Title:

A new Method for determining Compound Specific Carbon Isotope of Chlorinated Solvents in Porewater

Article Impact Statement:

Enhanced method for CSIA of chlorinated solvents in porewater, based on solvent extraction and GC-IRMS with SPME

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Abstract

A new method for the extraction of chlorinated solvents (CSs) from porewater with dimethylacetamide (DMA) used as a solvent and the determination of $\delta^{13}C$ by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) with solid-phase microextraction (SPME) are presented. This method was used for the determination of $\delta^{13}C$ of chloroethenes and chloromethanes. The extraction of the CSs from porewater with DMA led to a minimal loss of mass of solvent and chlorinated compounds. The accuracy of the method was verified with the analysis of the pure injected compounds using elemental analyser - isotope ratio mass spectrometry (EA-IRMS). It has been effectively applied in a study area in saturated soil samples of a pollutant source zone of perchloroethylene (PCE) and trichloroethylene (TCE). The limit of quantification of the new method was 0.034 µg/g for PCE and TCE for 10-20 g of soil sample. This new method allows for compound-specific isotope analysis (CSIA) of CSs in porewater, which can be beneficial in sites where the identification of contamination sources and the behaviour of the contaminants are not clear.

Keywords

1. Introduction

Chlorinated solvents (CSs) belong to the group of dense nonaqueous-phase liquids (DNAPLs) and are involved in numerous episodes of soil and groundwater contamination of industrial and urban areas (Tiehm and Schmidt 2011; Yu, Lee, and Hwang 2015). Given their physical and chemical properties (Mackay et al. 2006), these compounds migrate as a free phase through the materials in the subsoil. The source architecture is controlled by geological heterogeneities and decades of dissolution of DNAPLs due to groundwater flow (Parker et al. 2003; Guilbeault, Parker, and Cherry 2005; Puigserver et al. 2013), among other parameters. In addition, dissolved contaminants can penetrate low-conductivity materials by molecular diffusion (Chapman and Parker 2005; Filippini et al. 2020; Wanner, Parker, and Hunkeler 2018) and by vertical fractures (Fjordbøge et al. 2017; Chapman, Cherry, and Parker 2018), making the study of the distribution of CSs in the subsoil indispensable for studying contamination episodes in groundwater.

Compound-specific isotope analysis (CSIA) in CSs dissolved in groundwater allows for the identification of the source(s) of contamination by determining the initial isotopic composition of the compounds (Alberti et al. 2017; Zimmermann, Halloran, and Hunkeler 2020). It also makes quantification of the processes that produce isotope fractionation possible by using the approximation of the Rayleigh equation in open systems (Kuntze et al. 2020; Van Breukelen et al. 2017; Filippini et al. 2018). When the distribution of CSs in subsoil is complex, knowledge of this distribution is necessary in order to correctly interpret the distribution of the concentrations and isotopic compositions of DNAPLs dissolved in groundwater (Puigserver et al. 2013; Gilevska et al. 2019; Puigserver et al. 2014).

CSIA of CSs in porewater allows for the determination of the initial isotopic composition of the spilled contaminant and the presence or absence of degradation processes in the sediments (Passeport et al. 2016). This methodology has been successfully applied in saturated low-permeability sediments to differentiate and quantify the degradation pathways of CSs (Wanner et al. 2016; 2018) and to quantify the rate of degradation during enhanced reductive dehalogenation (Damgaard et al. 2013). Likewise, this technique is complementary to the CSIA of CSs in groundwater, and, until now, only the studies by Wanner et al. (2018 and 2016) have coupled the CSIA of porewater and groundwater. Wanner et al. (2018) studied low-permeability sediments to predict the potential magnitude of the impacts of back diffusion on adjacent aquifers . For the analysis of CSs

present in porewater, the extraction of the CSs and their subsequent concentrations in water (Damgaard et al. 2012, 2013; Wanner et al. 2018) and methanol (Wanner et al. 2016) were determined using the purge and trap analytical technique. Without the purge and trap technique, the methodology of passive samplers (or peepers) and their subsequent CSIA have been used effectively (Passeport et al. 2016; 2014).

Most of the methodologies used so far are based on the use of water as a solvent to extract the CSs, with the potential loss of the compounds through volatilisation. One methodology that reduces this volatilisation is the use of a methanol trap, which helps to avoid the loss of the CSs by volatilisation (Parker et al. 2003; USEPA 1996). This methodology is based on the quantification of the CSs in porewater, i.e. the CSs that are in the free and residual phase, dissolved in the interstitial water and sorbed out in the organic matter, by dissolving the CSs in methanol and favoured by the mechanical agitation and desorption steps. This methodology allows for more detailed sampling than passive samplers, since the samplers capture by rebalancing the CSs dissolved in the interstitial water and partially the compounds that are as free or residual phase. In addition, the recommended maximum storage time of soil samples at 4°C extracted with water is 4 days and with an organic solvent (methanol) the recommended maximum storage time is 1 month (ISO 18512 2007). Likewise, the extraction of the CSs with an organic solvent allows the analysis of free and residual phase, while extraction with water underestimates this phase as it is not dissolved.

The aim of this article is to define a method for the extraction and CSIA of CSs from porewater. The working hypothesis was that the extraction of CSs with an organic solvent and its subsequent CSIA would allow for the robust analysis of $\delta^{13}C$ of CSs, thus avoiding the loss of CSs by volatilisation and lowering the limits of quantification. This enhanced method allows for sampling of the CSs present in the porewater (sorbed, dissolved and free phase) on a centimetre scale. The main benefits of this method are the decrease in the risk of volatilisation and the subsequent increase in the recommended storage time, as well as its the high sensitivity, ease to use, simple mechanism, portability and low cost compared to other methods.

2. Study site

The saturated zone of a source area of perchloroethylene (PCE) pollution episode located in Figueres, in the northeast of Spain (Figure 1), was selected to test the method. The

contaminants selected for the test were chloroethenes (CEs), mainly PCE as the parental contaminant and trichloroethylene (TCE) as the major metabolite (Puigserver et al. 2016). Two boreholes, F1UB and F2UB (17.00 m and 20.20 m in depth, respectively), were drilled by rotary drilling with a diamond crown.
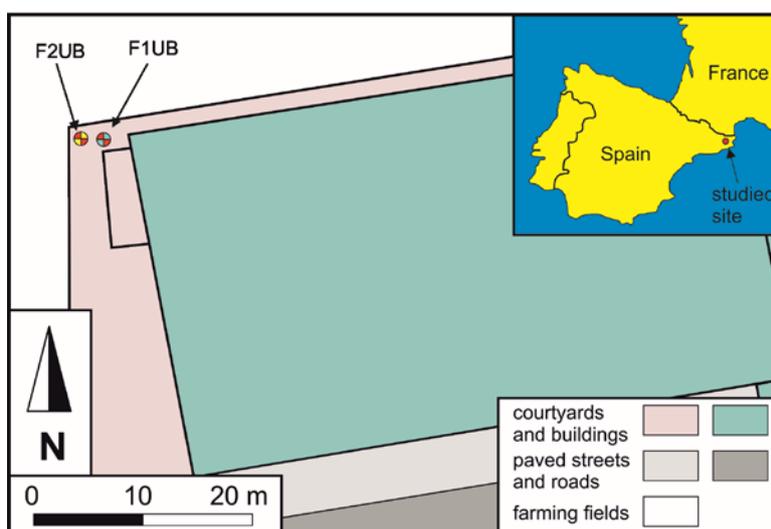

Figure 1: Location of the study site and the two boreholes (F1UB and F2UB)

The following five hydrostratigraphic units of different ages were differentiated from surface to bottom (Puigserver et al. 2016): (1) the unsaturated zone (UZ), made up of gravels and coarse, medium and fine sands, where trails of PCE were detected; (2) the upper discontinuous thin aquitard (UDTA), which consisted of clays, was crossed by subvertical microfractures and contained a high amount of PCE; (3) the upper part of the aquifer (UPA), where PCE was found to be trapped interstitially in the gravels and sands immediately below the contact with the aquitard; (4) the lower part of the aquifer (transition zone to basal aquitard, TZBA), made up of alternating gravels and coarse sands with numerous interbedded layers of medium to fine sands and silts at the centimetre to decimetre scale, where CEs concentrations remain elevated due to the high geological heterogeneity and the lower hydraulic conductivity compared to the upper part of the aquifer; and (5) lastly, the basal aquitard (BA), which consisted of fine laminar sands and silts crossed by a dense network of subvertical microfractures. This unit is affected by CEs until a minimum depth of 30 m.

3. Materials and Methods

   3.1. Chemicals and solutions

Methanol, dimethylacetamide (DMA), dimethylformamide (DMF), PCE, TCE, cis-dichloroethylene (cDCE), trans-dichloroethylene (tDCE), carbon tetrachloride (CT), chloroform (CF) and dichloromethane (DCM) were all analytical grade reagents obtained from Sigma Aldrich (St. Louis, MO, USA). Methanol, DMA and DMF were tested as solvents for the extraction of CEs from sediments from the study site. CSs (PCE, TCE, cDCE, tDCE, CT, CF and DCM) were used as standards to validate the method.

3.2. Sample collection and extraction

The drilling operations and the core sampling are described in detail by Puigserver et al., (2016). Around 10-20 g of soil was sampled with a stainless-steel spatula and poured into triplicate vials with 20 mL of solvent (methanol and DMA for the determination of the concentration and the isotopic composition of CE, respectively). To prevent cross-contamination, the subsamplers were cleaned with soapy water, methanol and distilled water between consecutive samples (Dincutoiu, Górecki, and Parker 2003). The methanol trap was used in accordance with EPA SW-846, Method 5035 (USEPA 1996). These vials were sealed, their weight was controlled, and they were stored at temperatures under 4 ºC. To validate the absence of cross-contamination and environmental contamination, the corresponding blanks were prepared with the same methodology except that the soil sample was absent.

The extraction of CEs from sediments was performed by a two steps procedure of mechanical agitation (10 rpm for 48 h) and use of an ultrasonic bath (5 h), following the method described by Puigserver et al. (2013), which is an adaptation of the method described in Dincutoiu et al. (2003), using DMA instead of methanol. Weight control during the extraction of CEs with methanol and DMA was performed before and after each step. No significant differences in the efficiency were observed between solvents.

3.3. Analytical method

The analysis of the concentration and the isotopic composition of CSs was carried at the laboratories of the Scientific and Technologic Centres of the University of Barcelona (CCiTUB).

The samples from the study area have only PCE and TCE in large enough amounts to perform CSIA. However, cDCE and tDCE were included in the standards during the

analysis of the field samples and chloromethanes (CMs; CT, CF and DCM) were tested as standards to prove that this technique could work for these compounds.

The analysis of the concentration of CEs from the field samples dissolved in methanol was done with a gas chromatograph TraceGC coupled to a mass spectrometer (DSQII) with an automatic injector (Triplus mode Head Space, Thermo Finnigan, Bremen, Germany).

Isotope data are reported using the delta notation, $\delta^{13}C = (R_s / R_{std}) - 1$ (Eq. 1), where R_s and R_{std} are the $^{13}C/^{12}C$ ratios of the sample and international standard (Vienna PeeDee Belemnite, VPDB), respectively. The determination of the isotopic composition of CSs was done using an adaptation of the technique described by Palau et al. (2007). This was used for the determination of $\delta^{13}C$ of volatile organic compounds dissolved in water by solid-phase microextraction (SPME) and by gas chromatography-isotope ratio mass spectrometry (GC-IRMS). When the CSs were dissolved in DMA, a 50 mL solution of Milli-Q water (Merck Millipore) was prepared, and 1-10 mL of DMA was added depending on the concentration. The samples were grouped according to concentrations in order to prepare the standards with the same volume of DMA and with a similar concentration of CE.

The GC-IRMS system consisted of an Agilent 6890 gas chromatograph (Palo Alto, CA, USA) equipped with a splitless injector coupled to a Delta Plus isotope-ratio mass spectrometer through a gas chromatograph combustion III interface (Thermo Finnigan). An SPB-624 (60 m × 0.32 mm, 1.8 m stationary phase; Supelco, Bellefonte, PA, USA) was used for the separation of the compounds, and helium was used as a carrier gas. The oven temperature program was 60ºC (5 min) to 200ºC (5 min) at a rate of 8 ºC/min. The injector temperature was 270ºC, and the injection was in the split mode (split ratio of 5:1). The combustion furnace temperature in the gas chromatograph combustion interface was 940 ºC.

This method uses a fine silica fibre coated with a thin layer of polydimethylsiloxane (PDMS, Supelco, Bellefonte, PA, USA) to extract CSs by adsorption from the headspace of the sample (HS-SPME). Before the first extraction, the fibre was located in the injector of the gas chromatograph for 30 min at 270 ºC to prepare and verify that there were no remnants of any substance that may interfere with the analysis.

Standards were prepared from a mother solution of 1000 mg/L of CEs and CMs in DMA. A 10 mg/L dilution was prepared daily from the mother solution, and the final standards were prepared from this dilution. Two standards of CEs dissolved in DMA were analysed at the beginning of the sequence to ensure repeatability. Then, the samples were analysed, and a standard was analysed every four samples. Each day ended with the analysis of a final standard to determine if there had been a drift of the $\delta^{13}C$ values of CEs throughout the day. The extraction time of HS-SPME was 25 min, plus 5 min of desorption.

The determination of the $\delta^{13}C$ values of the CSs from the standards was made by injecting the pure compound into an elemental analyser – isotope-ratio mass spectrometer (EA-IRMS, Flash EA1112 coupled to a Delta C isotope-ratio mass spectrometer through a ConFlo III interface; Thermo Finnigan). The combustion furnace temperature was 900ºC, and the column was kept at 45ºC.

4. Results and discussion.

   4.1. Solvent selection

Although it is useful for CS quantification (Dincutoiu, Górecki, and Parker 2003), methanol is not ideal for the HS-SPME technique: it saturates the fibre and masks the peaks of the DCE isomers and DCM and gives a poor reading of the TCE and CF (see retention times in Figure 2). In addition, due to the incompatibility between the polar methanol and the column of the GC, it is necessary to do a dilution of at least 100 times and pre-concentrate the samples with a purge-and-trap concentrator (Wanner et al. 2016). Two solvents—DMA and DMF—were tested, because of their properties as organic solvents, as well as their high molecular weights. DMA was chosen because within the GC column, the DMA peak comes out significantly later than the PCE and DMF peaks (Figure 2).
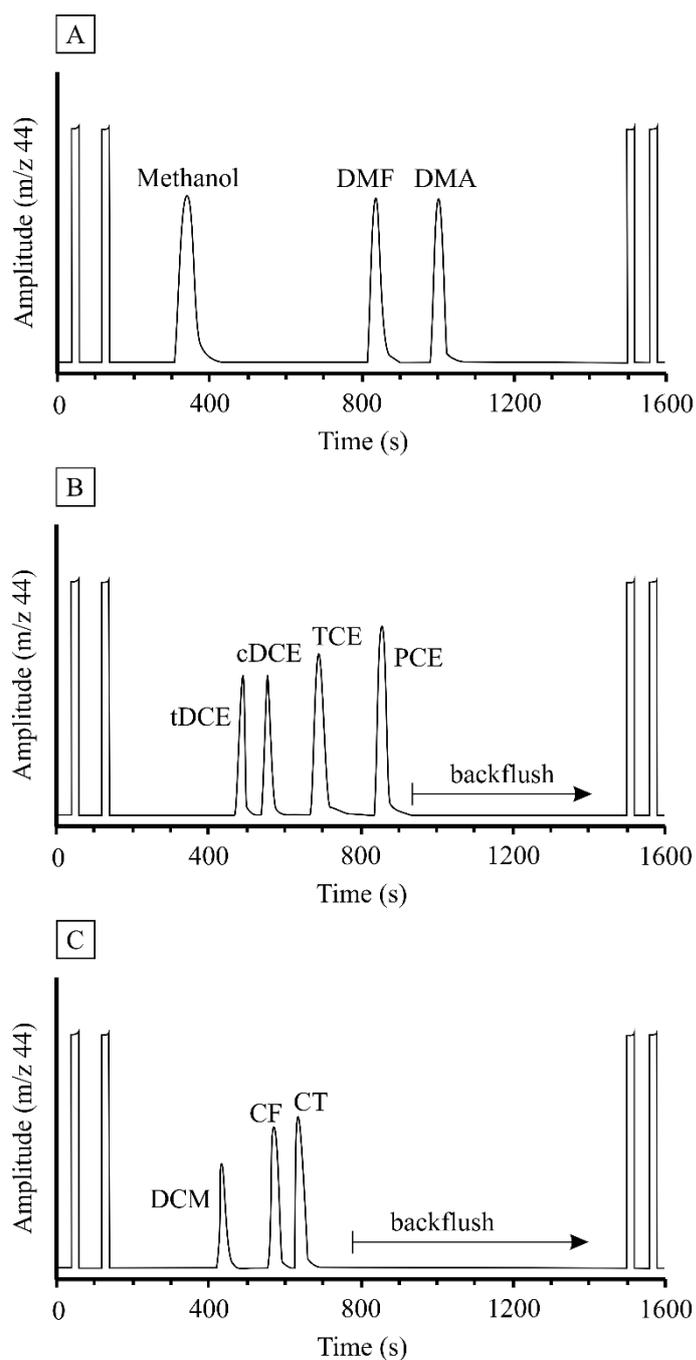
Figure 2: Distribution of the peaks for A) tested solvents (methanol, dimethylformamide and dimethylacetamide), B) Chloroethenes (trans- dichloroethylene, cis- dichloroethylene, trichloroethylene and perchloroethylene), and C) Chloromethanes (dichloromethane, chloroform and carbon tetrachloride)

4.2. Method precision

The method precision was determined by the analysis by HS-SPME and GC-IRMS of laboratory produced-samples with water, DMA and CS. Table 1 shows the isotopic composition, the standard deviation and the number of standards of each compound

analysed by both methods. The validation of the method with the injection of pure CSs by EA-IRMS showed that the process of adsorption of CSs by HS-SPME and the subsequent desorption by GC-IRMS produces a low isotopic shift, between 0.2 and 0.4, which is slightly lighter than the isotopic composition determined by HS-SPME and GC-IRMS. On the other hand, the same method used in aqueous samples (Palau et al. 2007) produces a similar isotopic shift in CSs. Therefore, the isotopic shift stated in Table 1 is probably due to the different analytical method. Nevertheless, the potential effect of the presence of DMA in the isotopic signature of the different CSs shown in the section 4.3.

Table 1: Average and standard deviation of $\delta^{13}C_{PCE}$ and $\delta^{13}C_{TCE}$ values measured in GC-IRMS and EA-IRMS

	$\delta^{13}C$ measured by HS-SPME and GC/IRMS			$\delta^{13}C$ measured by EA-IRMS			Isotopic shift
	$\delta^{13}C$ (‰)	Standard deviation	Nº standards	$\delta^{13}C$ (‰)	Standard deviation	Nº standards	
PCE	-27.0	0.4	56	-26.8	0.1	3	0.2
TCE	-26.9	0.3	56	-26.6	0.0	3	0.3
cDCE	-23.8	0.4	56	-23.6	0.1	3	0.2
tDCE	-25.3	0.4	56	-24.9	0.1	3	0.4
CT	-41.6	0.2	7	-41.2	0.1	3	0.4
CF	-51.2	0.3	7	-50.9	0.1	3	0.3
DCM	-41.4	0.3	7	-41.0	0.1	3	0.4

4.3. Potential effect of the amount of DMA on the isotopic composition of CEs

The variation in the amount of DMA used to prepare the standards did not produce isotopic fractionation in the CEs (Table 2), as shown by the minimum difference between the 20 and 100 µg/L standards. Therefore, there was no differential isotopic fractionation for saturation of PDMS coated fibre.

The limit of quantification tested with the standards was 20 µg/L of PCE and TCE (in a 1 mL sample of DMA with 49 mL of Milli-Q water). The method was consistent with standards between 20 and 100 µg/L of PCE and TCE and dilutions of DMA in Milli-Q water between 1:50 and 10:50.

Table 2: Standards of chloroethenes dissolved in DMA and Milli-Q water

Concentration (ppb)	100	80	60	40	20
mL DMA (of 50 mL solution)	10	5	5	2	1
nº standards	22	10	5	6	13

PCE	$\delta^{13}C$ (‰)	-26.8	-27.2	-27.1	-27.1	-27.1
	Standard deviation	0.4	0.4	0.3	0.3	0.3
TCE	$\delta^{13}C$ (‰)	-26.8	-26.9	-26.8	-27.1	-26.9
	Standard deviation	0.3	0.4	0.3	0.3	0.3
cDCE	$\delta^{13}C$ (‰)	-23.7	-23.8	-23.7	-23.8	-24.0
	Standard deviation	0.4	0.5	0.3	0.2	0.4
tDCE	$\delta^{13}C$ (‰)	-25.3	-25.4	-25.3	-25.4	-25.2
	Standard deviation	0.4	0.2	0.4	0.3	0.4

4.4. Application to a PCE-polluted source area

The method was applied in the saturated hydrostratigraphic units (UPA, TZBA and BA) in a PCE source zone (section 2 Study site). UPA presents a lower concentration of PCE and almost no concentration of TCE, compared to TZBA, where higher concentration of both compounds were detected, due to the higher presence of silty matrix. The distribution of PCE and TCE within the BA is ruled by the presence of vertical microfractures and stratification planes in the very fine sands with a silt-clay matrix.

The ranges of the $\delta^{13}C_{PCE}$ and $\delta^{13}C_{TCE}$ values were -25.2 to -22.5 ‰ and -31.1 to -28.3 ‰, respectively (Figure 3). The PCE found in the subsoil, which we consider to be less degraded, had a $\delta^{13}C_{PCE}$ value of approximately -24.7 ± 0.5 ‰ (Figure 3.A), which is considered to be $\delta^{13}C_0$ (initial isotopic composition of the parental compound). The $\delta^{13}C_0$ value of PCE was in accordance with Hunkeler and Aravena (2010), who defined the isotopic composition range of $^{13}C_{PCE}$ to be -37.2 to -23.2 ‰. The processes of biotic and abiotic reductive dehalogenation are the main processes that produce isotopic fractionation of PCE (Kuder et al. 2013; Centler, Heße, and Thullner 2013; Liang, Philp, and Butler 2009), causing an isotopic enrichment of $\delta^{13}C$ of the remaining PCE and producing mainly TCE (abiotic dehalogenation of PCE can produce other metabolites) with lighter values of $\delta^{13}C_{TCE}$ compared to $\delta^{13}C_0$ (Elsner 2010). In addition, physical processes (e.g. volatilisation, diffusion, sorption) can produce isotopic fractionation; although, they are less important than the processes that lead to PCE transformation (Braeckevelt, Fischer, and Kästner 2012; Wanner and Hunkeler 2015; Wanner et al. 2017). Several samples showed slight isotopic enrichment of PCE ($\delta^{13}C$ values heavier than -24.2‰, Figure 3.A), which can be related to the initial phase of the reductive dehalogenation and/or to physical processes that produce isotopic fractionation. Samples with values of $\delta^{13}C_{PCE}$ that are heavier than -23.0‰ (Figure 3.A) are related to areas

where reductive dehalogenation occurs and where there is the formation of TCE and cDCE (Puigserver et al. 2016).

On the other hand, the TCE found in the subsoil is a metabolite from PCE. TCE shows different extents of production; since the first TCE produced is isotopically lighter and it is expected that when the degradation of PCE is more advanced, $\delta^{13}C_{TCE}$ values should be heavier, reaching $\delta^{13}C_0$ when all PCE is degraded to TCE (Hunkeler and Morasch 2010). In addition, TCE degradation to cDCE occurs, but it is quantitatively not as important as the degradation from PCE to TCE, and the concentration of cDCE was not enough to determine its isotopic composition.

The limit of quantification of the soil samples was 0.034 µg of PCE and TCE per g of soil, considering that the sample interval was 1-20 g of sample and 20 mL of DMA (section 2.3). This limit was achieved with a final minimum concentration of 50 µg/L (PCE or TCE diluted in DMA), and the preparation of a 1:5 dilution with Milli-Q water resulted in a concentration of 10 µg/L in the laboratory sample for SPME.

Table 3: Maximum, minimum and average concentration of PCE and TCE for each hydrostratigraphic. Unsaturated zone (UZ and UDTA) was not sampled for CSIA of chlorinated solvents. UZ: Unsaturated Zone; UDTA: Upper Discontinuous Thin Aquitard; UPA: upper Part of the Aquifer; TZBA: Transition Zone to the Basal Aquitard; BA: Basal Aquitard; QL: quantification limit

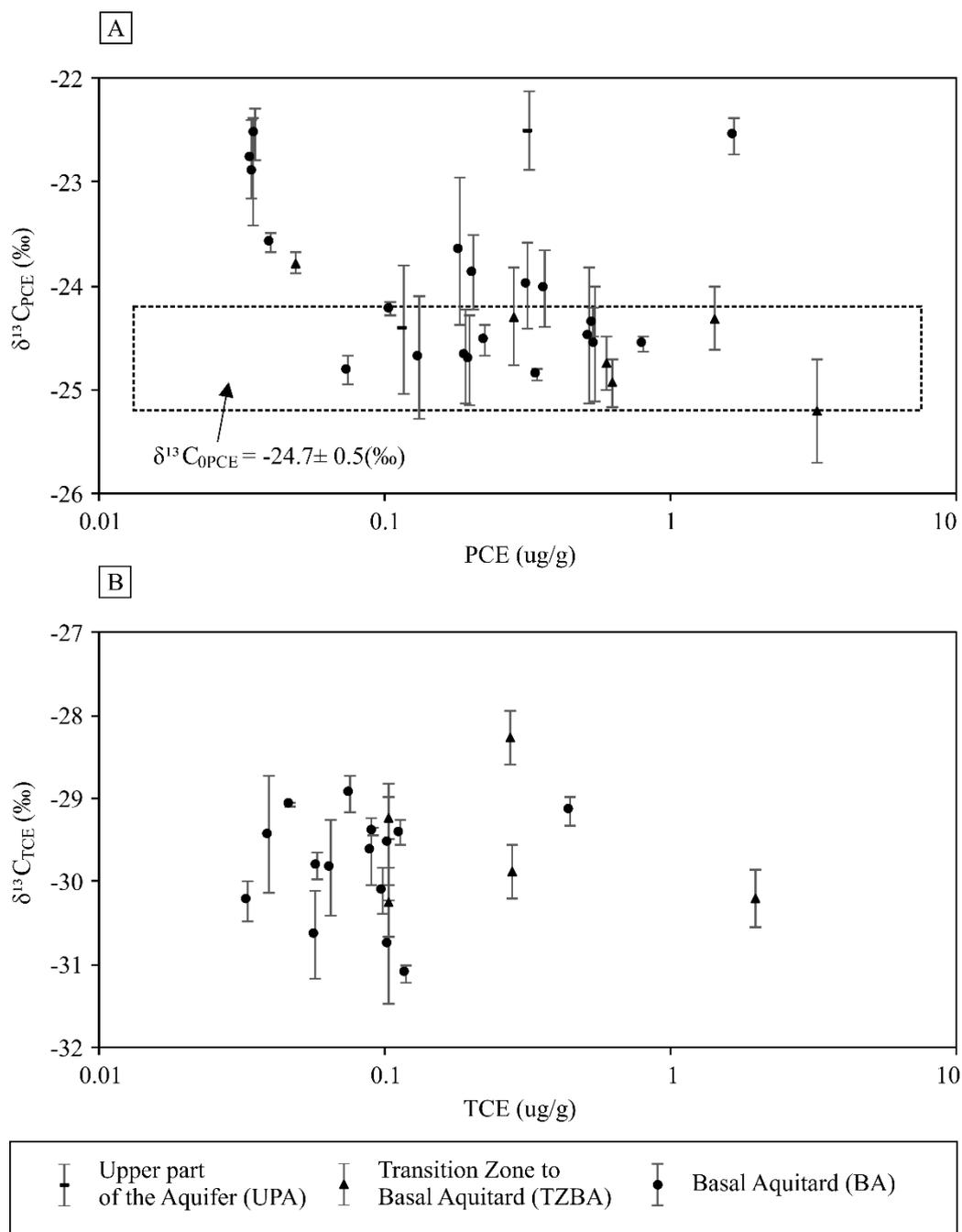|	Nº samples above the QL		PCE (µg/g)			TCE (µg/g)		
	Conc.	$\delta^{13}C$	Maximum	Minimum	Average	Maximum	Minimum	Average
UZ	25	-	2.71	0.002	0.183	0.006	0.001	0.002
UDTA	7	-	0.253	0.010	0.088	0.002	0.002	0.002
UPA	15	2	0.322	0.001	0.054	0.004	0.001	0.002
TZBA	17	8	3.28	0.001	0.373	1.98	0.001	0.151
BA	55	35	1.69	0.001	0.129	0.447	0.001	0.032

Figure 3: Concentration per gram of soil (µg/g) and isotopic composition (‰) of A) PCE and B) TCE of sediment samples.

5. Conclusions

The described method allowed for the determination of the isotopic composition of CSs in porewater while minimising the volatilisation of the volatile compounds, since an organic solvent trap was used instead of water.

The method was accurate, given that the standard deviation was below 0.5‰ for each compound and the difference was below 0.5‰ between the average of $\delta^{13}C$ values of CEs

and CMs found with the SPME method by GC-IRMS and with the pure injection of the compound into an EA-IRMS. In addition, the different amounts of DMA in the samples did not alter the results.

The applicability of this method to the determination of CEs present in porewater in a pollutant source zone was demonstrated. The method allowed for sampling at the centimetre level, taking samples between 10 and 20 g. It allowed for the determination of the initial isotopic composition of the CEs and the identification of the degradation zones in the porewater in the study area. This method is particularly suitable for hydrogeological units with low hydraulic conductivity where the sampling of groundwater is limited.

6. -Funding:

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