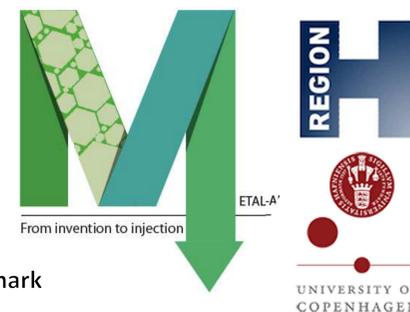


Extent of natural attenuation of chlorinated ethenes at a contaminated site in Denmark

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Introduction

- ❖ Chlorinated solvents contaminated soils and aquifers are a widespread problem and many require clean-up due to the risk of contaminating groundwater resources. Clean-up is costly and often invasive, thus there is high interest in stimulating natural attenuation processes.
- ❖ We present chemical, isotopic and microbial characterisation of a chlorinated ethene (CE) contaminated site in Denmark to evaluate these processes. The data give indication of complete microbial reductive dechlorination (RD) potential in hot spot areas, and reveal potential degradation due to aerobic co-metabolism and/or abiotic geochemical reduction. However, overall natural attenuation is low.



1. The site

- ❖ Contamination cause by operation of a drycleaning facility from 1960-1987 (2 buildings, Fig.1).
- ❖ Around 2 tons of PCE were gradually released into the underlying ~8 m thick clay layer, that overlays the sandy aquifer.
- ❖ Benzene, Ethylbenzene, Toluene and Xylenes (BTEX) are found as co-contaminants.
- ❖ Since 2014, a pump and treat facility (P01, Fig. 1) is operated to protect the sandy aquifer.

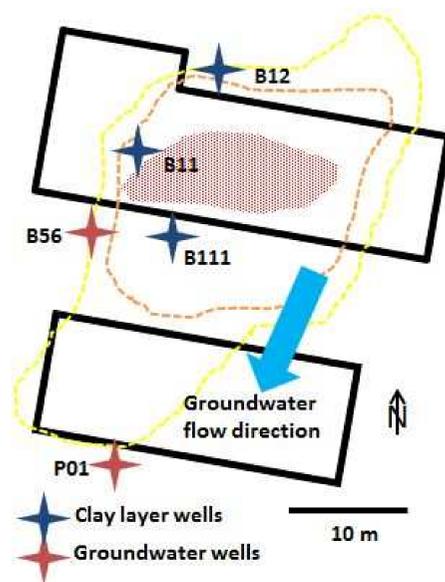


Figure 1: Schematic sketch of the field site, with well positions in the clay and sandy layers. Highlighted areas and contour lines indicate qualitative distribution of contamination in both x-y and z.

2. Chemical line of evidence

- ❖ The main contamination is situated in the clay layer, which in some locations seems aerobic (NO_x detected in B11 and B12) and anaerobic in others (B111, no NO_x).
- ❖ Anaerobic biological RD of CEs is only favorable under anaerobic conditions, and this is reflected by the molar ratios of CE intermediates (e.g., B111, B56).

	Clay layer			Groundwater		
	B11	B12	B111	B56	P01	
PCE	62000	35000	640	71	16	
TCE	2200	1800	710	69	5.8	
cDCE	1500	1400	8800	100	6.3	
VC	65	74	590	n.d.	n.d.	
Σ BTEX	3.7	1.2	1.9	<0.1	n.d.	
Σ C ₆ -C ₃₅	140000	7700	250	45	7	
NO_3	67	8.9	n.d.	n.d.	n.d.	
NO_2	0.46	0.10	n.d.	n.d.	n.d.	

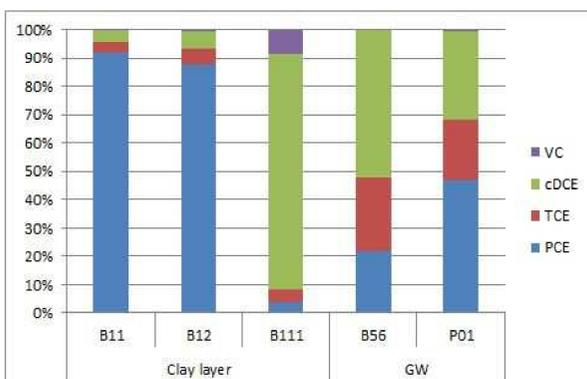


Figure 2: Molar ratios of PCE contaminant and the sequential degradation intermediates trichloro-, *cis*-dichloro- and monochloro ethylene (TCE, cDCE, VC) resulting from biological reductive dechlorination of PCE under anaerobic conditions.

3. Biological line of evidence

- ❖ Wells indicative of biological RD were investigated for the numbers of known CE degraders. Dehalococcoides (*Dhc*) is the only species known to carry out full RD beyond cDCE.
- ❖ The presence of *Dhc* and their enzymes (*tceA*, *vcr*, *bvc*) indicate potential for „full-degradation“.
- ❖ A potential exists in both wells but *Dhc* numbers are low and outnumbered by other degraders → degradation likely stalls at cDCE.

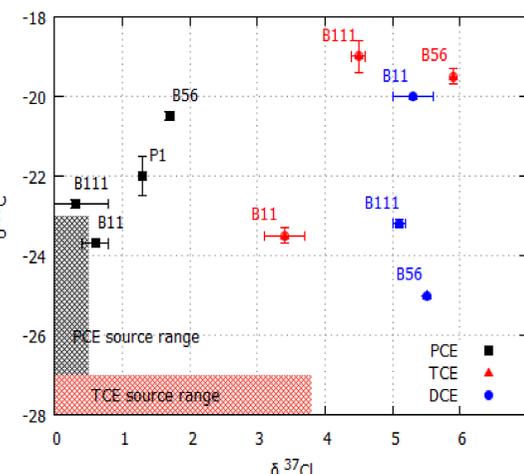
Table 2: Cell and enzyme numbers obtained via qPCR analysis of 1 L water samples. Low numbers of *Dhc* and high number of other degraders imply degradation stall at cDCE. Numbers are given in per ml. Bdl = below detection limit.

Bacteria/Enzymes [ml^{-1}]	Clay	GW
	B111	B56
Dehalococcoides (<i>Dhc</i>)	16	$3.1 \cdot 10^2$
TCE Reductase (<i>tceA</i>)	0.7	Bdl
VC Reductase (<i>bvc</i>)	0.9	2.2
VC Reductase (<i>vcr</i>)	1.7	22
Dehalobacter spp.	$3.3 \cdot 10^2$	$6.1 \cdot 10^2$
Dehalogenimones spp.	$2.7 \cdot 10^2$	$1.7 \cdot 10^3$
Desulfotobacterium spp.	66	$1.1 \cdot 10^4$
Desulfuromonas spp.	5.2	$9.3 \cdot 10^2$

4. Isotopic line of evidence

- ❖ A higher enrichment (more positive δ values) in ^{13}C confirm more degradation of PCE and also TCE in anaerobic wells compared to aerobic ones (B111, B56 vs B11), while cDCE values are low in anaerobic wells - indicating cDCE stall.
- ❖ In well B11 however, the high enrichment of cDCE shows significant degradation of this compound - presumably under aerobic conditions via aerobic co-metabolism.

As ^{13}C is conserved during biotic RD until full dechlorination, the change of its molar sum over all CEs is indicative of the total contaminant degradation by this process. Here, little change in ^{13}C shows the overall extent of contaminant removal is small.



$\delta^{13}\text{C}$ -MB	Clay layer		GW
	B11	B111	B56
	-23.5	-23.0	-22.4

Table 3: Carbon 13 mass balance (MB) over all measured chlorinated ethenes for three wells. Including data for VC in B111, data not shown.

Figure 3 (top): 2D-isotope plot of carbon and chlorine isotopes obtained for wells B11, B111, B56 and P01. Values are expressed in the δ -notation as ‰ relative to the international reference standards VPDB (Vienna Pee Dee Belemnite) and SMOC (standard mean ocean chloride). Areas for virgin PCE and TCE marked.

