



# Assessment of anaerobic biodegradation of bis(2-chloroethyl) ether in groundwater using carbon and chlorine compound-specific isotope analysis

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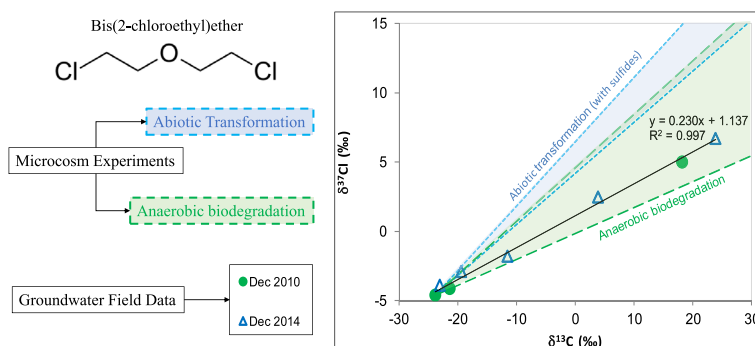
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## HIGHLIGHTS

- C and Cl isotopic analyses applied to BCEE transformation in groundwater plume
- Laboratory microcosms used to evaluate anaerobic biodegradation and abiotic reactions
- Anaerobic biodegradation likely main mechanism for BCEE attenuation in groundwater

## GRAPHICAL ABSTRACT



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## ABSTRACT

Carbon and chlorine compound specific isotope analysis (CSIA) of bis(2-chloroethyl) ether (BCEE) was performed to distinguish the primary processes contributing to observed concentration reductions in an anaerobic groundwater plume. Laboratory microcosms were constructed to demonstrate and obtain isotopic enrichment factors and dual-element CSIA trends from two potential transformation processes (1) anaerobic biodegradation using saturated sediment samples from the field site ( $\epsilon_{\text{C}} = -14.8$  and  $\epsilon_{\text{Cl}} = -5.0$ ) and (2) abiotic reactions with sulfide nucleophiles in water ( $\epsilon_{\text{C}} = -12.8$  and  $\epsilon_{\text{Cl}} = -5.0$ ). The results suggested a nucleophilic,  $\text{S}_{\text{N}}2$ -type dechlorination as the mechanism of biodegradation of BCEE. Identical dual-element CSIA trends observed in the field and in the microcosm samples suggested that the same degradation mechanism was responsible for BCEE degradation in the field. While biodegradation was the likely dominant mechanism of BCEE mass destruction in the aquifer, potential contribution of abiotic hydrolysis to the net budget of degradation could not be confidently excluded. To our knowledge, this is the first unequivocal demonstration of BCEE biodegradation at a field site.

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## 1. Introduction

Bis(2-chloroethyl) ether (BCEE) is a contaminant of concern due to its carcinogenic properties and its mobility and persistence when released into groundwater (Bednar et al., 2009; U.S. Environmental Protection

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Agency, 1993; U.S. Environmental Protection Agency, 1999). BCEE has historically been used as a solvent and as a precursor in production of insecticides and other chemicals (McClay et al., 2007). While US EPA has not established Maximum Contaminant Level (MCL) for BCEE, it has been the subject of enforcement actions by US EPA and other regulatory agencies.

To date, few studies have focused on the mechanisms of BCEE biodegradation. BCEE was found to biodegrade aerobically by *Ancylobacter aquaticus* (van den Wijngaard et al., 1993). McClay et al. reported biodegradation of BCEE by a *Xanthobacter* sp. strain ENV481, proceeding through sequential dechlorination (presumably, nucleophilic substitution of a chlorine atom by a hydroxyl group) to form 2-(2-chloroethoxy) ethanol (2-CEE) and eventually diethylene glycol (DEG) (McClay et al., 2007). The same products were detected in the presence of oxygen and under anaerobic conditions. *Pseudonocardia* sp. strain ENV478 was found to degrade BCEE by a monooxygenase-mediated O-dealkylation (McClay et al., 2007). BCEE was also susceptible to abiotic hydrolysis (Payne and Collette, 1989) with reaction products similar to those reported for ENV481, but the rate of the reaction was relatively slow, with estimated half-life of 22 years at 25 °C (Mabey et al., 1982).

Degradation of BCEE in groundwater is difficult to document through traditional methods, such as through detections of degradation products CEE and DEG, since the products are hard to detect at low concentrations. Compound-specific Isotope Analysis (CSIA) provides an alternative method for assessing in-situ mass reduction, relying on detection of characteristic heavy isotope (e.g.,  $^{13}\text{C}$ ) enrichments in the remaining parent contaminant. Dual-element CSIA, combining analysis of two isotope ratios (e.g.,  $^{13}\text{C}/^{12}\text{C}$  and  $^{37}\text{Cl}/^{35}\text{Cl}$ ) can be a particularly valuable tool for identification of the mechanisms of (bio)chemical transformations and has been extensively used in the studies of priority contaminants, including chlorinated ethenes (Cretnik et al., 2014; Hunkeler et al., 2011; Lojkasek-Lima et al., 2012; Renpenning et al., 2014; Wiegert et al., 2013), BTEX compounds (Fischer et al., 2008; Hunkeler et al., 2001; Steinbach et al., 2004), MTBE (Kuder et al., 2005; Zwank et al., 2005), and 1,2-dichloroethane (Palau et al., 2014).

Although BCEE is known to biodegrade aerobically (McClay et al., 2007), it frequently occurs in groundwater under anaerobic conditions. As such, it is important to understand whether anaerobic biodegradation of BCEE can occur and whether natural attenuation under anaerobic conditions is a viable option for remediation of BCEE in groundwater. In addition to biodegradation, abiotic transformation processes could be significant in the overall budget of BCEE attenuation under anaerobic conditions. These include abiotic hydrolysis and similar  $\text{S}_\text{N}2$ -type reactions with dissolved sulfide species and abiotic transformation on mineral surfaces, by analogy to previous studies of other halogenated compounds (Barbash and Reinhard, 1989; Butler and Hayes, 2000; VanStone et al., 2007).

To date, with a possible exception of one report on anaerobic incubation of strain ENV481 (McClay et al., 2007), there is limited evidence of BCEE degrading under anaerobic conditions and no reports of isotope fractionation of BCEE in relevant reactions. Consequently, the main objectives of this work were to test if BCEE would degrade under anaerobic conditions and if it was feasible to document that such degradation was occurring in the environment. The study combined laboratory experiments (to obtain reference carbon and chlorine isotope data on anaerobic biodegradation, reactions with sediment minerals, reactions with sulfide nucleophiles and hydrolysis) and CSIA of samples from a BCEE-contaminated field site to test whether the same reaction-specific dual-element CSIA signatures could be detected in the controlled lab experiments and in the environmental samples.

## 2. Materials & methods

### 2.1. Study site

The study site is an active chemical manufacturing facility in Texas where historical operations resulted in groundwater impacted

with multiple chlorinated compounds, including chlorinated alkenes and alkanes: tetrachloroethene (PCE), trichloroethene (TCE), cis-dichloroethene (cis-DCE), vinyl chloride (VC), 1,2-dichloroethane (1,2-DCA) and 1,2-dichloropropane (1,2-DCP), as well as chlorinated ethers: bis(2-chloroethyl) ether (BCEE) and bis(2-chloro-isopropyl) ether (BCIE). The likely sources of BCEE releases were in operation from mid 1940s through mid-1980s.

The groundwater plume is present in a sandy horizon at depths between 6.7 m and 8.5 m underlying ~1 m of till followed by ~5 m of sandy clay and clay. The hydraulic gradient is relatively flat (up to 0.0036 m/m) and seasonal fluctuation of <1.6 m in groundwater elevation is observed. Monitoring data collected since 2002 indicated that concentrations of chlorinated compounds in groundwater were either stable or decreasing with time. Fig. 1 shows the site map including the locations of monitoring wells described in this study. Groundwater geochemistry data (Table SI-1) indicated elevated concentrations of ferrous iron (0.4 to 8.4 mg/L), dissolved methane (0.1 to 16 mg/L), and dissolved manganese (0.16 to 9 mg/L), suggesting prevalence of anaerobic conditions. In addition, low to moderate concentrations of sulfate (2.5 to 60 mg/L) and sulfide (<0.01 to 0.4 mg/L) were observed. These data in combination with elevated concentrations of dissolved ethene (0.0025 to 83 mg/L), ethane (0.0062 to 2.2 mg/L), chloride (120 to 6000 mg/L), presence of elevated total organic carbon (1.7 to 243 mg/L) and stable or decreasing concentration trends of various chlorinated alkanes and alkenes suggested ongoing reductive dechlorination of PCE and TCE. Given the prevailing groundwater geochemistry and the ongoing evidence of reductive dechlorination of PCE and TCE, it was important to evaluate the fate of BCEE under anaerobic conditions.

### 2.2. Groundwater and sediment sample collection

To evaluate carbon and chlorine isotope fractionation patterns for BCEE in the field, groundwater samples from monitoring wells were sampled. BCEE concentrations ranged from <1 µg/L to 55,000 µg/L in these four sampling events (June and December 2009, December 2010 and December 2014). The wells were sampled using low-purge sampling procedure after achieving stable conditions of dissolved oxygen and oxygen reduction potential. Groundwater was collected in 40 mL VOA vials, preserved with sulfuric acid to pH < 2 and shipped on ice to University of Oklahoma for analysis.

Saturated sediment for the laboratory microcosm experiments was collected using a hollow stem auger with a 10-cm diameter split-spoon sampler, from 5 to 8 m below ground surface and adjacent to monitoring well MW-18. This well was selected based on a 1000-fold decrease in BCEE concentration along with >10‰ enrichment in  $\delta^{13}\text{C}$  of BCEE (compared to the presumed source area well, MW-17, see Table 3). The sampling depth interval coincided with the screened interval for MW-18. The sediment was immediately transferred to two 1-L glass Mason jars and the remaining headspace was filled with groundwater from MW-18 to minimize the possibility of introducing oxygen into the samples. In addition, groundwater from MW-18 was collected in two 1-L jars with blue Teflon-lined lids. The sealed jars containing sediment and groundwater were shipped overnight on ice to the University of Oklahoma for setting up sediment microcosms.

### 2.3. Laboratory experiments

Laboratory degradation experiments were set up to establish the presence or the lack of isotope fractionation patterns associated with various likely mechanisms of BCEE transformation. Table 1 summarizes the different treatments used in the laboratory experiments to generate carbon and chlorine CSIA data in conjunction with the likely concentration changes. Sediment free incubations were conducted to test the susceptibility of BCEE to reactions with sulfur nucleophiles and to hydrolysis. While the reported rate of hydrolysis of BCEE at 25 °C is

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