SNOWMAN

Sustainable ma**N**agement of s**O**il and ground**W**ater under the pressure of soil pollution and soil conta**M**in**A**tio**N**

Project No. SN-01/24

ENACT

Extending the Monitored Natural Attenuation Toolbox for Chlorinated Solvents

Final Research Report

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Toolbox for Chlorinated Solvents

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Project No. SN-01/24

ENACT

Extending the Monitored Natural Attenuation

Toolbox for Chlorinated Solvents

Final Research Report

Contributing authors

Boris van Breukelen (Vrije Universiteit Amsterdam)
Martin Elsner (Hemholz Zentrum München)
Johan Gemoets (VITO)
Toon De Ceuster (VITO)
Kaori Sakaguchi-Söder (Technische Universität Darmstadt)
Harry Veld (Deltares TNO)
Frank Volkering (Tauw bv)*

*: Project manager

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1 The ENACT project

1.1 Scope of the project

With chlorinated solvents being by far the most occurring groundwater contaminants from point sources, the natural attenuation (NA) of the compounds is increasingly recognized as an important issue in protecting groundwater reserves.

Studying the natural attenuation is focused on the occurrence of biological reductive dechlorination, the well-known process involving a stepwise removal of chlorine atoms until harmless compounds such as ethene and ethane are formed.

Extensive practical experience at contaminated sites has learned that in up to 53% of the cases contaminated with PCE or TCE, incomplete reductive dechlorination may occur, see the figure below for an overview of NA characteristics at PCE-contaminated sites in western Europe. This incomplete degradation leads to the accumulation of the intermediates *cis*-dichloroethene (cDCE) and/or vinyl chloride (VC). Since these degradation products are more mobile and more toxic than the original contaminants, application of monitored natural attenuation (MNA) is generally considered not to be a viable option for these cases.
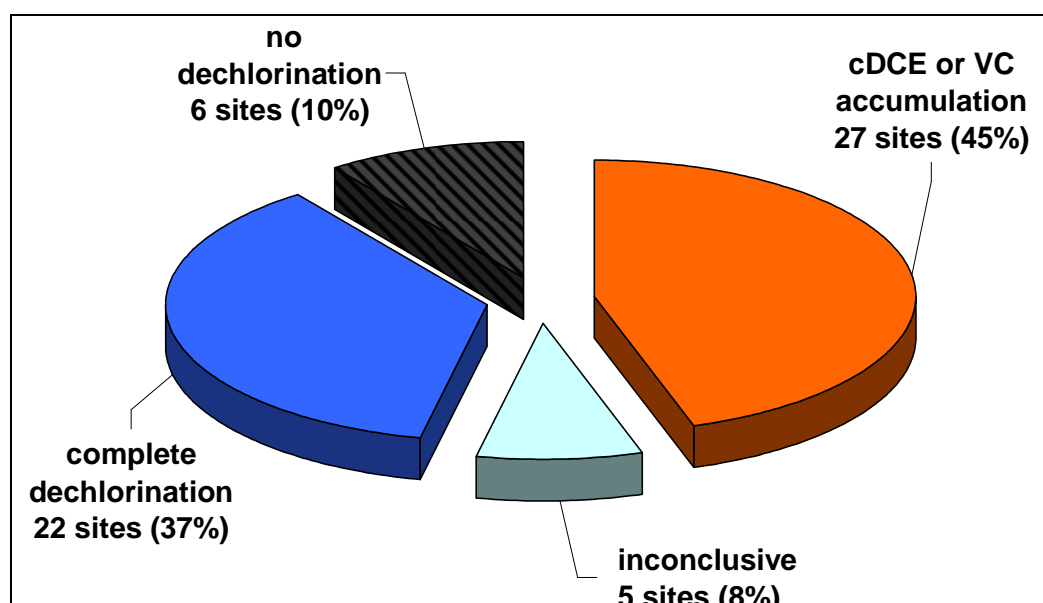

no dechlorination 6 sites (10%)

cDCE or VC accumulation 27 sites (45%)

complete dechlorination 22 sites (37%)

inconclusive 5 sites (8%)

Figure 1.1 Natural attenuation characteristics at 60 PCE-contaminated sites in western Europe (source: internal R&D project Tauw)

Recent scientific studies have shown that for chlorinated solvents, degradation mechanisms other than biological dechlorination may play a role: abiotic reduction by Fe(II)minerals (Ferrey et al, 2004; Wilson 2004) and biological anaerobic oxidation of lower chlorinated intermediates (Bradley, 2000). The figure below gives an overview of these "new" MNA mechanisms

Providing evidence for the occurrence of abiotic reduction and anaerobic oxidation is not straightforward. Biological oxidation does not lead to the formation of specific end products. Chloroacetylene and acetylene, the main products of abiotic reduction, are expected to be instable in the subsurface.

In a recent project, a toolbox for demonstrating the occurrence of these new MNA mechanisms for chlorinated hydrocarbons has been developed. In this SKB- project, stable carbon isotope analysis and detection of new intermediates/end products are used for studying abiotic reduction by Fe(II)minerals and biological anaerobic oxidation of the lower chlorinated degradation products. Compoundspecific stable carbon isotope analysis (^{13}C-CSIA), which has been shown a very versatile tool for studying complex MNA-cases with chlorinated hydrocarbons, is the more powerful of these two methods.

^{13}C-CSIA is increasingly becoming an accepted method for studying natural attenuation and ^{2}H-CSIA has been applied successfully to study natural attenuation of aromatic hydrocarbons and MTBE. The USEPA has recently published a guide on application of CSIA which provides an excellent overview (USEPA, 2008). For VOCl, however, ^{2}H-CSIA is not suited.

Very recently, compoundspecific stable chlorine isotope analysis (^{37}Cl-CSIA) has become practically available. By including ^{37}Cl-CSIA, it will be possible to construct two-dimensional isotope plots, which are known to provide strong evidence on the processes occurring in the subsurface. For example, two-dimensional isotope analysis with both stable carbon and stable hydrogen analysis allowed the discrimination of aerobic versus anaerobic degradation of MTBE (Zwank et al, 2005, see the figure below) and provided clear evidence on anaerobic natural attenuation of benzene (Mancini et al., 2001).
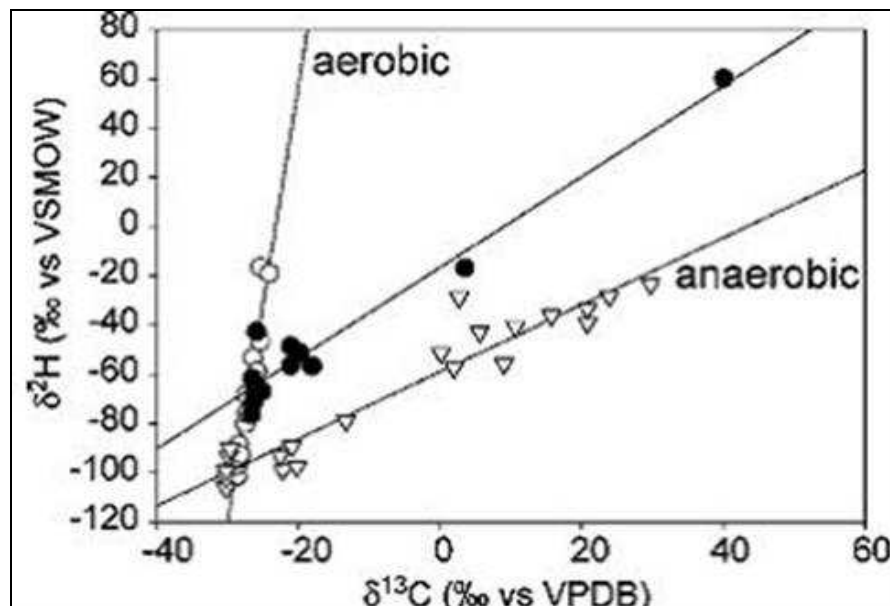
Figure 1.2 Example of the use of two-dimensional isotope plots: differentiation of aerobic and anaerobic MTBE biodegradation by combined carbon and hydrogen isotope analysis (Zwank et al., 2005)

The objective of the ENACT project is to enhance the toolbox for MNA of chlorinated solvents by including stable chorine isotope analysis and to demonstrate its use at contaminated sites.

References

Bradley P.M. (2000) Microbial degradation of chloroethenes in groundwater systems. Hydrogeology Journal 8, 104-111.

Ferrey M.L et al (2004). Nonbiological Removal of cis-Dichloroethylene and 1,1-Dichloroethylene in Aquifer Sediment Containing Magnetite. Environmental Science & Technology.38:1746-1753.

Mancini et al (2002) Hydrogen isotopic enrichment: a definitive indicator of biodegradation at a petroleum contaminated site. Environmental Science and Technology 36: 2464-2470

Wilson J.T. (2003) Abiotic reactions may be the most important mechanism in natural attenuation of chlorinated solvents. AFCEE Technology Transfer Workshop, Feb. 2003, Brooks Air force Base, San Antonio, TX

US EPA (2008) A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA). Available via www.epa.gov/ada

Zwank et al., 2005; New Evaluation Scheme for Two-Dimensional Isotope Analysis to Decipher Biodegradation Processes: Application to Groundwater Contamination by MTBE. Environmental Science & Technology 39(4) 1018-1029

1.2 Stable isotope theory

Chlorinated hydrocarbons consist of carbon, chlorine and hydrogen. All these elements consist of two stable isotopes: carbon consists of ^{12}C and ^{13}C, chlorine of ^{35}Cl and ^{37}Cl and hydrogen of ^{1}H and ^{2}H. The different isotopes behave slightly different in various processes and by measuring the isotope

ratio, it can be determined to which extent the compounds involved have been subject to degradation processes

Physical, chemical and biological processes may affect this stable isotope ratio. This so-called fractionation results in a difference in the isotopic signature of the original compound and that of the residual compound. In this report the enrichment factor ε will be used to characterize isotopic fractionation. For carbon, this factor is defined as:

$$\varepsilon \; = \; \frac{^{13}C/^{12}C_{freshly\,formed\,product}}{^{13}C/^{12}C_{residual\,substrate}} - 1 \; (‰)$$

In a closed system, fractionating processes can be described with the Rayleigh equation:

$$R = R_0 * f^{\varepsilon}$$

In which R is the isotope ratio (-) and f is the fraction of remaining reactant. A graphical example of the fractionation during a biological or chemical reaction with an enrichment factor of 6‰ is given in **Figure 1.3**. During the reaction, the parent compound (having an initial δ of -30‰) is enriched in ^{13}C. The product formed initially has a δ-value of -30 – ε = -36‰. When the reaction is completed, the product has the same δ-value as the parent compound at the start of the reaction.
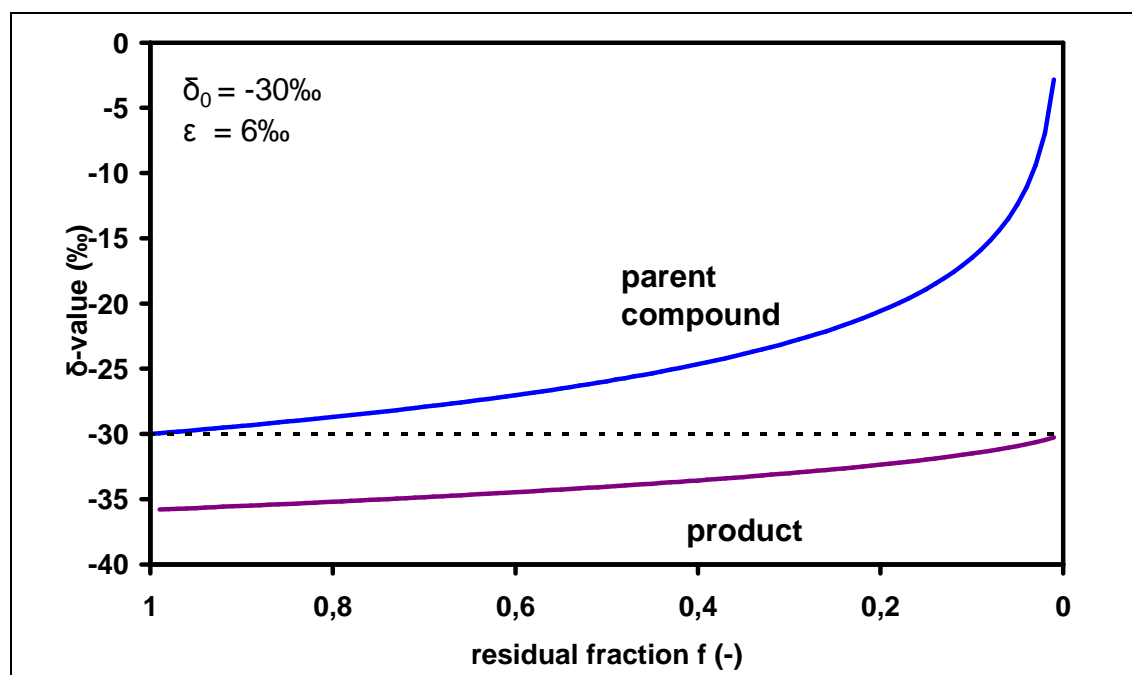

Figure 1.3: Carbon isotope composition of parent compound and product according to the Rayleigh equation during the course of a fractionating reaction.

For chlorine, the situation is different from carbon since the dechlorination reaction causes the removal of the chlorine atom from the molecule. The effect of this on the stable chlorine isotope was not know at the start of the ENACT project.

Other processes such as dissolution, sorption, dilution and transport with groundwater have no significant effect on the isotopic composition. In cases with PCE and TCE in groundwater, degradation processes can be considered the only natural processes affecting the isotope signature of the VOCl.

1.3 ENACT consortium and activities

The ENACT consortium consisted of the following partners:

Tauw bv, The Netherlands   Frank Volkering (project manager)

Technische Universität Darmstadt, Gemany   Kaori Sakaguchi-Söder

VITO, Belgium   Johan Gemoets, Toon De Ceuster

Vrije Universiteit Amsterdam, The Netherlands   Boris van Breukelen

DeltaresTNO, The Netherlands   Harry Veld

Helmholtz Zentrum München, Germany   Martin Elsner

The activities of the ENACT project were divided in six work packages (WPs):

WP 1   Project management.

WP 2   Optimization of the stable chlorine isotope analysis, making it suited for application at field sites

WP 3   Laboratory experiments to determine the chorine isotope fractionation factors of biological reductive dechlorination and the carbon and chlorine isotope fractionation factors of abiotic reduction

WP 4   Modeling chlorine isotope fractionation during reductive dechlorination of chloroethenes

WP 5   Application of the natural attenuation toolbox, including stable carbon and chlorine isotope analysis, at three VOCl-contaminated demonstration sites

WP6   Dissemination of the results

The results of the WPs 2-5 have been published in separate reports. In the next chapters of this report, the results are summarized, followed by a concluding chapter.

2 Optimizing measurement conditions for chlorine isotope analyses

2.1 A simple online method for compound-specific stable chlorine isotope analysis

In 2004, the Institut WAR at Darmstadt University of Technology (TUD) developed a simple and quick method for compound-specific stable chlorine isotope analysis (^{37}Cl-CSIA) while working on a sub-project of the BMBF funding priority KORA (Förderschwerpunkt "KORA - Kontrollierter natürlicher Rückhalt und Abbau von Schadstoffen bei der Sanierung kontaminierter Grundwässer und Böden) between 2003 and 2007. Using this new method, compound-specific chlorine isotope analysis can be performed by direct injection using a conventional quadrupole GC/MS. Unlike other chlorine isotope method, the new method requires neither up-stream chemical conversions (e.g. CAH $\rightarrow$ CH$_3$Cl) nor a special analytical instrument. Instead, the chlorine isotope ratio can be determined simply by analyzing peak areas of selected molecular and fragment ions of a substance of interest.

In the BMBF KORA project, it was verified that the method is applicable to determine chlorine isotope ratio of chlorinated ethenes as well as fractionation factors during abiotic and biological reductive degradation processes of PCE and TCE. The results showed that compound-specific stable chlorine isotope analysis can be performed with sufficient precision by means of a conventional quadrupole GC/MS when significant fractionation takes place during biochemical transformation processes. Concept of the method as well as major outcomes of the project were published in a technical paper entitled "Monitoring and evaluation of dechlorination processes using compound-specific chlorine isotope analysis" in *Rapid Communications in Mass Spectrometry* in 2007.

Advantages of the new chlorine isotope methods are:

- No upstream, offline sample pretreatment is necessary
- A standard quadrupole GC/MS can be used for ^{37}Cl-CSIA
- By direct injection of headspace, ^{37}Cl-CSIA of a mixture of PCE, TCE, DCE-isomers and VC can be completed within 30 minutes
- In principle, the method is applicable to any chlorine-containing compounds that can be separated by GC

2.2 Objectives

Through KORA project it was demonstrated that ^{37}Cl-CSIA on chlorinated ethenes can be performed with sufficient precision (< ±1 ‰) by direct headspace injection. In the ENACT project, the method was optimized to make it suited for analyzing field samples, specifically for chlorinated ethenes in aqueous solutions with a concentration lower than 200 µg/L. Important aspects with respect to this WP are defining the lower limits of quantification and the precision of the method under optimized measurement conditions using an enrichment technique Purge and Trap (P&T).

2.3 Results

The use of the P&T system could significantly improve the sensitivity in determining chlorine isotope compositions (δ^{37}Cl-values) for VC, tDCE, cDCE, TCE and PCE. When the ^{37}Cl-CSIA was performed with a certain concentration, a high internal precision was achievable for these chlorinated ethenes with a lower concentration:

- VC: ±0,2‰ (1σ, n=4) at the concentration of 33 µg/L
- tDCE: ±0,3‰ (1σ, n=4) at the concentration of 3,6 µg/L
- cDCE: ±0,9‰ (1σ, n=4) at the concentration of 14 µg/L
- TCE: ±0,3‰ (1σ, n=4) at the concentration of 10,7 µg/L
- PCE: ±0,4‰ (1σ, n=4) at the concentration of 9,1 µg/L

Further, a linearity test was carried out for each chlorinated ethene to determine peak area dependency of the method for ^{37}Cl-CSIA. To some extent δ^{37}Cl values were influenced by peak area, i.e. injected masses. For TCE and PCE, δ^{37}Cl values were stable by the change in peak areas whereas a significant change in δ^{37}Cl values was observed for VC, tDCE and cDCE. In all cases, the relationship between the δ^{37}Cl and peak areas could be well described using a polynomial regression line. A high correlation coefficient (R^2>0,9) was obtained when the regression was performed in a certain range of peak areas.

To obtain constant and comparable results, it is recommended to work with a constant peak area.When ^{37}Cl-CSIA cannot be performed with a fixed concentration (i.e. a constant peak area) peak area correction should be applied and raw δ^{37}Cl values should be corrected using a polynomial regression derived by a linearity test for each chlorinated ethenes.

For chlorine isotope analysis for field as well as batch samples for the project ENACT, the following measures were taken to obtain comparable data sets:

(1) Chlorine isotope analysis was carried out using the P&T system; purging conditions were set at temperature of 40 ℃ for 10 min.
(2) Sample concentrations were adjusted before the P&T analysis so that the chlorine isotope analysis could be done with a fixed concentration (or a narrow range in concentration).
(3) Raw δ^{37}Cl values were corrected using polynomial regression formulas derived through linearity tests to obtain comparable a data set

With this, the compound-specific stable chlorine isotope analysis of VOCl meets the requirements of the ENACT project.

An important point of attention is the need for ^{37}Cl-VOCl standards. Standard Mean Ocean Chloride (SMOC), which generally used as a reference substance to determine δ^{37}Cl values, is not appropriate for the GC/MS method. Since international ^{37}Cl-VOCl standards are currently not available, the δ^{37}Cl values in this project were determined using a commercial PCE standard as a reference substance. Because the δ^{37}Cl value determined relative to SMOC of this standard is unknown, δ^{37}Cl values reported in this project are relative to this PCE standard; not absolute values. Delta values obtained were reasonable to derive fractionation factors as well as to determine the degree of fractionation for a given substance when ^{37}Cl-CSIA was carried out by analyzing a certain mass, i.e. peak area or when peak area correction was performed on raw data to be compared. However, to compare the isotope ratio or δ^{37}Cl values between substances (e.g., a substrate and its degradation products), the method should be calibrated using standards of known δ^{37}Cl values.

As a follow-up of the ENACT project, VOCl chorine isotope standards are presently being developed in an international cooperation.

3 Laboratory experiments

Work package 3 of the ENACT project consisted of laboratory experiments on the biotic and abiotic degradation of chlorinated ethenes to determine the stable carbon and chlorine isotope fractionation caused by these processes.

3.1 Biodegradation

In the biodegradation tests, PCE, TCE, cDCE and VC were used as starting compounds. Biodegradation proceeded in all cases to ethene; production of acetylene and ethane was not observed in this test. Since the carbon isotope fractionation of biological reductive dechlorination is well-known, only the chlorine isotope behaviour was studied.

Analysis of the ^{37}Cl-content of the original chloroethenes during the experiments showed a significant fractionation for PCE, TCE and VC, but not for cDCE. Modelling of the results including those of intermediates, however, suggests that cDCE-reduction must be associated with a fractionating effect. Figure 3.1 gives a plot of the isotope fractionation as a function of the degradation of the original compound. The slope of the linear line in this plot is a represents the overall isotope enrichment factor ε, which is the most commonly used parameter for characterizing isotope fractionation.
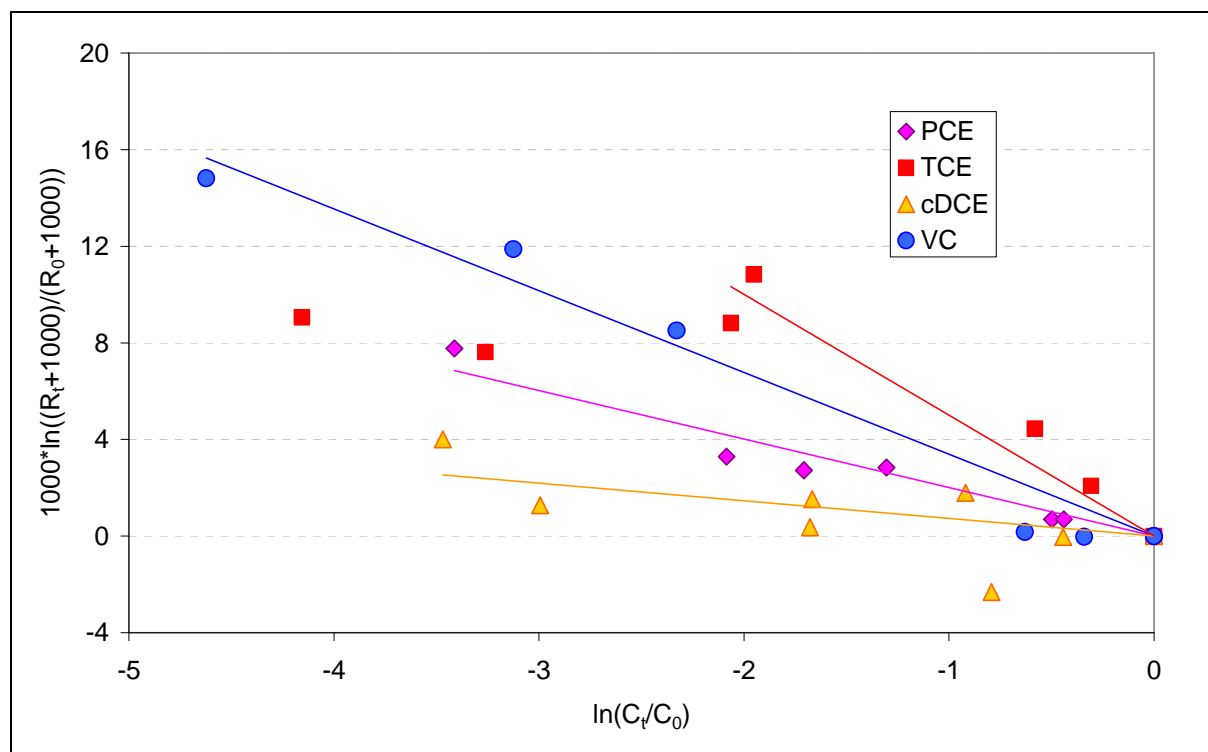

Figure 3.1 linear plot of ^{37}Cl-fractionation of chloroethenes by biological reductive dechlorination

The enrichment factors determined for the individual chloroethenes are given in table 3.1

Table 3.1 chlorine istope enrichment factors redcutive dechlrinmation of individual VOCl

compound	chlorine isotope enrichment factor ε_{Cl} (‰)
PCE	-2.2 (R = 0.975)
TCE	-5.0 (R = 0.94)
cDCE	-0.9 (R= 0.695)
VC	-3.6 (R =0.956)

3.2 Abiotic reduction

In the abiotic experiments the reduction of the individual chloroethenes PCE, TCE, cDCE and VC by two different minerals was studied: iron sulphide (FeS) and pyrite.

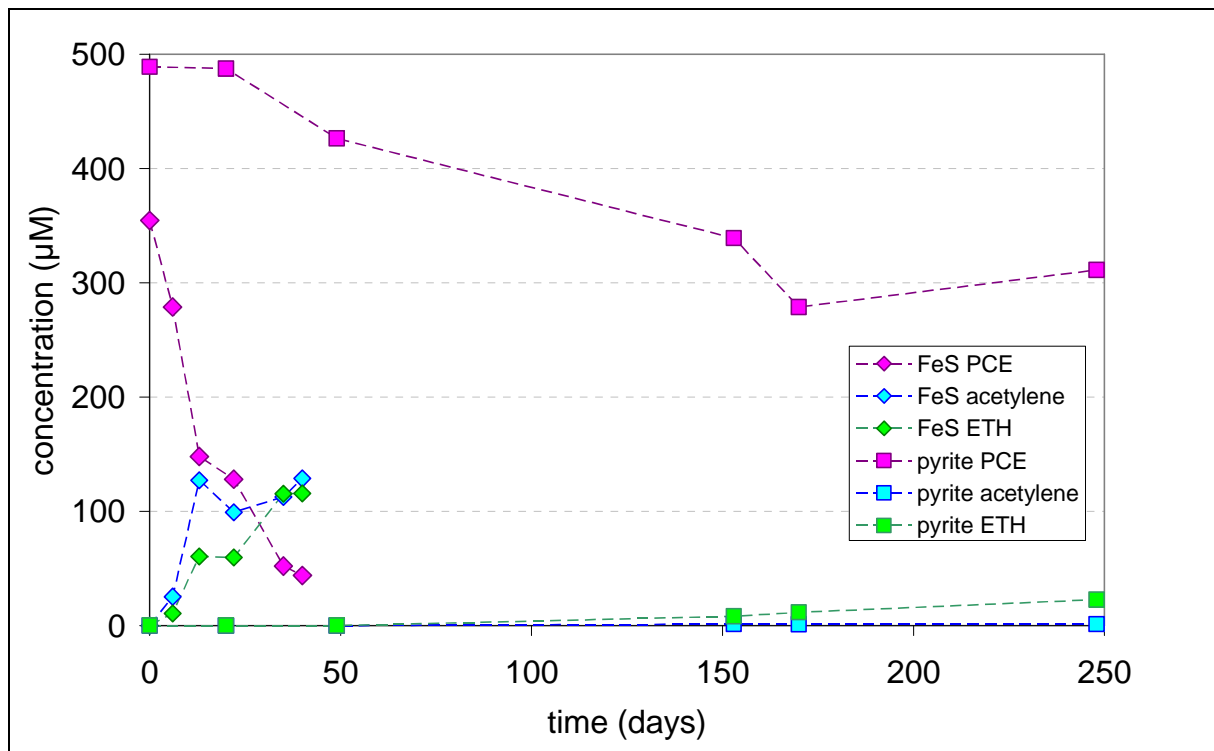Figure 3.2.gives a typical example of results of the abiotic experiments.

Figure 3.2 Degradation of PCE and formation of acytylene and ethene (ETH) in microcosms with FeS (diamonds) and pyrite (squares)

Degradation of PCE and TCE by FeS was fast; further degradation of the reaction products (cDCE, VC and acetylene) was much slower. Formation of acetylene was observed when parent compounds were PCE, TCE and cDCE, but not with VC as starting material. Vinyl chloride was not detected as a reaction product from PCE, TCE or cDCE with FeS. During the abiotic dechlorination of the chloroethenes by FeS (except for VC) many reaction products were formed:

- TCE (from PCE)
- cDCE (from TCE and PCE)
- acetylene (from PCE, TCE and cDCE)
- ethene and ethane (from PCE, TCE, cDCE and VC)

- a number of unidentified compounds.

Reliable isotopic enrichment factors for carbon and chlorine have been determined for reduction of PCE and TCE by FeS. Reduction of cDCE and VC by FeS also causes isotopic fractionation, but the data did not allow calculation of enrichment factors.

Abiotic dechlorination by pyrite was observed, but at much slower reaction rates than with FeS. The number of unidentified reaction products was limited. Contrary to the results with FeS, production of VC was observed. The main end products found were ethane and ethane, while acetylene accounted only for a very small fraction of dechlorination products. Reduction by pyrite caused significant carbon and chlorine isotope fractionation in most, but not all chloroethenes. Due to the slow reaction rates and the limited timeframe, it was not possible to obtain samples with sufficient degradation to determine reliable enrichment factors.

Figure 3.3 shows the double isotope plots for reduction of PCE and TCE by FeS and pyrite. Reduction by FeS causes stronger carbon isotope fractionation than chlorine isotope fractionation for both PCE and TCE. In contrast, isotope fractionation in PCE during reduction by pyrite appears to be stronger for chlorine than for carbon.
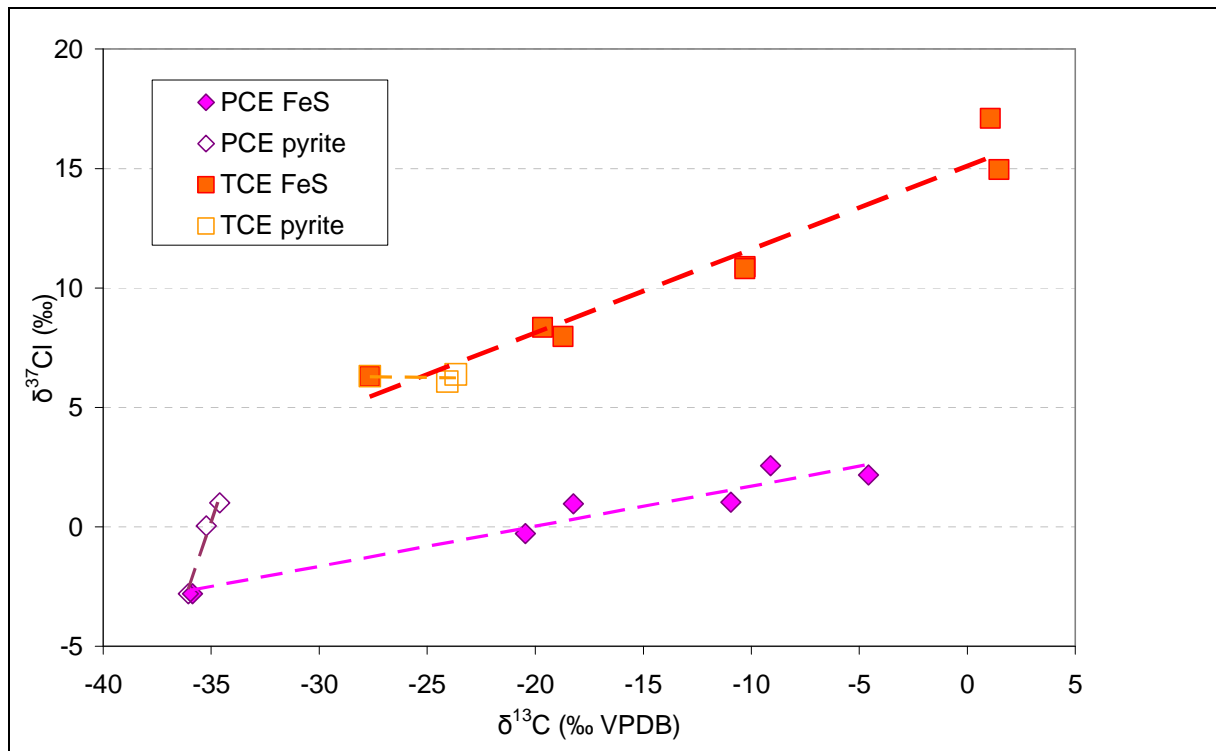

Figure 3.3 chlorine-carbon stable isotope plot for reduction of PCE and TCE by FeS and pyrite

Table 3.2 charateristics of carbon and chlorine isotope enrichment of chloroethenes during reduction by FeS and pyrite

compound	FeS		pyrite	
	$\varepsilon\ ^{13}C$ (‰)	$\varepsilon\ ^{37}Cl$ (‰)	^{13}C fractionation	^{37}Cl fractionation
PCE	-19.1 (R^2 = 0.80)	-3.14 (R^2 = 0.65)	significant	significant
TCE	-10.8 (R^2 = 0.98)	-3.30 (R^2 = 0.97)	significant	not significant
cDCE	High	high	not significant	not significant
VC	Significant	significant	significant	unclear

3.3 Conclusions from the lab experiments

In the biological experiments, chlorine isotope enrichment factors have been determined for the individual chloroethenes. Interpretation of the results intermediates is hampered by the relative nature of the chlorine isotope data.

In the abiotic experiments, fast reduction of PCE and TCE was found with FeS and slow reduction was found with pyrite. For reduction by FeS reliable carbon and chlorine isotope enrichment factors have been obtained. Reduction by pyrite was shown to have a fractionating effect, but the reaction rates were too low to determine enrichment factors.

The results of the abiotic experiments suggest a different reaction mechanism for the reactions with FeS and with pyrite.

4   Modelling chlorine isotope fractionation

4.1   Theory

Describing chlorine isotope fractionation during reductive dechlorination can not be done using the approach taken before by Van Breukelen et al. (2005) for simulation of carbon isotope fractionation. Chloroethenes only contain two carbon atoms and the chance that both of them are heavy ^{13}C isotopes is very low (~1% $\times$ ~1% = ~0.01%). Carbon isotope fractionation can, therefore, be simplified as the simulation of the individual carbon isotopes in a pool of bulk compound. In contrast to carbon, simulation of chlorine isotope fractionation must consider all the possible isotopologues (molecules that differ only in their isotopic composition) because:

1. The abundance of the 'rare' and heavy chlorine isotope is high with 24.2 % (^{37}Cl/[^{37}Cl +^{35}Cl])
2. Higher chlorinated ethenes contain up to four chlorine atoms (PCE) making isotopologues with multiple heavy chlorine isotopes likely
3. At each degradation step a chlorine atom (isotope) is removed from a chlorinated ethene.

This has far-reaching consequences for describing stable chorine isotope behaviour during reductive dechlorination. The theory behind this is described in detail in the report of WP 3 and in the publications by Elsner and Hunkeler et al 2008, and Hunkeler , Elsner and Van Breukelen (2009). The latter of these two publications is a direct result of the ENACT project. The most important effects are:

  – the behaviour of the parent compound can, as for carbon, be describe using he Rayleigh equation
  – in contrast to carbon, the product is not depleted in heavy chorine isotopes and has the same chlorine isotope signature as the parent compound
  – the TCE to DCE reduction is different from the other reactions because this is a stereo-selective reaction with preferential production of *cis*-DCE over *trans*-DCE

In figure 3.1 the differences between the carbon and chorine isotope behaviour is shown for the reductive dechlorination of PCE to TCE.
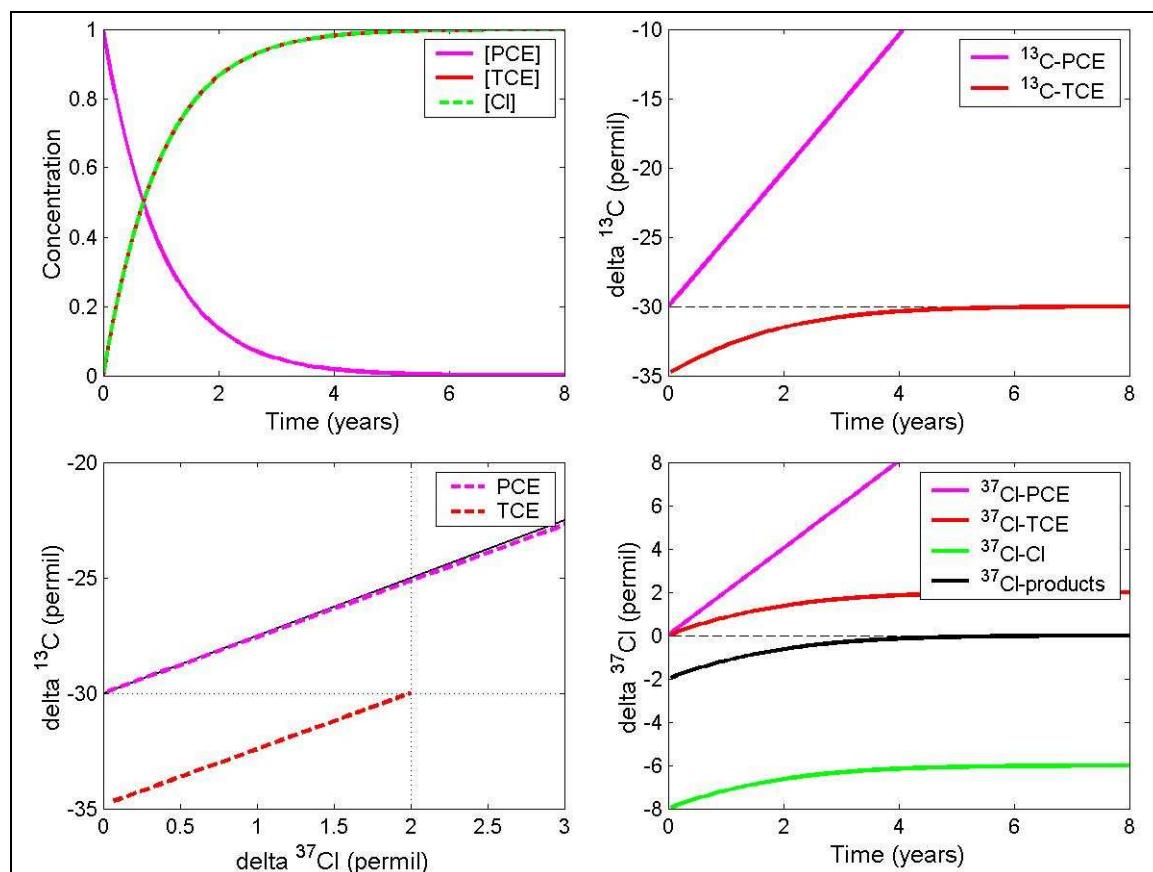
Figure 4.1 PCE to TCE reductive dechlorination (first-order PCE degradation rate constant = 1 per year; ε_C = -5‰; ε_{Cl} = -2‰ ($\varepsilon_{Cl, KIE}$ = -8‰)). TCE is not further degraded.

4.2 Scenario modelling

The theoretical considerations above have been used to construct a 1D-model in the model code PHREEQC, suited for describing both the carbon and the chlorine isotope fractionation during reactive transport of chloroethenes in groundwater. Using this 1D-model, simulation of various realistic field scenarios has been performed. Figure 3.2 gives an example of the results for the case of a constant PCE source with complete dechlorination to ethene with decreasing degradation rates.

It is known from application of ^{13}C-CSIA that the results of more complicated cases can be very difficult to interpret and that modelling is highly useful or even required in such cases. The model developed in this project is suited for interpreting combined carbon and chlorine isotope data from field sites and forms en essential tool in filed application of double isotope analysis for VOCl.
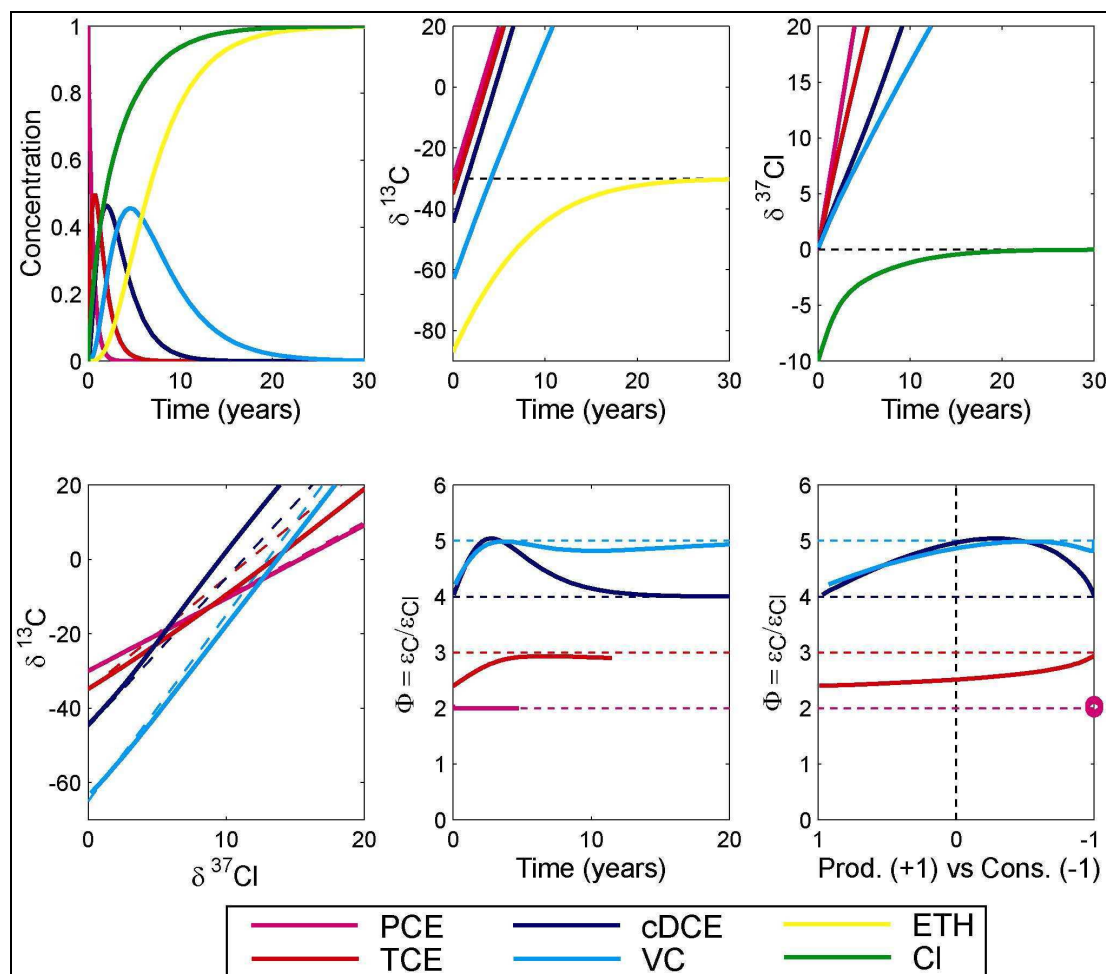
Figure 4.2 Sequential chlorinated ethene degradation ([PCE] initial = 1; δ¹³C-PCE initial = -30‰; δ³⁷Cl-PCE initial = 0‰; decreasing first-order rate constants in the order PCE to VC, The lower graphs on the right hand show how the effective εC/εCl (= Φ)changes as function of time, while graph F shows how Φ changes as function of production versus consumption ratio (= [production rate (PR) – consumption rate (CR)] / [PR+CR]).

References

van Breukelen, B.M., Hunkeler, D., Volkering, F. (2005) Quantification of Sequential Chlorinated Ethene Degradation by Use of a Reactive Transport Model Incorporating Isotope Fractionation. Environmental Science & Technology, 39, 11, 4189 – 4197

Elsner M; Hunkeler D (2008) Evaluating Chlorine Isotope Effects from Isotope Ratios and Mass Spectra of Polychlorinated Molecules. Anal. Chem., 2008, 80 (12), pp 4731–4740

Hunkeler, D; van Breukelen, BM; Elsner, M (2009); Modeling Chlorine Isotope Trends during Sequential Transformation of Chlorinated Ethenes. Accepted for publication in Environmental Science and Technology

5 Demonstration sites

For the ENACT project, three demonstration sites have been selected. It concerns VOCl-contaminated site with very different natural attenuation characteristics. :

- Amsterdam, a PCE-contaminated site with evidence of complete dechlorination
- Brabant, a TCE-contaminated site where reductive dechlorination stalls at cDCE
- Antwerp, a PCE-contaminated site with mixed dechlorination characteristics

Figure 5.1 demonstration sites

At these sites, the complete natural attenuation toolbox for VOCL, including stable carbon and chlorine analysis of all VOCL present in concentrations above the detection limit. The results have been interpreted by the isotope specialist s in the ENACT consortium and, if feasible, modelled using the reactive transport model including carbon and chorine isotope fractionation.

5.1 Demonstration site Amsterdam

The VOCl-contaminated site in Amsterdam has been selected as an example for a case where complete natural dechlorination is occurring. All the available chemical, biochemical, and biological evidence is indicative of very favourable conditions for natural attenuation. The groundwater is highly reduced and the groundwater has a high DOC content. The original contaminants are restricted to the source zone and the plume consists solely of degradation products with high concentrations of ethene and ethane. DNA encoding for VC reductase is present in the groundwater.

In contrast to what was expected, the isotope data showed very little variation. Figure 5.2 presents the data for TCE. Both for carbon and for chlorine no significant isotope fractionation was found in PCE and TCE. In the degradation products cDCE and VC somewhat more variation was measured, but the pattern is not a typical for cases with extensive dechlorination. Despite intensive efforts of the specialists in the ENACT consortium, no sound explanation for the isotope results could be brought forward.
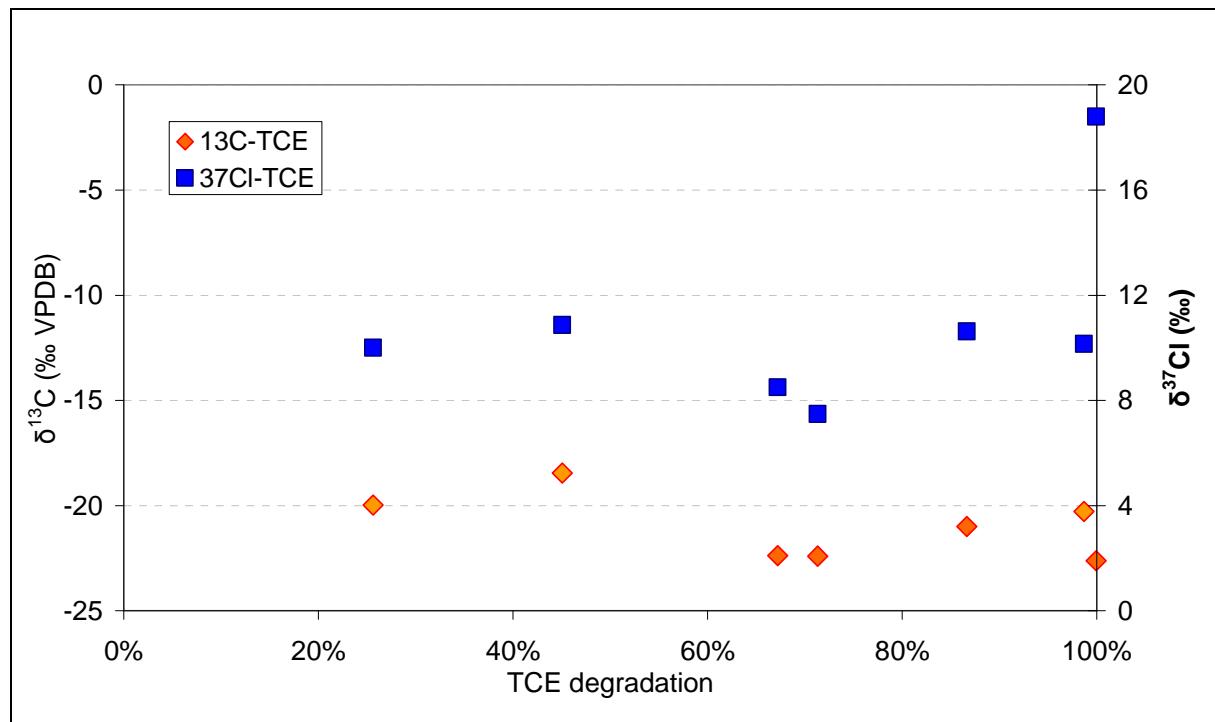

Figure 5.2 Stable carbon and chlorine data of TCE at the Amsterdam site a as a function of the TCE degradation percentage, calculated by assuming that all DCE, VC, ethene, and ethane in a single monitoring well are degradation products of the TCE in that well.

5.2 Demonstration site Brabant

The demonstration site Brabant is a typical example of a TCE-contamination where only partial reductive dechlorination is occurring. In the source zone, both TCE and cDCE is found, whereas the plume consists mainly of cDCE. VC is found in low concentrations only and ethene and ethane are below the detection limit. In such cases, an alternative degradation mechanism for cDCE would be very important. Anaerobic biological oxidation is often speculated upon in cases like this.

The results of both the carbon and the chlorine isotopes from the Brabant site confirm the conceptual model of the site with reductive dechlorination of TCE to CDCE without further degradation, as illustrated in figure 5.3. TCE follows typical behaviour with increasing enrichment in ^{13}C and [37]Cl with increasing degradation. The ^{13}C-content of the degradation product cDCE is never significantly higher than that of there original product, showing that no degradation mechanism is playing a significant role in the behaviour of cDCE at this site. The results of the [37]Cl-data are somewhat less clear due to the relative nature of the data, but the limited variation in the dataset and the good correlation between the carbon and chlorine isotope data provide strong support for the "cDCE stall" in this case.
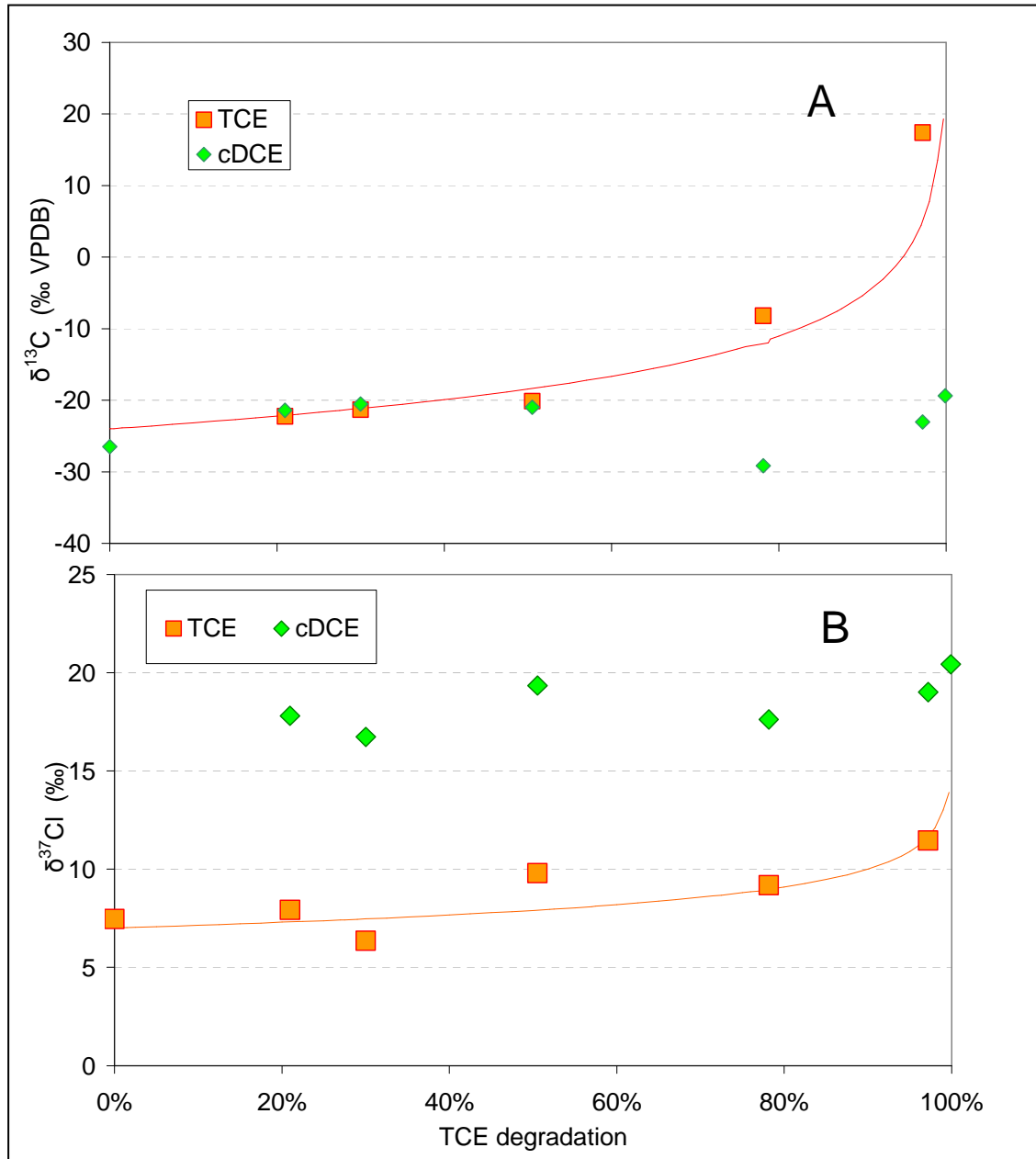
Figure 5.3 Carbon istope (A) and chlorine isotope (B) data for TCE and cDCE in samples from the Brabant site as a function of the TCE degradation percentage, calculated by assuming that all DCE, VC, ethene, and ethane in a single monitoring well are degradation products of the TCE in that well.

5.3 Demonstration site Antwerp

The Antwerp demonstration site is typical for a VOCl-contamination with mixed natural attenuation conditions. At some parts of the site the groundwater is highly reduced and dechlorination to ethene is observed, whereas at other parts the redox condition are less favourable and degradation appears to stall at cDCE or VC. Double isotope analysis has the potential to provide a strong independent line of evidence in such complex cases.

The data on the carbon isotopes show a somewhat unusual pattern with little variation in the δ^{13}C-PCE, despite clear evidence for PCE degradation. Assuming a low carbon isotope enrichment factor for PCE degradation, the ^{13}C-data from TCE can be described. cDCE shows the typical behaviour of an intermediate compound, with a large variation in δ^{13}C-values and with the higher values in samples with evidence for complete dechlorination. The δ^{13}C of VC could only be determined for three samples, which is insufficient for a meaningful interpretation.

The chlorine isotope data show enrichment in ^{37}Cl in PCE in samples with stronger degradation, but the data show more scattering than wanted (Figure 5.4). The relative nature of the chlorine isotope data hampered the interpretation of the results of the degradation products. The double isotope plots for PCE and TCE show patterns that support the assumption of PCE degradation with a low carbon isotope fractionation is occurring at this site.
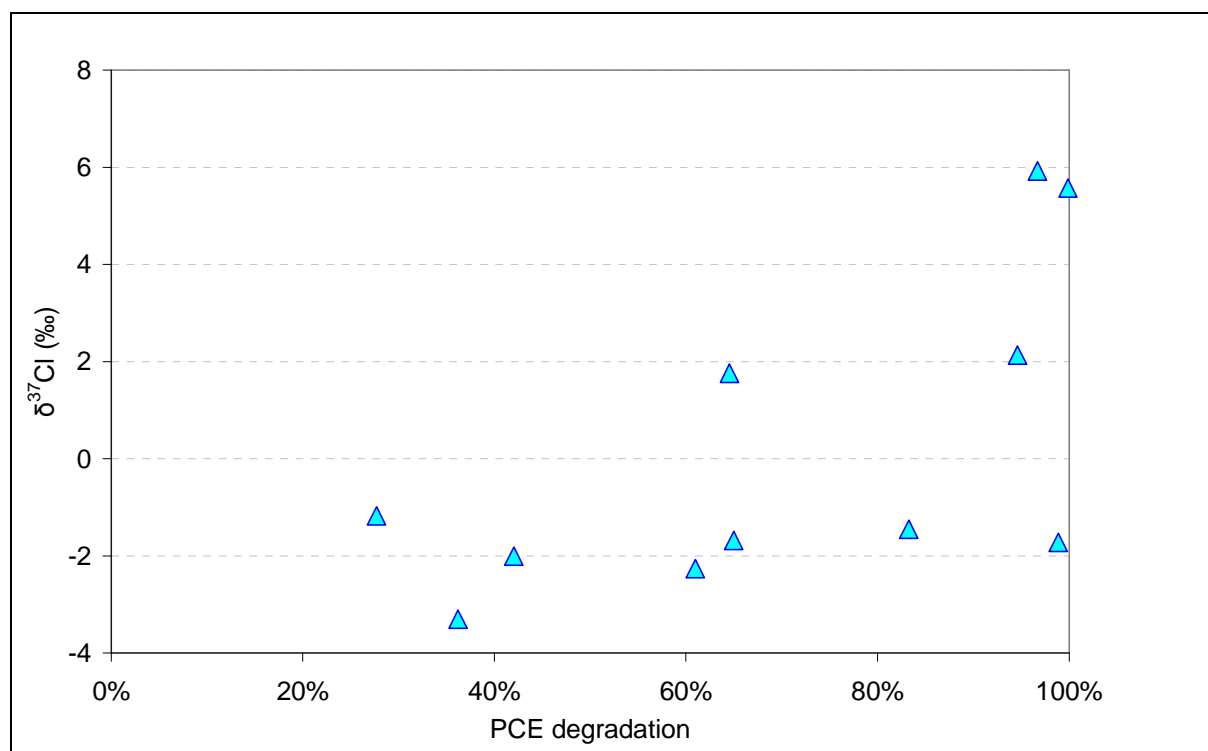

Figure 5.4 Chlorine isotope data for PCE in samples from the Antwerp site as a function of the PCE degradation percentage, calculated by assuming that TCE, DCE, VC, ethene, and ethane in a single monitoring well are all degradation products of the PCE in that well

5.4 Demonstration site conclusions

The conclusions from the application of the natural attenuation toolbox for VOCl including double isotope analysis at the three demonstration sites are:

− The Brabant case shows that chlorine isotope data can provide useful results which are in line with the existing site conceptual model and the view of the natural attenuation processes at the site. The double isotope data present a crucial line of evidence for this case, showing that cDCE is not subject to further degradation

− In the Antwerp case the data show a somewhat unusual pattern. Assuming a low ^{13}C-fractionating effect for PCE degradation, the results for PCE and TCE confirm the conceptual site model with varying conditions for natural attenuation. The relative nature of the chlorine isotope date complicate the interpretation of the chlorine isotope results from the degradation products

− The results of the Amsterdam site are highly unsatisfactory. Both the carbon and chlorine isotope results seem to be in clear contrast with all the other data. The specialists in the ENACT consortium have not been able to forward a sound explanation for the results. For the chlorine isotope analysis, this could be due to the fact that it is a new method being demonstrated for the first time in the ENACT project. Stable carbon isotope of VOCl, however, has proven to be powerful and reliable method for studying natural attenuation processes in many similar cases. Sampling procedures are simple and the analytical method applied is reliable. It is known that the presence of chloroethanes can interfere with stable carbon isotope analysis of chloroethenes, but in this case these compounds are not present in significant concentrations.

− The interpretation of the chlorine isotope data from the degradation products is hampered by the relative nature of the results of the chlorine isotope. In the Brabant case with only one degradation product (cDCE) the interpretation is rather straightforward and this is not a major problem. In cases where further transformation of VC and ethene is occurring, however, the interpretation is more complex and requires model calculations. Without absolute data, this is not possible.

Overall, combining stable carbon and stable chlorine is concluded to be a potentially very valuable tool for assessing the natural attenuation processes at VOCl-contaminated sites. Further development of the method for chlorine isotope analysis is needed and further application at demonstration sites is required to increase the experience with this new method.

6 General conclusions

The aim of the ENACT project was to improve the toolbox for natural attenuation of chlorinated solvents by including double isotope analysis. To do this, different activities have been performed:

− Optimization of the method for stable chlorine isotope analysis to make it suited for field application

− Development of a theory for stable chlorine isotope fractionation in chlorinated solvents and construction of a reactive transport model that can describe chlorine isotope fractionation in field situations

− Laboratory experiments to determine the stable chlorine isotope enrichment caused by the different relevant degradation processes

− Application of the toolbox at three demonstration sites

The stable chlorine isotope method developed at the Darmstadt University of Technology was optimized and meets the requirements for application at field sites. The analysis is currently commercially available. Due to a lack of ^{37}Cl-VOCl standards, the method can only provide relative chlorine isotope data. It is reasonable to derive chlorine isotope enrichment factors by batch experiment in the lab, yet complicates interpretation of the data from the degradation products. Chlorine isotope compositions (δ^{37}Cl-values) obtained by this method should be therefore calibrated to derive absolute values. This problem is currently being addresses as a follow-up of the ENACT project. Further validation in demonstration cases is required

A theory for stable chlorine isotope analysis during VOCl degradation has been developed and a reactive transport model has been constructed that can be used to describe stable chlorine isotope data from field sites.

The laboratory experiments have resulted in chlorine isotope fractionation factors for biological reductive dechlorination and abiotic reduction by FeS. In addition, the occurrence of chemical reduction processes has been verified.

The application at field sites has shown that double isotope analysis can be a very valuable tool for the interpretation of natural attenuation processes at VOCl -contaminated sites. In the most straightforward case with a TCE contamination and a one-step degradation to cDCE, the double isotope method provided clear evidence supporting the existing conceptual site model. A more complex case with unequivocal natural attenuation characteristics showed the need for absolute ^{37}Cl-data. On the other hand, at one of the three sites the results of both the carbon and the isotope analysis were in clear conflict with all other information an could not be explained.

Summarizing it can be said that combining compound-specific stable carbon and chlorine isotope analysis is a potentially very valuable method and that the ENACT project has been an important step in the development of it. With further optimization and validation, the method can become a unique tool that can be used to identify natural attenuation processes for VOCl and to characterize source zones.

7 Dissemination

The results of the ENACT project have been presented at various occasions and published in an outstanding scientific journal. Since the project is only recently finished, it is expected that further dissemination will follow. The list below gives a current overview of the presentations and publications related to the ENACT project.

− van Breukelen BM (2008) Modeling carbon and chlorine stable isotope fractionation to assess and quantify degradation of chlorinated ethenes in groundwater". Geochimica et Cosmochimica Acta, Volume 72, Issue 12, p.A971

− Hunkeler, D; van Breukelen, BM; Elsner, M (2009); Modeling Chlorine Isotope Trends during Sequential Transformation of Chlorinated Ethenes. Accepted for publication in Environmental Science and Technology

− Sakaguchi-Söder K, J. Jager, F. Volkering, J. Gemoets, T. De Ceuster, B.M. van Breukelen, H. Veld, M. Elsner. SNOWMAN-Projekt „ENACT: Extending the Monitored Natural Attenuation Toolbox for Chlorinated Solvents. Poster presented at the DECHEMA conference on natural attenuation, Frankfurt, Germany, November 24/25 2008

− Volkering F, van Breukelen BM, Gemoets J, Sakaguchi-Söder K, Veld H, Elsner M (2008) SNOWMAN project ENACT: extending the natural attenuation of chlorinated solvents toolbox. Platform paper presented at ConSoil 2008, 24-26 September 2008, Milano, Italy

The SNOWMAN partners are:

Austria

Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft (BMLFUW)

http://www.lebensministerium.at/

Belgium (Flanders)

Openbare Vlaamse Afvalstoffenmaatschappij (OVAM)

http://www.ovam.be

France

Agence De l'Environnement et de la Maîtrise de l'Energie (ADEME)

http://www.ademe.fr

Germany

Umweltbundesamt (UBA)

http://www.umweltbundesamt.de

Netherlands

Stichting Kennisontwikkeling en Kennisoverdracht Bodem (SKB)

http://www.skbodem.nl/

Sweden

Naturvårdsverket (SEPA, Swedish Environment Protection Agency)

http://www.naturvardsverket.se/

United Kingdom

The Environment Agency of England and Wales

http://www.environment-agency.gov.uk/