Science of the Total Environment 626 (2018) 497–506

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Remediation of chlorinated ethenes in fractured sandstone by natural and enhanced biotic and abiotic processes: A crushed rock microcosm study

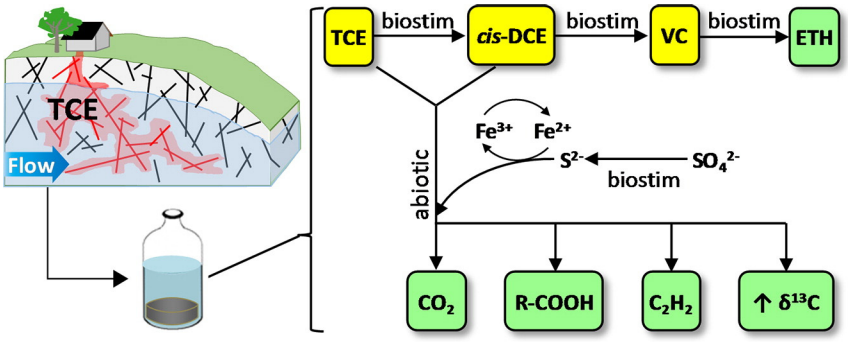
Rong Yu [a], Richard G. Andrachek [b], Leo G. Lehmicke [c], David L. Freedman [a,*]

[a] Department of Environmental Engineering and Earth Sciences, Clemson University, Clemson, SC 29634-0919, USA
[b] MWH, Now part of Stantec, 2121 N California Boulevard, Suite 600, Walnut Creek, CA 94596, USA
[c] CO_2 &Water, 295 Kenilworth Drive, Akron, OH. 44313, USA

HIGHLIGHTS

- TCE and cDCE degradation in sandstone was enhanced by three electron donors.
- TCE was reduced to cDCE by *Geobacter* and then to VC and ethene by *Dehalococcoides*.
- CSIA and 14C-tracking demonstrated abiotic transformation of TCE and cDCE.
- First order abiotic degradation rates were calculated based on 14C analysis.
- Sulfate did not enhance abiotic degradation but inhibited reductive dechlorination.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 October 2017
Received in revised form 6 January 2018
Accepted 8 January 2018
Available online 19 February 2018

Editor: Holden

Keywords:
Abiotic transformation
Biogeochemical processes
Compound specific isotope analysis
Fractured sandstone
Reductive dechlorination
Trichloroethene

ABSTRACT

Biostimulation was identified as a potential technology to treat a fractured sandstone aquifer contaminated with trichloroethene (TCE) and *cis*-1,2-dichloroethene (*cis*-DCE). Most of the mass of TCE and *cis*-DCE resides within the rock matrix and strategies to restore groundwater to pre-existing conditions are severely limited by back diffusion. A microcosm study using crushed rock and groundwater from the site was performed to assess biostimulation and natural attenuation. Lactate, hydrogen release compound® (HRC), and emulsified vegetable oil (EVO) significantly increased the rate of TCE reduction to *cis*-DCE. Lactate also stimulated dechlorination of *cis*-DCE to vinyl chloride (VC) and ethene, suggesting the presence of indigenous *Dehalococcoides*. Illumina sequencing and qPCR analyses suggest that reductive dechlorination of TCE to *cis*-DCE is mediated by *Geobacter* spp. while *Dehalococcoides* spp. perform reduction of *cis*-DCE to VC and ethene. The rate of VC reduction to ethene was much slower than the reduction of TCE to *cis*-DCE and *cis*-DCE to VC, indicating the indigenous *Dehalococcoides* perform the final step co-metabolically. This was confirmed in enrichment cultures fed with only VC. Consequently, biostimulation may create an elevated risk due to transient accumulation of VC. Abiotic transformation of TCE and *cis*-DCE was observed based on accumulation of ^{14}C-labeled products from ^{14}C-TCE and ^{14}C-*cis*-DCE, as well as enrichment in δ^{13}C-*cis*-DCE in the absence of reductive dechlorination. Based on accumulation rates for ^{14}C-products in unamended microcosms, pseudo-first-order rates for abiotic transformation were 0.038 yr^{-1} for TCE and 0.044 yr^{-1} for *cis*-DCE. These rates within the rock matrix may be sufficient to support natural attenuation in this diffusion controlled system.

* Corresponding author.
E-mail address: dfreedm@clemson.edu (D.L. Freedman).

https://doi.org/10.1016/j.scitotenv.2018.01.064
0048-9697/

1. Introduction

Fractured bedrock aquifers with rock matrix porosity >4 to 5% tend to be more recalcitrant to active remediation compared to unconsolidated aquifers due to their complex flow systems and the fact that most of the contaminant mass tends to reside within a low permeability matrix (Parker et al., 2010) Monitored natural attenuation (MNA) and biostimulation are potentially favorable treatment methods due to their cost effectiveness.

Anaerobic attenuation of chlorinated ethenes may occur via biotic and abiotic pathways, including reductive dechlorination, β-elimination, α-elimination, and hydrogenation (Arnold and Roberts, 2000; Brown et al., 2009). Reductive dechlorination is typically mediated by organohalide respiring microbes, most of which reductively dechlorinate trichloroethene (TCE) only as far as *cis*-1,2-dichloroethene (*cis*-DCE) (Adrian, 2016). Dechlorination of TCE to vinyl chloride (VC) and ethene requires *Dehalococcoides*, although the potential role of *Dehalogenimonas* should also be considered (Adrian, 2016).

Reductive dechlorination may be affected by the unique features of porous fractured bedrock aquifers, where most of the contaminant mass typically resides within the rock matrix. Contaminant mass within the matrix reduces the prospect for contact with microbes (Nelson, 2009). Nevertheless, dechlorinating microbes have been detected in low permeability media, including clay (Takeuchi et al., 2011) and fractured sandstone-dolostone (Lima et al., 2012). Other factors that affect reductive dechlorination include unfavorable redox conditions; a lack of electron donor; and preferential use of sulfate as an electron acceptor.

Abiotic transformation of chlorinated ethenes may contribute to natural attenuation but is difficult to document. For example, a decrease in contaminant mass may be attributable to other attenuation mechanisms, including biodegradation, diffusion, adsorption, and dilution. Unlike other short chain hydrocarbons (e.g., ethene and ethane), acetylene is an unambiguous indicator of abiotic degradation of chlorinated ethenes (USEPA, 2009), but is hard to track due to its volatility and biodegradability (Mao et al., 2017; Schink, 1985). Daughter products from abiotic degradation such as CO_2 and organic acids (e.g., glycolate, formate, and acetate) are not unique to transformation of chlorinated ethenes (Darlington et al., 2008, 2013). Geochemical and geophysical measurements (e.g., mineralogy and magnetic susceptibility) may be predictive of abiotic transformation mediated by iron-bearing minerals; however, the minerals may be present at concentrations too low to detect. Use of compound specific isotope analysis (CSIA) to document abiotic degradation is complicated by the co-occurrence of biotic degradation processes, although advances in multiple isotope analyses are helping to sort this out. Use of microcosm studies to evaluate abiotic degradation makes it possible to eliminate the contribution of biotic activity; furthermore, use of ^{14}C-labeled contaminants permits identification of products such as CO_2 and organic acids.

Biostimulation may enhance both biotic and abiotic transformation. Substrate addition generates redox conditions that are sufficiently low for reductive dechlorination, and fermentation yields hydrogen, a universal electron donor for chlororespiration. Acetate is also produced and used as the carbon source for *Dehalococcoides*. Biostimulation may also enhance abiotic transformation and interactions of biotic and abiotic processes that benefit overall remediaton (Brown et al., 2009; Chaudhuri et al., 2001; Kennedy et al., 2006; Kennedy et al., 2005; Moore, 2003; Sale et al., 2013).

An industrial site in southern California is contaminated with TCE to depths in excess of 244 m. Most of the mass is present in the sandstone rock matrix (Cherry et al., 2009). Field (Pierce, 2005; Zimmerman, 2010) and laboratory evidence (Darlington et al., 2008) strongly supports that reductive dechlorination to *cis*-DCE is a major attenuation process. However, further reduction to VC and ethene is limited, potentially because of a lack of electron donor or trace nutrients, a low and/or heterogeneous population of indigenous *Dehalococcoides* with the necessary functional genes, or a high background level of sulfate. Abiotic transformation mediated by the sandstone has been reported in microcosms amended with ^{14}C-labeled TCE and *cis*-DCE (Darlington et al., 2008).

The objectives of this study were to evaluate the effect of biostimulation on the rate of biotic and abiotic transformation of TCE and *cis*-DCE in fractured sandstone. Crushed rock microcosms were prepared with and without ^{14}C-labeled TCE and *cis*-DCE. This permitted quantification of ^{14}C-labeled product formation and quantification of δ^{13}C enrichment.

2. Material and methods

2.1. Site geology and sample collection

The site is underlain by a geological unit referred to as the Chatsworth formation, consisting of highly fractured interbedded sandstone, siltstone and mudstone deposited by marine turbidities that were uplifted during the Upper Cretaceous. Groundwater flow at this site is complex due to topography, faulting, bedrock strike (northeast) and dip (~30° northwest) and historic groundwater withdrawals. The majority of groundwater flow occurs in the fracture network with much higher hydraulic conductivity (average of 5E-4 cm/s) than in the rock matrix (4.1E-7 cm/s). Most of the groundwater resides in the porous rock body, because matrix porosity (13.6%) is almost four orders of magnitude larger than the fracture porosity (Cherry et al., 2009).

Sandstone samples were collected from a corehole at the site, crushed onsite and shipped to Clemson University. Groundwater was collected from two monitoring wells, one in the source zone and one near the plume periphery. Information concerning the sampling locations and collection methods is provided in Appendix A.1.

2.2. Chemicals and medium

The following chemicals (purity, source) were used: TCE (99%, Alfa Aesar), ^{14}C–TCE (99%, specific activity = 2 mCi/mmol, uniformly labeled, American Radiolabeled Chemicals, Inc.), *cis*-DCE (99%, TCI America), ^{14}C-*cis*-DCE (99.1%, specific activity = 5 mCi/mmol, uniformly labeled, Moravek Biochemicals), VC (99.5%, Fluka), polymer grade ethene (99.9%, Airgas), ethane (99.95%, Matheson), methane (99%, Matheson), hydrogen (99.995%, Airgas), and acetylene (99%, Matheson). Sodium lactate syrup was obtained from EM Science (58.8 to 61.2% sodium lactate; specific gravity 1.31). Sodium sulfide nonahydrate was obtained from Acros Organics (98%). NewmanZone® emulsified vegetable oil (EVO) was obtained from RNAS. Hydrogen release compound (HRC®) was obtained from Regenesis. All other chemicals were reagent grade. An anaerobic mineral salts medium was used to grow enrichment cultures (Appendix A.2).

2.3. Crushed rock microcosms

Table 1 summarizes the experimental design, including five control treatments: water controls (WC), autoclave controls (AC), autoclave controls amended with sulfide (AS), unamended live (UN), and unamended live with sulfate added (S). Donor amended treatments included lactate (L), lactate plus sulfate (LS), EVO (E), EVO plus sulfate (ES), HRC (H), and HRC plus sulfate (HS). With 11 treatments, two compounds (TCE and *cis*-DCE), and microcosms with and without ^{14}C-TCE and ^{14}C-*cis*-DCE, 528 bottles were prepared. Microcosms were constructed in an anaerobic chamber as previously described (Darlington, 2008), with minor modifications. Each 160-mL serum bottle contained 20 g of crushed rock and 50 mL of groundwater. Water controls were prepared with 50 mL of distilled deionized water plus an equivalent volume of glass beads as a surrogate for crushed rock. The initial concentration of TCE and *cis*-DCE was ~1 mg/L. For bottles that received ^{14}C-labeled TCE or *cis*-DCE, approximately 0.5 μCi/bottle was added.