Technical University of Denmark

Integrated characterization of NA of PCE plume after thermal source zone remediation

- microbial techniques and dual CSIA

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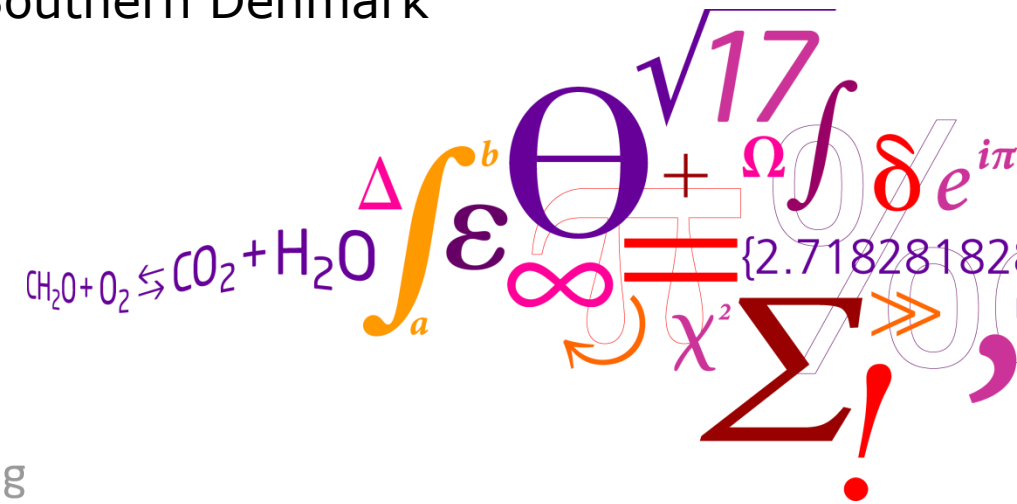
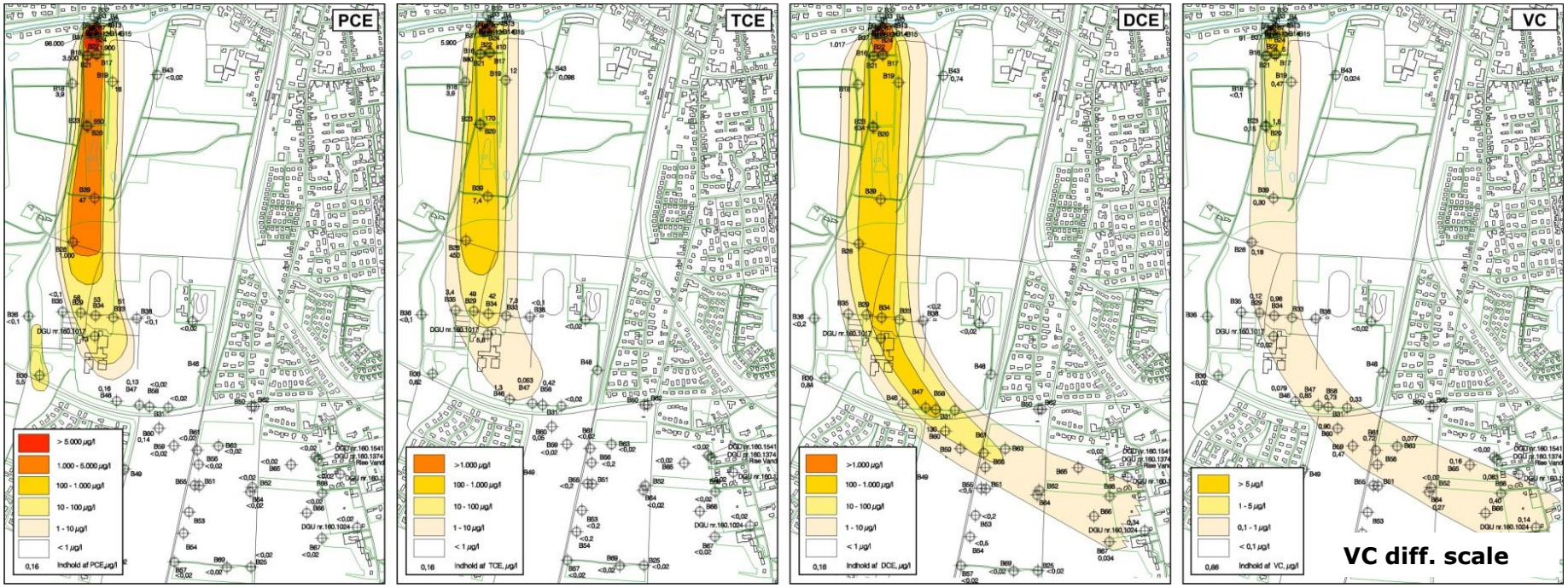


DTU Environment
Department of Environmental Engineering

Degradation of PCE in plume

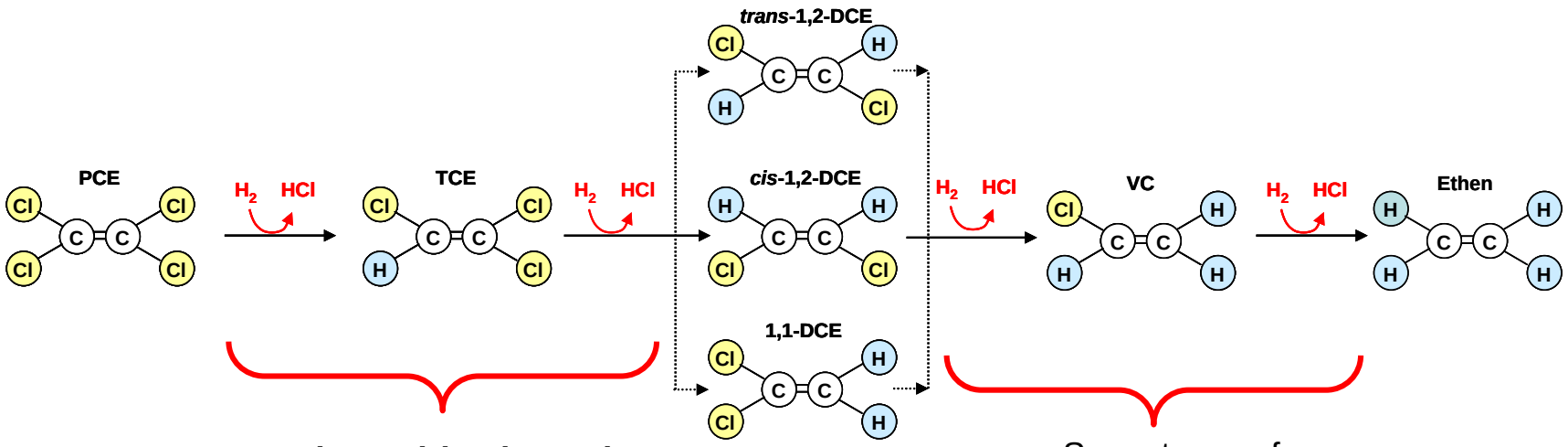


- Former central dry cleaning facility in Denmark
- PCE DNAPL in source area, plume in sand aquifer
- Degradation products TCE, DCE and a tiny bit of VC

- Thermal remediation of source area in late 2006. Effect in plume?
- Studies in 2006-7, 2014 (7-8 yr) and 2017 (11-12 yr, in progress). Change in risk?

- Tools: Dual CSIA, *Dhc* (+*Dhg*) activity, sequencing

Reductive dechlorination of PCE

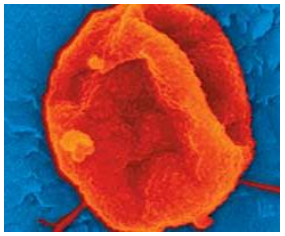


Halorespiring bacteria:
Dehalobacter (Dhb)
Dehalospirillum
Desulfitobacterium
Desulfuromonas
Dehalococcoides (Dhc)

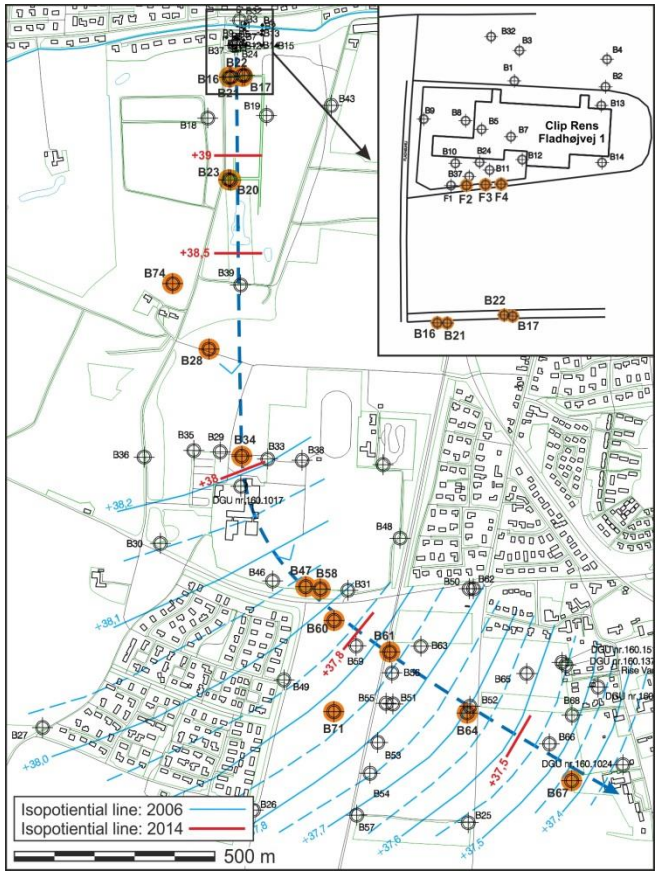
Some types of
Dehalococcoides *(Dhc)*
Dehalogenimonas (Dhg) (tDCE)

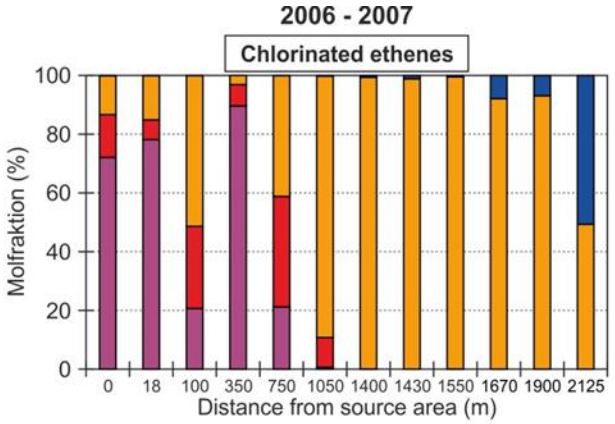
Dhc with vinylchloride reductase gene *(vcrA, bvcA), Dhg (tdrA?)*

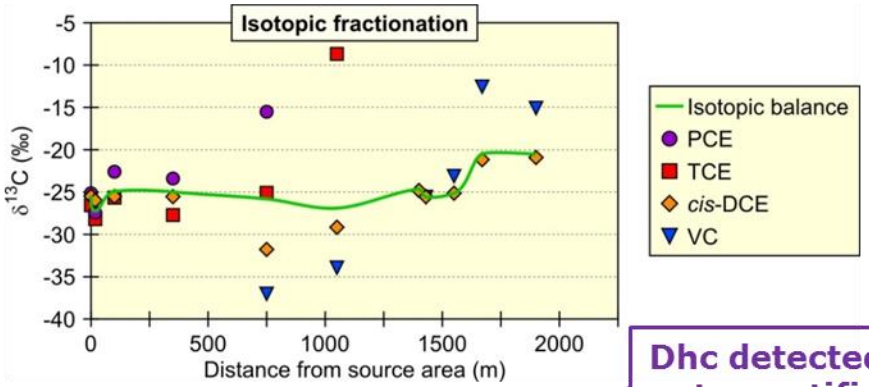
- Anaerobic conditions and hydrogen/organic donor
- Specific degraders
  - Risk of cDCE and/or VC accumulation, if Dhc or Dhg with vcr genes are not present

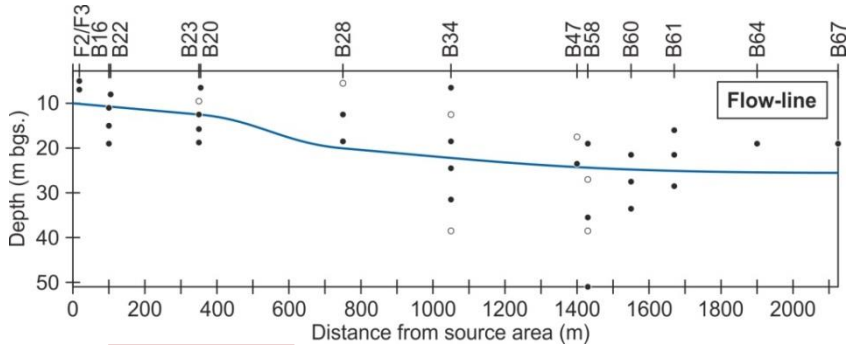


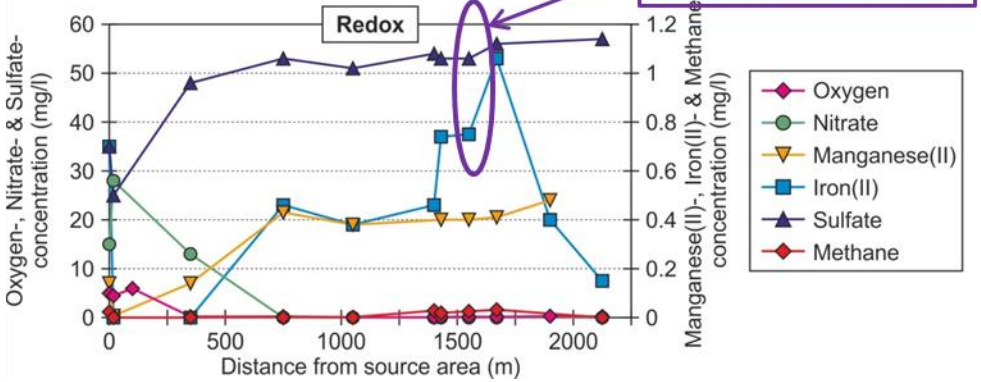
NA in plume prior to source remediation









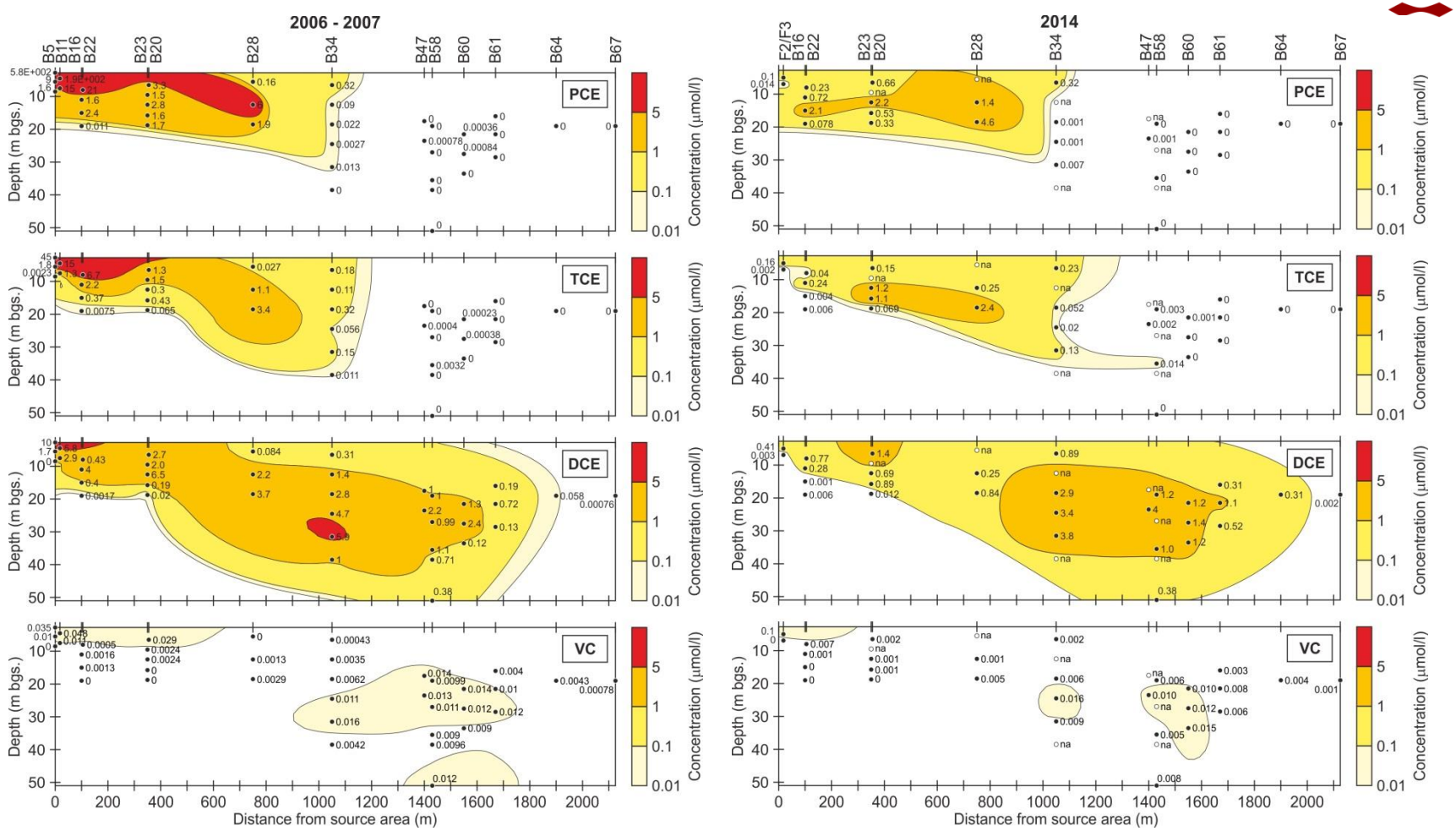


Thermal remediation of source zone

- Steam treatment
  - Vapor extraction
  - DNAPL condensation
  - AC gas treatment
- 1-2 ton PCE removed

- Dissolved organic matter released from soil by boiling
- Stimulation of NA?
- Change in risk?

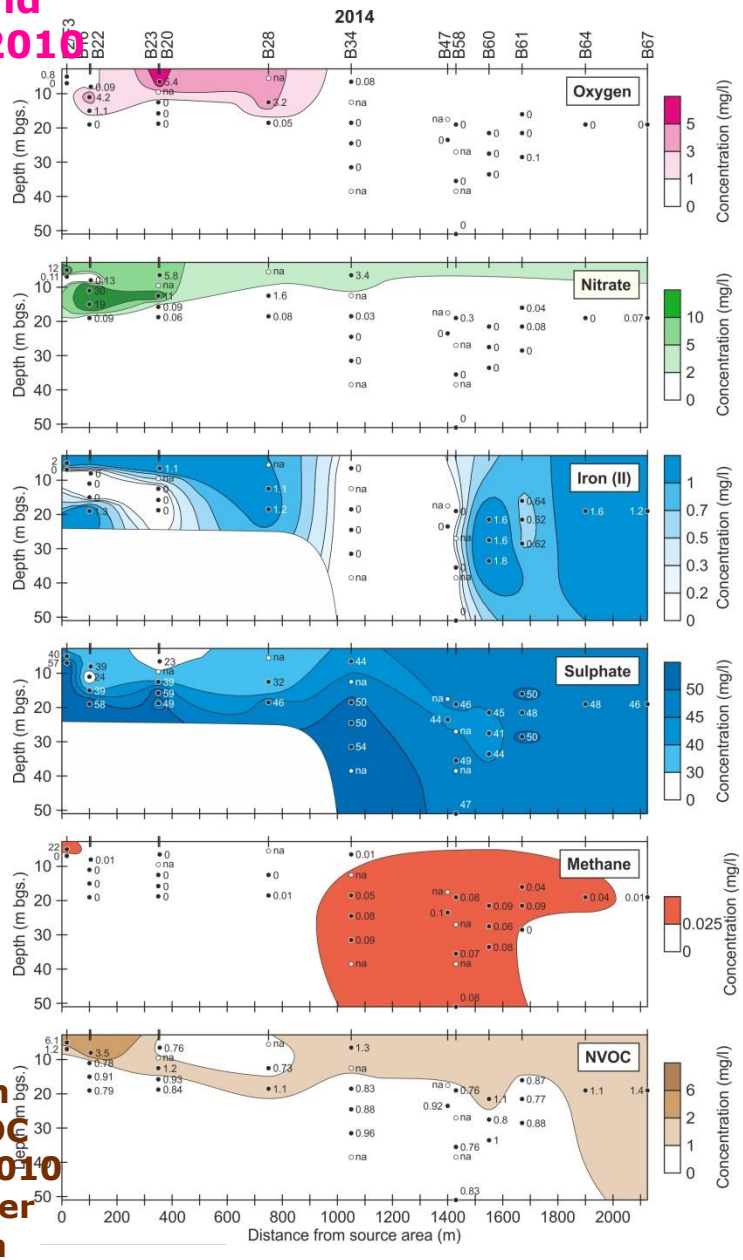
Effect on concentrations in plume



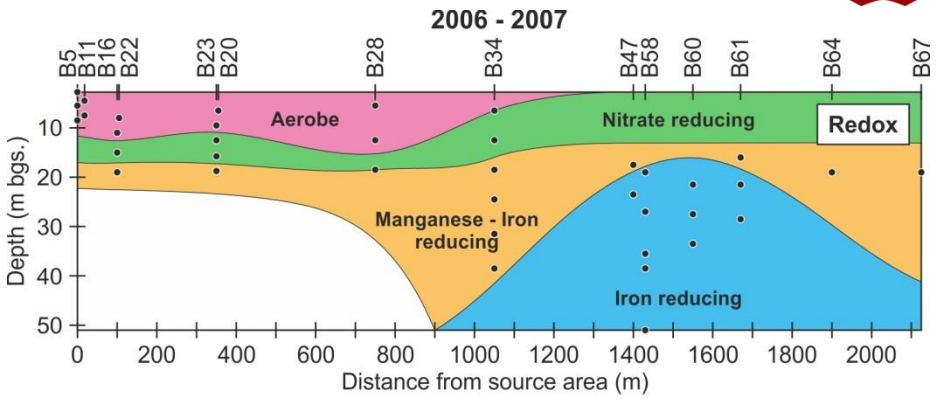
- PCE in source area is 2 orders of magnitude lower
- In the upper part of the aquifer a significant decrease in concentrations is observed to >750 m
- Centrally in the plume (1050 m) DCE and VC has decreased
- DCE continue to spread in downgradient direction

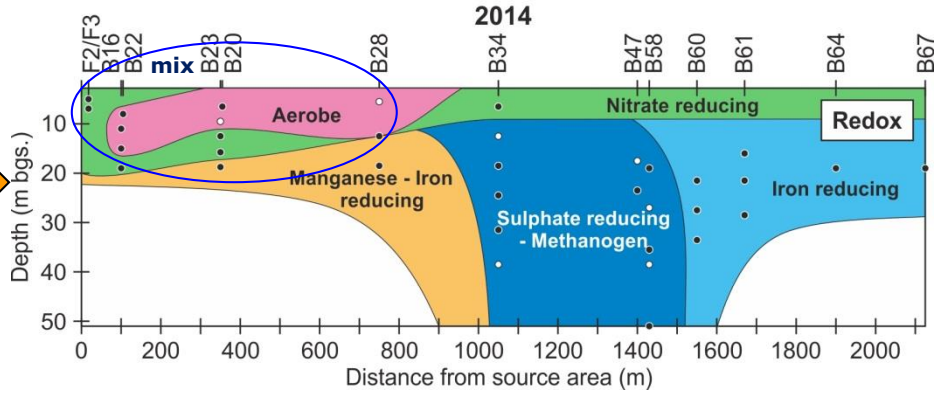
Effect on redox conditions

O_2 nd in 2010



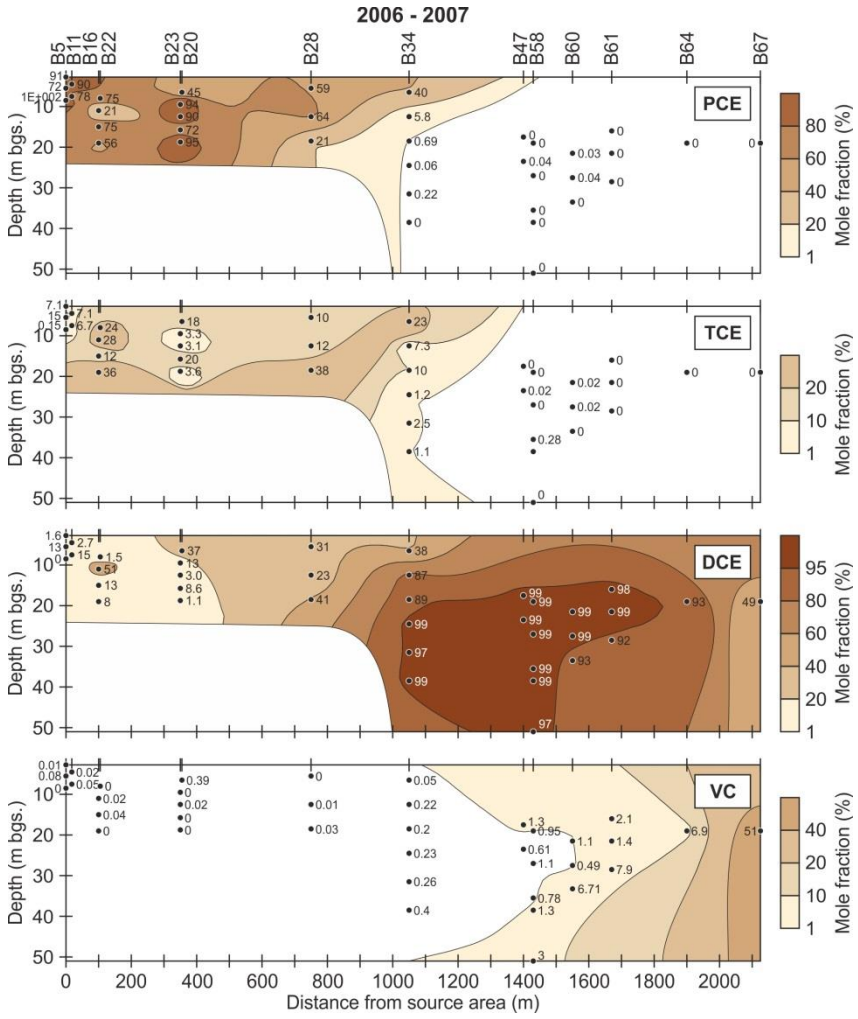
High NVOC in 2010 larger area

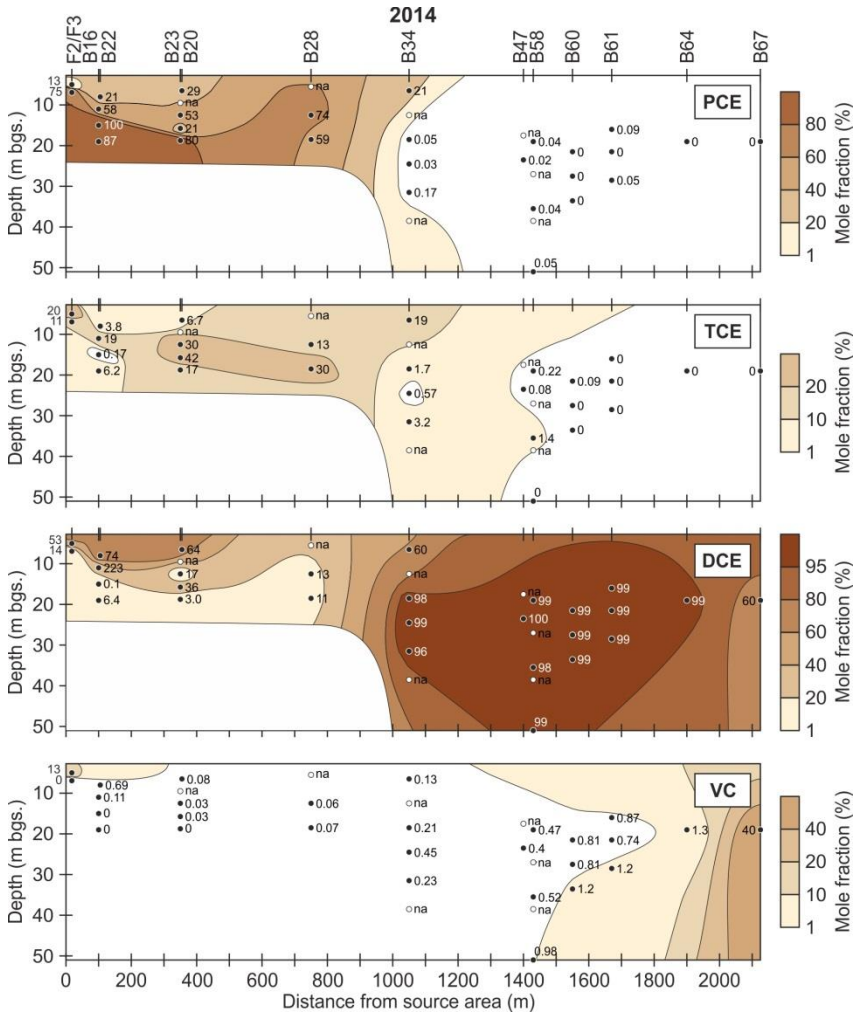




- Increased NVOC in/near source area
- Local reduction of redox conditions
- In 1050-1450 m change in redox
  - Pyrite oxidation lacking
  - More reduced
    - Methane indicate reduction

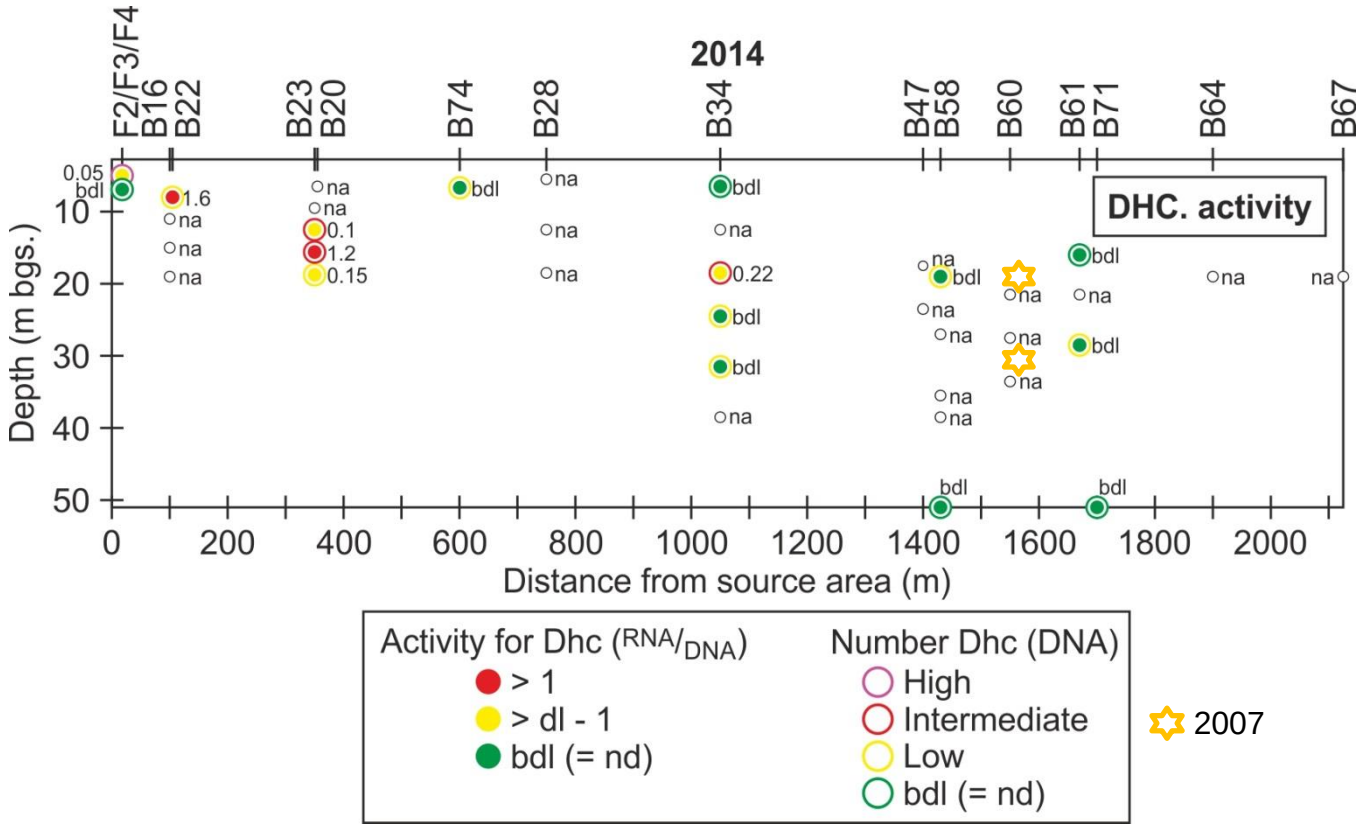
Effect on molar composition - degradation





- PCE degradation near source
- cDCE increase near source, little VC
- cDCE increase at 1050 m
- cDCE downgradient expansion - small (mostly less VC)

Specific degraders and activity (mRNA/DNA) in the plume after source remediation



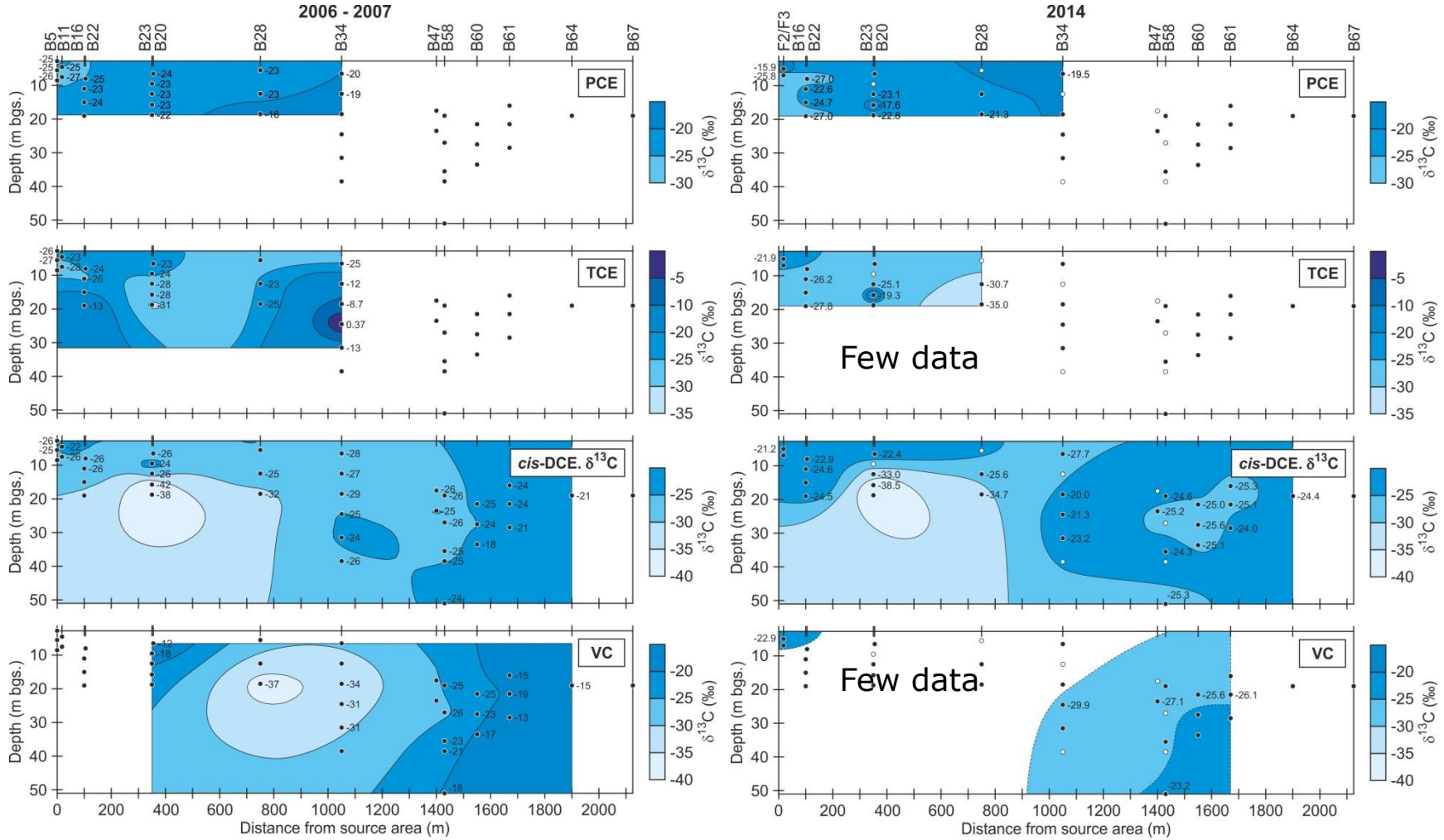
- **Dhc more widespread in 2014**, generally low level (except F4-3)
- VcrA and bvcA not detected
- **Dhc activity 0-350 m and 1050 m**

Sequencing. Chlorinated ethene degraders

Potential degradation Genus	Complete RD			RD of PCE+TCE							Ox VC+DCE			
	Dhc	**Dhg**	f_Dehalococcoidetes* (m.Dhc&Dhg)	**Dhb** Dehalobacter	**Gb** Geobacter	Clostridium	Acetobacterium	Desulfovibrio	Sporomusa	Methanosarcina	**Po** Polaromonas	Mycobacterium	Nocardioides	Methylosinus
B23-2	$5.21 \cdot 10^4$	$1.66 \cdot 10^6$	$3.04 \cdot 10^6$	$1.30 \cdot 10^5$	Nd	Nd	$5.21 \cdot 10^4$	Nd	Nd	Nd	$7.42 \cdot 10^5$	$2.60 \cdot 10^4$	$2.61 \cdot 10^4$	Nd
B23-3	Nd	$1.63 \cdot 10^5$	$3.72 \cdot 10^6$	Nd	Nd	Nd	Nd	Nd	$9.18 \cdot 10^4$	Nd	$2.04 \cdot 10^5$	$1.33 \cdot 10^5$	$4.38 \cdot 10^5$	$2.04 \cdot 10^4$
B34-2	$7.05 \cdot 10^4$	$8.28 \cdot 10^5$	$4.72 \cdot 10^6$	$2.64 \cdot 10^5$	$9.70 \cdot 10^5$	$4.58 \cdot 10^5$	$1.76 \cdot 10^5$	$7.05 \cdot 10^4$	$8.81 \cdot 10^4$	Nd	$3.88 \cdot 10^5$	$2.52 \cdot 10^4$	$3.52 \cdot 10^4$	Nd
B34-3	$9.28 \cdot 10^4$	$3.31 \cdot 10^5$	$1.78 \cdot 10^6$	$3.18 \cdot 10^5$	$2.66 \cdot 10^5$	$6.65 \cdot 10^4$	Nd	Nd	Nd	Nd	$5.70 \cdot 10^5$	Nd	Nd	Nd
B34-4	Nd	$3.74 \cdot 10^5$	$2.50 \cdot 10^6$	Nd	$1.50 \cdot 10^4$	Nd	$1.95 \cdot 10^5$	Nd	Nd	Nd	Nd	Nd	Nd	Nd
B34-6	Nd	$4.61 \cdot 10^5$	$9.99 \cdot 10^5$	Nd	$5.77 \cdot 10^4$	Nd	Nd	Nd	Nd	Nd	Nd	Nd	$3.85 \cdot 10^4$	Nd
B58-2	Nd	$8.34 \cdot 10^4$	$5.17 \cdot 10^5$	Nd	$3.33 \cdot 10^4$	Nd	Nd	Nd	Nd	$3.33 \cdot 10^4$	$1.12 \cdot 10^6$	Nd	$1.76 \cdot 10^4$	Nd
B58-6	$1.06 \cdot 10^5$	$6.60 \cdot 10^4$	$9.78 \cdot 10^5$	Nd	$9.24 \cdot 10^4$	$5.28 \cdot 10^4$	Nd	$2.64 \cdot 10^4$	$2.64 \cdot 10^4$	Nd	$1.66 \cdot 10^6$	Nd	Nd	Nd
B61-1	$4.40 \cdot 10^4$	$5.50 \cdot 10^3$	$1.76 \cdot 10^5$	$6.05 \cdot 10^4$	$1.26 \cdot 10^5$	$1.65 \cdot 10^4$	$5.50 \cdot 10^3$	$5.50 \cdot 10^3$	$7,.2 \cdot 10^5$	$5.50 \cdot 10^3$	$1.65 \cdot 10^4$	Nd	Nd	Nd
B61-3	Nd	$5.90 \cdot 10^3$	$4.66 \cdot 10^5$	Nd	$1.77 \cdot 10^4$	Nd	Nd	Nd	Nd	Nd	$4.60 \cdot 10^5$	Nd	$5.90 \cdot 10^4$	Nd
B74-3	$8.30 \cdot 10^4$	$2.77 \cdot 10^4$	$1.80 \cdot 10^5$	$1.94 \cdot 10^5$	$8.29 \cdot 10^4$	$1.24 \cdot 10^4$	$1.81 \cdot 10^6$	$2.76 \cdot 10^4$	Nd	Nd	$1.11 \cdot 10^6$	$2.77 \cdot 10^4$	Nd	Nd
kontrol	Nd	Nd	$1.24 \cdot 10^6$	$5.52 \cdot 10^4$	Nd	Nd	Nd	Nd	Nd	$3.36 \cdot 10^6$	Nd	Nd	Nd	$5.52 \cdot 10^4$

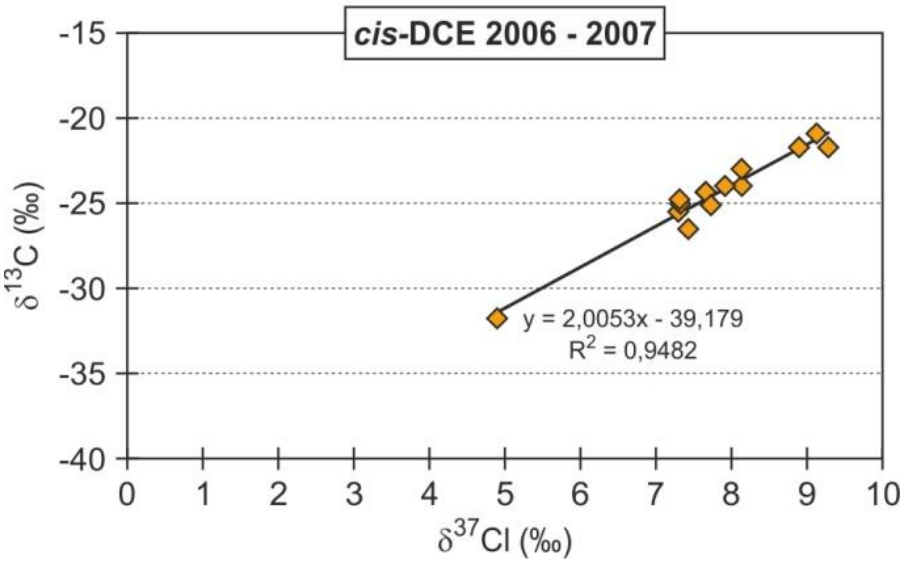
- >5000 OUT, searched for specific chlorinated ethene degraders
- 2 Complete RD: *Dhc, Dhg*
- 7 RD of PCE+TCE
- 4 Aerobic oxidation of VC, 1 VC&cDCE: Polaromonas.
- Very complex composition of bacteria in many samples suggest **several different concurrent degradation processes**

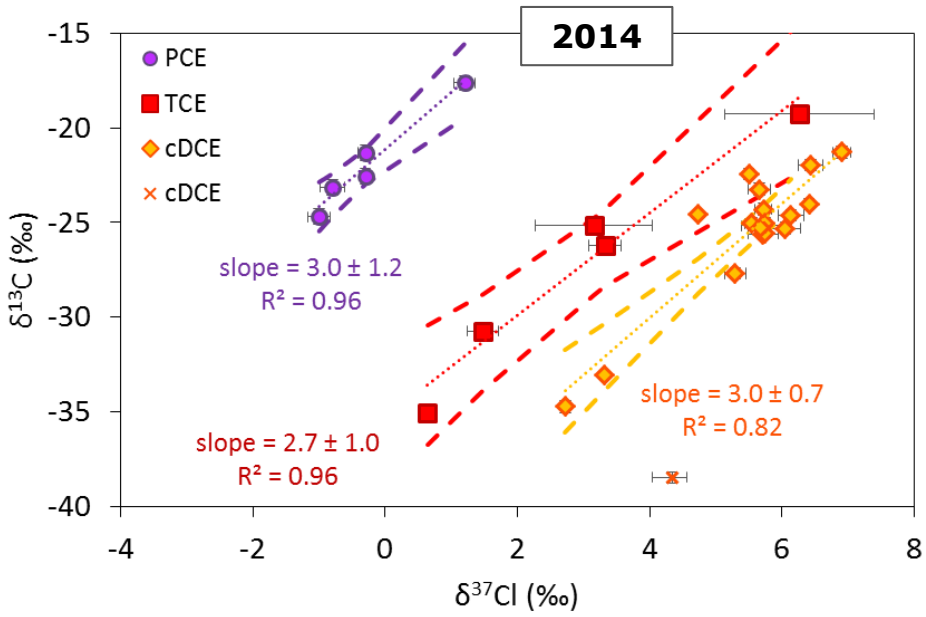
Effect on degradation. Isotopic fractionation



- PCE: Little left. Little change. Very little TCE.
- **cDCE**: Significant change. **0-350 m Degradation occurs.**
- **cDCE**: **1050 m Degradation has increased** (400 m before).
- VC: Few detect.

Dual stable isotopes – C and Cl





- Linear correlation – could indicate dechlorination?
- Correlation coefficient indicative of degradation process

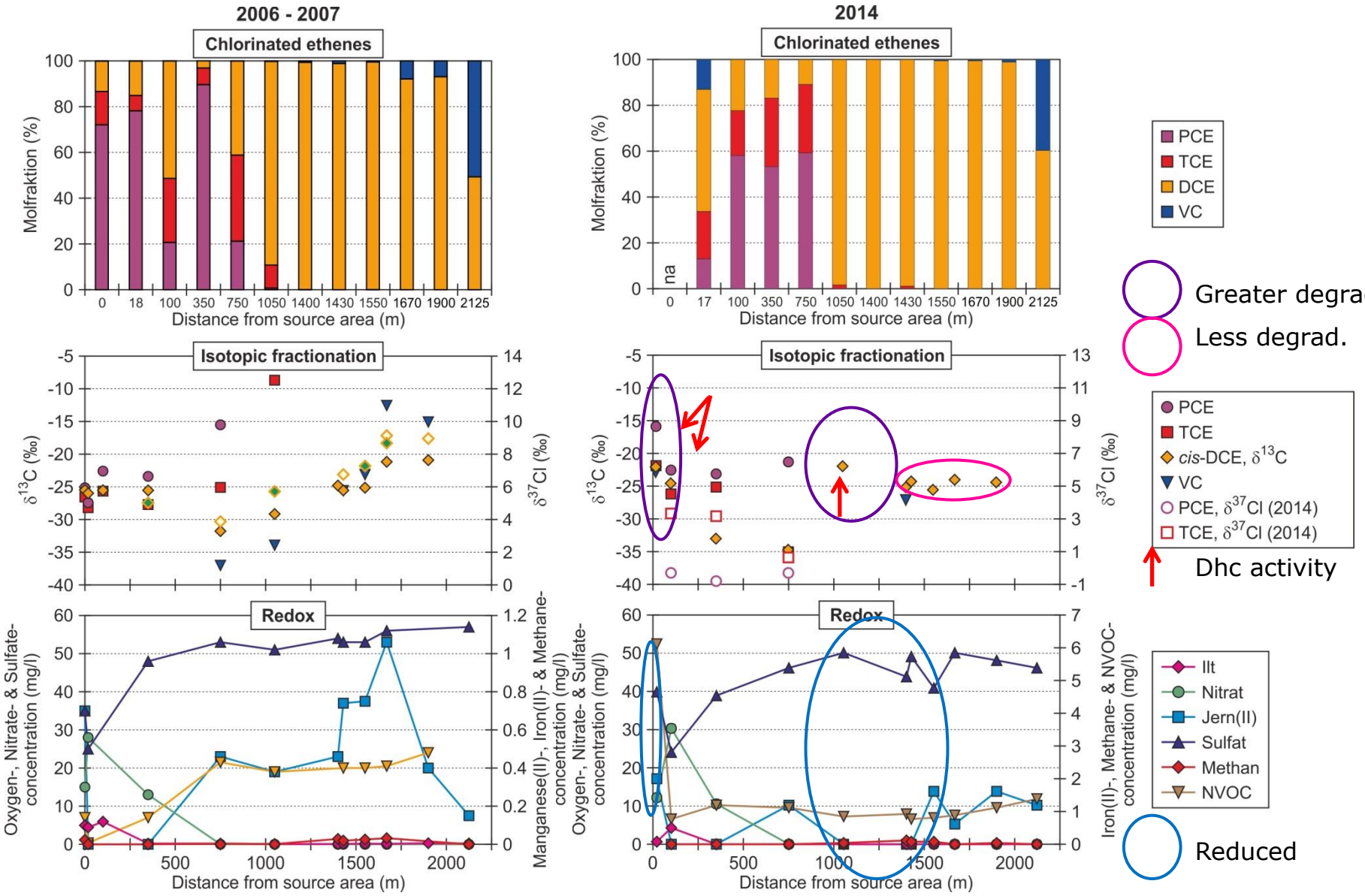
- PCE (**3**):
  - **Biotic RD**
  - PCE→TCE, Sulfurospirillum: **2.7**
  - PCE→DCE, Sulfuroospirillum: 0.7
  - PCE→DCE, Desulfitobacterium:**2.5**

TCE (**2,7**):
- **Biotic RD:** 4.8; 3.4-3.8
- Abiotic RD: 5.2

DCE (**2-3**):
- **Abiotic RD**: **3.0; 3.1**
- Biotic RD, Dhc-vcr: 11.6
- Aerobic biotic oxidation: 32.3

Badin 2014, Wiegert 2013, Audi-Miro 2013, Abe 2009, Kuder 2013, Cretnik 2013

Summary 2014



2017 Preliminary results

- Sampled March-April 2017
- Redox
  - Near source, upper part: oxic-anoxic i.e. back to 2006 status
  - 1050+ m: As reduced as in 2014
- Near source conc. and degradation
  - Conc. nearly as 2014, but less VC
  - Continued stimulation of degradation
- Far plume degradation
  - Comparable to 2014
  - Maybe a bit more VC?
  - Continued stimulation of degradation
- Plume expansion
  - Maybe small increase
- Specific degraders (4 samples)
  - **Dhc and Dhg** as in 2014
  - Now **vcrA/bvcA** quantifiable
  - Other Dehalogenating bact. as 2014
  - Sulfate reducing, bit of methanogenic, bacteria present
- Activity
  - Analysis in progress
- Dual CSIA
  - Analysis in progres

Conclusion and perspectives

- Mass much smaller after source remediation and decreasing
- Reduced conditions induced by NVOC release
- Degradation increased
- Mixed degradation processes on-going
- cDCE abiotic as well as biotic degradation
- Risk decreased (not eliminated)

- Future evolution in conditions and degradation?
  - Preliminary 2017 data so far appear promising

- Stimulation potential revealed for:
  - Biotic (ERD) degradation
  - Biotically induced (FeS) abiotic degradation (ISCR)

References

Badin et al. 2016. J. Contam. Hydrol., 192, 1-19.

Hunkeler et al. 2011. J. Contam. Hydrol., 119, 69-79.

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