C and Cl-CSIA for elucidating chlorinated methanes biotic and abiotic degradation at a polluted bedrock aquifer

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Abstract

In this study, concentration and δ¹³C and δ³⁷Cl values of chloroform (CF) and carbon tetrachloride (CT) measured in groundwater samples are related to redox conditions to elucidate natural attenuation processes in a polluted site. Shifts in δ¹³C and δ³⁷Cl of CF and CT were detected over time. δ¹³CCF values found in the potential sources were -34.5 ± 0.6 ‰ (tank near S3 well), -37.3 ± 0.6 ‰ (in a fracture near S1 well) and -46.2 ± 0.4 ‰ (barrels) in 2004, whereas in later sampling campaigns, δ¹³CCF enriched values such as -25.2 ± 0.5 ‰ were measured in S3 in 2013. 2D plots (δ¹³CCF vs δ³⁷ClCF) showed different isotopic patterns in different wells and depths. δ³⁷ClCF values let distinguish that the former sources evolved towards completely different isotopic signatures, whilst δ³⁷ClCF values of +1.3 ± 0.3 ‰ were reached in 2013 for S3, S1 moved towards more depleted δ³⁷ClCF values (down to -3.9 ± 0.6 ‰). These data indicate that different reductive dechlorination processes might occur.

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1. Introduction

Chlorinated methanes are persistent pollutants in groundwater compared with other volatile organic compounds. However, they have received less attention than other chlorinated compounds such as chlorinated ethenes or ethanes. CT has been used in fungicide formulation and as a commercial degreaser for almost 100 y. CF was initially used as an anesthetic and as a chemical precursor to nowadays banned refrigerants. CT and CF are toxic and also considered possible carcinogenic substances. In Europe, environmental water quality standards of 12 and 2.5 μg/L for CT and CF, respectively, have been established in the framework of water policy (Directive 2008/105/EC).

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Up to now, microbial CT degradation is only known to occur by cometabolic reduction under anoxic conditions. Although CF and dichloromethane (DCM) are the most common detected metabolites of CT reduction, the presence of sulphate reducing bacteria and high sulphite systems leads to the biologically-mediated transformation of CT to carbon disulphide (CS$_2$) as main final product. Regarding pure abiotic processes, several studies reported carbon isotopic fractionation associated with the reductive dechlorination of CT by Fe(II) sorbed onto iron minerals or by Zn(0). Stable carbon isotopic fractionation values ($\varepsilon$C) ranged from -10 to -32‰. CF biotic and abiotic reductive dechlorination occurs in anoxic environments. However, CF biodegradation has been also described under oxic conditions. Chan et al. (2012) obtained the first biotic carbon isotopic fractionation of CF ($\varepsilon$C value of -27.5 ± 0.9‰) during dehalorespiration to DCM by Dehalobacter cultures. In addition, CF could also be abiotically degraded by Fe-bearing minerals with slower dechlorination rates than CT. For field studies, in situ abiotic reduction of CT has been proved based on the average ratio of CF:CS$_2$ and on CT metabolites and their spatial distribution to detect possible sources an comingling plumes. However, little information about isotope effects on biotic or abiotic in situ degradation of CF and CT is currently available. Some C-CSIA measurements for CT are published in the vadose zone of a polluted site but no data have been obtained for long-term field demonstrations of CT and CF degradation using 2D-CSIA.

The study site is an unconfined fractured bedrock aquifer with low permeability in Òdena (Barcelona, Spain) (Fig. 1). Contamination originated from a former chemical plant between 1978 and 1985. The aquifer is contaminated by chlorinated volatile compounds (ethenes, methanes, aromatic hydrocarbons and ethanes), BTEX and traces of pesticides with the highest concentrations measured close to the former waste disposal areas: an underground wastewater tank (S3 well) and a disposal pit (S1 well) (Fig. 1). Both sources were removed in 2006 and the concentration of most pollutants decreased. Emptied space was filled with recycled aggregates from construction and demolition waste. Ten multilevel nested wells leading to a total of 147 sampling points were installed in 2006.

This study is focused on chlorinated methanes. CT and CF field isotope data is used to elucidate natural attenuation processes. In order to assess and predict the extent of the target compounds biodegradation due to indigenous microbial community, microcosm studies are being carried out in the laboratory. In addition, the role of Fe-bearing minerals in the abiotic dechlorination reactions of CT and CF is also being investigated. 2D-CSIA slopes obtained from field data will be compared with those determined in laboratory experiments.

2. Methods

2.1. Sampling

Above mentioned potential sources as well as abandoned barrels inside the factory were sampled in 2004 before their removal. Groundwater samples for plume characterization by concentration and isotopic measurements were collected from ten multilevel nested wells in four main campaigns (2006, 2010, 2013 and 2014). In some field campaigns, samples for analyzing redox sensitive compounds (NO$_3^-$, NO$_2^-$, dissolved Mn, dissolved Fe and SO$_4^{2-}$) were taken. Moreover, soil and groundwater samples impacted with CF, CT and DCM among other pollutants were collected from the bottom part of the well S3 (Fig. 1) in order to set up microcosms experiments.

2.2. Chlorinated methanes concentration and isotope data

Volatile organic compounds concentrations were determined by headspace (HS) analysis using a FOCUS gas chromatograph coupled with a DSQ II mass spectrometer (Thermo Fisher Scientific, Waltham, MA). For C-CSIA, the analyses were performed by headspace solid-phase microextraction (HS-SPME) in a Thermo Finnigan Trace GC Ultra instrument coupled via a GC-Isolink interface to a Delta V Advantage isotope ratio mass spectrometer (Thermo Scientific GmbH, Bremen, Germany). Volatile organic compounds concentrations and carbon isotope...
measurements were performed in the Scientific and Technological Center of the University of Barcelona (CCiT-UB). The Cl-CSIA analyses were performed GC-qMS system (Agilent) located in the laboratories of the Centre d’Hydrogéologie et Géothermie (CHYN) from the University of Neuchâtel (UNINE) (Switzerland) according to the method of Sakaguchi-Söder et al. (2014).15

2.3. Biotic and abiotic laboratory-scale degradation experiments

To explore the feasibility of achieving CF and CT detoxification in the field as well as their associated isotopic fractionation patterns, anoxic microcosm experiments were conducted in batch with slurry material from the bottom of S3 well. Moreover, batch experiments were also performed to assess and determine the magnitude of carbon and chlorine isotopic fractionation of CT and CF due to abiotic dechlorination processes mediated with Fe-bearing minerals taking pyrite and magnetite in anoxic conditions as model systems.

3. Preliminary results

After the removal of the pollution sources in 2006, a significant decrease in CT and CF concentrations was detected accompanied by shifts in δ13C values. In the case of CF, δ13CCF values found in the potential sources were -34.5 ± 0.6 ‰ (wastewater tank), -37.3 ± 0.6 ‰ (in a fracture near S1) and -46.2± 0.4 ‰ (barrels) in 2004, whereas in later sampling campaigns, δ13CCF enriched values were measured in zone S3 and S1, e.g. -25.2 ± 0.5 ‰ and -27.0 ± 0.5 ‰ respectively in 2013.

The most negative δ13CCF values observed in S6 (-44.6 ± 0.5 ‰) are similar to those found in some solvent barrels stored in the factory (-46.2 ± 0.4 ‰). As a preliminary hypothesis, depleted δ13CCF values found in S6 and S10 wells might be explained as slightly degraded CF or due to mixing of CF from wastewater tank and pit areas (Fig. 2). A contribution of CT degradation in δ13CCF values should not be discarded. In S3, additionally to the enriched δ13CCF (-25.2 ± 0.5 ‰) and δ37ClCF (+1.3 ± 0.3 ‰) values in the bottom part, high concentrations of CS 2 and a spatial and temporal accumulation of DCM were observed, suggesting that both CT and CF degradation may be occurring. δ37ClCF values show differences among wells and let distinguish that the two main former sources (S1 and S3 zones) evolved towards completely different isotopic signatures: while δ37ClCF values of +1.3 ± 0.3 ‰ could be reached in S3 in 2013, S1 moved towards more depleted δ37ClCF values down to -3.9 ± 0.6 ‰ (Fig. 3). These differences might indicate that processes affecting CF in S1 are different than those of S3 and S7 (the wells with more positive values of δ37ClCF, Fig. 3) and may suggest that similar degradation processes are taking place in these last two wells. Moreover, S3 and S7 were those with higher dissolved Fe concentrations and whose redox system seems to be regulated totally or partially by equilibrium between Fe(II)aq and Fe-oxyhydroxides. The isotopic enrichment tendency observed in this 2D-CSIA plot for S3 and S7 will be compared with the slopes obtained in ongoing laboratory scale experiments in order to see if it is possible to discriminate between biotic and abiotic degradation processes.
Fig. 3. $\delta^{13}$CCF vs. $\delta^{37}$ClCF data from wells on March 2013 and November 2014. Error bars are related to standard deviation of the measurements.

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