



Multi-isotope (carbon and chlorine) analysis for fingerprinting and site characterization at a fractured bedrock aquifer contaminated by chlorinated ethenes



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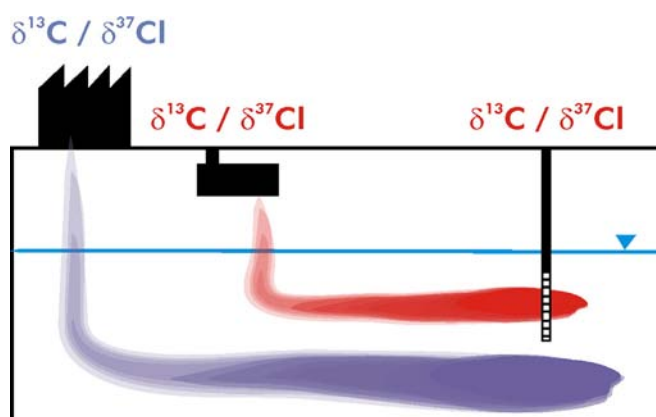
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HIGHLIGHTS

- Origin and fate of CAHs in groundwater by means of multi CSIA (¹³C, ³⁵Cl) survey
- Innovative/new approach tested in a fractured bedrock site
- Differentiation of distinct CAH sources
- Biodegradation and source mixing recognition in the aquifer

GRAPHICAL ABSTRACT



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ABSTRACT

The use of compound specific multi-isotope approach (C and Cl) in the characterization of a chlorinated ethenes contaminated fractured aquifer allows the identification of several sources and contaminant plumes, as well as the occurrence of biodegradation and mixing processes. The study site is located in Spain with contamination resulting in groundwater concentrations of up to 50 mg/L of trichloroethene (TCE), the most abundant chlorinated ethene, and 7 mg/L of tetrachloroethene (PCE). The potential sources of contamination including abandoned barrels, an underground tank, and a disposal lagoon, showed a wide range in $\delta^{13}\text{C}$ values from -15.6 to -40.5% for TCE and from -18.5 to -32.4% for PCE, allowing the use of isotope fingerprinting for tracing of the origin and migration of these contaminants in the aquifer. In contrast, there is no difference between the $\delta^{37}\text{Cl}$ values for TCE in the contaminant sources, ranging from $+0.53$ to $+0.66\%$. Variations of $\delta^{37}\text{Cl}$ and $\delta^{13}\text{C}$ in the different contaminant plumes were used to investigate the role of biodegradation in groundwater. Moreover, the isotopic data were incorporated into a reactive transport model for determination of whether the isotopic pattern observed downstream from the tank's source could be explained by the simultaneous effect of mixing and biodegradation. The results demonstrate that a multi-isotope approach is a valuable tool for

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characterization of complex sites such as fractured bedrock aquifer contaminated by multiple sources, providing important information which can be used by consultants and site managers to prioritize and design more successful remediation strategies.

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1. Introduction

Chlorinated aliphatic hydrocarbons such as TCE and PCE are among the most widespread contaminants in soil and groundwater as they are commonly used as solvents in heavy industries and dry cleaning facilities (Squillace et al., 1999). These compounds can migrate over long distances in aquifers and can also be degraded under specific conditions (Pankow and Cherry, 1996; Wiedemeier, 1999). The potential degradation along the flow path and the fact that there often are multiple sources of contaminants produce complex plumes of dissolved chlorinated solvents and degradation products, such as *cis*-1,2-dichloroethene (cDCE) and vinyl chloride (VC), which are difficult to trace. This phenomenon may be amplified in fractured aquifers, where fractures complicate the prediction of the contamination extent (Vroblesky et al., 1996). Consultants and site managers at contaminated sites might want to assess the impact of different sources and link them to downstream contamination in order to prioritize remediation strategies; for example, by treating particular sources or plumes to minimize the risk to the environment and potential receptors and to set remediation goals.

The rationale for using compound specific isotope analysis (CSIA) in environmental forensic studies is based on the wide isotopic composition ($\delta^{13}\text{C}$, but also $\delta^{37}\text{Cl}$) range of manufactured chlorinated compounds (Jendrzewski et al., 2001; Numata et al., 2002; Shouakar-Stash et al., 2003). During recent years, compound specific carbon isotope analysis has been used to fingerprint sources of chlorinated solvents and trace their migration in groundwater (Blessing et al., 2009; Hunkeler and Aravena, 2010). Recently, the development of CSIA for chlorine isotopes (Aeppli et al., 2010; Bernstein et al., 2011; Sakaguchi-Soder et al., 2007; Shouakar-Stash et al., 2006; Van Acker et al., 2006) enables a multi-isotope approach.

Isotopic fingerprinting of chlorinated ethenes can even be used on old contaminated sites because of the small or insignificant changes in the isotopic signature occurring during phase transfer processes such as dissolution, sorption, and volatilization (Braeckvelt et al., 2012; Hunkeler et al., 2004; Poulson and Drever, 1999; Slater et al., 2000; Thullner et al., 2012). Recently, chlorine isotopic fractionation was determined to be small for dissolved PCE and TCE during air-water partitioning ($\epsilon_{\text{Cl}} = -0.20 \pm 0.04\%$ and $-0.06 \pm 0.05\%$ respectively) (Jeannotat and Hunkeler, 2012, 2013) resulting in negligible variations of $\delta^{37}\text{Cl}$ in the saturated zone (Braeckvelt et al., 2012). Moreover, contaminant removal due to volatilization from groundwater is low in many aquifers under natural conditions (Thullner et al., 2012). In contrast, substantial isotopic fractionation leading to progressive enrichment in carbon and chlorine heavy isotope is produced during abiotic or biotic degradation (Abe et al., 2009; Audí-Miró et al., 2013; Hunkeler et al., 2011; Lojkasek-Lima et al., 2012a,b; Wiegert et al., 2013). By the combined use of isotope data for two elements – chlorine and carbon for chlorinated solvents – it may be possible to identify different sources even if they contain the same contaminants and are subject to ongoing degradation processes (Hunkeler et al., 2009; Lojkasek-Lima et al., 2012a). Furthermore, additional information about plume mixing in complicated groundwater flow systems such as fractured aquifers may be obtained using a multi-isotope approach. Several authors have recently employed reactive transport models to help analyse isotope data and quantify degradation and fate of chlorinated solvents at complex field sites (Hoheney and Atteia, 2010; Pooley et al., 2009; Van Breukelen et al., 2005; Wiegert et al., 2012). This approach is essential to interpret isotopic values of parent and degradation compounds at

sites where sequential degradation occurs (Van Breukelen et al., 2005; Wiegert et al., 2012).

To date, field studies including CSIA of carbon and chlorine are scarce in the literature and this approach has not yet been applied to link sources and plumes in contaminated sites where several sources are present. Our study investigates the origin and fate of chlorinated ethenes in a fractured bedrock site impacted by different sources using compound-specific carbon and chlorine isotope analysis and reactive transport modelling. The characterization of redox conditions of the aquifer was based on concentrations of redox sensitive compounds. The isotope signatures of the potential sources were determined and compared with the manufacturers' reported range. Our goals were (i) to characterize the chlorinated ethenes plumes and to relate them to their sources even when parent compounds experience biodegradation, and (ii) to combine carbon and chlorine isotope data with numerical modelling to identify the occurrence of biodegradation and mixing processes.

2. Methods

2.1. Site description

The studied aquifer is located 50 km northwest of Barcelona (NE Spain). The contamination originated from a former chemical plant, where TCE and PCE were used as chemical intermediates for the manufacture of phytosanitary products and chemical compounds for the textile industry between 1978 and 1985. The site is highly complex due to the presence of multiple contaminant sources of chlorinated solvents: 1) an underground wastewater tank, 2) a disposal lagoon and 3) abandoned solvent barrels inside the manufacturing building (Fig. 1). It is probable that some barrels were filled with waste solvent. Moreover, several spills detected around the plant building were also potential sources of contamination. The disposal lagoon was emptied and refilled with sand and gravel prior to the closure of the manufacturing facility, while the tank remained partially full.

The aquifer is an unconfined fractured bedrock mainly consisting of an Eocene blue-grey limestone bed which forms a low permeability matrix with conductive fractures and fissures (Fig. 1). The water table is located at depths ranging between 3.2 and 11.7 m below ground surface (BGS). The hydraulic conductivity, estimated with pumping tests at the site, is highly variable ranging from 1.44×10^{-3} to 0.6 m/day (Table S1 in supplementary information (SI)). The hydraulic gradient has shown significant seasonal variation and an average value of approximately 10% (Fig. 1). More details about the contaminant sources, subsurface geology, and the aquifer are available in the SI (Section 1).

2.2. Sample collection

Groundwater samples for plume characterization were collected (mostly in March 2006) from ten multilevel nested wells leading to a total of 147 sampling points. The use of multilevel samplers helps in avoiding groundwater mixing in sampling wells as samples from long screen monitoring wells are generally a mixture of contaminants from different parts of the plume with varying degrees of degradation, isotope values and redox conditions, complicating data interpretation. Eh, pH, dissolved oxygen (DO) and temperature were measured in situ and samples for dissolved organic carbon (DOC) were collected from all sampling points. Samples for other parameters were obtained from selected depths: 86 samples for volatile organic compounds

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