



Use of dual carbon–chlorine isotope analysis to assess the degradation pathways of 1,1,1-trichloroethane in groundwater



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ARTICLE INFO

Article history:

Received 2 October 2015
Received in revised form
27 January 2016
Accepted 30 January 2016
Available online 2 February 2016

Keywords:

Volatile organic contaminants
Chlorinated solvents
Compound-specific isotope analysis
Contaminant fate
Groundwater remediation
Abiotic degradation

ABSTRACT

Compound-specific isotope analysis (CSIA) is a powerful tool to track contaminant fate in groundwater. However, the application of CSIA to chlorinated ethanes has received little attention so far. These compounds are toxic and prevalent groundwater contaminants of environmental concern. The high susceptibility of chlorinated ethanes like 1,1,1-trichloroethane (1,1,1-TCA) to be transformed via different competing pathways (biotic and abiotic) complicates the assessment of their fate in the subsurface. In this study, the use of a dual C–Cl isotope approach to identify the active degradation pathways of 1,1,1-TCA is evaluated for the first time in an aerobic aquifer impacted by 1,1,1-TCA and trichloroethylene (TCE) with concentrations of up to 20 mg/L and 3.4 mg/L, respectively. The reaction-specific dual carbon–chlorine (C–Cl) isotope trends determined in a recent laboratory study illustrated the potential of a dual isotope approach to identify contaminant degradation pathways of 1,1,1-TCA. Compared to the dual isotope slopes ($\Delta\delta^{13}\text{C}/\Delta\delta^{37}\text{Cl}$) previously determined in the laboratory for dehydrohalogenation/hydrolysis (DH/HY, 0.33 ± 0.04) and oxidation by persulfate (∞), the slope determined from field samples (0.6 ± 0.2 , $r^2 = 0.75$) is closer to the one observed for DH/HY, pointing to DH/HY as the predominant degradation pathway of 1,1,1-TCA in the aquifer. The observed deviation could be explained by a minor contribution of additional degradation processes. This result, along with the little degradation of TCE determined from isotope measurements, confirmed that 1,1,1-TCA is the main source of the 1,1-dichloroethylene (1,1-DCE) detected in the aquifer with concentrations of up to 10 mg/L. This study demonstrates that a dual C–Cl isotope approach can strongly improve the qualitative and quantitative assessment of 1,1,1-TCA degradation processes in the field.

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1. Introduction

Groundwater contamination by chlorinated aliphatic hydrocarbons (CAHs) is a major environmental problem and it has an adverse impact on water resources (Moran et al., 2007). 1,1,1-trichloroethane (1,1,1-TCA) and trichloroethene (TCE) are toxic and persistent contaminants commonly found in polluted aquifers because of their widespread use as solvents (ATDSR, 2003, 2006a). TCE is frequently a co-contaminant in aquifers with 1,1,1-TCA due to their similar industrial applications and both compounds are considered as priority pollutants by the United States

Environmental Protection Agency (USEPA, 2013). In groundwater, 1,1,1-TCA may be transformed by multiple biotic and abiotic reactions (Fig. 1) (Scheutz et al., 2011), making it challenging to elucidate active degradation pathways. This knowledge is necessary to evaluate contaminant degradation and potential formation of toxic intermediates. Identifying pathways is further complicated in sites contaminated by mixed CAHs because some products of 1,1,1-TCA such as 1,1-dichloroethylene (1,1-DCE) can be formed from different precursors (Fig. 1). Hence, identification of pathways based solely on substrate-product concentration relationships may lead to erroneous interpretations. Therefore, development of innovative strategies for 1,1,1-TCA degradation pathways elucidation and evaluation in the field is warranted.

In groundwater, 1,1,1-TCA is abiotically degraded to 1,1-DCE and acetic acid (HAc) via dehydrohalogenation and hydrolysis (DH/HY),

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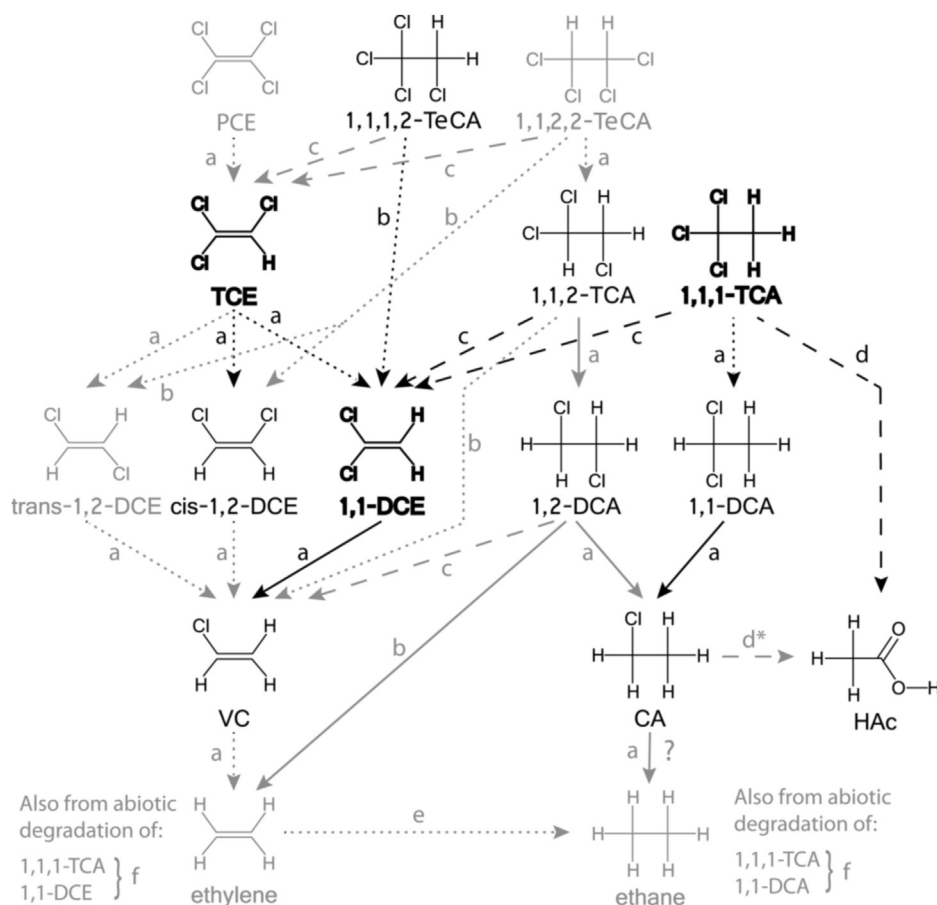


Fig. 1. Degradation pathways of chlorinated ethanes and ethenes. Aerobic biodegradation pathways are not shown. In grey color are indicated the compounds and pathways that are not mentioned explicitly in the text. Compounds in bold represent the main contaminants investigated in this study. Dotted lines show reactions that can be both abiotically or biotically mediated whereas solid lines indicate biodegradation pathways (Culubret et al., 2001; Field and Sierra-Alvarez, 2004) and dashed lines abiotic transformations catalyzed by iron bearing minerals (Butler and Hayes, 2000; Han et al., 2012; Lee and Batchelor, 2002) and zero valent iron (Arnold and Roberts, 2000; Hara et al., 2005; Song and Carraway, 2005). For chlorinated ethanes, abiotic hydrolysis and dehydrohalogenation in water are included (Jeffers et al., 1989; Scheutz et al., 2011). Chlorinated and non-chlorinated acetylenes and higher molecular compounds (i.e. C₄–C₆) produced during metal catalyzed reactions are not shown. (a) hydrogenolysis, (b) dihaloelimination, (c) dehydrohalogenation, (d) hydrolysis, (e) hydrogenation and (f) reactions that proceed via α -elimination. (d*) Transformation of CA to HAc evolves via hydrolysis of CA to ethanol and subsequent fermentation to HAc.

respectively (Scheutz et al., 2011) (Fig. 1). Thermal enhancement of DH/HY has been recently proposed for in situ remediation of 1,1,1-TCA contamination (Suthersan et al., 2012). Generally, reductive dechlorination of TCE (biotic and abiotic) also results in the formation of 1,1-DCE as minor product via hydrogenolysis (Arnold and Roberts, 2000; Field and Sierra-Alvarez, 2004). However, Zhang et al. (2006) found 1,1-DCE as the predominant intermediate in microcosm degradation experiments of TCE prepared with a microbial culture derived from a landfill site. In addition, 1,1-DCE may also result from dehydrohalogenation of 1,1,2-trichloroethane (1,1,2-TCA) (Pagan et al., 1998) and from dihaloelimination of 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA) (Culubret et al., 2001; O'Loughlin and Burris, 2004) (Fig. 1). 1,1-DCE is also a contaminant of environmental concern because it may be transformed to vinyl chloride (VC) in anaerobic conditions (Fig. 1), a confirmed carcinogenic compound (ATDSR, 2006b). In anaerobic conditions, 1,1,1-TCA may undergo metal catalyzed reduction either by naturally occurring reductants such as iron sulfide (Butler and Hayes, 2000) and iron hydroxides (O'Loughlin and Burris, 2004) or by zero valent iron (Fe(0)) in engineered systems (Fennelly and Roberts, 1998). Reduction of 1,1,1-TCA by Fe(0) leads to the formation of 1,1-dichloroethane (1,1-DCA), ethene and ethane in parallel pathways (Fennelly and Roberts, 1998) (Fig. 1). Biodegradation of

1,1,1-TCA under both aerobic and anaerobic conditions has been reported in a number of studies (Field and Sierra-Alvarez, 2004; Scheutz et al., 2011). Dehalorespiration of 1,1,1-TCA by the anaerobic bacterium *Dehalobacter* sp. strain TCA1 was demonstrated by Sun et al. (2002). 1,1,1-TCA was transformed into chloroethane (CA) with transient formation of 1,1-DCA as intermediate. In aerobic conditions, cometabolic oxidation of 1,1,1-TCA has been observed in several studies with pure and enrichment cultures (Field and Sierra-Alvarez, 2004; Yagi et al., 1999).

For a given compound, different degradation pathways are sometimes related to distinct subsurface redox environments and, therefore, redox conditions may help elucidating reaction pathways. However, for 1,1,1-TCA different reaction pathways may be active under the same redox conditions. For instance, 1,1,1-TCA biodegradation, via either reductive dechlorination or cooxidation, and DH/HY can occur simultaneously in anaerobic or aerobic conditions, respectively, complicating their evaluation. In addition, redox zones characterization may be difficult due to the presence of micro-redox environments and/or strong redox gradients with depth within the contaminant plume (Christensen et al., 2000). In this case, groundwater samples collected from conventional long screen wells may be a mixture of water from different parts of the plume with distinct redox conditions.

Compound-specific isotope analysis (CSIA) is an innovative tool to investigate degradation pathways of organic contaminants because the extent of isotope fractionation (ϵ_{bulk}) during compound transformation is highly reaction-specific (Hirschorn et al., 2004; Hunkeler et al., 2005; Vanstone et al., 2008). The isotope fractionation of the substrate can be quantified in laboratory studies using the Rayleigh equation, which can be approximated by the following expression, Eq. (1):

$$\delta^h E_S \approx \delta^h E_{S0} + \epsilon_{\text{bulk}} (\%) \cdot \ln f \quad (1)$$

where $\delta^h E_S$ is the isotopic composition of element E at a remaining fraction (f) and $\delta^h E_{S0}$ is the initial isotopic composition.

In aquifers, transformation-induced isotope fractionation is generally larger than the one related to phase transfer processes such as sorption or volatilization (Braeckvelt et al., 2012). While isotope fractionation of one element alone (e.g. ϵ_{bulk}^C) could provide pathway distinction in laboratory experiments (Elsner et al., 2007), this is not possible under field conditions. Here, contaminant concentration changes related to processes other than its transformation (such as sorption and dispersion) cannot be excluded, preventing accurate calculation of ϵ_{bulk} values. However, contaminant degradation pathways differentiation in the field may be addressed using a dual isotope approach (Whiticar, 1999; Zwank et al., 2005). Recent development of analytical methods for online CI-CSIA, either by continuous flow gas chromatography isotope ratio mass spectrometry (GC-IRMS) (Shouakar-Stash et al., 2006) or GC-quadrupole mass spectrometry (GC-qMS) (Aeppli et al., 2010; Bernstein et al., 2011; Jin et al., 2011; Palau et al., 2014a; Sakaguchi-Soder et al., 2007) has facilitated the measurement of chlorine isotope ratios in chlorinated ethenes and ethanes. These novel methods open new possibilities for a dual C–Cl isotope approach, which has not yet been applied to investigate the fate of chlorinated ethanes in the field.

During the course of a reaction, combined changes in isotope ratios (e.g. $\Delta\delta^{13}\text{C}$ vs. $\Delta\delta^{37}\text{Cl}$) for a given reactant generally yield a linear trend in a dual element isotope plot (Abe et al., 2009; Cretnik et al., 2013; Palau et al., 2014a). The dual element isotope slope ($\Delta = \Delta\delta^{13}\text{C}/\Delta\delta^{37}\text{Cl} \approx \epsilon_{\text{bulk}}^C/\epsilon_{\text{bulk}}^{\text{Cl}}$) reflects isotope effects of both elements and, thus, different slopes may be expected for distinct transformation mechanisms involving different bonds with distinct elements (Elsner, 2010). Following this approach, dual isotope slopes observed in the field can be compared to the slopes determined in laboratory experiments to identify degradation pathways. A significant advantage of the dual isotope approach is that the Δ value often remains constant, regardless of the occurrence of transport and retardation processes (Thullner et al., 2013). The reason is that such processes are generally non- or slightly-isotope-fractionating so that both elements are affected similarly. In this case, by taking the ratio of the isotope shift for the two elements (e.g., $\Delta\delta^{13}\text{C}/\Delta\delta^{37}\text{Cl}$) their effect is canceled out (Elsner et al., 2005). In addition, if a given contaminant is simultaneously degraded by two different pathways, the dual isotope approach could allow determining the portion of reaction occurring through each pathway (Centler et al., 2013; van Breukelen, 2007). For 1,1,1-TCA, distinctly different dual C–Cl isotope trends were determined during oxidation with persulfate, reduction by Fe(0) and DH/HY in a recent laboratory study (Palau et al., 2014b), illustrating the potential of this approach for 1,1,1-TCA degradation pathways differentiation. The dual C–Cl isotope approach has been applied to a limited number of chlorinated ethenes contaminated sites (Badin et al., 2014; Hunkeler et al., 2011; Lojkasek-Lima et al., 2012a; 2012b; Wiegert et al., 2012) but, to our knowledge, not to sites with chlorinated ethanes.

In this study, dual C–Cl isotope analysis of 1,1,1-TCA in

groundwater samples was performed for the first time with the purpose of elucidating the fate of 1,1,1-TCA in a contaminated aquifer. In order to evaluate the potential of the multi-isotope analysis and the dual C–Cl isotope slopes to identify degradation pathways of 1,1,1-TCA in the field, the isotope ratios of 1,1,1-TCA ($\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$) and 1,1-DCE ($\delta^{13}\text{C}$) from field samples, in conjunction with concentration data, were compared to the isotope patterns determined from a previous laboratory experiment of 1,1,1-TCA transformation by DH/HY (Palau et al., 2014b). In addition, the isotopic composition of TCE ($\delta^{13}\text{C}$ and $\delta^{37}\text{Cl}$) detected in the aquifer was also determined to assess its transformation.

2. Field site

The dual C–Cl isotope approach was evaluated at a site where the subsurface is impacted by a mixture of CAHs. A detailed hydrogeological site characterization and complementary information about subsurface contamination are available in the [Supplementary material \(SI\)](#). The origin of the contamination was related to an industrial plant where 1,1,1-TCA and TCE were used as solvents for cleaning and degreasing metal parts since the 60's. In the late 80's, an environmental survey at the site revealed important subsurface contamination in the north-eastern part of the plant, where the waste disposal and the delivery zones were located (Fig. 2).

The lithology at the site consists of, from top to bottom, Quaternary loess deposits (from 5 to 18 m thick), a layer of flint conglomerate resulting from chalk alteration and dissolution (from 4 to 8 m thick), Senonian chalks forming the fractured bedrock aquifer (thickness of ~30 m) and Campanian smectite clay corresponding to the low permeability basis of the aquifer. The chalk unit can be considered as a dual porosity aquifer composed of high matrix porosity (up to 45%) and much lower fracture porosity (on the order of 1–5%) (Brouyère et al., 2004; Orban et al., 2010). Despite the relatively low fracture porosity, its contribution to the hydraulic conductivity is predominant (see SI). In the studied area, the chalk aquifer is unconfined and the groundwater table is found between 16.9 and 28.6 m below ground surface, showing an annual fluctuation of up to 2 m and inter-annual variations of approximately 5 m. Groundwater flows towards north-west and the average hydraulic gradient is ~1% (Fig. 2). According to the hydraulic conductivity range determined at the site by pumping tests (see SI) and assuming an effective porosity of 0.01 (Orban et al., 2010), the groundwater seepage velocity can be estimated to be 0.3–8.6 m d⁻¹ (SI).

3. Material and methods

3.1. Groundwater sampling

The sampling methods are described in detail in the [SI](#). Briefly, the field site is equipped with a groundwater monitoring network consisting of 30 wells situated along the CAHs plume. Water samples from selected wells (18 wells, Fig. 2A) were collected for chemical and isotope analysis in February 2011 (first campaign) and March 2013 (second campaign). Prior to samples collection, monitoring wells were purged (3–5 well volumes) until temperature, pH, redox potential, electrical conductivity and dissolved oxygen (DO) stabilized. Samples for CAHs concentration and isotope analysis were collected in 40 mL glass vials closed without headspace using screw caps with Teflon coated septa, preserved at pH ~2 with HNO₃ (10%) and stored at 4 °C in the dark until analysis. Concentration analysis of CAHs was performed within 48 h after samples collection.

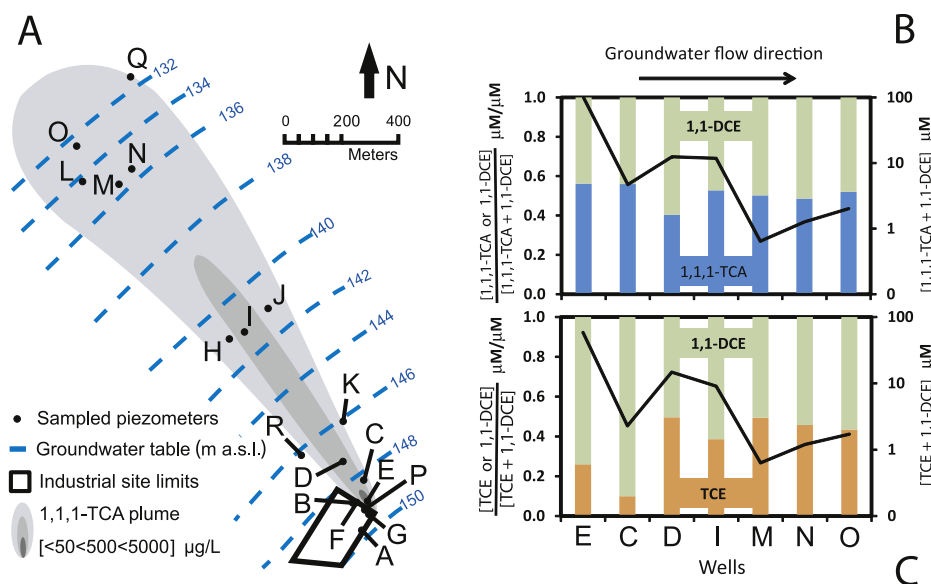


Fig. 2. (A) Site map and groundwater monitoring wells network. Dashed lines correspond to the groundwater surface (in m above sea level) and contour lines depict the 1,1,1-TCA concentrations in the aquifer. (B) Total concentration (i.e. 1,1,1-TCA+1,1-DCE) (right y-axis, line) and concentration of 1,1,1-TCA and 1,1-DCE normalized by the total concentration (left y-axis, bars). (C) Total concentration (i.e. TCE+1,1-DCE) (right y-axis, line) and concentration of TCE and 1,1-DCE normalized by the total concentration (left y-axis, bars). The data indicated were obtained in March 2013 but similar concentration patterns were observed in February 2011 (Fig. S2, SI).

3.2. Chemical and isotope analysis

Detailed descriptions of analytical methods are available in the SI. The DH/HY experiments preparation and analysis for concentration and isotope ratios are thoroughly described in Palau et al. (2014b) (see a summary in the SI). Concentration analysis of CAHs in groundwater samples was performed by GC-MS in an accredited commercial laboratory. The analysis of redox sensitive species in groundwater samples was performed by ion chromatography (nitrate and sulfate) and atomic absorption spectrometry (iron and manganese) at the University of Liège.

Carbon isotope ratios (i.e. $^{13}\text{C}/^{12}\text{C}$) of 1,1,1-TCA, TCE and 1,1-DCE were determined by GC-IRMS, whereas chlorine isotope ratios (i.e. $^{37}\text{Cl}/^{35}\text{Cl}$) of 1,1,1-TCA and TCE were measured by GC-MS (Bernstein et al., 2011; Palau et al., 2014b) at the University of Neuchâtel (see SI). Isotope ratios of individual compounds were reported using the delta notation, Eq. (2),

$$\delta^{\text{hE}}_{\text{sample}} = \frac{R^{\text{(hE/lE)}}_{\text{sample}}}{R^{\text{(hE/lE)}}_{\text{standard}}} - 1 \quad (2)$$

where R is the isotope ratio of heavy ($^{\text{hE}}$) to light ($^{\text{lE}}$) isotopes of an element E (e.g., $^{13}\text{C}/^{12}\text{C}$ and $^{37}\text{Cl}/^{35}\text{Cl}$). The δ values are usually expressed in per mil. For chlorine, the raw $\delta^{37}\text{Cl}$ values were obtained by referencing against two external laboratory standards of 1,1,1-TCA and TCE according to Eq. (2). These standards were dissolved in water and measured similarly to the samples interspersed in the same sequence (Aeppli et al., 2010). Samples and standards were diluted to a similar concentration and each of them was measured ten times. Further details about samples and standards analysis scheme as well as raw $\delta^{37}\text{Cl}$ values (two-point) calibration to the standard mean ocean chloride (SMOC) scale are available in the SI. Precision (1σ) of the analysis was 0.3‰ for $\delta^{13}\text{C}$ and 0.4‰ for $\delta^{37}\text{Cl}$.

3.3. Calculation of substrate remaining fraction

In order to evaluate if the observed isotope pattern of primary

compounds and potential metabolites is related to reactive processes, measured concentrations are transformed to relative concentrations taking into account reaction equations and related to isotope ratios in analogy to the Rayleigh equation (Eq. (1)). As several reactive processes might occur simultaneously, the slope of such a plot will not necessarily correspond to a specific laboratory enrichment factor (ϵ_{bulk}). The substrate remaining fraction (f) at a certain well is estimated according to Eqs. (3) and (4) for 1,1,1-TCA and TCE, respectively:

$$f_{1,1,1\text{-TCA}} = \frac{[1,1,1\text{-TCA}]}{[1,1,1\text{-TCA} + \text{HAc} + 1,1\text{-DCE}]} = \frac{[1,1,1\text{-TCA}]}{[1,1,1\text{-TCA} + 3.6 \times 1,1\text{-DCE}]} \quad (3)$$

$$f_{\text{TCE}} = \frac{[\text{TCE}]}{[\text{TCE} + 1,1\text{-DCE}]} \quad (4)$$

where [1,1,1-TCA] and [TCE] are the aqueous concentration of 1,1,1-TCA and TCE, respectively, and [1,1,1-TCA + HAC + 1,1-DCE] and [TCE + 1,1-DCE] are the total concentration of 1,1,1-TCA, TCE and their respective products for the DH/HY and hydrogenolysis pathways, respectively (Fig. 1). Mole fractions are used instead of absolute concentrations as the first take into account the effect of dilution. Regarding the hydrogenolysis products of TCE, *cis*-1,2-DCE is not considered in Eq. (4) as its concentration in groundwater (up to 14 $\mu\text{g/L}$) is much smaller than that of 1,1-DCE (up to 10 mg/L). For 1,1,1-TCA, HAC produced by hydrolysis was not analyzed in groundwater samples. In the aquifer, HAC is readily biodegraded because it is used as electron donor and carbon source by the microorganisms. Therefore, for $f_{1,1,1\text{-TCA}}$ the expression $[1,1,1\text{-TCA}]/[1,1,1\text{-TCA} + 3.6 \times 1,1\text{-DCE}]$ is used, which accounts for the produced HAC. The yield of HAC (hydrolysis product) relative to 1,1-DCE (dehydrohalogenation product) was estimated by first order curve fitting of concentration-time data series obtained in a previous laboratory study (Palau et al., 2014b) (see SI). Previous studies showed that hydrolysis of 1,1-DCE in water is negligible at environmental conditions (Gerken and Franklin, 1989; Jeffers et al.,

1989). The uncertainty of the calculated $f_{1,1,1\text{-TCA}}$ and f_{TCE} in the field, i.e. 39% and 17%, respectively, was estimated by error propagation in Eqs. (3) and (4), and an uncertainty of 10% was assumed for commercial concentration analysis of volatile organic compounds (Hunkeler et al., 2008).

4. Results and discussion

4.1. Field geochemical conditions and CAHs concentration

High DO and nitrate concentrations were measured in groundwater, ranging between 2.6 and 8.4 mg/L for DO and from 51.6 to 94.4 mg/L for nitrate, which indicate the presence of aerobic conditions in the aquifer. Concentrations of dissolved Mn and dissolved Fe are low (≤ 0.01 and ≤ 0.07 mg/L, respectively), which is in agreement with the presence of oxygen. Aerobic conditions are unfavorable for microbial reductive dechlorination of CAHs.

The main CAHs present in groundwater, i.e. 1,1,1-TCA, TCE and 1,1-DCE, are detected at concentrations > 1 mg/L, reaching a value of up to 20 mg/L for 1,1,1-TCA in the source area (well E in February 2011) and forming a CAHs plume spreading northwest (see the 1,1,1-TCA plume in Fig. 2A). Several compounds are detected at lower concentrations, including 1,1,2-TCA (up to 500 $\mu\text{g/L}$), 1,1-DCA (up to 140 $\mu\text{g/L}$), 1,2-dichloroethane (1,2-DCA, up to 270 $\mu\text{g/L}$) and *cis*-1,2-dichloroethene (*cis*-1,2-DCE, up to 14 $\mu\text{g/L}$), and their mole fractions relative to the total concentration of chlorinated ethanes and ethenes are $< 7\%$. The presence of 1,1,1-TCA and TCE reductive dechlorination products such as 1,1-DCA and *cis*-1,2-DCE, respectively (Fig. 1), could be related to the occurrence of micro-anaerobic environments in the aquifer. The contribution of 1,1,2-TCA dehydrohalogenation to 1,1-DCE concentration (Fig. 1) is probably very small according to the low molar concentration of 1,1,2-TCA relative to 1,1,1-TCA ($< 8\%$).

Concentrations of 1,1,1-TCA, TCE and 1,1-DCE show a similar distribution in the aquifer and a large concentration range of two orders of magnitude is observed for all of them in the wells situated close to the plume centerline (Fig. S1, S1). High concentrations of 1,1-DCE are already present in the wells located in the source area, up to 10 mg/L in well E in February 2011 (Fig. 2A and Fig. S1). Changes in aqueous CAH concentrations in the plume can be related to transformation processes but also to non-degradative processes such as hydrodynamic dispersion and sorption. To account for dispersion, relative variations in 1,1,1-TCA, TCE and 1,1-DCE concentrations along the plume can be expressed as mole fractions. Increasing mole fractions of 1,1-DCE downgradient from the source would be indicative of 1,1,1-TCA and/or TCE degradation during transport. However, the mole fractions of 1,1-DCE in several wells located close to the plume centerline show a small variation relative to $[1,1,1\text{-TCA} + 1,1\text{-DCE}]$, from 0.41 to 0.60 (Fig. 2B and Fig. S2), and the fractions of 1,1-DCE relative to $[\text{TCE} + 1,1\text{-DCE}]$ are higher for the wells situated close to the source, i.e. wells E and C (Fig. 2C and Fig. S2). Therefore, additional data is necessary to confirm the contribution of degradation processes to the observed changes in mole fractions.

4.2. Isotope patterns of 1,1,1-TCA, TCE and 1,1-DCE in the aquifer

The chlorine isotope composition of 1,1,1-TCA in groundwater range from $+2.4$ to $+7.6\text{‰}$. In previous studies, chlorine isotope ratios of pure phase 1,1,1-TCA from different manufacturers showed values ranging from -3.54 to $+2.03\text{‰}$ (Shouakar-Stash et al., 2003). Compared to the manufacturers' range, the higher range of $\delta^{37}\text{Cl}$ values in groundwater suggests that 1,1,1-TCA could be affected by degradation processes. Similarly, the carbon isotopic composition of 1,1,1-TCA in groundwater, which ranges from -21.1 to -25.1‰

(with the exception of the value of -26.3‰ measured in the well E in February 2011), is also higher than the manufacturers' range, which varies between -25.5 and -31.6‰ (Hunkeler and Aravena, 2010), supporting 1,1,1-TCA transformation in the aquifer. To evaluate in more detail whether the variations of isotope ratios of 1,1,1-TCA in groundwater are due to degradation, $\delta^{37}\text{Cl}$ and $\delta^{13}\text{C}$ values are related to the concentration data according to the Rayleigh equation (Eq. (1)) in Fig. 3C and D. Chlorine and carbon isotope ratios of 1,1,1-TCA exhibit an enrichment in heavy isotopes (i.e. ^{37}Cl and ^{13}C) with decreasing mole fractions, with the exception of data from wells A, E and G (red markers in Fig. 3C and D), confirming that isotope variations of 1,1,1-TCA are related to its degradation. The $\delta^{13}\text{C}$ values of 1,1-DCE in groundwater, from -18.5 to -25.3‰ , are generally depleted in ^{13}C compared to those of 1,1,1-TCA (Fig. 3D), which is consistent with the abiotic formation of 1,1-DCE from 1,1,1-TCA via dehydrohalogenation. In addition, this isotope pattern also suggests that 1,1-DCE is not further degraded in most of the wells.

In well A, carbon and chlorine isotopes ratios of 1,1,1-TCA are significantly enriched in both ^{13}C and ^{37}Cl . These higher values could be explained either by a distinct source of 1,1,1-TCA with a heavier isotope composition or by the effect of biodegradation. Relatively low DO values varying from 1.0 to 1.7 mg/L were measured in this well between 2005 and 2008, which could indicate that micro-anaerobic environments favorable to microbial reductive dechlorination of 1,1,1-TCA took place at that time and that 1,1,1-TCA affected by biodegradation is still present in the vicinity of well A. In contrast, for wells E and G, $\delta^{13}\text{C}_{1,1,1\text{-TCA}}$ values are slightly depleted in ^{13}C (up to -26.3‰ in E-February 2011), while $\delta^{37}\text{Cl}_{1,1,1\text{-TCA}}$ values are lightly enriched in ^{37}Cl (up to $+5.8\text{‰}$ in G-March 2013). Such behavior could be related to the effect of vaporization and diffusion processes on the residual 1,1,1-TCA contamination in the unsaturated zone (Jeannotat and Hunkeler, 2012). Wells E and G are located in the vicinity of the source area (Fig. 2A) and previous reports at the site showed that, when the water level rises, it sometimes reaches highly contaminated parts of the unsaturated zone in the source area (see SI), leading to a direct input of residual contaminants into the aquifer. For the remaining 15 out of 18 wells investigated (i.e. B-D, F and H-R), observed variations with regard to both Cl and C isotope values are well described by a linear trend ($r^2 \geq 0.75$, Fig. 3C and D). The intercepts of the correlation lines, i.e. $-0.7 \pm 1.9\text{‰}$ for Cl and $-27 \pm 1\text{‰}$ for C (the uncertainties were estimated by error propagation in the regression equations for Cl and C isotope data indicated in Fig. 3C and D), can be considered as an estimate of the initial isotopic composition of 1,1,1-TCA ($\delta^{37}\text{Cl}_0$ and $\delta^{13}\text{C}_0$, respectively, Eq. (1)), which agree very well with the ranges reported for pure 1,1,1-TCA from different manufacturers, i.e. between -3.54 and $+2.03\text{‰}$ for Cl (Shouakar-Stash et al., 2003) and between -25.5 and -31.6‰ for C (Hunkeler and Aravena, 2010).

In order to compare the field and laboratory isotope patterns, the isotope data of 1,1,1-TCA and 1,1-DCE measured during 1,1,1-TCA transformation by DH/HY in the laboratory (Palau et al., 2014b) were reevaluated in this study according to Eqs. (1) and (3) (Fig. 3A and B). In general, the field $\delta^{13}\text{C}$ values of 1,1,1-TCA and 1,1-DCE (Fig. 3D) exhibit a pattern similar to the one observed in the laboratory batch experiment (Fig. 3B), providing further evidence for 1,1,1-TCA dehydrohalogenation in the aquifer. Compared to the laboratory experiment, the correlation lines for field isotope data show a smaller slope for Cl, i.e. $-3.3 \pm 0.8\text{‰}$ (field, Fig. 3C) and $-4.8 \pm 0.2\text{‰}$ (laboratory, Fig. 3A), and a larger slope for C, i.e. $-2.5 \pm 0.5\text{‰}$ (field, Fig. 3D) and $-1.6 \pm 0.2\text{‰}$ (laboratory, Fig. 3B). However, when taking their uncertainty into consideration, the slopes for field and laboratory data are relatively similar for both elements. The larger slope obtained from field carbon isotope data compared to the laboratory DH/HY experiment can be associated

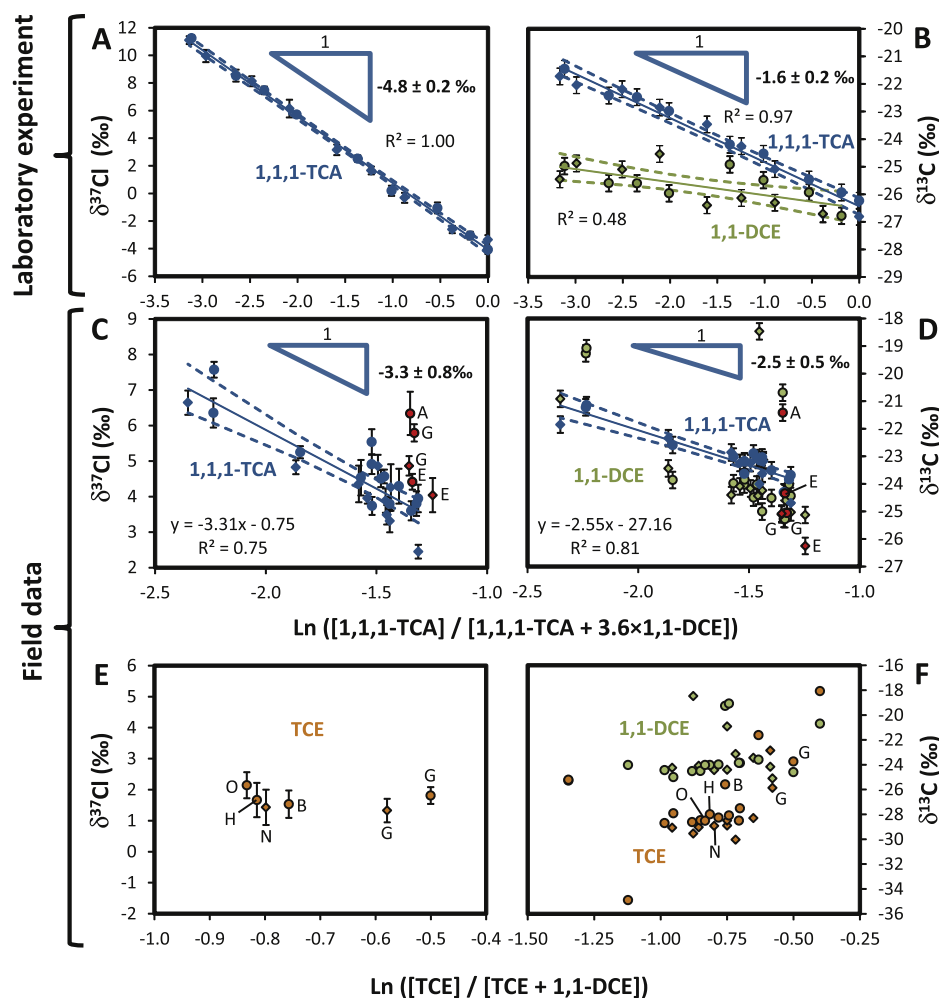


Fig. 3. A, B) Isotopic composition of 1,1,1-TCA ($\delta^{37}\text{Cl}$ and $\delta^{13}\text{C}$) and 1,1-DCE ($\delta^{13}\text{C}$) during DH/HY of 1,1,1-TCA in batch experiments. Data from duplicate experiments are combined (i.e. rhombus and circle symbol marks). C, D) Isotopic composition of 1,1,1-TCA ($\delta^{37}\text{Cl}$ and $\delta^{13}\text{C}$) and 1,1-DCE ($\delta^{13}\text{C}$) in groundwater samples. Dashed lines correspond to the 95% confidence intervals of regression parameters. E, F) Isotopic composition of TCE ($\delta^{37}\text{Cl}$ and $\delta^{13}\text{C}$) and 1,1-DCE ($\delta^{13}\text{C}$) in groundwater samples. For field samples, data from both sampling campaigns are combined, i.e. rhombus (February 2011) and circles (March 2013).

with the simultaneous occurrence of biodegradation processes of 1,1,1-TCA in addition to DH/HY in the field, which is further investigated using a dual isotope approach (Section 4.3).

For TCE, several groundwater samples with different $\delta^{13}\text{C}$ values (data points labeled in Fig. 3F) were selected for chlorine isotope analysis, showing similar $\delta^{37}\text{Cl}$ values (from $+1.3 \pm 0.4\text{‰}$ to $+2.1 \pm 0.4\text{‰}$, Fig. 3E). The $\delta^{37}\text{Cl}$ values of TCE in groundwater fall within the reported range of pure TCE from different manufacturers which varies between -3.19 and $+3.90\text{‰}$ (Hunkeler and Aravena, 2010), suggesting little transformation of TCE. The carbon isotopic composition of TCE varied from -21.6 to -30.0‰ , with an average of $-27 \pm 2\text{‰}$ ($\pm 1\sigma$, $n = 24$), except for the wells A (-18.1‰) and K (-34.9‰) on March 2013. As observed for chlorine, most of the $\delta^{13}\text{C}_{\text{TCE}}$ values fall within the range of TCE from different manufacturers, i.e. between -24.5 and -33.5‰ (Hunkeler and Aravena, 2010), supporting little degradation of TCE in groundwater. Contrary to the isotope patterns of 1,1,1-TCA, $\delta^{37}\text{Cl}_{\text{TCE}}$ and $\delta^{13}\text{C}_{\text{TCE}}$ values do not show any enrichment in ^{37}Cl and ^{13}C with decreasing mole fractions of TCE (Fig. 3E and F), confirming that TCE is not significantly degraded in the aquifer. This result is in agreement with the aerobic conditions determined in the aquifer. In addition, the $\delta^{13}\text{C}$ values of 1,1-DCE are generally enriched in ^{13}C compared to TCE (Fig. 3F). According to the normal carbon isotope fractionation of

TCE during reductive dechlorination (Hunkeler and Morasch, 2010), the $\delta^{13}\text{C}$ values of produced 1,1-DCE would be lower than those of TCE. Therefore, for most of the samples, the observed changes in $\delta^{13}\text{C}_{\text{TCE}}$ can probably be associated with some variability in the carbon isotopic composition of source TCE.

4.3. Dual C–Cl isotope approach to investigate degradation pathways in the field

Carbon and chlorine δ isotope values of 1,1,1-TCA in groundwater samples were combined in a dual isotope plot (Fig. 4). Isotope values from wells A, E and G are not included because, as indicated above (Section 4.2), isotope data from these wells could be affected by processes different than compound transformation. The plotted data show a linear trend ($r^2 = 0.75$) with a dual isotope slope ($\Lambda = \Delta\delta^{13}\text{C}/\Delta\delta^{37}\text{Cl} \approx e_{\text{bulk}}^{\text{C}}/e_{\text{bulk}}^{\text{Cl}}$) of 0.6 ± 0.2 , confirming that transformation of 1,1,1-TCA is an important process in the aquifer. This field Λ value is very different from that determined in a recent laboratory study for oxidation (Fig. 4), clearly indicating that oxidation cannot be the main process involved (Palau et al., 2014b). In contrast, the field slope is closer to the one determined for 1,1,1-TCA transformation via DH/HY in the laboratory (0.33 ± 0.04 , Fig. 4) (Palau et al., 2014b). The significant difference between the dual

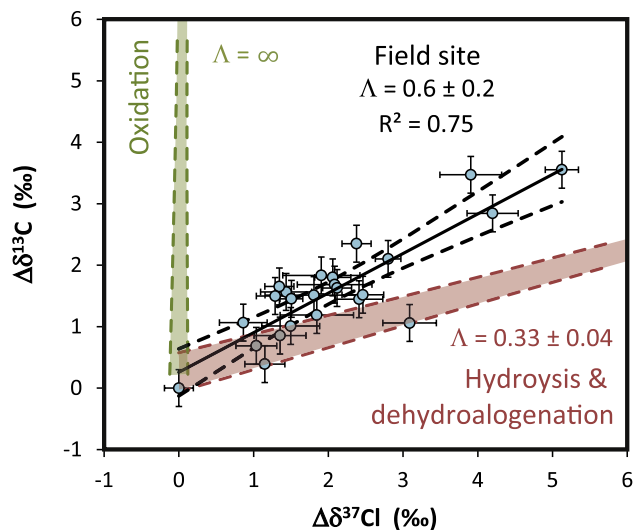


Fig. 4. Dual C–Cl isotope trends during transformation of 1,1,1-TCA in the investigated test site and in two experimental systems. Data from both campaigns are combined (blue circles). Λ values ($\pm 95\%$ C.I.) are given by the slope of the linear regressions and the black dashed lines correspond to the 95% C.I. Shaded areas (95% C.I.) indicate exclusive occurrence of either one of the two pathways. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

isotope slopes determined for the field and the DH/HY experiment (ANCOVA, $P = 0.0003$) suggests that additional degradation processes of 1,1,1-TCA likely occur in the aquifer, as pointed out by the carbon isotope patterns in Fig. 3. A higher Λ value (1.5 ± 0.1) associated with the reduction of 1,1,1-TCA by zero-valent iron was previously reported (Palau et al., 2014b), however, significant biotic and/or abiotic reductive dechlorination of 1,1,1-TCA are discarded due to the aerobic conditions in the aquifer. On the other hand, in aerobic conditions, microbial cooxidative degradation of 1,1,1-TCA to 2,2,2-trichloroethanol via C–H bond cleavage in the first reaction step has been reported in several studies (Field and Sierra-Alvarez, 2004; Yagi et al., 1999). The occurrence of microbial oxidation of 1,1,1-TCA would be consistent with the different slopes determined from $\delta^{13}\text{C}_{1,1,1\text{-TCA}}$ data for the field and the DH/HY experiment in Fig. 3. As observed during abiotic oxidation of 1,1,1-TCA in a recent study (Palau et al., 2014b), a much higher isotope effect associated with C–H bond cleavage is expected for C compared to Cl. This might explain, taking as a reference the slopes determined from the laboratory experiment, the higher slope obtained for C, $-2.5 \pm 0.5\%$ (field) and $-1.6 \pm 0.2\%$ (laboratory) (Fig. 3B, D), compared to the smaller slope observed for Cl, $-3.3 \pm 0.8\%$ (field) and $-4.8 \pm 0.2\%$ (laboratory) (Fig. 3A, C). Therefore, a combination of DH/HY and microbial oxidation may be taking place.

In this case, oxidation and DH/HY pathway-specific contributions to total 1,1,1-TCA degradation may be estimated using the expression derived by van Breukelen (2007), Eq. (5),

$$F = \frac{\Lambda \cdot \varepsilon_{\text{O}}^{\text{Cl}} - \varepsilon_{\text{O}}^{\text{C}}}{\left(\varepsilon_{\text{D/H}}^{\text{C}} - \varepsilon_{\text{O}}^{\text{C}}\right) - \Lambda \left(\varepsilon_{\text{D/H}}^{\text{Cl}} - \varepsilon_{\text{O}}^{\text{Cl}}\right)} \quad (5)$$

where F is the distribution of DH/HY and oxidation pathways, $\varepsilon_{\text{D/H}}^{\text{C}}$ and $\varepsilon_{\text{D/H}}^{\text{Cl}}$ are the C and Cl isotope fractionation values during DH/HY of 1,1,1-TCA and $\varepsilon_{\text{O}}^{\text{C}}$ and $\varepsilon_{\text{O}}^{\text{Cl}}$ correspond to the C and Cl isotope fractionation values for 1,1,1-TCA oxidation. For this equation, in addition to the $\varepsilon_{\text{bulk}}$ values of 1,1,1-TCA for both reactions involved, only the dual isotope slope determined from field data

($\Lambda = 0.6 \pm 0.2$) is necessary. The $\varepsilon_{\text{bulk}}^{\text{C}}$ and $\varepsilon_{\text{bulk}}^{\text{Cl}}$ values of 1,1,1-TCA during DH/HY and oxidation reactions were reported in a recent study (Palau et al., 2014b), showing values of $-1.6 \pm 0.2\%$ and $-4.7 \pm 0.1\%$ (DH/HY), $-4.0 \pm 0.2\%$ and no chlorine isotope fractionation (Oxidation). In this previous study, the isotope fractionation values of 1,1,1-TCA during oxidative C–H bond cleavage were determined abiotically by reaction with persulfate. Chlorine isotope fractionation values for microbial oxidation of 1,1,1-TCA are still not available in the literature, however, isotope fractionation values determined from abiotically mediated oxidation may be used as a rough approximation. In fact, isotope fractionation values from abiotic reactions are often considered closest to the intrinsic isotope effects (Lollar et al., 2010). According to the reported reaction-specific $\varepsilon_{\text{bulk}}$ values, the contribution of DH/HY was of $80 \pm 10\%$ (the uncertainty was estimated by error propagation in Eq. (5)). This result indicates a relatively small contribution of the oxidation pathway, provided that the $\varepsilon_{\text{bulk}}$ values for microbial oxidation of 1,1,1-TCA by indigenous microorganisms at the site are confirmed in future biodegradation studies. Eq. (5) assumes simultaneous activity of both pathways, which is a likely assumption in our case judging by the good linear correlation between $\delta^{37}\text{Cl}$ and $\delta^{13}\text{C}$ values (Fig. 4).

The expected rate of 1,1,1-TCA degradation by DH/HY at the measured groundwater temperature can be estimated using the Arrhenius equation, Eq. (6),

$$k = A \cdot \exp(-E_a/RT) \quad (6)$$

where k is the first order rate constant (s^{-1}), A is the frequency factor (s^{-1}), R is the gas constant ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$), E_a is the activation energy ($\text{kJ} \cdot \text{mol}^{-1}$) and T is the absolute temperature (K). According to the E_a ($122.8 \text{ kJ mol}^{-1}$) and A ($8.7 \times 10^{13} \text{ s}^{-1}$) values determined by Gauthier and Murphy (2003) from several previous studies and the average groundwater temperature at the site ($284 \pm 1 \text{ K}$, $\pm 1\sigma$, $n = 34$), the transformation rate is estimated to be $1.95 \times 10^{-4} \text{ d}^{-1}$ (i.e. half-life of around 10 years). This slow reaction rate contrasts with the relatively fast groundwater seepage velocity in the saturated zone (up to 8.6 m d^{-1}), suggesting that significant contaminant retardation would be necessary to explain the high concentrations of 1,1-DCE in the source area. In this site, owing to the high chalk matrix porosity (up to 45%), 1,1,1-TCA is probably subject to retardation by diffusion into the matrix pore water (Parker et al., 1997). In addition to degradation of 1,1,1-TCA in the saturated zone, dehydrohalogenation of 1,1,1-TCA to 1,1-DCE might also occur in the unsaturated part of the aquifer (up to 28 m thick). Here, downward migration for dissolved compounds in groundwater was estimated at $\sim 1 \text{ m y}^{-1}$ by different studies (Brouyère et al., 2004; Orban et al., 2010). Degradation of 1,1,1-TCA in the unsaturated zone is supported by the detection of 1,1-DCE in relatively high concentrations in soil samples from the unsaturated zone analyzed in previous reports (see SI).

5. Conclusions

The demonstration and evaluation of CAHs degradation processes is necessary to predict their fate and long-term impact on contaminated sites. The chlorine and carbon isotopic composition of 1,1,1-TCA exhibited clear correlations with its varying mole fractions, revealing the contribution of degradation processes of 1,1,1-TCA in the aquifer. Dual C–Cl isotope data showed that, while the slope obtained from field samples is very different from that seen in the laboratory for oxidation, the field Λ value is closer to the one determined for DH/HY, pointing to DH/HY as the dominant degradation pathway. In addition, the observed deviation from the dual isotope trend expected for DH/HY suggests the occurrence of

additional degradation processes of 1,1,1-TCA in groundwater. A minor contribution of microbial cooxidation of 1,1,1-TCA via C–H bond cleavage could be a feasible explanation according to the isotope results and the aerobic conditions of the aquifer. Contrary to 1,1,1-TCA, the chlorine and carbon isotopic composition of TCE suggest little degradation, which is in agreement with the aerobic conditions and the product concentration analysis.

Considering the time scale of cost-efficient contaminant remediation strategies like monitored natural attenuation, low rate abiotic reactions such as DH/HY have the potential to contribute significantly to 1,1,1-TCA attenuation in contaminated sites. However, low rate transformation processes are typically difficult to monitor and to evaluate based on concentration measurements only. This study shows that the dual C–Cl isotope analysis is a valuable tool to assess degradation pathways of 1,1,1-TCA in the field. Such information is crucial to improve contaminant attenuation estimates and to delineate adequate remediation strategies.

Acknowledgments

We would like to thank Johan Derouane and Vincent Lebrun (Service publique de Wallonie, DGO3-DGARNE, Direction de l'Eau, Service des Eaux Souterraines) for providing access to the reports and for their contribution on the discussions on the case study. We also would like to thank Dr. Barbara Sherwood Lollar (University of Toronto) and an anonymous reviewer for their comments and suggestions, which improved the quality of the manuscript. A.B. is financed by the European Commission, Marie Curie Actions Project 265063, and J.P. was supported by the University of Neuchâtel via direct university funding.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.01.057>.

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