



## Review

# Tracking chlorinated contaminants in the subsurface using compound-specific chlorine isotope analysis: A review of principles, current challenges and applications



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## HIGHLIGHTS

- Chlorine CSIA enables process and source differentiation.
- Successful field applications illustrate the potential of chlorine CSIA.
- Isotope fractionation models enable further applications for chlorine CSIA data.
- Physical and chemical Cl isotope fractionation processes are detailed.
- Methods for measuring Cl isotopic enrichment in contaminants are summarized.

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## ABSTRACT

Many chlorinated hydrocarbons have gained notoriety as persistent organic pollutants in the environment. Engineered and natural remediation efforts require a monitoring tool to track the progress of degradation processes. Compound-specific isotope analysis (CSIA) is a robust method to evaluate the origin and fate of contaminants in the environment and does not rely on concentration measurements. While carbon CSIA has established itself in the routine assessment of contaminated sites, studies incorporating chlorine isotopes have only recently become more common. Although some aspects of chlorine isotope analysis are more challenging than carbon isotope analysis, having additional isotopic data yields valuable information for contaminated site management. This review provides an overview of chlorine isotope fractionation of chlorinated contaminants in the subsurface by different processes and presents analytical techniques and unresolved challenges in chlorine isotope analysis. A summary of successful field applications illustrates the potential of using chlorine isotope data. Finally, approaches in modelling chlorine isotope fractionation due to degradation, diffusion, and sorption processes are discussed.

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## 1. Introduction

Chlorinated hydrocarbons (CHC) are a diverse group of compounds, occurring as both aliphatic and aromatic hydrocarbons. These compounds have at least one covalently bonded chlorine atom in place of a hydrogen atom. Synthetic organochlorines have found widespread use as pesticides, pharmaceuticals, plastics, refrigerants, industrial solvents, lubricants, dielectric and dry-cleaning agents. They also appear as intermediates in chemical syntheses or as the result of combustion processes (Häggbloom and Bossert, 2004).

The chemical inertness, stability and lipid solubility of chlorinated hydrocarbons make them suitable for many industrial processes and has led to their large-scale production. These properties dominate the behaviour of these compounds in the environment and are the reason that many of them have become known as persistent organic pollutants (POP). In addition to resisting degradation for long periods, many of these pollutants accumulate in the fatty tissue of organisms and show various degrees of toxicity for humans and ecosystems (Häggbloom and Bossert, 2004; Koenig et al., 2015).

Volatile chlorinated aliphatic hydrocarbons are short hydrocarbon chains containing at least one covalently bonded chlorine atom and include chlorinated methanes, ethanes and ethenes (Stroo and Ward, 2010). These volatile organic compounds (VOCs) have been used in the past for degreasing, cleaning and dry-cleaning on the basis of their apolar nature, rapid evaporation and low flammability (Doherty, 2000). Chlorinated solvents are among the most common persistent contaminants in the environment, owing to their extensive application and often improper handling and disposal (Philp, 2007; Cincinelli et al., 2012). Although certain chlorinated solvents such as chloroform (CF) have been proven to occur naturally (Häggbloom and Bossert, 2004; Gribble, 2010), the natural production for many of these compounds is dwarfed by their release from anthropogenic sources (Lecloux, 2003; Hunkeler et al., 2012).

Among chlorinated solvents, chlorinated ethenes or ethylenes have been the subject of great interest in the field of contaminant hydrochemistry. They include vinyl chloride (VC), *trans*- and *cis*-dichloroethene (DCE), trichloroethene (TCE), and tetrachloroethene/perchloroethene (PCE). Chlorinated ethenes, especially TCE and PCE, have been used as industrial degreasing agents with PCE continuing to be used as a solvent in dry-cleaning applications. All chlorinated ethenes display some degree of toxicity, with TCE and VC being classified as known human carcinogens (Bradley, 2003; Guha et al., 2012).

Being able to differentiate sources and understand transformation processes is key in assessing the impact of contamination by chlorinated solvents on groundwater and ecosystems

(Cincinelli et al., 2012). Compound-specific isotope analysis (CSIA) has emerged as a powerful tool to track contaminants in the subsurface. The concept involves measuring variations in the isotopic composition of each compound of interest and/or their degradation products by combining a mass spectrometer with a chromatographic separation system. Using this approach, additional information can be gathered that allows a deeper understanding of transformation processes when compared with measuring concentration levels exclusively. While carbon CSIA has become a routine technique in the assessment of contaminant degradation, studies incorporating chlorine CSIA are still relatively rare.

This review provides an overview of the current knowledge about isotope fractionation effects of chlorinated contaminants in the subsurface, as well as the analytical challenges in using Cl CSIA as a routine approach in the assessment of contaminated sites. Field applications, including source differentiation, tracking, degradation pathway evaluation, and degradation quantification, are also discussed. Finally, considerations related to modelling Cl isotope fractionation due to various subsurface processes are detailed.

## 2. Measuring chlorine isotope ratios

Chlorine has two stable isotopes,  $^{35}\text{Cl}$  with a natural abundance of 75.8% and  $^{37}\text{Cl}$  with an abundance of 24.2%. This ratio can vary slightly due to various physico-chemical processes. Since minuscule differences can be resolved, the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotope ratio of a sample  $R_{\text{sample}}$  is reported using the  $\delta$  notation as permille (‰) difference from the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotope ratio in a reference standard  $R_{\text{SMOC}}$ , which is standard mean ocean chlorine (SMOC):

$$\delta^{37}\text{Cl} = \frac{R_{\text{sample}}}{R_{\text{SMOC}}} - 1 \quad (\text{‰}) \quad (1)$$

Similarly, in any chlorinated compound, chlorine atoms can either be of the light ( $^{35}\text{Cl}$ ) or the heavy ( $^{37}\text{Cl}$ ) variety. Molecules of the same compound that differ in their isotopic composition are referred to as isotopologues.

Chlorine isotope ratios in compounds are obtained using mass spectrometric techniques. Measuring the molecular mass of a molecule is a three step process, which is shared by every type of mass spectrometer. In the first step, the ionization step, the molecules of interest are converted to ions. Different ionization methods are used depending on the volatility and ionization potential of the molecule or atom of interest. Electron ionization is a common method for ionizing molecules of relatively volatile compounds. Thermal ionization can be used to create atomic as well as molecular ions of inorganic analytes. Inductively coupled plasma ionization is a versatile method than can be applied to solid as well as solved samples. In the ionized argon plasma, the analyte undergoes

a complete vaporization, atomization and ionization. The ionization energy of this method is adequate to ionize many elements, while ensuring that mostly only single-charged species are produced (Dass, 2007; Westman-Brinkmalm and Brinkmalm, 2008; Sparkman et al., 2011).

The second step is the acceleration and separation of the species according to their ratio of mass to charge ( $m/z$ ) in a mass analyzer. Common mass analyzers are the magnetic sector mass spectrometer and the quadrupole mass spectrometer (qMS). Magnetic sector mass analyzers include isotope ratio mass spectrometers (IRMS), where it is possible to compare the obtained isotope ratios to those of standardized reference values by introducing a reference gas. The two common types of IRMS are continuous flow (CF-IRMS) and dual-inlet (DI-IRMS). In the former, the reference gas is introduced into a stream of carrier gas before and after the sample gas which also contains the sample gas. In the latter, sample gas and reference gas are introduced alternately in a rapid succession, leading to a higher precision. Quadrupole mass spectrometers are compact benchtop instruments, where masses are separated according to their trajectory through an oscillating electromagnetic field.

In the third and final step, the mass spectrum is obtained by measuring the mass-resolved ion current in a detector, either consecutively in a single collector (common for quadrupole MS) or simultaneously with a multicollector (MC) setup.

Prior to chlorine mass spectrometric analysis of organic compounds, an extraction and conversion of the chlorine in the compound to an inorganic chloride may be necessary. This so-called offline measurement (Fig. 1a) has the advantage that the extraction/conversion steps are independent of the kind of mass spectrometer that will be used to determine the isotope ratio, but for mixtures usually only bulk isotope ratios and not compound-specific isotope ratios can be reported. The counterpart, an online measurement (Fig. 1b), allows analyzing samples directly in real-time and offers the possibility for compound-specific isotope measurements, a larger potential for automation and a higher sample throughput, but has the disadvantage that the extraction/conversion step is directly linked to the isotope measurement, thereby limiting the choice of mass spectrometer. Table 1 gives an overview of off- and online methods, including sample sizes and precisions obtained.

### 2.1. Offline chlorine isotope measurements

There exist several sample preparation paths for offline chlorine isotope analysis of chlorinated hydrocarbons (Fig. 1a). Most offline methods require cryogenic, chromatographic or ion exchange purification of the product to remove unwanted reagents and byproducts prior to mass spectrometric analysis. Table 1 gives an overview of offline  $\delta^{37}\text{Cl}$  measurements of organic compounds presented in this section. Apart from the limited possibilities of automating the conversion process, a main drawback is that offline methods cannot be coupled to a simple method that allows isotopically resolving mixtures of contaminants. There is the possibility of using preparative capillary gas chromatography (pcGC) to extract target analytes from mixtures at amounts sufficiently high for offline analysis. This method has so far been only applied to chlorine CSIA of semi-volatile organochlorine compounds such as the insecticide dichlorodiphenyltrichloroethane (DDT) by Holmstrand et al. (2006) and polychlorinated biphenyls (PCB) by Reddy et al. (2000) and Mandalakis et al. (2008). All three aforementioned works did not observe a significant chlorine isotope fractionation during this preparative step. Holmstrand et al. (2006) and Mandalakis et al. (2008) emphasize that the complete eluting peak must be collected due to slight differences in the GC retention times between isotopologues. Gas chromatographic isotope effects are a well-known phenomenon (Brand, 1996) and have also been

observed for carbon (Ricci et al., 1994; Meier-Augenstein et al., 1996) and hydrogen isotopes (Jancsó and Van Hook, 1974). As an alternative method, Numata et al. (2002b) suggest that there the possibility of using compound-specific degradation techniques to resolve chlorine isotope data in complex mixtures. Direct coupling of a separation device, e.g. a gas chromatograph, to a mass spectrometer is however reserved for online methods. Nevertheless, offline methods are still essential to reference organic molecules to molecularly different, even inorganic molecules (Gilevska et al., 2015).

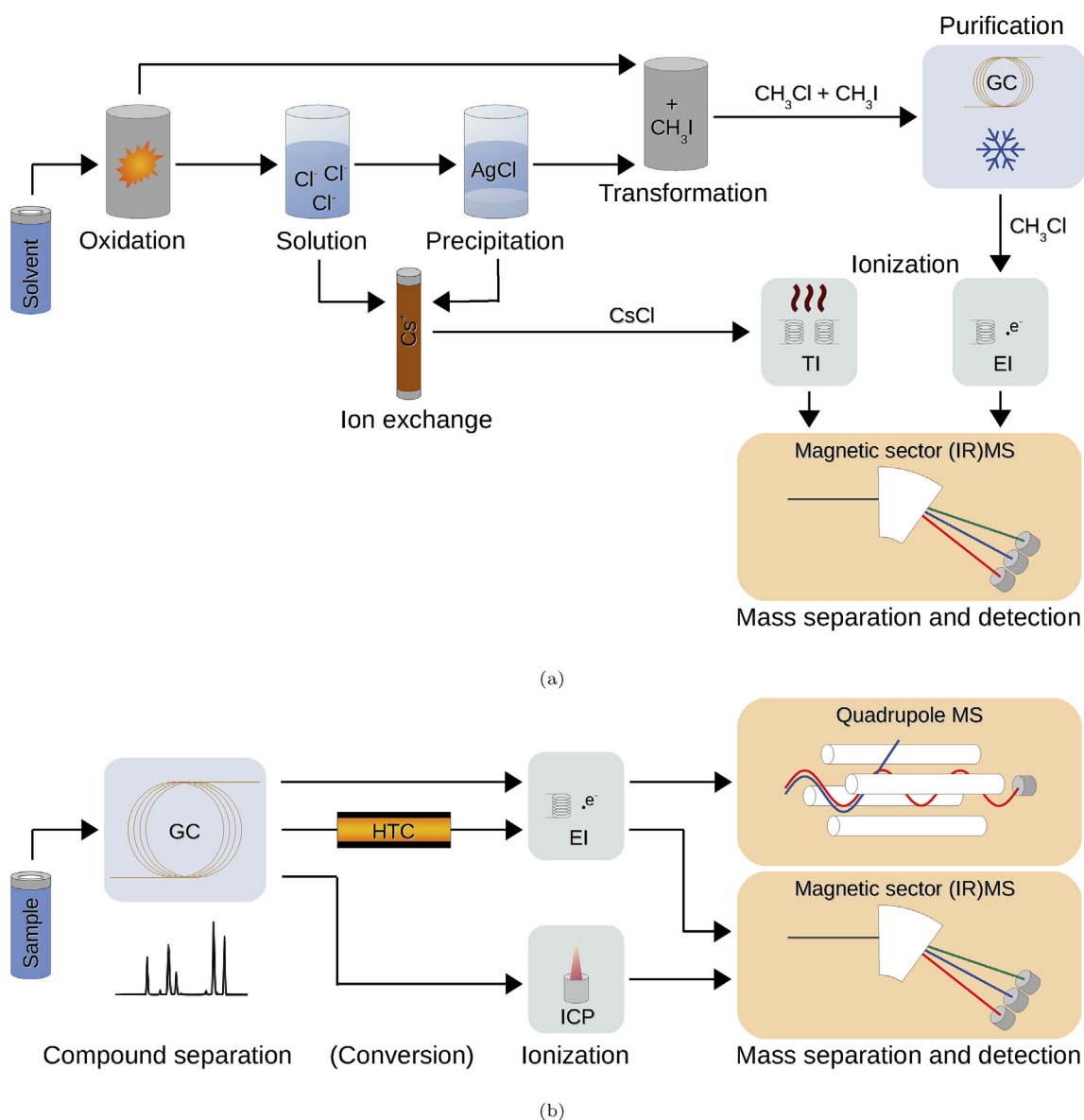
Some of the first measurements of organic chlorine isotope ratios were reported by Baertschi et al. (1953), who studied the chlorine isotope fractionation in chloroform and carbon tetrachloride during distillation. The chlorine isotope analysis was performed using a magnetic sector mass spectrometer with two collectors. The conversion step involved having the organic compounds undergo a reaction to yield gaseous hydrogen chloride (HCl).

Bartholomew et al. (1954) were the first to observe reactive isotope effects in a chlorinated organic compound, *tert*-butyl chloride ( $(\text{CH}_3)_3\text{CCl}$ ). The compound was allowed to react with silver nitrate, and the kinetic isotope effect ( $k_{35\text{Cl}}/k_{37\text{Cl}}$ ) for light and heavy chlorine isotopes was observed by converting the initial compound and the silver nitrate to chlorine gas ( $\text{Cl}_2$ ), which was subsequently measured in a magnetic sector mass spectrometer. Masses of 70 ( $^{35}\text{Cl}^{35}\text{Cl}$ ), 72 ( $^{35}\text{Cl}^{37}\text{Cl}$ ), and 74 ( $^{37}\text{Cl}^{37}\text{Cl}$ ) were recorded. Bartholomew et al. (1954) also pointed out the memory effect that is observed when using chlorine gas in a mass spectrometer – a disadvantage it shares with hydrogen chloride, as both tend to adhere to the interior of the mass spectrometer (Eggenkamp, 2014).

Being aware of this memory effect, Owen and Schaeffer (1955) were – together with Langvad et al. (1954) – some of the first researchers to establish chloromethane/methyl chloride ( $\text{CH}_3\text{Cl}$ ) as a suitable gas in mass spectrometric analysis of chlorine isotopes. Chloromethane remains the gas of choice in modern offline chlorine isotope ratio mass spectrometry. When using chloromethane in an IRMS, either positively or negatively charged ions can be analyzed, by switching the acceleration voltage to either a negative or a positive value respectively. Taylor and Grimsrud (1969) undertook some promising studies using negatively charged ions in DI-IRMS, since it results in a very simple mass spectrum consisting mainly of  $^{35}\text{Cl}^-$  and  $^{37}\text{Cl}^-$  ions. The downside is a lower intensity. Tanaka and Rye (1991) used this method to measure referenced chlorine isotope ratios in anthropogenic chlorinated hydrocarbons, at the same time being one of the first to propose the use of chlorine isotope mass spectrometry as a tool in fingerprinting of pollutants. Nowadays, it has become common practice to analyze positively charged ions of chloromethane, as most IRMS are set up like this for routine measurements of other compounds.

Jendrzewski et al. (1997) developed an offline conversion technique to measure chlorine isotope ratios in chlorinated organic compounds by oxidizing them with cupric oxide, yielding inorganic chloride which was then measured as described by Long et al. (1993) by precipitation as  $\text{AgCl}$  and conversion to chloromethane, which was measured in positive ion mode. The method was also applied to a mixture of chlorinated hydrocarbons, but as there was no prior separation step only a bulk chlorine isotope ratio was reported. Positive ion IRMS was also the method of choice for van Warmerdam et al. (1995) and Beneteau et al. (1999) for organic compounds, though the offline conversion step differed. The compounds were oxidized offline and the resulting chloride trapped in a calcium carbonate solution.

Holt et al. (1997) developed a non-aqueous offline conversion process especially for VOC which is still in widespread use, since it



**Fig. 1.** Overview of common (a) offline and (b) online chlorine isotope measurement methods for chlorinated hydrocarbons. TI, thermal ionization; EI, electron ionization; MS, mass spectrometer; GC, gas chromatograph; HTC, high temperature conversion; ICP, inductively coupled plasma; IR, isotope ratio; MS, mass spectrometer.

also allows offline measuring of carbon isotope ratios. Here, the compound of interest undergoes a high-temperature reaction with cupric oxide to yield copper(I) chloride (CuCl), which further reacts with methyl iodide (CH<sub>3</sub>I) in the same reaction tube resulting in chloromethane (CH<sub>3</sub>Cl), omitting the step of precipitation of the chlorine as silver chloride. Yields of CH<sub>3</sub>Cl from a variety of chlorinated organic compounds were 89±4%. [Shouakar-Stash et al. \(2003\)](#) used a modified Holt method to convert 1,1,1-Trichloroethane (1,1,1-TCA) and TCE to chloromethane for isotopic analysis. The chloromethane was separated chromatographically from the excess methyl iodide and measured in a DI-IRMS.

[Gilevska et al. \(2015\)](#) identified the incomplete dissolution of the chlorine salt after the oxidation step to be the main reason leading to inaccurately lower  $\delta^{37}\text{Cl}$  values when measuring chlorine isotope ratios of the insecticide  $\gamma$ -hexachlorocyclohexane (Lindane).

A different approach to offline chlorine isotope ratio measurements of chlorinated hydrocarbons that does not require

transformation to chloromethane was brought up by [Numata et al. \(2002b\)](#), using the thermal ionization (TI) method developed by [Magenheim et al. \(1994\)](#) for inorganic chlorides. [Numata et al. \(2002b\)](#)'s method involves a step where free chlorine is extracted from the compounds by treating them with sodiumbiphenyl. This chlorine is then transformed to CsCl by ion exchange. The solution is deposited directly onto a filament, the thermal ionization source of the mass spectrometer, and masses 301 ( $^{133}\text{Cs}_2^{35}\text{Cl}^+$ ) and 303 ( $^{133}\text{Cs}_2^{37}\text{Cl}^+$ ) are measured. The method required only 2.8  $\mu\text{mol Cl}$  for highly precise measurements.

TIMS was also applied to more complex chlorinated hydrocarbons such as DDT by [Holmstrand et al. \(2004, 2006\)](#) and PCBs by [Reddy et al. \(2000\)](#) and [Mandalakis et al. \(2008\)](#). [Holmstrand et al. \(2004\)](#) observed that TIMS is very sensitive to impurities and matrix effects which stem from the intricate offline conversion.

**Table 1**

Comparison of offline and online  $\delta^{37}\text{Cl}$  analytical precision for organic compounds (only cases where SMOC-referenced  $\delta^{37}\text{Cl}$  values were reported and  $n \geq 3$ ). TCA, trichloroethane; DDT, dichlorodiphenyltrichloroethane; PCP, pentachlorophenol; DCM, dichloromethane; CF, chloroform; CT, carbon tetrachloride.

MS method	Compound	Analyzed ions/masses	Sample size	Replicates $n =$	Best $1\sigma$ (‰)	Reference
<b>Offline</b>						
DI (+)-ion IRMS	1,1,1-TCA	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	1500 $\mu\text{mol Cl}$	21	0.29	van Warmerdam et al. (1995)
DI (+)-ion IRMS	1,1,1-TCA	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	not reported	4	0.17	Beneteau et al. (1999)
DI (+)-ion IRMS	1,1,1-TCA	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	150 $\mu\text{mol Cl}$	3	0.07	Shouakar-Stash et al. (2003)
DI (+)-ion IRMS	TCE	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	1700 $\mu\text{mol Cl}$	3	0.26	van Warmerdam et al. (1995)
DI (+)-ion IRMS	TCE	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	33 $\mu\text{mol}$ to 66 $\mu\text{mol Cl}$	8	0.15	Jendrzewski et al. (1997)
DI (+)-ion IRMS	TCE	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	not reported	3	0.08	Beneteau et al. (1999)
DI (+)-ion IRMS	TCE	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	166 $\mu\text{mol Cl}$	4	0.05	Shouakar-Stash et al. (2003)
DI (+)-ion IRMS	PCE	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	2000 $\mu\text{mol Cl}$	6	0.10	van Warmerdam et al. (1995)
DI (+)-ion IRMS	PCE	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	40 $\mu\text{mol}$ to 80 $\mu\text{mol Cl}$	4	0.10	Jendrzewski et al. (1997)
DI (+)-ion IRMS	PCE	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	not reported	4	0.15	Beneteau et al. (1999)
DI (+)-ion IRMS	Lindane	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	250 $\mu\text{mol Cl}$	3	0.04	Gilevska et al. (2015)
DI (+)-ion IRMS	Various CHC	$\text{CH}_3^{35}\text{Cl}^+$ , $\text{CH}_3^{37}\text{Cl}^+$	10 $\mu\text{mol}$ –70 $\mu\text{mol Cl}$	8	0.07	Holt et al. (1997)
(+)-ion TIMS	TCE	$\text{Cs}_2^{35}\text{Cl}^+$ , $\text{Cs}_2^{37}\text{Cl}^+$	2.8 $\mu\text{mol Cl}$	3	0.22	Numata et al. (2002b)
(+)-ion TIMS	PCE	$\text{Cs}_2^{35}\text{Cl}^+$ , $\text{Cs}_2^{37}\text{Cl}^+$	2.8 $\mu\text{mol Cl}$	4	0.08	Numata et al. (2002b)
(+)-ion TIMS	DDT	$\text{Cs}_2^{35}\text{Cl}^+$ , $\text{Cs}_2^{37}\text{Cl}^+$	85 nmol Cl	3	0.46	Holmstrand et al. (2004)
<b>Online</b>						
GC-IRMS	DCE isomers	96, 98	6 nmol to 9 nmol Cl	15	0.08	Shouakar-Stash et al. (2006)
GC-IRMS	TCE	95, 97	6 nmol to 9 nmol Cl	30	0.06	Shouakar-Stash et al. (2006)
GC-IRMS	TCE	95, 97	40 pmol Cl	10	< 0.15	Bernstein et al. (2011)
GC-IRMS	PCE	94, 96	6 nmol to 9 nmol Cl	30	0.12	Shouakar-Stash et al. (2006)
GC-qMS	TCE	60, 62, 95, 97, 130, 132	150 pmol Cl	10	< 0.5	Bernstein et al. (2011)
GC-qMS	TCE	60, 62, 95, 97, 130, 132	75 pmol Cl	10	< 0.5	Bernstein et al. (2011)
GC-qMS	TCE	60, 62, 95, 97, 130, 132	95 pmol Cl	5	< 1.0	Bernstein et al. (2011)
GC-qMS	TCE	60, 62, 95, 97, 130, 132	3 pmol Cl	5	< 0.85	Bernstein et al. (2011)
GC-qMS	TCE	130, 132	>275 pmol Cl	10	< 0.5	Bernstein et al. (2011)
GC-qMS	PCE	164, 166	1.6 pmol Cl	10	0.6	Aeppli et al. (2010)
GC-qMS	DDT	352, 354	1100 pmol Cl	9	1.2	Aeppli et al. (2010)
GC-qMS	PCP	264, 266	40 pmol Cl	9	1.3	Aeppli et al. (2010)
GC-HTC-IRMS	TCE	36, 38	30 nmol Cl	16	0.24	Renpenning et al. (2015)
GC-HTC-IRMS	PCE	36, 38	30 nmol Cl	16	0.37	Renpenning et al. (2015)
GC-MC-ICPMS	DCM	35, 37	2 nmol to 3 nmol Cl	10	0.15	Horst et al. (2017)
GC-MC-ICPMS	CF	35, 37	2 nmol to 3 nmol Cl	10	0.15	Horst et al. (2017)
GC-MC-ICPMS	CT	35, 37	2 nmol to 3 nmol Cl	10	0.13	Horst et al. (2017)
GC-MC-ICPMS	VC	35, 37	2 nmol to 3 nmol Cl	8	0.14	Horst et al. (2017)
GC-MC-ICPMS	<i>cis</i> -1,2-DCE	35, 37	2 nmol to 3 nmol Cl	8	0.10	Horst et al. (2017)
GC-MC-ICPMS	TCE	35, 37	200 nmol to 1300 nmol Cl	26	0.06	van Acker et al. (2006)
GC-MC-ICPMS	TCE	35, 37	2 nmol to 3 nmol Cl	34	0.12	Horst et al. (2017)
GC-MC-ICPMS	PCE	35, 37	175 nmol to 350 nmol Cl	10	0.09	van Acker et al. (2006)
GC-MC-ICPMS	PCE	35, 37	2 nmol to 3 nmol Cl	9	0.12	Horst et al. (2017)

## 2.2. Online chlorine isotope measurements

Compound-specific isotope analysis is simplified by online coupling of a separation device to a mass spectrometer. The prior separation step before measuring the isotope ratios has several benefits, including being able to report isotope ratios of the initial compounds as well as of the degradation products in the same sample. Different separation techniques and mass spectrometers are usually only applicable to certain groups of compounds.

Fig. 1b gives an overview of the methods that so far have been applied in chlorine CSIA of (semi-)volatile compound mixtures. The mixture is separated chromatographically, after which each compound is ionized by either electron ionization or inductively coupled plasma ionization, and finally the fragment ions are separated by  $m/z$  ratio and detected in a quadrupole or magnetic sector mass spectrometer. High-temperature conversion of the compounds after separation is also an option; however, an online conversion interface that would yield the desired chloromethane has not yet been developed. Table 1 gives an overview of the results obtained with some of the online methods discussed here.

It has become possible to obtain compound-specific chlorine isotope ratios of organic compounds directly by analyzing fragment ions in a mass spectrometer. The fragment ions are produced by the ion source of a mass spectrometer during electron ionization. The

isotope ratio of the compound is then related to the isotope ratio of the fragment ion. Shouakar-Stash et al. (2006) used an IRMS that was equipped for both continuous flow and dual inlet operation and reported chlorine isotope ratios for several chlorinated ethenes. The gaseous reference standards, identical to the compounds, were referenced to SMOC in dual-inlet operation by the Holt et al. (1997) method. Compound mixtures were separated by means of gas chromatography, and by injecting a reference gas peak at appropriate times during the chromatographic run in continuous-flow operation, it was possible to report compound-specific SMOC-referenced chlorine isotope ratios. This, however, also required adjusting the tuning parameters for each compound during a run. In addition to using headspace analysis for pure phase samples, chlorinated ethenes could also be extracted from aqueous samples and measured with the help of a solid-phase micro-extraction (SPME) fiber.

The work of Sakaguchi-Söder et al. (2007) paved the way for a simple online approach to measuring chlorine isotope ratios of chlorinated volatile organic compounds, analyzing the headspace of the samples. This approach uses a quadrupole mass spectrometer coupled to a gas chromatograph (GC-qMS) and is made possible by the high relative abundance of the  $^{37}\text{Cl}$  isotope. Compound-specific fragment ions are analyzed in the mass detector, and the chlorine isotope ratio of the compound is calculated



from intensities of these fragment ions through sets of stochastically derived Equations (2) and (3). Using the example of PCE, the ratio  $R_{PCE}$  of  $^{37}\text{Cl}$  to  $^{35}\text{Cl}$  in the molecule can be calculated as a weighted average by taking into account the measured intensities or peak areas  $I$  of the fragment ions produced in the mass spectrometer (Sakaguchi-Söder et al., 2007; Jin et al., 2011):

$$R_{PCE} = a \cdot \frac{1}{4} \cdot \frac{I_{166}}{I_{164}} \cdot b \cdot \frac{1}{3} \cdot \frac{I_{131}}{I_{129}} \cdot c \cdot \frac{1}{2} \cdot \frac{I_{96}}{I_{94}} \cdot d \cdot \frac{1}{1} \cdot \frac{I_{61}}{I_{59}} \quad (2)$$

The weight factors  $a, b, c, d$  can be calculated through different means taking into account some or all fragment ion intensities (Jin et al., 2011). Alternatively the ratio  $R_{PCE}$  can be calculated by only taking into account the measured intensities or peak areas  $I_{166}$  and  $I_{164}$  of the two most abundant fragment ions with masses 166 respectively 164 (Aeppli et al., 2010) or any pair of isotopologues (Elsner and Hunkeler, 2008):

$$R_{PCE} = \frac{1}{4} \cdot \frac{I_{166}}{I_{164}} = \frac{1}{3} \cdot \frac{I_{131}}{I_{129}} = \frac{1}{2} \cdot \frac{I_{96}}{I_{94}} = \frac{1}{1} \cdot \frac{I_{61}}{I_{59}} \quad (3)$$

It has been shown by Elsner and Hunkeler (2008) that this proportionality remains valid even if isotopologue ratios change due to a reactive processes. It is, however, important to note that Equation (3) is based on the assumption that all isotopes are distributed stochastically, i.e. randomly, among all possible isotopologues of a compound. A non-stochastic distribution of isotopes may occur when isotopologues contain more than one heavy isotope, which is referred to as isotope clumping (Eiler, 2007). The relevance of this effect for chlorinated hydrocarbons and, consequently, the question of whether all or only the most abundant pairs of isotopologue fragment ions need be taken into account during mass spectrometric analysis has not yet been conclusively answered. Given the elevated temperatures of  $>400^\circ\text{C}$  at which most organochlorine compounds are synthesized (Dreher et al., 2011), it can be argued that the influence of clumped isotopes effects on the distribution of isotopes among isotopologues is of minor importance, as clumped isotope effects become less pronounced at higher temperatures (Wang et al., 2004; Eiler, 2007). Furthermore, clumped isotope effects decrease with mass (Eiler, 2007). Hence, they are expected to be much smaller for isotopologues where chlorine is multiply isotopically substituted, compared to, e.g., the multiple substitution of hydrogen by deuterium.

Sakaguchi-Söder et al. (2007) did not report  $\delta^{37}\text{Cl}$  values relative to SMOC but relative to the internal standard trichlorofluoromethane ( $\text{CFCl}_3$ ), not providing an estimate for the trueness of the values by comparing them to those obtained by established offline methods. The required sample size of about 1 nmol makes this a sensitive method, at the expense of a lower precision than most other offline and online methods exhibit.

Aeppli et al. (2010) refined this method, realizing that in order to produce accurate results the samples need to be analyzed together with a molecularly identical SMOC-referenced standard. In addition to PCE, more complex molecules such as the pesticides dichlorodiphenyltrichloroethane (DDT) and pentachlorophenol (PCP) could also be analyzed with this approach. The chlorinated hydrocarbons were injected on-column following dilution in solvents. Only the two most abundant fragment ions were taken into account when calculating the chlorine isotope ratio, e.g. masses 164 and 166 for PCE (Equation (3)). To assess the trueness,  $\delta^{37}\text{Cl}$  values were compared to those obtained by offline TIMS. It was shown that the concentrations of the standards and the samples had to be within 20% of each other, otherwise the accuracy of the obtained  $\delta^{37}\text{Cl}$  values was compromised.

This necessity of matching the concentrations of standards and

samples was also observed by Bernstein et al. (2011). The reproducibility of the direct qMS method was investigated in an inter-laboratory study, comparing qMS and CF-IRMS methods coupled to GC. The IRMS instruments generally achieved a higher precision, which was attributed to their multiple detector configuration. The qMS instruments exhibited a temporal drift in the instrument  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio. The effect of this drift on the  $\delta^{37}\text{Cl}$  values was negligible when samples were bracketed with two referenced, molecularly identical standards of differing isotopic composition. Further, a mismatch between the difference in  $\delta^{37}\text{Cl}$  values and the known  $\delta^{37}\text{Cl}$  difference of the two standards was observed, which could also be corrected when using two standards. The authors advised against drawing any kind of conclusions about isotope enrichments based on raw, non-referenced isotope ratios.

A qMS can furthermore be coupled to an online thermal conversion interface. Hitzfeld et al. (2011) developed a setup for combusting chlorinated ethenes at a high temperature (HTC) of  $>1300^\circ\text{C}$ , yielding gaseous HCl which was analyzed in the mass detector as  $^1\text{H}^{35}\text{Cl}^+$  and  $^1\text{H}^{37}\text{Cl}^+$ . No SMOC-referencing procedure was implemented at the time and the precision ( $1\sigma$ ) for non-referenced  $^{37}\text{Cl}$  was on the order of 1%. Renpenning et al. (2015) later used this HTC interface in combination with an IRMS to report referenced values of TCE and PCE. The severe memory effects that are linked to using HCl as analyte in a mass spectrometer (see Section 2.1) were not resolved, though.

An entirely different method was brought up by van Acker et al. (2006), using an inductively coupled plasma (ICP) ionization source which made it possible to directly measure  $^{35}\text{Cl}^+$  and  $^{37}\text{Cl}^+$  ions of TCE and PCE in the multicollector (MC) setup. The method offered high sensitivity and precision. No sample concentration step was applied, thus only pure compounds were injected. PCE was referenced to SMOC by comparison to TCE of known  $\delta^{37}\text{Cl}$  value, and both compounds were separated by GC. As the ionization source runs on argon, the author points out one of the drawbacks of this kind of this ionization source: There is the possibility of interference of  $^1\text{H}^{36}\text{A}^+$ , which has a similar  $m/z$  (36.97537) as  $^{37}\text{Cl}^+$  (36.96590). A high mass resolution was needed to overcome this issue.

The issue was solved with Horst et al. (2017)'s approach to GC-MC-ICPMS. Care was taken to inhibit the ingress of water into the ionization source to avoid the formation of  $^1\text{H}^{36}\text{A}^+$ . The hydrogen atoms bonded to the chlorinated hydrocarbons were shown to have a negligible influence on its formation. As a lower mass resolution could be applied, a better sensitivity was achieved. The referenced standards used in the two-point calibration were not always identical to the analyte.

Same as for offline pcGC (see Section 2.1), a chlorine isotope effect may occur during online GC separation of organochlorine compound mixtures due to slight differences in retention times for different isotopologues. Similarly, care must be taken during integration of the eluting peaks in order to register the complete signal of all isotopologues (Tang et al., 2017). Chlorine isotope fractionation also takes place during ionization (Tang et al., 2019). The effects can, however, be mitigated when bracketing with molecularly identical standards (Aeppli et al., 2010), which are expected to fractionate in the same manner as the samples when ionized.

Online methods do not only simplify compound-specific isotope analysis, but also require a far lower amount of target compound. GC-qMS is a versatile routine method as it makes it possible to analyze a wide range of masses, providing a good sensitivity and acceptable precision. Difficulties lie in obtaining suitable sets of molecularly identical reference standards which have shown to be indispensable (Bernstein et al., 2011; Elsner et al., 2012; Ebert et al., 2017), since most instruments do not allow to introduce a reference gas. GC-IRMS uses detector configurations specific to each

compound, which allows for better precision but limits the compounds that can be analyzed. Online mass spectrometric methods employing a combustion interface have not yet proved themselves for routine chlorine isotope ratio measurements. They could, however, be applicable to a wide range of compounds, while at the same time their mass detectors only need to be optimized for a single analyte – an advantage they share with GC-MC-ICPMS.

### 2.3. Accuracy, linearity and calibration strategies

Positive evidence that degradation processes are occurring is given when the isotopic fractionation as shift in  $\delta^{37}\text{Cl}$  exceeds a certain threshold. An important question when comparing the capability of analytical methods to resolve this shift is hence that of the measurement uncertainty or accuracy of the method, which takes into account both the precision and the trueness. While some mass spectrometers report  $\delta$ -values by comparison with a working gas of known isotopic composition, this so-called single point anchoring versus the working gas often does not yield sufficiently accurate results (Paul et al., 2007). Therefore, isotopically referenced standards, preferably molecularly identical to the compound of interest, are used. These isotopic standards must be stable and homogeneous in isotopic composition (Coplen, 2011). They are required for two principal reasons. Firstly, they serve to account for isotopic fractionation processes during sample preparation and analysis. These processes may occur for example during incomplete conversion of the compound of interest to a molecule suitable for mass spectrometry. Under the principle of identical treatment, standard and sample are prepared and analyzed in the same way yielding repeatable results. Secondly, they enable reporting of reproducible and standardized results across laboratories.

Depending on the accuracy of the instrument, two or more isotopically different reference standards can be necessary due to a distortion of instrument isotope ratios relative to the SMOC scale (Bernstein et al., 2011). These standards are analyzed within a run to bracket the samples, i.e. the samples should have an isotope ratio that lies within the range given by the standards' isotope ratios. Obtaining said standards can often prove challenging.

In isotopic analysis, the term linearity describes whether the measured isotope ratio is independent of the quantity that is injected into the measuring device (Sherwood Lollar et al., 2007; Hunkeler et al., 2008; Jochmann and Schmidt, 2015). A large linearity range is advantageous as samples and standards are often not measured at exactly the same concentration or signal intensity. The limit of detection of an isotopic measurement method therefore involves identifying the lower limit of the linearity range or the lowest concentration for which no amount dependency is observed. Jochmann et al. (2006) have published guidelines to determine this so-called method detection limit using a moving mean approach, which gives the lower limit for which both the precision and trueness criteria are met. With all instruments, amount dependency effects of isotope measurements must be evaluated, in some cases requiring that the concentrations of samples and standards be closely matched.

## 3. Current knowledge about chlorine isotope fractionation

### 3.1. Basic concepts

The minor mass difference of isotopes leads to small changes in the physical and chemical properties of the molecules they are part of, which, in turn, is the cause of isotope fractionation or isotope effects. Isotope fractionation is described using the isotope ratio  $R_A$  in phase/educt  $A$  and  $R_B$  in phase/product  $B$  as the fractionation factor  $\alpha$ :

$$\alpha = \frac{R_B}{R_A} = \frac{\delta^{37}\text{Cl}_B + 1}{\delta^{37}\text{Cl}_A + 1} \quad (\text{‰}) \quad (4)$$

or, since  $\alpha$  is generally close to 1, as the enrichment factor  $\epsilon$ :

$$\epsilon = \alpha - 1 \quad (\text{‰}) \quad (5)$$

During a reversible equilibrium reaction  $A \rightleftharpoons B$ , different isotopologues have a slightly different equilibrium constant, which in turn causes an isotopic fractionation of isotopologues between the phases/educts  $A$  and phases/products  $B$ . This equilibrium isotope effect (EIE), expressed as the equilibrium fractionation factor  $\alpha_{eq}$ , is often not very large, though highly temperature-dependent.

Isotope effects for a non-equilibrium reaction  $A \rightarrow B$  are caused by differences in the reaction rates for isotopologues having a light ( $^{35}\text{Cl}$ ) or a heavy ( $^{37}\text{Cl}$ ) isotope at the reactive position and are expressed as the kinetic fractionation factor  $\alpha_{kin}$ . The difference in reaction rates  $k$  is expressed as the kinetic isotope effect (KIE):

$$KIE = \frac{k_{35\text{Cl}}}{k_{37\text{Cl}}} \quad (6)$$

A normal kinetic isotope effect is observed if  $KIE > 1$ , i.e. the isotopologue with the lighter isotope(s) at the reactive position(s) will react more rapidly, while the isotopologue with the heavier isotope(s) at the reactive position(s) will accumulate in the educt. The opposite is true if  $KIE < 1$ , which is denoted as a inverse kinetic isotope effect. In addition to this primary isotope effect, secondary isotope effects are observed when isotopic substitution takes place at non-reactive positions. Secondary isotope effects are however usually at least one order of magnitude weaker than primary isotope effects (Meckenstock et al., 2004; Elsner et al., 2005; Aelion, 2010).

Using the isotope enrichment factor  $\epsilon$ , the isotope fractionation during a transformation process can be described by the Rayleigh equation (Elsner and Hunkeler, 2008):

$$\frac{R_t}{R_0} = f^\epsilon = f^{(\alpha-1)} \quad (7)$$

where  $R_0$  describes the initial isotope ratio at the beginning of the transformation process,  $R_t$  the isotope ratio and  $f$  the remaining fraction of the compound at a point in time  $t$ .

In a well-constrained, homogeneous system, Equation (7) is the basis to calculate a compound-specific bulk chlorine isotope enrichment factor  $\epsilon_{\text{Cl,bulk}}$ , specific to a given transformation mechanism. This bulk enrichment factor accounts for the change in isotope ratios averaged over the whole compound. Crucially, the remaining concentration of the compound must only be influenced by the transformation process, thus laboratory batch experiments are preferable for obtaining said enrichment factors over field studies where processes such as dilution and dispersion affect the measured concentration data (Abe and Hunkeler, 2006). If the transformation process on the field site is known, the degree of degradation can be quantified by inserting  $\epsilon_{\text{Cl,bulk}}$  and the measured shift in isotope ratios into Equation (7). Uncertainties in field data due to multiple unconstrained processes at play can be reduced when isotopic data of multiple elements is considered (Zwank et al., 2005). More specifically, the ratio of the shift in delta values ( $\Delta\delta$ ) for the isotopes of two elements during a transformation process is, for the most part, not affected by non-reactive processes, as well as being specific to the reaction pathway (Palau et al., 2017). This ratio corresponds to the slope of a fitted linear relationship using least squares or, preferably, the York method (Ojeda et al., 2019), obtained by plotting the  $\delta$  values for the two

elements, e.g.  $\delta^{13}\text{C}$  and  $\delta^{37}\text{Cl}$  against each other (Abe et al., 2009a), and provides a good approximation of the ratio of enrichment factors:

$$\frac{\Delta\delta^{13}\text{C}}{\Delta\delta^{37}\text{Cl}} = \frac{\varepsilon_{\text{C,bulk}}}{\varepsilon_{\text{Cl,bulk}}} \quad (8)$$

The dual element approach is useful for identifying the dominant degradation process, which allows to constrain the element-specific range of enrichment factors to be inserted into Equation (7).

CSIA has been widely used for low molecular mass compounds. In larger chlorinated molecules such as certain aromatic compounds and pesticides, the isotope effect can be diluted as the heavy isotope is more likely to be at a non-reactive position in the molecule (see Section 5), leading to a smaller bulk isotope enrichment factor than would be expected from cleavage of a bond involving the heavier isotope. Another process, which is especially relevant to biotic degradation reactions, is masking. Being enzyme-catalyzed, biotic degradation reactions always involve multiple steps, where the isotope effect from the actual catalytic reaction can be masked by preceding rate-limiting steps such as extra- and intracellular mass transfer (Elsner, 2010).

### 3.2. Chlorine isotope fractionation by physical processes

Physical processes, such as evaporation (volatilization/liquid-vapor partitioning), diffusion, sorption and dissolution can lead to an isotopic fractionation due to slight differences in the thermodynamic properties of isotopologues (Aelion, 2010). Table 2 summarizes the chlorine isotope enrichment factors caused by physical processes that have been obtained through laboratory studies.

Liquid-vapor chlorine isotope fractionation in chlorinated VOCs has been studied from an early date in the laboratory. Baertschi et al. (1953) and Bradley (1954) observed that for carbon tetrachloride (CT) and chloroform (CF), the liquid phase became enriched in  $^{37}\text{Cl}$ , while  $\delta^{13}\text{C}$  showed an inverse isotope trend, leading to an enrichment in the vapor phase. These opposite trends were confirmed by Huang et al. (1999) for TCE and dichloromethane (DCM) as well as by Poulson and Drever (1999) and Jeannotat and Hunkeler (2012) for TCE. They are believed to be caused by the differing effects of isotopic substitution on intermolecular forces in the condensed phase. In general, heavy isotope substitution leads to weaker intermolecular forces and thus a lower boiling point due to lower frequencies of internal vibration (Van Hook, 2005), however the effect of  $^{13}\text{C}$  substitution is considerably larger than that of  $^{37}\text{Cl}$  substitution (Jancsó and Van Hook, 1974). The weak inverse chlorine isotope effect is thus counteracted by other intermolecular forces in the condensed

phase, while it is possible to observe the strong inverse carbon isotope effect. When the chlorinated VOC is dissolved in water, hydrogen bonding and dipole-dipole interactions, which are relevant between the more polar molecules, may become strong enough to completely cancel out the inverse carbon isotope effect (Horst et al., 2016).

Vapor-phase diffusion has been shown to cause a significant chlorine isotope fractionation in laboratory experiments (Jeannotat and Hunkeler, 2012). This arises due to heavier isotopocules generally being less mobile than their lighter counterparts. The difference of two atomic units between stable chlorine isotopes compared to only one atomic unit between stable carbon isotopes explains the pronounced chlorine isotope fractionation.

Isotope fractionation due to aqueous-phase diffusion also occurs in the subsurface. Several models for the diffusion coefficient have been proposed. Wanner and Hunkeler (2019) presented a comprehensive review of five relevant models and existing experimental data that have been obtained for several compounds. In general, models for the mass dependency of a compound's diffusion coefficient reduce to the form:

$$D \propto m^{-\beta} \quad (9)$$

where  $m$  is the isotopologue molecular mass and  $\beta$  is a number generally between 0 and  $\sim 1/2$ . This relation is sometimes written as a function of the reduced mass ( $\mu_r = m \cdot m_{\text{solvent}} / (m + m_{\text{solvent}})$ ). However, as many theories that assume that the water molecule network acts as a massive effective particle ( $m_{\text{solvent}} \gg m$ ) (Bourg and Sposito, 2007; Wanner and Hunkeler, 2019), Equation (9) is generally valid.

Various models such as the well-known Chapman-Enskog relation (Chapman and Cowling, 1970) have been developed for diffusion. However, only some are relevant in the case of aqueous solutions in porous media. Extensions of classical Fickian kinetic theory (Fick, 1855) imply that  $\beta = 1/2$  in Equation (9) (Alder et al., 1974). The Einstein (1905) and Langevin (1908) models of diffusion are based on the random trajectory of a single solute particle (i.e., Brownian motion), but do not integrate mass effects. The Maxwell-Stefan diffusion model (Maxwell, 1867), like the Fick model, considers the ensemble behaviour of solute particles. In this model, mass is explicitly taken into account with the resulting relationship of  $\beta = 1/2$ . This theory assumes that solute molecules move according to solute concentration gradients, but are subject to a friction-like force from the solvent molecules. A final theory of note is mode-coupling theory analysis (MCTA) (Bhattacharyya and Bagchi, 1997; Ali et al., 2001) wherein  $0 < \beta < 1/2$ . In MCTA, the diffusion coefficient depends on the interplay between extremely frequent intermolecular collisions, which are strongly mass-dependent, and longer-term hydrodynamic modes which exhibit

**Table 2**  
Bulk carbon and chlorine isotope enrichment factors by physical processes based on laboratory experiments.

Mechanism	Compound	$\varepsilon_{\text{C,bulk}}$ (‰)	$\varepsilon_{\text{Cl,bulk}}$ (‰)	Reference
Continuous evaporation of pure compound	DCM	+ 0.65±0.02	- 0.48±0.06	Huang et al. (1999)
Continuous evaporation of pure compound	TCE	+ 0.31±0.04	- 1.82±0.22	Huang et al. (1999)
Continuous evaporation of pure compound	TCE	+0.24±0.06 to + 0.35±0.02	- 1.64±0.13	Poulson and Drever (1999)
Continuous evaporation of pure compound	TCE	+ 0.28±0.03	- 1.35±0.03	Jeannotat and Hunkeler (2012)
Stepwise evaporation of pure compound	TCE	+ 0.75±0.04	- 0.39±0.03	Jeannotat and Hunkeler (2012)
Diffusion-controlled evaporation of pure compound	TCE	+ 0.10±0.05	- 1.39±0.06	Jeannotat and Hunkeler (2012)
Stepwise evaporation of aqueous phase compound	TCE	+ 0.38±0.04	- 0.06±0.05	Jeannotat and Hunkeler (2012)
Aqueous phase back-diffusion (enrichment in reservoir)	cis-1,2-DCE		-0.28 to - 1.33	Vakili (2017)
Aqueous phase back-diffusion (enrichment in reservoir)	1,2-DCA	- 0.23±0.04	- 0.61±0.03	Wanner and Hunkeler (2015)
Aqueous phase sorption (enrichment in solution)	1,2-DCA	- 0.40±0.06	- 0.55±0.13	Wanner et al. (2017)
Aqueous phase sorption (enrichment in solution)	cis-1,2-DCE	<0.1	- 0.2	Vakili (2017)
Aqueous phase sorption (enrichment in solution)	TCE	<0.1	- 0.85	Vakili (2017)



little mass dependence (Wanner and Hunkeler, 2019).

Finally, sorption can also induce isotopic fractionation in the adsorbed and desorbed substances. While Vakili (2017) detected only an insignificant carbon isotope effect, the chlorine isotope enrichment in the solution reached  $-0.2\%$  for *cis*-1,2-DCE and  $-0.85\%$  for TCE, which may also be explained by the difference of two atomic units between stable chlorine isotopes compared to only one atomic unit between stable carbon isotopes. The preferential sorption of the light isotopologues leads to an enrichment of  $^{37}\text{Cl}$  in the solution. Similarly to evaporation, this may be explained by the weaker intermolecular forces between heavy isotopologues and the sorbent compared to light isotopologues. Sorption is of concern primarily in organic-rich sediments as well as low-permeability sediments with small pore sizes, such as shales and clays, due to their high specific surface area. It is also relevant in zero-valent iron systems (Dries et al., 2007) which are of increasing interest in remediation efforts (Crane and Scott, 2012).

Physical processes are often not well constrained to a single process. In laboratory experiments, Jeannotat and Hunkeler (2012) found a cumulative normal chlorine isotope effect by both liquid-vapor partitioning and vapor phase diffusion. Vakili (2017) investigated chlorine isotope effects caused by back-diffusion from a low-permeability zone as well as sorption on the laboratory scale, although it is unclear how the set-up discriminated between diffusion and sorption processes. Wanner et al. (2017) attempted to isolate the isotopic effects of these processes by including field data into a numerical model. The theoretical sorption-induced isotope shift was calculated to reach up to 2%.

Chlorine isotope effects caused by physical processes have not been widely studied on the field scale. While gas-phase diffusion (Jeannotat and Hunkeler, 2012) may cause a significant chlorine isotope effect, its relevance in vadose zone transport has not been established (Hunkeler et al., 2011b). The isotope effects of physical processes are believed to have a minor influence compared to the isotope effects observed during (bio-)chemical degradation processes and are less pronounced once steady-state conditions are reached (Schmidt and Jochmann, 2012). Numerical considerations related to modelling physical processes are discussed in Section 5.

### 3.3. Chlorine isotope fractionation during biotic processes

Biotic degradation of chlorinated contaminants in the subsurface is a process that causes isotope fractionation due to bond cleavage. Chemical bonds involving the heavier isotope are slightly stronger than those involving the light isotope, thus the lighter isotopologue of a molecule degrades preferentially resulting in a heavy isotope enrichment in the residual compound. Fig. 2 gives an overview of potential degradation pathways for the example of PCE. One advantage of compound-specific isotope analysis is that degradation can be proven even if there are no characteristic degradation products. If they however do occur, it is advisable to monitor them, also their isotope ratios, to provide confirmation about the degradation path.

The biotic degradation pathway is a function of the redox potential in the soil and the availability of electron donors and adapted bacteria. Chlorinated hydrocarbons either serve as electron acceptors during anaerobic organohalide respiration or else as electron donors during anaerobic as well as aerobic metabolic degradation (Dolinová et al., 2017). If degradation of xenobiotics is not the primary metabolic process, it is referred to as co-metabolism and attributed to the activity of non-specific enzymes. Anaerobic dechlorination is usually the predominant process in biotic degradation on the field scale, as aerobic dechlorination is limited by the lack of electron donor, specifically molecular oxygen (Numata et al., 2002a). The aerobic process does

however become more relevant with decreasing chlorination, e.g. during the sequential degradation of PCE, where a purely anaerobic process may stall at the highly toxic degradation product VC (Tiehm and Schmidt, 2011). Aerobes on the other hand have a higher potential to further degrade VC to non-chlorinated, non-toxic compounds through epoxide formation.

Table 3 gives an overview of some of the chlorine isotope enrichment factors that were measured in laboratory microcosms. It is noticeable that the chlorine isotope fractionation is almost always smaller in magnitude than the carbon isotope fractionation, as opposed to the trends observed for physical processes. Furthermore, different reactive processes lead to remarkably different carbon and chlorine isotope enrichment factors for the same compound. As commonly observed, the exact reaction mechanism dictates whether a large primary or lower secondary chlorine isotope effect is observed or whether dilution and masking (see Section 3.1) have an influence on the magnitude of fractionation.

During aerobic oxidation of DCM, a considerable carbon and chlorine isotope effect was observed by Heraty et al. (1999). The first and rate-limiting step was proposed to involve breaking of a C-Cl bond by nucleophilic substitution ( $\text{S}_{\text{N}}2$ ), leading to  $\text{CH}_2\text{O}$  (formaldehyde) and HCl via the unstable intermediate  $\text{CH}_2\text{ClOH}$ . VC and 1,2-DCA on the other hand undergo a different reaction mechanism during aerobic oxidation, which manifests itself in the smaller enrichment factors (Abe et al., 2009b). Here, the first step does not involve C-Cl bond cleavage but C-C bond cleavage and the formation of an epoxide between the two carbon atoms.

Two distinct aerobic degradation pathways for 1,2-DCA can be distinguished using dual carbon-chlorine isotope plots (Palau et al., 2014a). Only a small carbon isotope effect is measured with C-H bond cleavage as the initial step, which is the case for the reaction with the monooxygenase enzyme used by the *Pseudomonas* sp. strain. The dehalogenase enzyme that is employed by *Xanthobacter autotrophicus* and *Ancylobacter aquaticus* causes a large carbon isotope effect, as here the initial step is C-Cl bond cleavage via nucleophilic  $\text{S}_{\text{N}}2$  substitution. For both pathways, Palau et al. (2014a) observed a similar chlorine isotope effect  $\epsilon_{\text{Cl,bulk}}$ . During anaerobic degradation by *Dehalococcoides* and *Dehalogenimonas*, 1,2-DCA exhibits a significant chlorine isotope effect (Palau et al., 2017). The reason is thought to be a dichloroelimination pathway, where not one but two C-Cl bonds are cleaved. This dichloroelimination pathway also appears during anaerobic degradation of 1,1,2-TCA to VC (Rosell et al., 2019). Compared to 1,2-DCA, the chlorine isotope effect is not quite as pronounced due to masking effects (see Section 3.1) caused by differences in the enzyme kinetics.

The anaerobic reductive dechlorination of chlorinated ethenes can either proceed via single-electron transfer or nucleophilic addition as initial step (Aelion, 2010). The former would lead to primary carbon and chlorine isotope effects due to C-Cl bond cleavage, while the latter would attack the C=C double bond resulting in a large primary carbon isotope effect and secondary chlorine isotope effects (Cretnik et al., 2014). For TCE, Kuder et al. (2013) applied triple element hydrogen-carbon-chlorine isotope analysis and observed secondary chlorine isotope effects consistent with the nucleophilic addition pathway.

Masking effects may also have a major impact on the observed isotope fractionation during reductive dechlorination. For PCE, Renpenning et al. (2014) obtained significantly different dual carbon-chlorine isotope slopes for the culture *Sulfurospirillum multivorans* ( $\epsilon_{\text{C}}/\epsilon_{\text{Cl}}$  ranging from 2.2 to 2.8) versus the culture's enzyme corrinoid cofactor ( $\epsilon_{\text{C}}/\epsilon_{\text{Cl}}$  ranging from 4.6 to 7.0), which was attributed to the preceding rate-limiting steps. Interestingly, this masking effect was not observed during reductive dechlorination of TCE.

While considerable work has been done in measuring chlorine

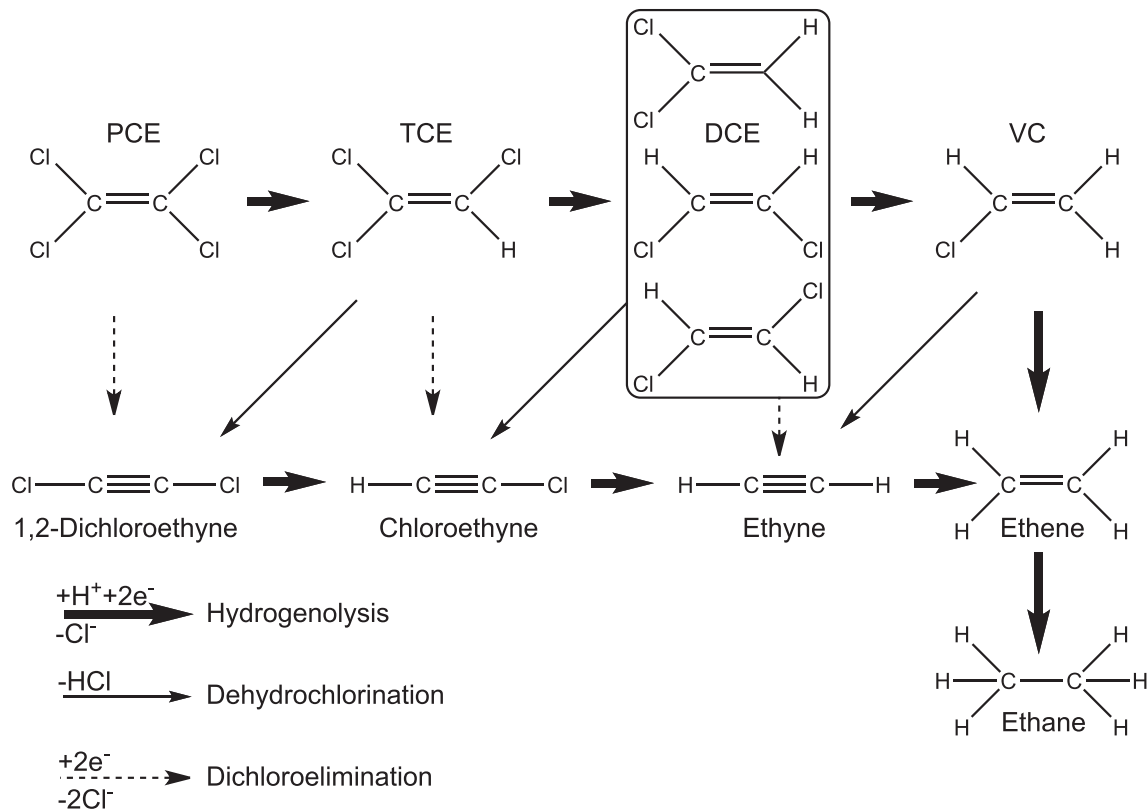


Fig. 2. Potential biotic and abiotic degradation pathways for PCE adapted from Brown et al. (2006). Biotic degradation typically takes the hydrogenolysis pathway from PCE to VC.

isotope fractionation during biotic degradation, the masking effects that are inherent to biotic processes as well as the ambiguity of some dual carbon-chlorine isotope slopes can complicate the attribution of specific mechanisms to observed isotope fractionations. Improvements in analytical methods (see Section 2) can assist in lowering the uncertainty of chlorine CSIA data, especially for TCE.

#### 3.4. Chlorine isotope fractionation during abiotic processes

Abiotic degradation of chlorinated contaminants in soil is usually slower than biotic degradation, but has the advantage that it is likely to result in completely dechlorinated, generally non-toxic compounds (Tobiszewski and Namieśnik, 2012). There are many different constituents of natural soil that can be relevant to abiotic degradation during natural remediation, namely iron-bearing sulfide, oxide, hydroxide and clay minerals (He et al., 2015). Additionally, engineered remediation at polluted sites often involves reactive barriers that employ zero-valent metals or compounds that contain metals at their reduced state (Hara, 2012). Table 3 gives an overview of some of the chlorine isotope enrichment factors that were measured in the laboratory for abiotic degradation.

The isotope effects associated with abiotic degradation in chlorinated hydrocarbons are often very pronounced for carbon isotopes (Slater et al., 2003; Liang et al., 2007) and for chlorine isotopes. Audi-Miró et al. (2013) studied the chlorine isotope effect during degradation of chlorinated ethenes in an engineered reactive barrier that used zero-valent iron (ZVI). The process is based on an electron transfer where the chlorinated ethenes are dechlorinated reductively, while the ZVI is oxidized. Abiotic TCE degradation yielded *cis*-1,2-DCE via a hydrolysis pathway as well as ethene and ethane via dichloroelimination (Fig. 2). This additional

pathway is often observed during abiotic degradation and involves the simultaneous cleavage of two chlorine substituents, explaining the large chlorine isotope effect. Torrentó et al. (2017) explored different abiotic degradation mechanisms for chloroform (CF). The oxidation reaction was proposed to involve C-H bond cleavage as the initial step, hence only a small secondary chlorine isotope effect was observed (Table 3). Rodríguez-Fernández et al. (2018) investigated the suitability of different iron minerals in engineered remediation, and observed a pronounced pH dependence of the chlorine isotope enrichment factors (Table 3), which was suspected to be caused by surface passivation of the iron minerals at alkaline pH.

Most chlorine isotope enrichment data for abiotic processes have so far been obtained with a focus on zero-valent iron in engineered remediation. The question of which pathways are taken during reaction of chlorinated contaminants with natural constituents of soils could be investigated using dual carbon-chlorine isotope analysis.

## 4. Field applications

Chlorine CSIA has rarely been used in source differentiation field applications. A more common field application is the tracking of reactive processes, usually in combination with carbon isotope analysis. Table 4 provides an overview of field studies where chlorine CSIA has been applied.

### 4.1. Source differentiation

Due to differences in the methods and raw materials used in manufacturing, certain chlorinated hydrocarbons can exhibit a range of  $\delta^{37}Cl$  values. For example, van Warmerdam et al. (1995)

**Table 3**

Bulk carbon and chlorine isotope enrichment factors as well as dual element isotope slopes (C/Cl) by biotic and abiotic degradation based on laboratory microcosm studies.

Compound	Proposed mechanism (rate-limiting step)	Culture (enzyme) for biotic or reactant for abiotic degradation	$\epsilon_{C,bulk}$ (‰)	$\epsilon_{Cl,bulk}$ (‰)	C-Cl isotope slope	Reference
Biotic						
DCM	aerobic oxidation (nucleophilic substitution)	<i>Methylobacterium/Ochrobactrum</i> MC8b	-42.4±1.5	-3.8±0.3	11.2	Heraty et al. (1999)
1,2-DCA	aerobic oxidation (C-H bond cleavage)	<i>Pseudomonas</i> sp.	-3.5±0.1	-3.8±0.2	0.78±0.03	Palau et al. (2014a)
1,2-DCA	aerobic oxidation (nucleophilic substitution)	<i>Xanthobacter autotrophicus</i> GJ10 & <i>Ancylobacter aquaticus</i> AD20	-31.9±0.7 to -32.0±0.9	-4.2±0.1	7.7±0.2	Palau et al. (2014a)
1,2-DCA	dichloroelimination	<i>Dehalococcoides</i>	-33.0±0.4	-5.1±0.1	6.8±0.2	Palau et al. (2017)
1,2-DCA	dichloroelimination	<i>Dehalogenimonas</i>	-23±2	-	1.89±0.02	Palau et al. (2017)
1,1,2-TCA	dichloroelimination	<i>Dehalogenimonas</i> sp.	-6.9±0.4	-2.7±0.3	2.5±0.2	Rosell et al. (2019)
VC	aerobic oxidation (epoxide formation)	<i>Nocardioides</i> strain JS614	-7.2±0.16	-	25.6±3.6	Abe et al. (2009b)
VC	reductive dechlorination	<i>Dehalococcoides</i>	-25.0±0.72	-	13.7±0.3	Abe et al. (2009b)
VC	reductive dechlorination	<i>Dehalococcoides</i>	-26.7±1.9 to -28.1	-2.7±0.4	10±10	Kuder et al. (2013)
cis-1,2-DCE	aerobic oxidation (epoxide formation)	$\beta$ -Proteobacterium strain JS666	-8.5±0.10	-	32.3±6.4	Abe et al. (2009b)
cis-1,2-DCE	reductive dechlorination	<i>Dehalococcoides</i>	-18.5±1.80	-	11.4±0.6	Abe et al. (2009b)
cis-1,2-DCE	reductive dechlorination	<i>Dehalococcoides</i>	-26.8	-3.2	8.3	Kuder et al. (2013)
TCE	reductive dechlorination	<i>Geobacter lovleyi</i>	-12.2±0.5	-3.6±0.1	3.4±0.2	Cretnik et al. (2013)
TCE	reductive dechlorination	<i>Desulfitobacterium hafniense</i>	-9.1±0.6	-2.7±0.6	3.4±0.2	Cretnik et al. (2013)
TCE	reductive dechlorination	<i>Desulfitobacterium</i> sp.	-12.2±1.0	-3.6±0.2	3.4±0.2	Cretnik et al. (2014)
TCE	reductive dechlorination	<i>Clostridium</i> sp. & <i>Desulfitobacterium aromaticivorans</i>	-8.8±0.2	-3.5±0.5	2.7±0.8	Wiegert et al. (2013)
TCE	reductive dechlorination	<i>Dehalococcoides</i>	-15.3 to -16.4±0.4	-3.6±0.3	4.8±4.5	Kuder et al. (2013)
TCE	reductive dechlorination	<i>Sulfurospirillum multivorans</i> (PceA-norpseudo-B12 enzyme)	-20.0±0.5	-3.7±0.2	5.3±0.3	Renpenning et al. (2014)
TCE	reductive dechlorination	<i>Sulfurospirillum multivorans</i> (PceA-nor-B12 enzyme)	-20.2±1.1	-3.9±0.6	5.0±0.8	Renpenning et al. (2014)
PCE	reductive dechlorination	<i>Desulfitobacterium</i> sp.	-19.0±0.9	-5.0±0.1	3.8±0.2	Cretnik et al. (2014)
PCE	reductive dechlorination	<i>Clostridium</i> sp. & <i>Desulfitobacterium aromaticivorans</i>	-5.6±0.7	-2.0±0.5	2.9±0.9	Wiegert et al. (2013)
PCE	reductive dechlorination	<i>Sulfurospirillum multivorans</i> (PceA-norpseudo-B12 enzyme)	-1.4±0.1	-0.6±0.2	2.2±0.7	Renpenning et al. (2014)
PCE	reductive dechlorination	<i>Sulfurospirillum multivorans</i> (PceA-nor-B12 enzyme)	-1.3±0.05	-0.4±0.1	2.8±0.5	Renpenning et al. (2014)
PCE	reductive dechlorination	consortium SL2-PCEc <i>Sulfurospirillum</i> (PceATCE)	-3.6±0.2	-1.2±0.1	2.7±0.3	Badin et al. (2014)
PCE	reductive dechlorination	consortium SL2-PCEb <i>Sulfurospirillum</i> (PceADCE)	-0.7±0.1	-0.9±0.1	0.7±0.2	Badin et al. (2014)
Abiotic						
CF	oxidation (C-H bond cleavage)	persulfate	-8±1	-	17±2	Torrentó et al. (2017)
CF	hydrolysis (E1cB elimination)	pH 12 buffer	-57±5	0.44±0.06	-	Torrentó et al. (2017)
CF	hydrogenolysis (C-Cl bond cleavage)	ZVI pH 7	-33±11	-4.4±0.4	13.0±0.8	Torrentó et al. (2017)
CF	hydrogenolysis/reductive elimination	ZVI pH 12	-20±9	-3±1	8±1	Rodríguez-Fernández et al. (2018)
CT	hydrogenolysis	ZVI pH 7	-3.7±0.1	-	6.1±0.5	Rodríguez-Fernández et al. (2018)
CT	hydrogenolysis	ZVI pH 12	-3.4±0.1	0.58±0.04	-	Rodríguez-Fernández et al. (2018)
CT	hydrogenolysis/hydrolysis	magnetite pH 12	-2±1	-	5.8±0.4	Rodríguez-Fernández et al. (2018)
CT	hydrogenolysis/thyolitic reduction	pyrite pH 7	-5±2	-0.8±0.2	2±1	Rodríguez-Fernández et al. (2018)
CT	hydrogenolysis/thyolitic reduction	pyrite pH 12	-4±1	-1.5±0.4	2.9±0.5	Rodríguez-Fernández et al. (2018)
1,1,1-TCA	hydrolysis/dehydrohalogenation	water	-1.6±0.2	-0.9±0.4	3.7±0.9	Rodríguez-Fernández et al. (2018)
1,1,1-TCA	(C-Cl bond cleavage)	ZVI	-7.8±0.4	-4.7±0.1	0.33±0.04	Palau et al. (2014c)
cis-1,2-DCE	dichloroelimination & hydrogenolysis	ZVI	-20.5±1.8	-5.2±0.2	1.5±0.1	Palau et al. (2014c)
TCE	dichloroelimination & hydrogenolysis	ZVI	-14.8±0.6	-6.2±0.8	3.1±0.2	Audí-Miró et al. (2013)
TCE	(nucleophilic addition)	magnetite + H <sub>2</sub> O <sub>2</sub>	-2.9±0.3	-2.6±0.1	5.2±0.3	Audí-Miró et al. (2013)
				-0.9±0.1	3.1±0.2	Liu et al. (2014)

**Table 4**  
Field studies where chlorine CSIA has been applied.

Compound	Isotopes		Objective			Reference
	<sup>13</sup> C	<sup>37</sup> Cl	Source differentiation	Process assessment	Quantification of degradation	
1,2-DCA	✓	✓		✓		Wanner et al. (2017)
1,2-DCA	✓	✓		✓		Palau et al. (2017)
1,1,1-TCA	✓	✓		✓		Palau et al. (2016)
cis-1,2-DCE	✓	✓		✓		Hunkeler et al. (2011a)
cis-1,2-DCE	✓	✓		✓		Hunkeler et al. (2011b)
TCE		✓		✓		Sturchio et al. (1998)
TCE	✓	✓		✓		Hunkeler et al. (2011b)
TCE	✓	✓	✓	✓	✓	Wiegert et al. (2012)
TCE	✓	✓		✓	✓	Wiegert et al. (2013)
TCE	✓	✓		✓		Badin et al. (2016)
TCE	✓	✓	✓	✓		Palau et al. (2014b)
PCE	✓	✓	✓	✓		Beneteau et al. (1999)
PCE	✓	✓		✓		Hunkeler et al. (2011b)
PCE	✓	✓	✓	✓	✓	Wiegert et al. (2012)
PCE	✓	✓		✓	✓	Wiegert et al. (2013)
PCE	✓	✓		✓	✓	Badin et al. (2014)
PCE	✓	✓	✓	✓		Palau et al. (2014b)
PCE	✓	✓		✓		Badin et al. (2016)
PCE	✓	✓		✓	✓	Murray et al. (2019)

reported  $\delta^{37}\text{Cl}$  SMOC values from  $-2.4\text{‰}$  to  $4.4\text{‰}$  for TCE sourced from different manufacturers. Based on these findings, Beneteau et al. (1999) used isotopic methods to distinguish two potential sources of PCE at a field site, with  $\delta^{37}\text{Cl}$  SMOC values ranging from 0.2 to 1.1‰. The plume at this particular field site was however not affected by biodegradation. To assess whether a plume could be affected by biodegradation, where the resulting isotopic fractionation would hamper fingerprinting applications, a field site should be first characterized geochemically with regard to the redox conditions (Aelion, 2010). Furthermore, a dual element isotope approach should be employed to exclude degradation. Dual carbon and chlorine isotope analysis was applied to field site in a fractured bedrock aquifer by Palau et al. (2014b). Here, multiple sources as well as biodegradation had to be identified. The initial contaminants could be sampled at several different potential sources, yielding  $\delta^{13}\text{C}$  values ranging from  $-40.5\text{‰}$  to  $-15.6\text{‰}$  for TCE, while  $\delta^{37}\text{Cl}$  only varied between 0.53‰ and 0.66‰, though. The isotope ratios in groundwater samples downgradient of the sources showed that certain parts of the plumes were affected by biodegradation, while in others the isotope ratios remained stable. A systematic study of the  $\delta^{37}\text{Cl}$  range is still lacking for many compounds, some of the values that have so far been reported are summarized in Table S1 (in SI).

#### 4.2. Assessing reactive processes

In contaminated sites, isotope effects can be caused by physical processes (see Section 3.2) or reactive processes (see Sections 3.3 and 3.4). For assessing reactive processes, the typical analytical uncertainties for chlorine isotope analysis as discussed in Section 2 need to be considered carefully, in view of the generally smaller magnitudes of chlorine isotope fractionation compared to carbon isotope fractionation. A compound for which it is especially feasible to differentiate biotic and abiotic pathways using dual carbon-chlorine isotope slopes (see Table 3) is *cis*-1,2-DCE, while for TCE the slopes for both processes may fall into the same range. For 1,2-DCA, VC, *cis*-1,2-DCE and PCE different biotic pathways can easily be distinguished, and abiotic pathways can be differentiated for CF and CT. Data on abiotic degradation of PCE is still lacking.

As a basis for assessing reactive processes, the effect of non-reactive processes has to be taken into account. Chlorine isotope effects due to physical processes on the field scale were

investigated by Hunkeler et al. (2011b), who observed neither carbon nor chlorine isotopic fractionation by either liquid-vapor partitioning at the boundary layer or vapor phase diffusion in the unsaturated zone of a sandy aquifer for *cis*-1,2-DCE, TCE and PCE. This was taken as justification to relate isotope ratios measured in soil gas to those measured in groundwater, under the condition of a steady-state system. Wanner et al. (2017) used dual carbon-chlorine isotope plots to find out whether sorption of 1,2-DCA is associated with an isotope effect, this was however only possible because degradation could be excluded. Desorption from saturated low-permeability sediments was shown to have normal isotope effect for carbon and for chlorine, as expected from laboratory experiments (see Section 3.2).

Reactive processes on the field scale were assessed by Sturchio et al. (1998) using compound-specific chlorine isotope analysis at a site contaminated with TCE, where an enrichment in <sup>37</sup>Cl provided evidence for natural attenuation. Hunkeler et al. (2011a) measured stable isotope fractionation at a field site that exhibited varying redox conditions and the potential for abiotic degradation. Dual carbon-chlorine isotope plots made it possible to exclude an abiotic degradation pathway for TCE and PCE, while the fate of the degradation product *cis*-1,2-DCE remained unclear. In a follow-up study at this field site, Badin et al. (2016) applied dual carbon-chlorine isotope plots, giving evidence for abiotic degradation of *cis*-1,2-DCE by pyrite (FeS<sub>2</sub>) or other iron sulfide species as suggested by Hunkeler et al. (2011a) for this field site. A difficulty was observed here when investigating a compound that is a degradation product as well as a primary contaminant. It is possible to resolve these issues with dual carbon-chlorine isotope plots of both the initial contaminant and the degradation product, where both will follow a linear trend if no further degradation of the product is occurring (Hunkeler et al., 2009). Further dual carbon-chlorine isotope analysis by Murray et al. (2019) at this field site confirmed the biotic degradation pathway for PCE.

Wiegert et al. (2012) encountered a wide range of chlorine isotope enrichment factors for chlorine when calculating it through dual carbon-chlorine isotope slopes from field data and  $\epsilon_{\text{C,bulk}}$  literature values according to Equation (8), hence in their following study Wiegert et al. (2013) used bacteria culture from the field site in batch reactors to help constrain  $\epsilon_{\text{Cl,bulk}}$  for TCE and PCE and hereby lowering the uncertainty in calculating the degree of degradation. Badin et al. (2014)'s field study showed that similar



bacterial culture do not necessarily lead to similar dual carbon-chlorine isotope plots during reductive dechlorination. This was attributed to a different reaction mechanism, which resulted in either primary or secondary isotope effects. Applying dual element isotope analysis when quantifying the degree of degradation proved advantageous at this field site. Taking into account the chlorine isotope data helped to narrow down the choice of enrichment factor when quantifying the degree of degradation.

A common problem that was encountered during the application of chlorine CSIA at the aforementioned field studies is the lack of published dual carbon-chlorine isotope slopes for different compounds and processes. If laboratory-derived reaction-specific enrichment values for the isotopes of multiple elements are available, even relative contributions of different reactive processes, such as aerobic and anaerobic degradation, can be assessed (Palau et al., 2016, 2017). New developments in modelling degradation and physical processes (e.g., Jin et al., 2014; Badin et al., 2018; Halloran et al., 2019) show promise for more robust integration of chlorine CSIA data into quantitative assessments.

## 5. Modelling chlorine fractionation processes

### 5.1. General considerations

Interpretation of CSIA data requires an understanding of the fractionation processes. Two major factors differentiate the modelling of chlorine isotopic fractionation from that of carbon. Firstly, the ratio of heavy to light chlorine atoms in nature ( $\sim 0.320$ ) is far higher than that of heavy to light carbon atoms ( $\sim 0.0112$ ). Secondly, for chlorinated compounds of interest in contaminant hydrology, relevant degradation reactions involve dechlorination. Thus, for most molecules, including all of those considered here, a chlorine atom can be in a reactive position.

One of the implications of the  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio is that for a compound with multiple chlorine atoms (e.g., PCE), significant proportions of the molecules will have one or more heavy isotopes present (Fig. S1 in S.I.). Thus, while considering only two species (i.e., “heavy” and “light” molecules) may introduce negligible error for carbon isotope modelling, for chlorine, a greater number of species may need to be considered. For example, in modelling PCE, to avoid errors in  $\delta^{37}\text{Cl}$  (Fig. S1 in S.I.), isotopologue modelling would need to include five isotopologues (if only chlorine is of interest). While a large body of work exists on the modelling of carbon isotope fractionation (e.g. Clayton, 1991; Cramer et al., 1998; Yu and Semprini, 2004), the explicit treatment of chlorine isotopes has become of interest only more recently, corresponding to advances in chlorine CSIA methods.

As discussed in Section 3, both degradation and physical processes lead to detectable isotope fractionation. Thus, a comprehensive modelling approach needs to take them into account. Degradation effects stem from the relative differences of reaction rates involving heavy and light Cl isotopes. Similarly, diffusive effects are caused by the relative effects of heavy and light Cl isotopes on diffusive transport. Sorption effects stem from the relative tendency of compounds with heavy or light Cl isotopes to adsorb onto or desorb from the matrix surfaces of porous media.

The behaviour of concentration  $C$  of a given species  $\gamma_i$  (e.g., a given isotopocule or isotopologue) can be described by the convection-diffusion-degradation equation:

$$\frac{\partial(\varepsilon C_{\gamma_i})}{\partial t} = \nabla \cdot (D_{\gamma_i} \nabla C_{\gamma_i}) - \vec{v} \cdot \nabla C_{\gamma_i} + \left[ \frac{\partial C_{\gamma_i}}{\partial t} \right]_{\text{reactions}} + Q_{s,\gamma_i} \quad (10)$$

where  $D$  is the diffusion coefficient;  $\varepsilon$ , porosity;  $\vec{v}$ , the advective velocity; and  $Q_s$ , a source term. Here, the subscript  $i$  is used to refer

to a single species.

### 5.2. Chemical and physical processes

Degradation is often the primary cause of isotopic fractionation in groundwater contaminants (Barth et al., 2002; Abe and Hunkeler, 2006). Degradation will generally result in relative isotopic enrichment in the parent compound and relative isotopic depletion in the daughter compound due to heavier species being degraded more slowly than lighter ones. To illustrate, consider a simple case where compound  $A$  is degraded to stable compound  $B$ , and where each compound has a light ( $A_L$  and  $B_L$ ) and a heavy ( $A_H$  and  $B_H$ ) species. If the reactions



where  $k_H$  and  $k_L$  denote the reaction rates, are possible, then compound  $A$  will become enriched and  $B$  depleted if  $k_L > k_H$ . In practice, this condition is nearly always true because bonds with heavier isotopes generally have lower energy levels and consequently higher activation energies for bond cleavage.

As noted above, when chlorine is considered, more than two isotopocules or isotopologues may be present in non-negligible quantities (e.g. PCE, Fig. S1 in S.I.). There may also be multiple isotopocules to which a parent isotopocule can be degraded. Furthermore, compounds of interest may be both parent and daughter compounds in different reactions. These considerations necessitate a more rigorous mathematical definition of the mechanism for fractionation stemming from degradation (i.e., the  $[\partial C_{\gamma_i}/\partial t]_{\text{reactions}}$  term in Equation (10)).

To date, investigations involving modelling of isotopic fractionation in chlorinated compounds have focused on chlorinated ethenes (Table 5). Numata et al. (2002a) presented the first modelling study for chlorine isotope fractionation using the Rayleigh equation (Equation (7)). This equation holds for a first order degradation in a system without transport, but for more complex systems error may be introduced in using it (Abe and Hunkeler, 2006).

Further progress in Cl isotope fractionation modelling was made by Hunkeler et al. (2009), who described a modelling scheme for Cl isotopologues of chlorinated ethenes and another for simplified “light” and “heavy” molecules. The models included a single kinetic isotope effect for Cl and could be combined with similar models of C isotopologues, evaluated in parallel, to produce  $\delta^{37}\text{Cl}/\delta^{13}\text{C}$  plots (e.g. Wanner et al., 2016). Later, Van Breukelen et al. (2017) used the independent isotopologue approach of Hunkeler et al. (2009) for Cl while also introducing  $\delta^2\text{H}$  modelling and Monod kinetics (Kompala et al., 1984). Crucially, this study determined position-specific isotope enrichment factors in the model based on experimental data from Kuder et al. (2013).

Jin et al. (2013) developed a model that considered the four isotopically different combinations of Cl-C bonds and the differential rates at which each would be cleaved. This work was the first that considered Cl and C isotopes as interdependent. The authors used data from Aeppli et al. (2009) to show how their combined modelling method could describe  $\delta^{13}\text{C}$  trends better than the separate C/Cl isotopologue model of Hunkeler et al. (2009).

Recognising the practical aspects of independent isotope-level modelling, as well as the need for more detail to account for relative molecular positions of isotopes, Höhener (2016) presented a correction factor to the isotope model of Hunkeler et al. (2009)

**Table 5**  
Studies that have modelled isotopic fractionation of chlorine in groundwater contaminants. “(ind.)” denotes independent modelling of multiple elements. \* indicates that a correction factor was used.

Level of modelling	Molecules	Secondary effects?	Diffusion effects?	Reference
isotope, Cl	PCE, TCE	no	no	Numata et al. (2002a)
isotope, Cl/C (ind.)	PCE, TCE, <i>cis</i> -1,2-DCE, VC	no	no	Hunkeler et al. (2009)
isotopologue, Cl/C (ind.)	PCE, TCE, <i>cis</i> -1,2-DCE, VC	no	no	Hunkeler et al. (2009)
isotopologue, Cl/C	TCE, <i>cis</i> -1,2-DCE, VC	no	no	Jin et al. (2014)
isotope, Cl/C (ind.)	PCE, TCE, <i>cis</i> -1,2-DCE, VC	yes*	no	Höhener (2016)
isotopologue, Cl/C/H (ind.)	TCE, <i>cis</i> -1,2-DCE, VC	yes	no	Van Breukelen et al. (2017)
isotopologue, Cl/C (ind.)	PCE, TCE, <i>cis</i> -1,2-DCE	yes	no	Badin et al. (2018)
isotopomer, Cl/C	PCE, TCE, <i>cis</i> -1,2-DCE	yes	no	Badin et al. (2018)
isotopologue, Cl/C	PCE, TCE, <i>cis</i> -1,2-DCE	yes	$D \propto \mu_r^{-1/2}$	Halloran et al. (2019)

based on the results of Cretnik et al. (2014). This “Cretnik” correction factor accounted for the fact that in the degradation step TCE  $\rightarrow$  *cis*-1,2-DCE only one position can be reactive.

Badin et al. (2018) proposed a generalised model, including secondary isotope effects, for degradation-induced fractionation for a given isotopocule  $i$  of compound  $\gamma$  in the degradation sequence  $\gamma - 1 \rightarrow \gamma \rightarrow \gamma + 1$ :

$$\left[ \frac{\partial C_{\gamma_i}}{\partial t} \right]_{\text{reactions}} = \left[ \sum_{h=1}^{n_{\text{iso}}^{\gamma-1}} \kappa_{h,i}^{\gamma-1 \rightarrow \gamma} R_{\gamma-1} \frac{C_{(\gamma-1)_h}}{C_{(\gamma-1)}} \right] - \left[ \sum_{j=1}^{n_{\text{iso}}^{\gamma+1}} \kappa_{i,j}^{\gamma \rightarrow \gamma+1} \right] R_{\gamma} \frac{C_{\gamma_i}}{C_{\gamma}} \quad (12)$$

Here,  $R$  is the overall reaction rate, while  $n_{\text{iso}}^{\gamma-1}$  and  $n_{\text{iso}}^{\gamma+1}$  are the total number of isotopocules of compounds  $\gamma - 1$  and  $\gamma + 1$ , respectively. The most critical parts of this equation are the  $\kappa$  matrices, which describe the difference in reaction rates arising from isotopic effects. The first term in the right side of Equation (12) describes production of isotopocule  $\gamma_i$  from parent species, while the second term describes its degradation.

Halloran et al. (2019) presented an isotopologue-level version of this model, noting that, for chlorinated ethenes, this would reduce the number of modelled species from  $2^{n_c} 2^{n_{cl}}$  to  $(n_c + 1)(n_{cl} + 1)$  (where  $n_c$  and  $n_{cl}$  are the number of carbon and chlorine atoms in the molecule) when both Cl and C isotopes are considered concurrently.

The  $\kappa$  matrices integrate primary and secondary kinetic isotope effects in terms of apparent kinetic isotope effects (AKIE),  $A$ . The apparent kinetic isotope effect can be evaluated from measured enrichment factors (Elsner et al., 2005):

$$A = \frac{1}{1 + z\varepsilon_r/1000} \quad (13)$$

where  $z$  is the number of indistinguishable reactive sites. The primary AKIE,  $A_{Cl,p}$ , and secondary AKIE,  $A_{Cl,s}$ , are used in the definition of  $\kappa$  matrices for degradation of compound  $\gamma$  to compound  $\gamma + 1$ . At the isotopocule level (i.e., all isotopomers of all possible isotopologues), considering both Cl and C isotopes, this matrix (see Equation (3) in Badin et al., 2018) can be defined in a generalised way that is not specific to chlorinated ethenes.

For isotopologues of chlorinated ethenes, chlorine and carbon isotopes can be considered separately and the matrix for Cl be evaluated (refer to Equation (7) in Badin et al. (2018)).

These matrices are generally sparse due to the limited number of daughter isotopologues for a given parent isotopocule. When considering isotopologues rather than isotopocules (Equation (3) in Badin et al., 2018), these matrices reduce in size considerably (e.g., from  $64 \times 32$  to  $15 \times 12$  for PCE  $\rightarrow$  TCE) and have been evaluated explicitly for degradation of chlorinated ethenes (Halloran et al., 2019).

In practical terms, the only cases where isotopocule-level models would be needed instead are those where significantly different secondary isotopic effects occur at different non-reacting positions (Badin et al., 2018). However, this may not necessarily be true for other compounds. Future laboratory investigations of secondary isotope effects using NMR (e.g. Chan et al., 2010) or other tools may improve our understanding of these processes and the necessity of modelling them explicitly at the isotopocule or isotopologue level.

The degree to which diffusion contributes to isotopic fractionation is a current topic of interest (Wanner and Hunkeler, 2019). Jin et al. (2014) performed laboratory experiments of *cis*-1,2-DCE and TCE in an agar gel, obtaining values of  $\beta = 0.088 \pm 0.015$  for *cis*-1,2-DCE and  $\beta = 0.043 \pm 0.008$  for TCE (see Equation (9)). Wanner and Hunkeler (2015) used a modified Stokes diffusion cell to measure diffusion coefficients of 1,2-DCA and TCE. They obtained values of  $\beta = 0.031 \pm 0.002$  for 1,2-DCA and  $0.024 \pm 0.002$  for TCE. With respect to modelling, only one study (Halloran et al., 2019) thus far has combined diffusion and degradation effects.

The limited amount of experimental studies on chlorine diffusive fractionation make it difficult to draw broad conclusions. For example, it is not yet known whether there are scale effects on diffusive fractionation in porous media. Nonetheless, it appears that  $\beta = 1/2$  is not valid for the studied compounds and is unlikely to be valid for other similar compounds of concern here (e.g. PCE, TCA). In future modelling studies, it is therefore advisable to model diffusive fractionation with empirical  $\beta$  values (Jin et al., 2014; Wanner and Hunkeler, 2015), or, ideally, to allow  $\beta$  to vary over some reasonable range when performing parameter optimisation.

Finally, for sorption-induced fractionation, there have been modelling studies on carbon, but nothing yet on chlorine. For carbon, Slater et al. (2000) found that no significant fractionation effects were present for several compounds in equilibrium sorption with graphite and activated carbon. It is known that sorption is dependent on pH, salinity, temperature, and other factors (e.g. Michot, 1991; Oh et al., 2016) that are often difficult to constrain in field studies. Therefore, it is expected that future laboratory studies will provide the next advances in this domain.

In practical terms, modelling of sorption effects can be implemented by including additional adsorbed (immobile) isotopologues or isotopocules in a model which act as sources (the  $Q_s$  term in Equation (10)) of the individual isotopologues or isotopocules. For each isotopologue, the Freundlich isotherm (e.g., Dries et al., 2007) could be used to describe the equilibrium mass of the adsorbed material ( $m_{\text{sorbed}}$ ):

$$m_{\text{sorbed}} = K_F C^{1/n_F} \quad (14)$$

where  $K_F$  is the Freundlich sorption capacity, which may depend on the isotopologue's mass, and  $n_F$  is an empirically-determined constant. Other models, such as the Langmuir isotherm could also be

used, but in the absence of empirical data, constraining sorption processes with as few parameters as possible is advantageous.

## 6. Conclusions and outlook

As this review has shown, complementing carbon isotope data with chlorine isotope data has the potential to greatly improve our understanding of the fate of chlorinated contaminants in the subsurface. Additional efforts are needed to overcome the analytical challenges and lack of isotope fractionation factors in order to tap into this potential and further establish chlorine CSIA as routine method in the assessment of contaminated sites. In particular, there is an urgent need for a reliable method of producing isotopically different, compound-specific sets of reference standards.

While considerable progress has been made in  $\delta^{37}\text{Cl}$  measurement methods and chlorine isotope fractionation process understanding, there remain several knowledge gaps. Further progress in filling these gaps will continue to improve and widen the applicability of chlorine CSIA.

While recent work on diffusion (Wanner and Hunkeler, 2019) has shown its isotope effect to be generally weaker than previously thought, very few measurements (Jin et al., 2014; Wanner and Hunkeler, 2015) of these effects have been made for chlorinated hydrocarbons. As back-diffusion (Parker et al., 2008) is a widely observed phenomenon at contaminated sites with aquifer-aquitard interfaces, further investigation of diffusion isotope effects in other chlorinated hydrocarbons is needed. Furthermore, as noted, isotope effects due to sorption have not yet been reliably measured. Adsorption and desorption processes occur in many low-permeability hydrogeological units such as clay-rich sediments. Measurements of sorption isotope effects are therefore crucial for comprehensive assessment of contaminated sites. Additionally, more measurements of isotope effects during degradation by various biotic or abiotic mechanisms are always welcome.

There also remain open questions related to modelling chlorine isotope fractionation. As few such studies currently exist (Table 5), the value of chlorine CSIA data in informing models – which may drive remediation decisions – is currently not well understood. There is also a need to understand the level of model complexity in modelling isotope effects that is required to make accurate assessments of degradation and transport of chlorinated hydrocarbons. Efforts to improve the modelling of chlorine isotope fractionation processes will be most effective when combined with data from laboratory and field studies. Additionally, there is significant scope for the expansion of chlorine CSIA to other, larger compounds, especially those with few chlorine atoms. Here, the applicability of chlorine CSIA will be pronounced as carbon isotope fractionation is less significant in larger organic molecules.

Finally, there is clearly major potential for further applications of chlorine CSIA to evaluate degradation in field sites. After all, this is one of the main motivations for the development of the laboratory and modelling techniques discussed in depth here. In particular, chlorine CSIA in conjunction with carbon CSIA will surely see further applications in the differentiation of both sources and processes.

Chlorine CSIA is a relatively new tool for the assessment of groundwater contamination by chlorinated hydrocarbons. Research and development in this field is moving forward with continued progress on laboratory techniques, field applications, modelling approaches, and fundamental understanding.

## Declaration of competing interest

The authors declare no competing interests.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.125476>.

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