



# Assessing chlorohydrocarbon degradation using compound-specific isotope analysis (CSIA) at the RÄVEN Site, Helsingborg, Sweden

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## Sammanfattning

Denna studie syftar till att bedöma nedbrytningen av klorerade lösningsmedel i grundvattnet på den förorenade platsen Råven i Helsingborg, Sverige med hjälp av föreningsspecifik kolisotopanalys (CSIA). Området i Råven var förorenat av klorerade lösningsmedel under kemtvättsverksamheten mellan 1929 och slutet av 1970-talet. För att få detaljerad inblick i nedbrytningen av de klorerade lösningsmedlen på platsen, bestämdes högupplösta kol-CSIA-profiler från 9 flernivåbrunnar belägna i föroreningskällan och längre nedströms. I källzonen avslöjade CSIA-profilerna att nedbrytningsaktiviteterna generellt sett är låga och att trikloreten (TCE), som tidigare ansetts vara en nedbrytningsprodukt av tetrakloreten (PCE), troligen kommer från föroreningskällan. Dessutom visade CSIA kombinerat med koncentrationsprofilerna i källzonen att nedbrytning av klorerat lösningsmedel stannade vid cis-dikloreten (cDCE) och inte gick vidare till vinylklorid (VC). I nedströms brunnarna med flera nivåer minskade koncentrationerna av klorerade lösningsmedel med mer än två storleksordningar, och nedbrytningsaktiviteterna var högre i motsats till källzonen, som också till viss del fortsätter till VC. Trots de högre nedbrytningsaktiviteterna i nedströmsbrunnarna kunde dock koncentrationsminskningen jämfört med källzonen i högre grad hänföras till utspädning jämfört med nedbrytning.

## Summary

This study aims to assess the degradation of chlorohydrocarbon in the groundwater at the Råven site in Helsingborg, Sweden using compound-specific carbon isotope analysis (CSIA). The Råven site was contaminated by chlorohydrocarbons during dry cleaner activities between 1929 and the end of the 1970ties. To obtain detailed insight into the degradation of the chlorohydrocarbons at the site, high-resolution carbon CSIA profiles were determined from 9 multilevel wells located in the contamination source zone and farther downstream. In the source zone, the CSIA profiles revealed that the degradation activities are generally low and that trichloroethene (TCE), previously considered as a degradation product of tetrachloroethene (PCE), likely originates from the contamination source. Moreover, the CSIA combined with the concentration profiles in the source zone showed that chlorohydrocarbon degradation stalled at cis-dichloroethene (cDCE) and did not proceed further to vinyl chloride (VC). In the downstream multilevel wells, the chlorohydrocarbon concentrations decreased by more than two orders of magnitude, and the degradation activities were higher as opposed to the source zone, which also proceed to some extent to VC. However, despite the higher degradation activities in the downstream wells, the concentration decrease compared to the source zone could be attributed to a higher extent to dilution in comparison to degradation.

# 1. Introduction

Chlorohydrocarbons such as tetrachloroethene (PCE) or trichloroethene (TCE) are anthropogenically produced compounds occurring as dense nonaqueous phase liquids (DNAPLs) and being carcinogenic to humans. Despite their adverse effects on human health, chlorohydrocarbons were widely used at many industrial sites in Sweden and worldwide for various purposes including degreasing applications and dry cleaning. Due to improper handling, disposal and accidents, chlorohydrocarbons were often released at the surface as DNAPLs and rapidly migrated vertically into groundwater systems due to their high density and low viscosity (Schwille, 1988). Although the peak production and release of chlorohydrocarbons occurred in the 1970ties, chlorohydrocarbons are still present at thousands of sites in Sweden and worldwide demonstrating their long-term persistence for several decades.

The long-term persistence of chlorohydrocarbons poses a major challenge for the remediation of contaminated sites. To determine the best remediation strategy for chlorohydrocarbons contaminated sites, it is of major importance to determine whether chlorohydrocarbons are subject to degradation. Chlorohydrocarbons are degradable under reducing conditions since they can act as an electron acceptor under oxygen free conditions. For instance, chlorinated ethenes such as tetrachloroethene (PCE) or trichloroethene (TCE) can undergo sequential reductive dechlorination and degrade to cis-dichloroethene (cDCE), vinyl chloride (VC) and eventually to ethene, respectively (Fig. 1).

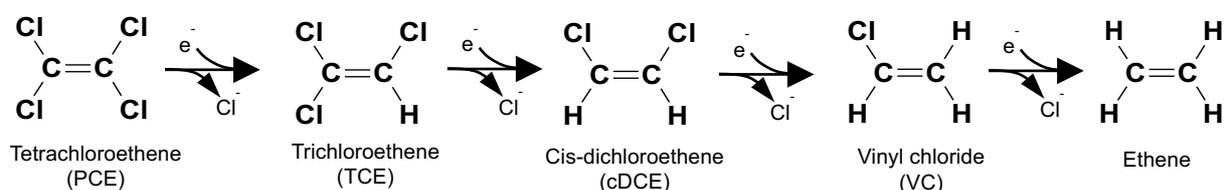


Figure 1. Sequential reductive dechlorination of chlorinated ethenes, whereby during each dechlorination step, one chlorine atom is replaced by one hydrogen atom.

If no chlorohydrocarbon degradation occurs at contaminated sites, the sites need to be decontaminated for example through excavation, thermal remediation and/or soil washing to lower the contaminant concentration below the remediation goal (Fig. 2A). The decontamination of contaminated site material is time-consuming and often related with high costs. In contrast, if chlorohydrocarbon degradation occurs such that the contamination concentration decreases below the remediation goal within a reasonable time frame, a monitored natural attenuation approach (MNA) can be applied (Fig. 2B). MNA includes the continuous monitoring of chlorohydrocarbon attenuation caused by degradation in the contaminated groundwater systems through frequent groundwater sampling. MNA is a much cheaper remediation option compared to the decontamination approach and shows that the costs of a remediation heavily depend on whether chlorohydrocarbons are subject to degradation.

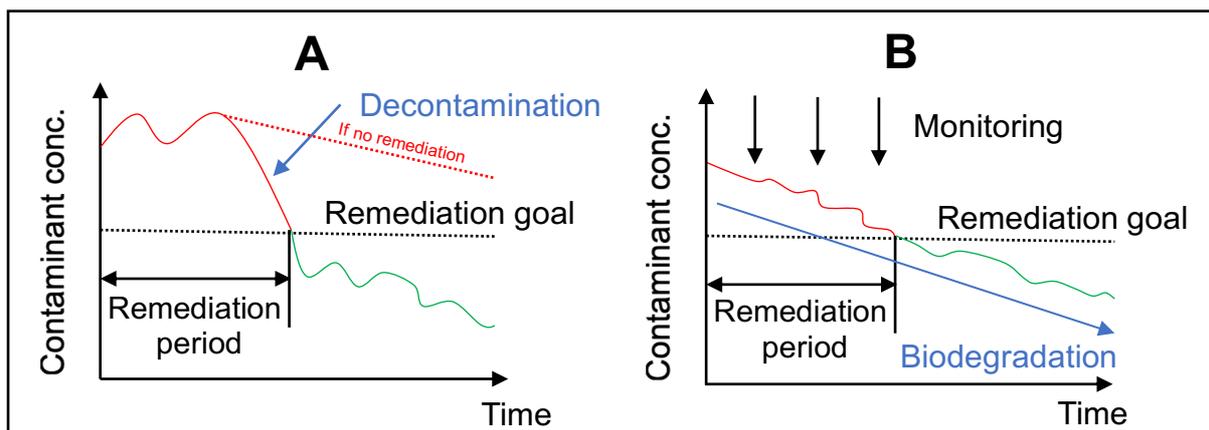


Figure 2. Different remediation scenarios for sites contaminated by chlorohydrocarbons. In scenario A no degradation occurs and hence, a decontamination of the aquifer material is necessary to reach the remediation goal. In scenario B, degradation is sufficiently high to reach the remediation goal by monitored natural attenuation (MNA) only.

Despite its high importance for applying the best remediation strategy and for its costs, the determination of chlorohydrocarbon degradation at contaminated sites is challenging based on concentration measurements only. Often, it remains unclear if chlorohydrocarbon concentrations decrease due to dilution or degradation and chlorohydrocarbon degradation rates are difficult to quantify. To overcome the shortcoming of concentration analysis only for determining chlorohydrocarbon degradation, compound-specific isotope analysis (CSIA) has been emerged in the last two decades has an effective tool to determine chlorohydrocarbon degradation (Hunkeler, 2008; Wanner et al., 2016; Wanner et al., 2018a; Wanner et al., 2018b). The method makes use of the preferential cleavage of bonds between light compared to heavy isotopes, leading to a progressive enrichment of heavy isotopes in the parent compared to the daughter compound (Fig. 3). Hence, an enrichment of heavy carbon isotopes in the parent compound over time provides unequivocal evidence for chlorohydrocarbon degradation.

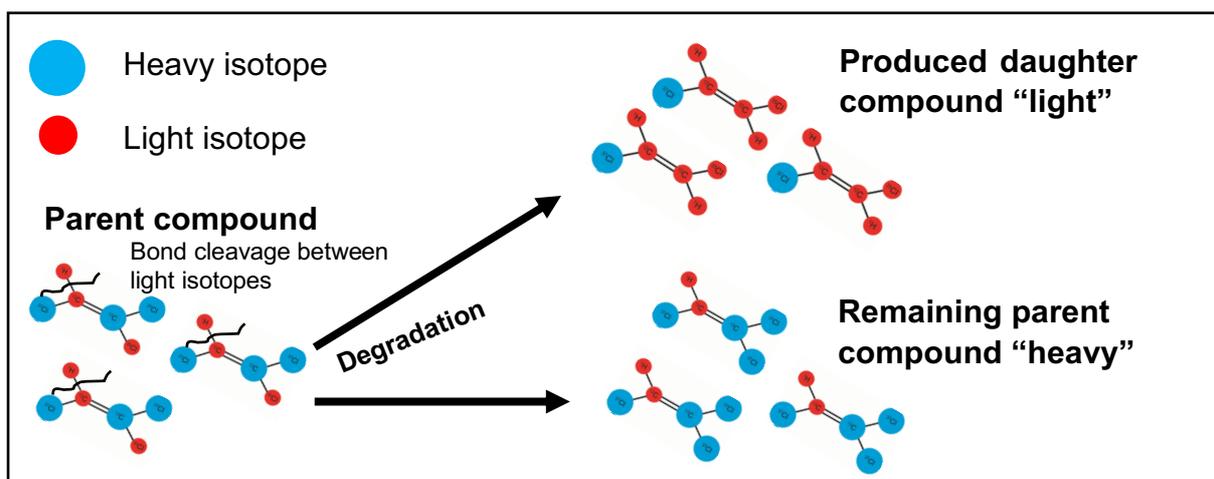


Figure 3. Concept of compound-specific isotope analysis (CSIA). During chlorohydrocarbon degradation, bonds between light isotopes are preferentially cleaved, leading to a continuous enrichment of heavy isotopes in the remaining parent compared to the produced daughter compound providing clear evidence for chlorohydrocarbon degradation.

The goal of this study is to determine chlorohydrocarbon degradation in the groundwater at a contaminated site named Råven in Helsingborg, Sweden using highly resolved compound-specific carbon isotope analyses (CSIA) data for selecting the most appropriate remediation approach. To the best of our knowledge, this is the first high-resolution CSIA study, which has been carried out in Sweden to determine chlorohydrocarbon degradation at a contaminated site.

## 2. Methods

### 2.1. Site description

The investigated Råven site is a historical dry cleaner facility in a residential area at the Blekingegatan in Helsingborg, Sweden. The hydrogeological conditions at the site consist of a sandstone aquifer, which serves as a reserve water source for the hospital in Helsingborg, which is located 500 meters downstream of the site, and as a water source for the Swedish mineral water producer Ramlösa being located a few kilometres downstream of the site. The Råven site was contaminated during dry cleaner activities between 1929 and the end of the 1970ties. During this time period, significant amounts of PCE and possibly TCE DNAPLs were released into the subsurface. Since 2011, several rounds of investigations of the extent of contamination have been carried out. The investigations at the site culminated in the retrieval of cores and the installation of 16 multilevel monitoring wells in 2019 and 2021, respectively, in the source and downstream of the source, zone whereby each of the multilevel wells contains 3 to 6 sampling ports resulting in 43 ports total (Fig. 2).

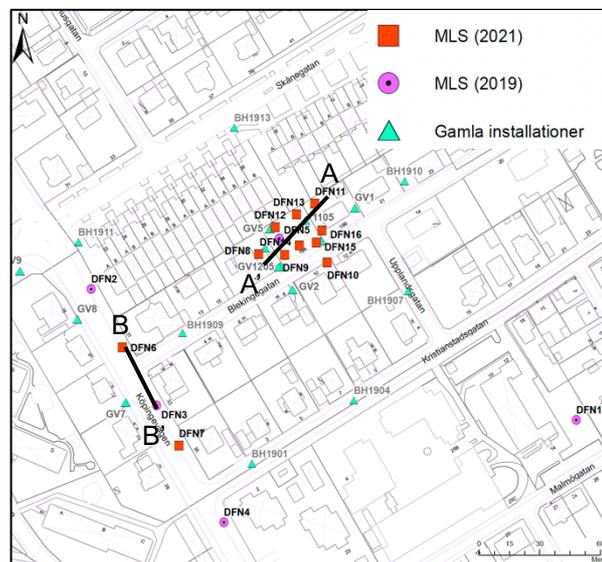


Figure 4. Locations of the installed multilevel wells being provided by Sweco®. The turquoise triangles are the locations of the conventional groundwater sampling wells, which were installed before 2019, the pink circles represent the locations, where the multilevel wells were installed in 2019 and the red squares the locations, where the multilevel wells were installed in 2021.

The previous investigations at the site revealed that a major part of the PCE DNAPL is present in the unsaturated zone. However, a substantial part of the PCE DNAPL also migrated to greater depth into the aquifer systems and its dissolution sustains a groundwater contamination plume in the direction of groundwater flow to the southwest until today (Fig. 3). Additionally, the presence of PCE daughter products

such as TCE, cDCE and VC indicate degradation activities at the site but the extent of chlorohydrocarbon degradation remained unclear based on the previous investigations.

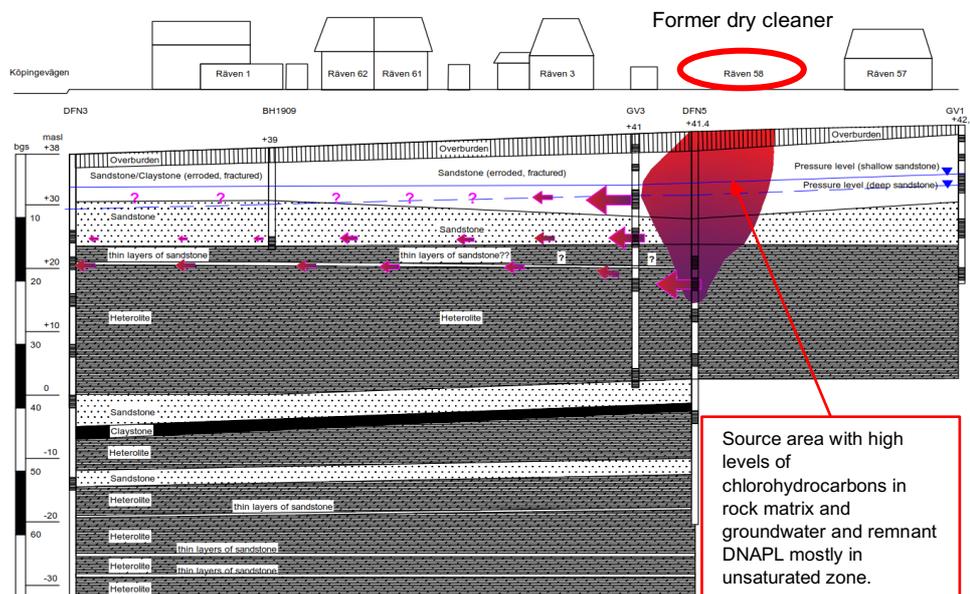


Figure 5. Updated conceptual site model of the Raven site based on previous conceptual site models provided by Sweco®.

## 2.2. Groundwater sampling

For this study, groundwater sampling was conducted during March 20 – 23, 2023 from 9 multilevel wells including DFN 3, 5, 6, 8, 9, 11, 12, 13, 15 (Fig. 2) using a bladder pump with dedicated polyethylene (PE) tubing. After measuring the field parameters (pH, dissolved oxygen (DO), temperature (T),  $\text{Fe}^{2+}$  concentrations), groundwater samples for chlorohydrocarbon, methane, ethane, and ethene concentrations as well as compound-specific carbon isotope analyses were collected in 40 mL (VOA) glass vials without headspace. Moreover, groundwater samples for total Fe and Mn concentration analysis were collected in 250 mL plastic bottles and groundwater samples for Na, K, Mg, and Ca were taken in 60 mL plastic bottles.

## 2.3. Concentration analysis

Chlorohydrocarbon, methane, ethane, and ethene concentration analysis as well as total Fe, Mn, Na, K, Mg, and Ca concentrations analysis were carried out by the commercial ALS laboratories in Sweden. Detailed description of the analytical methods for the concentrations analysis by ALS can be found elsewhere: <https://www.alsglobal.se>

## 2.4. Compound-specific carbon isotope analysis (CSIA)

Compound-specific carbon isotope analysis (CSIA) of PCE, TCE, and cDCE were performed at the Earth Science Department of the University of Gothenburg in Sweden. CSIA was conducted using a gaschromatograph (GC, Agilent 7890A) coupled to an isotope mass spectrometer (IRMS, Elementar Isoprime) via a combustion III interface (GC5, Elementar Isoprime). Samples were injected from the

headspace of a 20 mL vials filled with a 15 mL sample solution using a CombiPal Autosampler (CTC Analytics, Zwingen, Switzerland). For the chromatographic separation in the GC, a DB-VRX column (60 m, 0.25 mm, 1.40  $\mu\text{m}$ , Agilent) with a constant helium flow of 1,2 ml/min was used. The chromatographic separation in the GC was carried out by holding the GC oven at 50°C for 2 minutes, then by ramping it up at a rate of 5°C/min to 150°C and holding it for 5 minutes. After chromatographic separation, PCE, TCE, and cDCE were converted to CO<sub>2</sub> in the combustion interface and conveyed to the isotope ratio mass spectrometer (IRMS) for stable carbon isotope analyses. Stable carbon isotope analysis in the IRMS was conducted relative to a CO<sub>2</sub> gas being referenced to the international Vienna Pee Dee Belemnite (VPDB) standard, whereby the results were expressed in the delta notation according to:

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

where  $\delta^{13}\text{C}$  (‰) is the carbon delta value of the sample expressed in permill,  $\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Sample}}$  is the stable carbon isotope ratio of the sample, and  $\left(\frac{^{13}\text{C}}{^{12}\text{C}}\right)_{\text{Standard}}$  corresponds to the stable carbon isotope ratio of the VPDB international standard (0.01123720).

To maximise precision of the analysis water samples were diluted to identical concentrations of 300  $\mu\text{g/L}$ , whereas lower concentrations were measured undiluted. The detection limit for CSIA of PCE, TCE was at 60  $\mu\text{g/L}$  and for cDCE at 160  $\mu\text{g/L}$ . The analytical uncertainty for carbon isotope analysis (standard deviation of the mean:  $\text{SDM} = 1\sigma/(n)^{1/2}$ ;  $\sigma$ : standard deviation,  $n$ : sample number) of each PCE, TCE and cDCE measurements was determined based on triplicate measurements of each sample and was in average 0.12‰. To assess the degradation of chlorohydrocarbons by stable isotope methods at the site, the Rayleigh equation was used as the degradation of chlorohydrocarbons corresponds to a kinetic process:

$$\delta^{13}\text{C} = \delta^{13}\text{C}_0 + \varepsilon \cdot \ln f \quad \text{with} \quad \varepsilon = (\alpha - 1) \quad (2)$$

where  $\delta^{13}\text{C}$  is the stable carbon isotope ratio of the reactant at time  $t$ ,  $\delta^{13}\text{C}_0$  corresponds to the initial stable carbon isotope ratio of the reactant at time zero,  $\varepsilon$  is the stable carbon isotope enrichment factor, and  $\alpha$  is the stable carbon isotope fractionation factor corresponding to the ratio of the stable carbon isotope ratios ( $^{13}\text{C}/^{12}\text{C}$ ) of the instantaneously produced product and remaining educt, respectively.

### 3. Results and Discussion

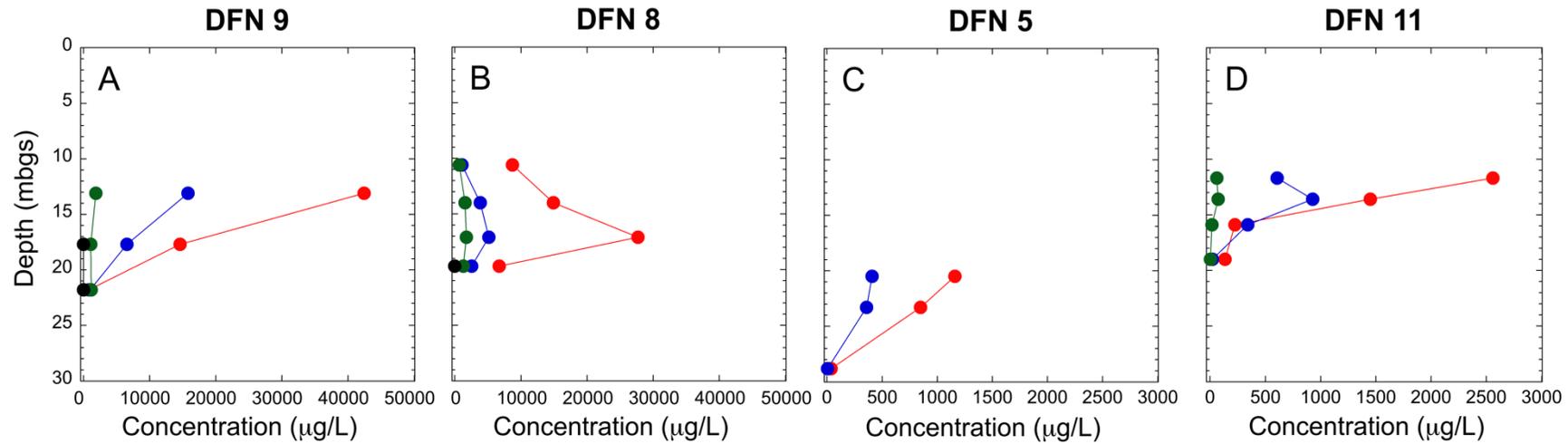
#### 3.1. Concentration data 2023

Figure 6 shows the chlorohydrocarbon profiles in the source zone along a long section (A-A'; Fig. 4) from northeast to southwest in DFN 9, 8, 5 and 11 (Figs. 6A - D) and in the downstream wells along a cross section (B-B') from northwest to southeast in DFN 3 and 6 (Figs. 6E and F) during in March 2023.

In the source zone, the highest chlorohydrocarbon concentrations were measured in groundwater at a depth ranging between 10 and 20 meters below ground surface (mbgs; Figs. 6A - D). The vertical location of this high chlorohydrocarbon concentration zone is consistent with previous investigations confirming the location of the groundwater contamination source at this depth range. In the source zone, PCE showed the highest concentrations of up to 42,000  $\mu\text{g/L}$ , followed by TCE of up to 15,800  $\mu\text{g/L}$  and cDCE of up to 1,880  $\mu\text{g/L}$  (Figs. 6A-D), whereby all peak chlorohydrocarbon concentrations in the source zone were measured in DFN 9 (Figs. 6A-D). The measured highest concentration of PCE among the different chlorohydrocarbon in the source zone is consistent with the assumption that PCE is the main constituent of the contamination source at the site. Moreover, the detection the degradation products including TCE and cDCE suggests that PCE was subject to degradation to TCE and further to cDCE (Fig. 1). However, based on the concentration data only it is difficult to determine if all detected TCE in the source zone originates from PCE degradation since there is the possibility that TCE was also part of the contamination source and that TCE was released from the contamination source into the groundwater system (SGU, 2020). Furthermore, the rare detection of the cDCE degradation product (VC) indicates that chlorohydrocarbon degradation in the source zones stalls at cDCE, which is often observed at sites contaminated by chlorohydrocarbons.

In the downstream wells, the peak chlorohydrocarbon concentrations were observed at a similar depth range as in the source zone (10 -20 mbgs; Figs. E and F). This indicates chlorohydrocarbon migration in the groundwater from the source zone to the downstream wells at this depth range. Moreover, compared to the source zone, the chlorohydrocarbon concentrations decreased by more than two orders of magnitude to below 1,000  $\mu\text{g/L}$  in the downstream wells. However, in contrast to the source zone, the chlorohydrocarbon concentration ratios were different in the downstream wells. TCE showed a higher concentration (up to 942  $\mu\text{g/L}$ ) compared to PCE (up to 616  $\mu\text{g/L}$ ) and the relative portion of the detected cDCE was increased with concentrations up to 152  $\mu\text{g/L}$ . Furthermore, small amounts VC was detected (up to 4.95  $\mu\text{g/L}$ ) in almost all the ports in the downstream wells, whereas in the source VC showed almost everywhere non-detects. The different chlorohydrocarbon concentration ratios in the downstream wells compared to the source zone indicate higher degradation activities in the downstream area. The higher TCE and cDCE concentrations portions compared to the source zone suggest degradation from PCE to TCE and from TCE to cDCE, respectively (Fig. 1). Moreover, the detection of small amounts of VC in the downstream wells indicate that at least to some extent cDCE is further degraded to VC. However, similar to the source zone, the occurrence of chlorohydrocarbon degradation cannot be completely unravelled based on concentration measurements only, especially not the degradation from PCE to TCE since TCE might also originate from the contamination source.

**Source zone multilevel wells:**



**Downstream multilevel wells:**

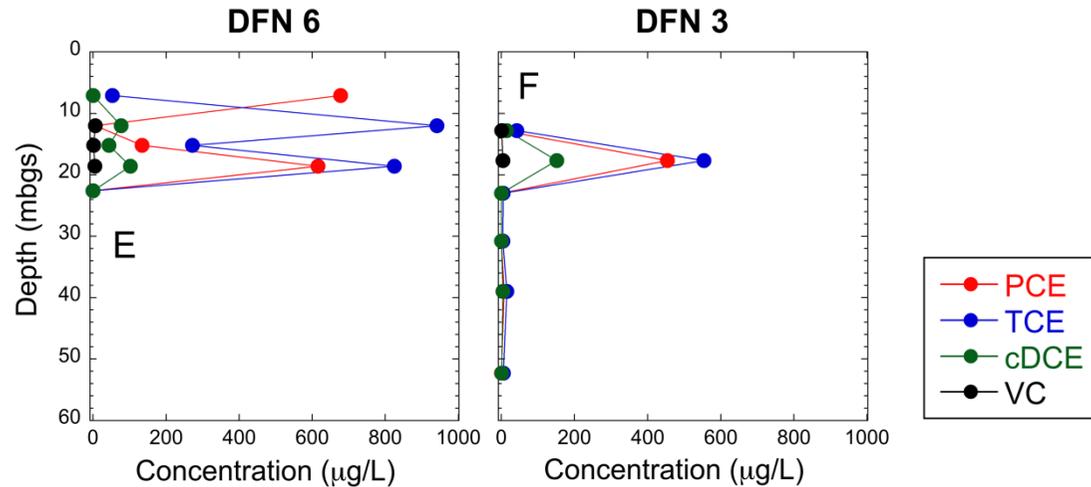


Figure 6. Measured chlorohydrocarbon concentration profiles in the multilevel wells in 2023 in the source zone (A-D) and farther downstream of the source (E-F). The filled red circles indicate the measured PCE concentrations, the blue filled circles the TCE, the filled green the cDCE, and the filled black circles the VC concentration.

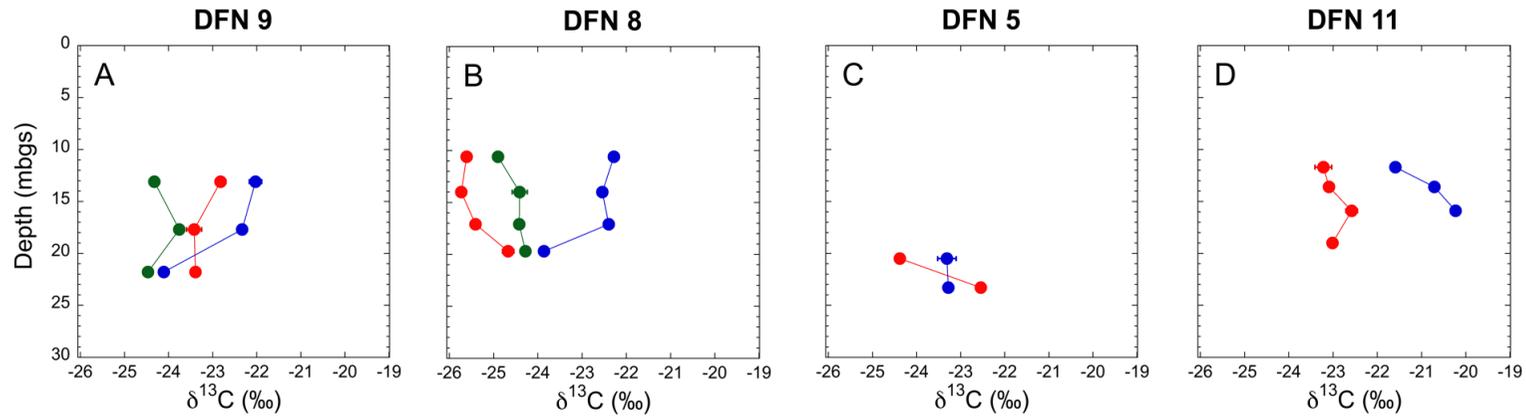
### 3.2. Compound-specific carbon isotope data 2023

To further explore the chlorohydrocarbon degradation at the Råven site, CSIA of the detected chlorohydrocarbons was carried out on the samples that were taken in 2023 (Tab. 1). Similar to the concentration profiles (Fig. 6), Figure 7 shows the CSIA profiles in the source zone along a long section (A-A') from northeast to southwest in DFN 9, 8, 5 and 11 (Figs. 7A-D) and in the downstream wells along a cross section (B-B') from northwest to southeast in DFN 3 and 6 (Figs. 7E and F).

In the source zone, at a depth shallower than 20 mbgs (Figs. 6A-D), TCE was more enriched in heavy carbon isotopes ( $^{13}\text{C}$ ) compared to PCE displaying  $\delta^{13}\text{C}$  values ranging between  $-23.86\text{‰}$  and  $-21.22\text{‰}$ , whereas PCE showed values between  $-25.73\text{‰}$  and  $-22.82\text{‰}$  (Tab. 1; Figs. 7A-D). This is opposite to what is expected for PCE degradation to TCE for which a higher enrichment of  $^{13}\text{C}$  in PCE compared to TCE would be anticipated. Hence, these opposite PCE and TCE  $\delta^{13}\text{C}$  trends suggest that the detected TCE in the immediate vicinity of the contamination source (<20 mbgs) mainly originates from the source dissolution and not from the degradation of PCE. In contrast, at a greater depth (>20 mbgs), TCE becomes more depleted in  $^{13}\text{C}$  compared to PCE in DFN 5 and 9 showing  $\delta^{13}\text{C}$  values ranging between  $-24.11\text{‰}$  and  $-23.28\text{‰}$  (Figs. 7A and C). The depletion of  $^{13}\text{C}$  in TCE compared to PCE at greater depth provides evidence for PCE degradation to TCE. This indicates that PCE degradation to TCE in the source zone predominantly occurs at a depth greater than 20 mbgs and to lower extent at shallower depth, closer to the contamination source, where the TCE likely originates mainly from the source itself. In addition to PCE and TCE, the presence of cDCE suggests further degradation of the TCE to cDCE, especially in wells DNF 9 and 8 (Figs. 7A and B). However, TCE degradation is likely not extensively occurring since TCE is not greatly enriched in  $^{13}\text{C}$  and the measured cDCE concentrations are rather low compared to the measured TCE concentrations. Moreover, also the  $\delta^{13}\text{C}$  cDCE values do not show a strong enrichment of  $^{13}\text{C}$  providing not much evidence for cDCE degradation to VC in the source zone, which is supported by the low or non-detects of VC in the source zone (Figs. 6A-D). Overall, the CSIA measurements in the source zone suggest only moderate to low chlorohydrocarbon degradation activities and only at a depth greater than 20 mbgs.

As opposed to the source zone, the CSIA of the chlorohydrocarbons in the downstream wells indicate higher degradation activities. PCE is mostly more enriched in  $^{13}\text{C}$  compared to TCE (Figs. 7E and F) showing  $\delta^{13}\text{C}$  values between  $-24.46\text{‰}$  and  $-19.94\text{‰}$ , whereas TCE shows lower  $\delta^{13}\text{C}$  values ranging between  $-27.09$  and  $-21.22\text{‰}$  (Tab. 1). The higher enrichment of  $^{13}\text{C}$  in PCE compared to TCE also in the high concentration zone indicates PCE degradation to TCE in the downstream wells, which contrast the source zone, where PCE degradation only occurs at a depth greater than 20 mbgs. The occurrence of PCE degradation to TCE in the downstream wells is further reinforced by the higher TCE concentrations in comparison to PCE (Figs. 6E and F). Moreover, the significant cDCE concentrations in the downstream wells indicate TCE degradation to cDCE, which are, however, not reflected by a strong enrichment of  $^{13}\text{C}$  in TCE (Figs. 7E and F). The low  $^{13}\text{C}$  enrichment in TCE despite its degradation to cDCE is likely related to the continuous production of isotopically light TCE from the degradation of PCE, which occurs at the same time as TCE degradation to cDCE. Furthermore, the presence of VC in the downstream wells suggests VC production by cDCE degradation. However, this could not be further substantiated by the CSIA data since the cDCE concentrations in the downstream wells were below the detection limit for CSIA.

**Source zone multilevel wells:**



**Downstream multilevel wells:**

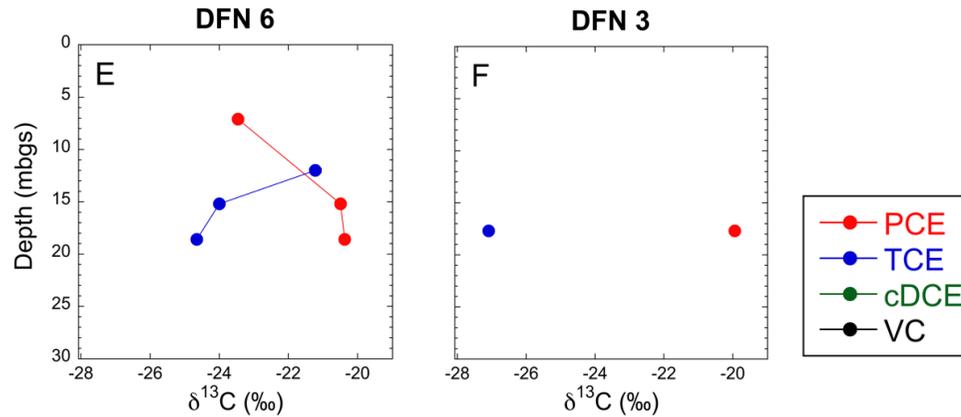


Figure 7. Measured compound specific carbon isotopes ratio (CSIA) profiles in the multilevel wells in 2023 in the source zone (A-D) and farther downstream of the source (E-F). The filled red circles indicate the measured PCE stable carbon isotope ratios, the blue filled circles the TCE and the filled green the cDCE stable carbon isotope ratios. The error bars indicate the CSIA uncertainties, whereas where the error bars are not visible, the uncertainty is smaller than the size of the symbol.

**Table 1. Compound-specific carbon isotope analysis results from the samples taken in March 2023**

Well	Port	Depth (mbgs)	PCE (µg/L)	$\delta^{13}\text{C}_{\text{PCE}}$ (‰)	TCE (µg/L)	$\delta^{13}\text{C}_{\text{TCE}}$ (‰)	cDCE (µg/L)	$\delta^{13}\text{C}_{\text{cDCE}}$ (‰)
DFN3	2	17.7	454	-19.94±0.15	554	-27.09±0.08	152	b.d.
DFN5	1	20.5	1160	-24.38±0.11	408	-23.31±0.21	b.d.	b.d.
	2	23.3	848	-22.54±0.07	358	-23.28±0.07	b.d.	b.d.
DFN6	1	7.1	678	-23.46±0.03	53.4	b.d.	0.618	b.d.
	2	12.0	6.61	b.d.	942	-21.22±0.16	76.9	b.d.
	3	15.2	134	-20.49±0.12	272	-24.00±0.11	43.9	b.d.
	4	18.6	616	-20.37±0.12	825	-24.65±0.13	102	b.d.
DFN8	2	10.6	8720	-25.61±0.07	1100	-22.28±0.11	695	-24.90±0.05
	3	14.0	14900	-25.73±0.07	3840	-22.54±0.08	1560	-24.41±0.17
	4	17.1	27700	-25.41±0.10	5160	-22.40±0.09	1740	-24.42±0.07
	5	19.7	6730	-24.67±0.13	2560	-23.86±0.06	1280	-24.28±0.05
DFN9	3	13.1	42400	-22.82±0.12	15800	-22.03±0.14	1880	-24.32±0.06
	4	17.7	14600	-23.42±0.17	6560	-22.33±0.08	1130	-23.76±0.01
	5	21.8	815	-23.39±0.05	1020	-24.11±0.08	1170	-24.47±0.09
DFN11	2	11.7	2560	-23.22±0.19	607	-21.59±0.02	60.7	b.d.
	3	13.6	1450	-23.09±0.05	929	-20.71±0.02	73.1	b.d.
	4	15.9	226	-22.58±0.13	341	-20.23±0.09	18.5	b.d.
	5	19.0	135	-23.01±0.03	20.3	b.d.	4.05	b.d.
DFN12	4	11.9	10000	-23.95±0.12	2680	-21.65±0.09	1040	-22.43±0.26
	6	18.2	65.5	-23.90±0.27	59.7	-20.04±0.43	49	b.d.
DFN13	5	15.9	59.2	-22.50±0.33	368	-20.16±0.09	b.d.	b.d.
DFN15	5	14.6	2010	-20.69±0.17	3080	-21.28±0.24	502	T.t.h.
	6	17.8	258	-20.52±0.01	626	-19.55±0.25	84.8	b.d.
	7	21.2	149	-22.09±0.19	169	-19.73±0.46	22.7	b.d.

b.d.: below detection limit

T.t.h.: Turbidity too high for CSIA

In the addition to the isotope profiles, the CSIA data can also be used for estimating to what extent, the observed chlorohydrocarbon concentration decrease with respect to the source zone is related to degradation and/or dilution. To this end, the measured PCE  $\delta^{13}\text{C}$  data was evaluated with a so-called Rayleigh plot according to equation 2 (Fig. 8). In this Rayleigh plot, the y-axis corresponds to the measured  $\delta^{13}\text{C}$  values, the x-axis to the natural logarithm of the remaining PCE fraction with respect to the source ( $\ln f$ ), and the slope to the isotope enrichment factor ( $\epsilon$ ), respectively (Fig. 8). For the starting point ( $\ln f = 0$ ) it was assumed that the PCE concentration in the contamination source corresponds to the PCE solubility limit (200,000 µg/L) being justifiable by PCE concentration measurements in 2021, being close the PCE solubility limit (178,000 µg/L). Moreover, for the initial  $\delta^{13}\text{C}$  value of the source ( $\delta^{13}\text{C}_0$  in eq. 2), the most negative measured  $\delta^{13}\text{C}$  value (-24.73‰) was used as an approximation. To evaluate if the observed PCE concentration decrease with respect to the source is related to degradation and/or dilution, the expected isotope evolution for PCE degradation only was plotted in the Rayleigh plot for a PCE isotope enrichment factor of -10.8‰ (solid black line, Fig. 8). This enrichment factor corresponds to the average PCE isotope enrichment factor found in the literature (Wanner et al., 2016). Moreover, the expected isotope evolution for PCE degradation only was also plotted for two other PCE isotope enrichment factors including -1.7‰ and -19.9‰ (dashed lines, Fig. 8) corresponding to the  $\pm 1\sigma$  standard deviation of the average isotope enrichment factor (-10.8‰). Finally, the isotope evolution for PCE for dilution only was added to the Rayleigh plot corresponding to the horizontal black line (Fig. 8).

Figure 8 shows that the measured PCE  $\delta^{13}\text{C}$  values plot generally closer to the dilution evolution and further away from the degradation evolution line of the average PCE average isotope enrichment factor ( $-10.8\text{‰}$ ) as well as of the  $\pm 1\sigma$  standard deviation PCE enrichment factors (Fig. 8). This indicates that although PCE degradation contributes to some extent to the PCE concentration decrease at the site compared to the source zone it is mainly triggered by dilution processes. This shows the extent of the plume is controlled by physical rather than reactive processes.

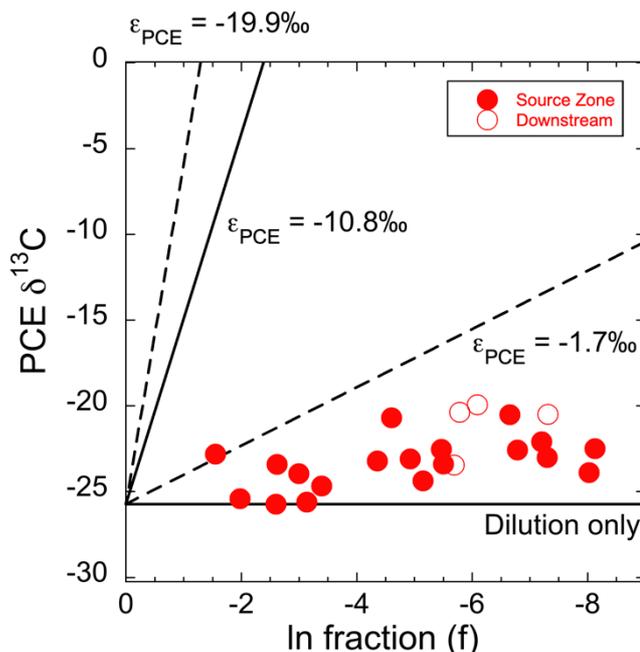


Figure 8. Rayleigh plot for the measured PCE stable carbon isotope data (eq. 2). The filled red circles are the source zone wells and the red open circles are the downstream wells. The solid line black line corresponds to the expected PCE carbon isotope evolution for degradation only with the average PCE isotope enrichment factor found in the literature ( $-10.8\text{‰}$ ). The dashed lines represent the expected isotope evolution for PCE degradation only for two other PCE isotope enrichment factors ( $-1.7\text{‰}$  and  $-19.9\text{‰}$ ) corresponding to the  $\pm 1\sigma$  standard deviation of the average isotope enrichment factor found in the literature. Moreover, the horizontal solid black line corresponds to the expected carbon isotope evolution if PCE concentrations were affected by dilution only.

## 4. Conclusions

In this study, we carried out for the first time high-resolution CSIA field measurements in Sweden at a chlorohydrocarbon-contaminated site in Helsingborg. The results show that in the source zone, only low chlorohydrocarbon degradation activities occur at a depth  $<20$  mbgs and that TCE, previously considered as a degradation product of PCE, was likely also part of the contamination source and was released simultaneously with PCE at the site. Moreover, in the source zone, the degradation stalled mainly at cDCE and did not proceed further to VC. In the downstream wells, the chlorohydrocarbon concentrations decreased by more than two orders of magnitude, and higher degradation activities were detected compared to the source zone, which also proceeded to some extent to VC. However, despite of the higher degradation activities in the downstream wells, the concentration decrease compared to the source zone was related to a higher degree to dilution compared to degradation.

## 5. References

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