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Anaerobic abiotic transformations of *cis*-1,2-dichloroethene in fractured sandstone

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HIGHLIGHTS

- cDCE was transformed abiotically under anaerobic conditions by typical sandstone.
- CO_2 and soluble compounds were the main products formed.
- Pyrite was present but was not likely responsible for abiotic transformation of cDCE.
- SEM/EDS analysis indicated goethite and magnetite are present in the rock.
- Autoclaving altered the sandstone but was preferable to chemical sterilization.

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ABSTRACT

A fractured sandstone aquifer at an industrial site is contaminated with trichloroethene to depths greater than 244 m. Field data indicate that trichloroethene is undergoing reduction to *cis*-1,2-dichloroethene (cDCE); vinyl chloride and ethene are present at much lower concentrations. Transformation of cDCE by pathways other than reductive dechlorination (abiotic and/or biotic) is of interest. Pyrite, which has been linked to abiotic transformation of chlorinated ethenes, is present at varying levels in the sandstone. To evaluate the possible role of pyrite in transforming cDCE, microcosms were prepared with groundwater, $\sim$40 mg L^{-1} cDCE + [^{14}C]cDCE, and crushed solids (pure pyrite, pyrite-rich sandstone, or typical sandstone). During 120 d of incubation, the highest level of cDCE transformation occurred with typical sandstone (11–14% $^{14}CO_2$, 1–3% ^{14}C-soluble products), followed by pyrite-rich sandstone (2–4% $^{14}CO_2$, 1% ^{14}C-soluble products) and even lesser amounts with pure pyrite. These results indicate pyrite is not likely the mineral involved in transforming cDCE. A separate experiment using only typical sandstone compared the rate of cDCE transformation in non-sterilized, autoclaved, and propylene-oxide sterilized treatments, with pseudo-first order rate constants of 8.7, 5.4, and 1.0 yr^{-1}, respectively; however, transformation stopped after several months of incubation. Autoclaving increased the volume of pores, adsorption pore diameter, and surface area in comparison to non-sterilized typical sandstone. Nevertheless, autoclaving was less disruptive than chemical sterilization. The results provide definitive experimental evidence that cDCE undergoes anaerobic abiotic and biotic transformation in typical sandstone, with formation of CO_2 and soluble products.

1. Introduction

At an industrial site in southern California underlain by fractured sandstone, thousands of kg of trichloroethene (TCE) were reportedly discharged to the surface for several decades following its use in degreasing operations. Field data indicate that nearly all of the TCE has diffused into the rock matrix and some has undergone reductive dechlorination to *cis*-1,2-dichloroethene (cDCE) to depths in excess of 244 m. Only minor amounts of vinyl chloride (VC) and ethene have been detected, suggesting that only a low percentage of the cDCE undergoes complete biological dechlorination, as has been observed at other sites. At some locations, field evidence suggests that cDCE undergoes natural attenuation by a pathway other than reductive dechlorination. Abiotic transformation of cDCE may play an important role in this process (Ferrey et al., 2004).

A microcosm study performed with crushed rock and groundwater from the site provided evidence that cDCE is transformed abiotically (Darlington et al., 2008). Non-sterile (live) microcosms

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confirmed field evidence for reductive dechlorination of TCE to cDCE, with only minor amounts of VC appearing. In both live and autoclaved microcosms that received ^{14}C-labeled TCE and cDCE there was transformation to $^{14}CO_2$ and ^{14}C-labeled soluble products. Glycolate, formate and acetate were identified as three components of the soluble products. The extent of transformation to CO_2 was greater in the live microcosms and the extent of transformation to soluble products was greater in the autoclaved microcosms. This suggested that soluble product formation was abiotic and was followed by biotic or abiotic transformation to CO_2. However, this does not rule out direct transformation of TCE and cDCE to CO_2, either by a biotic or abiotic process. Costanza et al. (2005) also observed abiotic formation of glycolate, formate and carbon dioxide, although the parent compound was tetrachloroethene and transformation was induced by thermal remediation under aerobic conditions.

Previous studies provide evidence for abiotic transformation of tetrachloroethene, TCE, cDCE and VC catalyzed by naturally occurring minerals (Butler and Hayes, 1999, 2001; Lee and Batchelor, 2002b). For example, pyrite, magnetite and green rust catalyzed the transformation of TCE and cDCE to as much as 71% acetylene and minor amounts of VC (Lee and Batchelor, 2002a,b); however, the mass balances did not account for all of the TCE or cDCE initially added, suggesting that soluble products and/or CO_2 may also be significant. Portions of the sandstone at the southern California site that is the subject of this research are enriched in pyrite.

Autoclaving is widely used as a method to sterilize soil and thereby create the conditions for observing abiotic transformation reactions, even though uncertainty exists regarding its efficiency. Another concern with autoclaving is the effect it has on the reactivity of the soil. Darlington et al. (2008) observed a greater extent of abiotic transformation in autoclaved microcosms than total transformation in live microcosms. Several studies have compared the characteristics of soil to autoclaved soil. Extractable manganese and pH levels increased in soils that were autoclaved (Skipper and Westermann, 1972; Lopes and Wollum, 1976; Wolf et al., 1989), while extractable iron levels decreased (Skipper and Westermann, 1972; Lopes and Wollum, 1976; Wolf et al., 1989). Ammonia and nitrate increased in autoclaved sandy loam soils (Lopes and Wollum, 1976).

The objectives of this study were to: (1) determine if pyrite or another mineral is responsible for catalyzing the anaerobic abiotic transformation of cDCE in fractured sandstone; (2) compare the rate and extent of cDCE abiotic transformation when sterilization is accomplished with propylene oxide versus autoclaving; and (3) determine first order rates for cDCE transformation under biotic and abiotic conditions. Although abiotic transformation occurred with TCE and cDCE in the prior study (Darlington et al., 2008), the current study focused on cDCE. Biotic reductive dechlorination is a significant pathway for TCE, whereas with cDCE abiotic transformation appears dominant. Also, the extent of transformation to soluble products was greater for cDCE than for TCE. The prior study (Darlington et al., 2008) used an initial cDCE concentration (0.62 mg L^{-1}) that is representative of groundwater conditions, while the current study used a higher initial concentration (40 mg L^{-1}) that is within the concentration range for pore water at the site (Pierce, 2005).

2. Materials and methods

2.1. Sample collection, processing, and storage

Groundwater was obtained from a well close to the core hole from which rock was obtained. Upon receipt, the groundwater contained ~1.3 μM TCE. The groundwater was stored for several wk at 4 °C prior to preparing the experiments; it was then warmed to room temperature and sparged (5–6 min with 70% N_2:30% CO_2) so that the only volatile compound present at time zero was the added cDCE. The groundwater pH was 7.0 before sparging and 6.3 after sparging.

Rock cores identified as pyrite-rich and typical sandstone on coring logs were collected from depths of 125–170 and 90–230 m at the site, respectively. Samples were collected as previously described (Darlington et al., 2008). One set of core samples was crushed at the University of Waterloo using a schedule 304 stainless steel cylinder and piston and shipped to Clemson University, where they were crushed further with a ceramic mortar and pestle and then passed through a series of sieves. Three fractions were obtained: <0.075; 0.075–0.25; and >0.25 mm. The crushed rock was stored in an anaerobic chamber for about 150 d until microcosms were prepared. Additional cores identified as typical sandstone were collected from the same core hole and shipped directly to Clemson University where they were crushed using a manual hydraulic press. The smaller pieces of core were then crushed with a grinding mill, passed through a 0.85 mm sieve, and stored in an anaerobic chamber for approximately 60 d prior to use.

2.2. Chemicals

[^{14}C]cDCE dissolved in toluene was purchased from Moravek Biochemicals (4 mCi mmol^{-1}). Research grade pyrite mineral (Zacatecas, Mexico) was obtained from Ward's Natural Science (Rochester, NY), crushed with a mortar and pestle, and sieved. The 0.075–0.25 mm fraction was acid washed and freeze dried (Lee and Batchelor, 2002b). The sources and purity of other chemicals were: propylene oxide (98%, VWR); VC (99.5%, Fluka); ethene (99.9%) and acetylene (99.6%, Matheson Tri Gas); and ethane (99.5%, National Welders). All other chemicals used were reagent grade.

2.3. Experimental design

Two experiments were conducted. Experiment I determined if pyrite catalyzes the abiotic transformation of cDCE to soluble products and CO_2, based on five treatments (duplicate bottles per treatment): (1) groundwater + typical sandstone; (2) groundwater + pyrite-rich sandstone; (3) buffered distilled deionized (DDI) water (10 mM $NaHCO_3$) (Lee and Batchelor, 2002b) + pure pyrite; (4) groundwater alone; and (5) buffered DDI water alone. All of the treatments except pure pyrite were sterilized by autoclaving. Pure pyrite was sterilized by washing twice with a 1 M HCl solution then rinsing with DDI water until the pH was above 6.7. The pyrite was then freeze dried before sieving and storing in an anaerobic glove box (Lee and Batchelor, 2002b). This method removed oxidized iron oxides from the surface of the pyrite.

Experiment II compared the effect of sandstone sterilization by autoclaving versus exposure to propylene oxide on the rate and extent of abiotic transformation of cDCE, based on four treatments (triplicate bottles per treatment): (1) groundwater + untreated typical sandstone, intended to simulate live conditions; (2) groundwater + typical sandstone that was autoclaved (see below); (3) groundwater + typical sandstone that was sterilized using propylene oxide; and (4) groundwater that was autoclaved (1 h, 121 °C).

Experiments were performed in glass bottles (2300 mL total volume) with a side arm attached, capped with a Mininert valve (Supplemental material (SM), Sec. SM-1). The treatments with sandstone contained 1400 g rock + 1200 mL groundwater per bottle. For experiment I, crushed rock (0.075–0.25 mm) was used. The treatment with pyrite contained 100 g pyrite + 1200 mL buffered