Abiotic dechlorination of chlorinated ethenes in natural clayey soils: Impacts of mineralogy and temperature

CrossMark

Charles E. Schaefer[a,*], Paul Ho[b], Christopher Gurr[c], Erin Berns[d], Charles Werth[d]

[a] CDM Smith, 110 Fieldcrest Avenue, #8, 6th Floor, Edison, NJ 08837, United States
[b] CDM Smith, 14432 SE Eastgate Way # 100, Bellevue, WA 98007, United States
[c] CDM Smith, 11490 Westheimer Rd #700, Houston, TX 77077, United States
[d] University of Texas at Austin, Civil, Architectural, and Environmental Engineering, 301 E. Dean Keeton St., Stop C1786, Austin, TX 78712, United States.

ARTICLE INFO

ABSTRACT

Laboratory batch experiments were performed to assess the impacts of temperature and mineralogy on the abiotic dechlorination of tetrachloroethene (PCE) or trichloroethene (TCE) due to the presence of ferrous minerals in natural aquifer clayey soils under anaerobic conditions. A combination of x-ray diffraction (XRD), magnetic susceptibility, and ferrous mineral content were used to characterize each of the 3 natural soils tested in this study, and dechlorination at temperatures ranging from 20 to 55 °C were examined. Results showed that abiotic dechlorination occurred in all 3 soils examined, yielding reduced gas abiotic dechlorination products acetylene, butane, ethene, and/or propane. Bulk first-order dechlorination rate constants (k_{bulk}), scaled to the soil:water ratio expected for in situ conditions, ranged from $2.0 \times 10^{-5}\,day^{-1}$ at 20 °C, to $32 \times 10^{-5}\,day^{-1}$ at 55 °C in the soil with the greatest ferrous mineral content. For the generation of acetylene and ethene from PCE, the reaction was well described by Arrhenius kinetics, with an activation energy of 91 kJ/mol. For the generation of coupling products butane and propane, the Arrhenius equation did not provide a satisfactory description of the data, likely owing to the complex reaction mechanisms associated with these products and/or diffusional mass transfer processes associated with the ferrous minerals likely responsible for these coupling reactions. Although the data set was too limited to determine a definitive correlation, the two soils with elevated ferrous mineral contents had elevated abiotic dechlorination rate constants, while the one soil with a low ferrous mineral content had a relatively low abiotic dechlorination rate constant. Overall, results suggest intrinsic abiotic dechlorination rates may be an important long-term natural attenuation component in site conceptual models for clays that have the appropriate iron mineralogy.

1. Introduction

Contaminant uptake and the subsequent slow release from low permeability (e.g., silt, clay) matrices serve as one of the greatest challenges facing the environmental remediation industry with respect to chlorinated solvents and impacted groundwater. This matrix back-diffusion process can sustain contaminant plumes for decades, even if proven technologies such as in situ chemical oxidation or biostimulation are applied to successfully remove contaminants in transmissive zones (Mundle et al., 2007; Parker et al., 2008). While thermal (Baker et al., 2016) and electrokinetic (Athmer, 2014) approaches have been demonstrated for effectively treating chlorinated ethenes in clays, these technologies are often cost-prohibitive when considered on a large scale. Thus, there is a need to consider or enhance naturally occurring removal mechanisms for chlorinated solvents such as tetrachloroethene

(PCE) or trichloroethene (TCE) from natural clays.

Multiple studies have demonstrated that, under anoxic conditions, ferrous iron minerals can facilitate the dechlorination of chlorinated ethenes and ethanes. The majority of these studies have used artificially prepared minerals (Butler and Hayes, 2001; Lee and Batchelor, 2002a; Elsner et al., 2004, O'Loughlin and Burris, 2004; Liang et al., 2009, He et al., 2015), yielding primarily acetylene or further reduced gases such as ethene or ethane via a reductive elimination pathway. Other studies have focused on the formation of iron sulfide minerals that form in response to enhanced biotic or abiotic reducing conditions, and the subsequent abiotic dechlorination enhancement that can occur from these precipitated minerals (Szecsody et al., 2004; Choi et al., 2009; Jeong et al., 2011; Hyun and Hayes, 2015).

Far fewer studies have been performed using natural aquifer materials that were not biotically or abiotically modified. Kenneke and

---

Weber (2003) measured the removal of halogenated methanes from pond sediments, and observed abiotic degradation. Ferrey et al. (2004) showed that autoclaved natural sands containing magnetite facilitated the reductive dechlorination of chlorinated ethenes. Recent studies have shown the ferrous minerals present in bedrock facilitate the reductive dechlorination of chlorinated ethenes (Schaefer et al., 2013; Schaefer et al., 2015; Darlington et al., 2013), and are likely important with respect to contaminant transport (Schaefer, 2016).

While the role of naturally-occurring ferrous minerals in rock matrices has been examined with respect to dechlorination of TCE, similar processes in low permeability un-altered natural clays and silts have not been reported, and it is unclear what mineral properties might be important for providing a screening-level assessment of the potential for abiotic dechlorination. Ferrous mineral content as determined via the 1,10-phenanthroline method (Amonette and Templeton, 1998) and magnetic susceptibility have been argued as a means to assess the potential for abiotic dechlorination in rock or sands (Ferrey et al., 2004, Schaefer et al., 2013, Lebrón et al., 2015), but it is currently unknown if these are appropriate screening tools for clays.

Methods to enhance abiotic dechlorination of chlorinated ethenes in natural sediments and clays have not been widely reported. Costanza and Pennell (2007) examined PCE dechlorination in a natural silty clay at temperatures up to 95 °C, but only showed trace levels of transient n-butene generation that stalled by 37 days into the batch study. Truex et al. (2007) showed that the abiotic dechlorination product acetylene was generated in laboratory experiments in the presence of TCE with sediments at 70 °C; no acetylene generation was observed in parallel experiments performed at 10 °C. These data suggest that the elevated temperatures likely enhanced the abiotic dechlorination of TCE to acetylene in the presence of ferrous minerals naturally present in the sediment. However, insight into the relationship between temperature and iron-facilitated abiotic dechlorination rates in natural clayey soils has yet to be explored, and the clay mineral properties that are conducive to such abiotic reactions remain poorly understood.

The overall goal of this study is to examine abiotic dechlorination in natural clayey materials, the relationship to the ferrous iron type and content, and the enhancement of this dechlorination via heating. Specifically, the generation rate and nature of the abiotic transformation products are evaluated as a function of temperature for natural clayey soils. The impact of soil mineralogy, and mineral screening methods as a predictor of abiotic dechlorination, also are evaluated.

2. Experimental

2.1. Materials

PCE (> 99.9% purity), TCE (> 99.5% purity), and reduced gas standards (15 PPM methane, ethane, ethene, acetylene, propane, propylene, methyl acetylene, butane in a nitrogen balance) were purchased from Sigma Aldrich (St. Louis, MO). An electrolyte solution consisting of 0.005 M $CaCl_2$ was used in all experiments. Three clayey aquifer materials were collected for this study. Details of the location and collection methods for the soils are provided in the SI.

2.2. Batch dechlorination testing

Using the soils and synthetic groundwater described in the above section, batch microcosms were prepared to evaluate abiotic dechlorination processes as a function of temperature and soil type. As described in Table 1, unsterilized soils were used for the Biotic conditions for Soils 1 and 3. Abiotic test conditions for Soils 1 and 2 were prepared via gamma-irradiation (2.5 M-rads) prior to use.

The experimental method employed was based on previously published methods that were used to determine abiotic TCE dechlorination in batch systems containing rock (Schaefer et al., 2015). Batch experiments were prepared under anoxic conditions, as all preparations were

Table 1
Experimental design for the batch experiments. Soils 1 and 2 were prepared in triplicate; Soil 3 was prepared in duplicate. Soil in the abiotic conditions was gamma-irradiated, while soil in the biotic conditions were not.

Condition	Biotic or Abiotic	Contaminant Addition	Temperature (°C)
Soil 1	Biotic	None	20, 35, 55
	Biotic	PCE	20, 35, 55
	Abiotic	PCE	20, 35, 55
Soil 2	Abiotic	None	20, 55
	Abiotic	PCE	20, 35, 55
Soil 3	Biotic	None	20
	Biotic	TCE	20

performed in an anaerobic chamber. The soil (6 g) was placed in 40 mL glass vials. The $CaCl_2$ electrolyte solutions were sparged with nitrogen gas prior to use in the anaerobic chamber for a minimum of 1 h. A contaminant spiking solution, which contained neat PCE or TCE in the electrolyte, was also prepared using this nitrogen-sparged electrolyte. Spiking solution was added (15 mL) to each vial that was targeted for PCE or TCE addition (Table 1); electrolyte (without PCE or TCE) was then added to each vial to bring the final aqueous volume to 30 mL. Use of both contaminant-spiked and non contaminant-spiked conditions served as a means to distinguish generation of PCE/TCE dechlorination products (e.g., ethene, ethane, acetylene, propane) due to current abiotic/biotic reaction from that of gas generation due to any other carbon sources and/or any accumulation of these gases in the soil samples from dechlorination that may have occurred in situ prior to sample collection. A similar approach was employed by Schaefer et al. (2015) to determine the current abiotic dechlorination activity of rock samples.

The vials were capped with Mininert® valves to allow for repeated headspace sampling while minimizing losses of chlorinated ethene and potential gaseous transformation products. After the vials were prepared and capped in the anaerobic chamber, the vials were removed from the anaerobic chamber and placed under a stream of nitrogen. The retaining ring on the cap was loosened while the valve was held in place, and a thin bead of epoxy was applied to the lower threads on the vial. This epoxy seal was used to further limit leakage losses during the experiment. The retainer ring was re-tightened, and the epoxy was spread through the threads. The vials were gently inverted several times to enhance mixing, then returned to the anaerobic chamber and placed on shakers at 50 RPM. For elevated temperature conditions, vials were placed in an Innova 44R incubator and shaker table (New Brunswick Scientific Co., Edison, NJ). Each condition (Table 1) for Soils 1 and 2 were prepared in triplicate; Soil 3 conditions were prepared in duplicate. Vial headspace was sampled as a function of time for chlorinated ethenes and reduced gases over an 8 week period; Soil 3 was sampled over a 10 week period. Following the final headspace sampling event, headspace in Soils 1 and 2 were analyzed for hydrogen. Final aqueous samples were analyzed for pH.

2.3. Analytical methods and soil characterization

PCE, TCE, cis-1,2-dichloroethene (DCE), vinyl chloride (VC), and reduced gas (methane, ethane, ethene, propane, acetylene, butane, methyl acetylene, and propylene) concentrations were determined via headspace analysis using a Shimadzu 2010+ gas chromatograph equipped with a Flame Ionization Detector (FID) and an RT-QS-BOND fused silica PLOT column. A chromatogram identifying the reduced gases is provided in the Supplemental materials. Aqueous concentrations were determined by applying Henry's Law, where the Henry's constant was adjusted for temperature. To account for any potential leakage losses over the duration of the experiment at 55 °C, losses in the spiked PCE were scaled using a Henry's Law based partitioning factor to account for losses of transformation products as follows: