TITLE: Abiotic Dechlorination of Chlorinated Ethenes in Natural Clayey Soils: Impacts of Mineralogy and Temperature

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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 x 10^{-5} day^{-1} at 20° C, to 32 x 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.

1.0 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 pahway. 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 et al., 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.

2.0 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.

2.2Batch 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 mega-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 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 one hour. 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:

$$\alpha_i = \frac{\varepsilon_v + \frac{\varepsilon_w}{H_{PCE}}}{\varepsilon_v + \frac{\varepsilon_w}{H_i}} \qquad \text{Eq. 1}$$

where α_i is the scaling factor by which PCE dechlorination product i is multiplied to correct for leakage losses, ε_v is the fraction of vapor volume in the vial (0.22), ε_w is the fraction of water volume in the vial (0.75), H_{PCE} is the dimensionless Henry's Law constant for PCE at 55° C (4.1) (Sander, 1999), and H_i is the Henry's Law constant at 55° C for dechlorination product i (Sander, 1999).

Mineral content was determined by MUD Geochemical, Inc. using x-ray diffraction (XRD) with a Bruker D2 Phaser. Magnetic susceptibility was determined by Microbial Insights, Inc. using a Barrington MS2B meter (Ferrey et al., 2004, USEPA, 2009). Ferrous mineral content was determined by McCampbell Analytical, Inc. using the 1,10-phenanthroline method (Amonette and Templeton, 1998). Sieve analysis was performed for each soil to determine the approximate particle size distribution. pH was determined by using an Orion 720A+ meter and Orion 9107BN pH probe. Hydrogen concentrations were determined via headspace analysis using a Shimadzu 2010+ gas chromatograph equipped with a Thermal Conductivity Detector (TCD) and a Carboxen-1010 PLOT capillary column.

3.0 Results and Discussion

3.1 Clay Mineralogy

Rock mineralogy, ferrous iron content, and magnetic susceptibility for each of the natural soils tested are presented in Table 2. The magnetic susceptibility value for Soil 1 is approximately 15-times greater than for Soils 2 and 3, suggesting that the presence of magnetic minerals is substantially greater in Soil 1 than the other soils. Based on a previously developed correlation between magnetic susceptibility and magnetite levels in soils (USEPA, 2009), if the magnetic susceptibility value in Soil 1 is due to magnetite, than the magnetite level in Soil 1 would be approximately 2%. Magnetite is not identified via the XRD analysis for any of the soils, thus the magnetic susceptibility response likely is due to other minerals present in the soils. Furthermore, since the magnetic susceptibility is likely not associated with magnetite content, it The magnetic susceptibility in Soil 1 is likely influenced by the presence of hematite and/or antigorite, while the magnetic susceptibility in Soils 2 and 3 is likely influenced by riebeckite, illite and/or goethite (USGS, 1999; Syono, 1960).

In contrast, the ferrous mineral content, as determined using the 1,10-phenanthroline method, is much greater in Soils 2 and 3 than in Soil 1. Comparison of the ferrous minerals identified via XRD and the ferrous mineral content among the 3 soils suggests that the ferrous mineral content is most sensitive to the riebeckite and/or chlorite content of the soil. The results presented in Table 2 also suggest that ferrous minerals such as antigorite and illite contribute little to the ferrous mineral content as measured via the 1,10-phenthroline method, at least for Soil 1. Ferrous iron content was related to greater dechlorination activity in rock samples (Schaefer et al., 2013), and its effect on dechlorination activity in Soils 1-3 is evaluated in section 3.2.

3.2 Batch Experiments and PCE Dechlorination

Measureable loss of PCE occurred only for the last two sampling events for the PCE-spiked experiments performed at 55° C (Figures S1 through S3 of the Supplemental Materials). These losses could not be explained by generation of any dechlorination products, and were assumed to be due to leakage. Thus, the correction shown in Equation 1 was used to assess the generation of the PCE transformation products for these last two sampling events at 55° C.

For Soil 1, no detectable levels of PCE were present in the unspiked samples, and no detectable levels of biotic PCE/TCE dechlorination products were observed under any conditions. For Soil 1, low levels of acetylene were initially (t=1 day) present in the PCE-spiked samples for both the Abiotic and Biotic conditions, but no increases over time in acetylene were observed in either condition (Figure S4). No acetylene was observed in the Soil 1 sample without the PCE spike. Thus, this acetylene may have been present due to a rapid but transient abiotic dechlorination reaction (acetylene is a known abiotic dechlorination product, and is not expected to be generated biologically), or more likely may have been present as an impurity or transformation product with the same elution time as acetylene associated with the PCE spiking solution. The absence of any of the expected biotic PCE dechlorination products (i.e., DCE, vinyl chloride, ethene) at any temperature suggests that heating did not stimulate any measurable biological reduction of PCE for this soil.

As shown in Figure S5, butane was the only gaseous product that was generated in Soil 1, where the generated butane levels were calculated based on the difference between the PCE spiked and unspiked samples. Butane generation was most clearly noted at 55° C. Butane generation was only observed in the Abiotic condition, and not the Biotic condition. The absence of butane in the Biotic condition likely was due to subsequent butane biotransformation.

For Soil 2, accumulation of PCE abiotic dechlorination products were observed at each temperature. Figure 1, which shows the generation of PCE dechlorination products for the PCE-spiked Soil 2 conditions (calculated as the difference in dechlorination product generation between the PCE-spiked and non-spiked conditions), indicates that the reduced gas transformation products consisted of a mixture of acetylene, butane, ethene, and trace levels of propane. Reduced gases in all bottles were at least 5-times less in the non-spiked samples than in the PCE-spiked samples, confirming that the bulk of the reduced gases generated were from the spiked PCE and not from any dechlorination reactions that had occurred from historic exposure (prior to sample collection) of the soil to chlorinated ethenes. Similar to Soil 1, acetylene was present at the initial sampling event for all temperatures in Soil 2; this acetylene may have been the result of an initial rapid and transient reaction, or (more likely) it was the result of an impurity or transformation product associated with the PCE spiking solution. Gas product generation in Soil 2 was approximately 100-times greater in Soil 2 than in Soil 1.

Acetylene and ethene have been identified as ferrous iron-induced abiotic dechlorination products of chlorinated ethenes in several studies (Lee and Batchelor, 2002a, Truex et al., 2007; Schaefer et al., 2013). Butane, propane and/or other short chain (3 or more carbons) hydrocarbons have been identified as likely abiotic coupling products from (chloro)acetylene or ethene transformation on zerovalent iron surfaces (Arnold and

Roberts, 2000; Elsner et al., 2008) and in ferrous rock minerals (Schaefer et al., 2015). With the exception of ethene, which can be generated abiotically or biotically from PCE or TCE (Maymó-Gatell et al., 1997; Schaefer et al., 2009), the other generated reduced gases observed in this study have not been reported as biotic PCE transformation products, thereby reinforcing their generation via abiotic processes.

Assuming the acetylene present at the initial sampling event was an artifact of the spiking solution, butane was the most abundant dechlorination product measured at both 20 and 35 degrees C in Soil 2, which is consistent with the results obtained for Soil 1. For Soil 2, both acetylene and butane showed an approximately linear increasing trend over time, thereby indicating that abiotic dechlorination of PCE was ongoing throughout the 8-week incubation period, yielding these reduced gases as transformation products.

At 55° C, butane remained the dominant dechlorination product for both Soils 1 and 2. For Soil 2, butane increased at a rate approximately 4-times greater than at the lower temperatures. Ethene generation in Soil 2 also became significant by 29 days at 55° C. By day 57, ethene generation surpassed that of acetylene, and acetylene levels began to decline. No ethene generation was observed at the lower temperatures. These results suggest that the elevated temperature facilitated the reduction of acetylene to ethene in Soil 2 by increasing the rate or extent of hydrogenation reactions, and increased the rate of butane generation by increasing the rate or extent of higher coupling reactions.

The dominant presence of higher coupling products (i.e., butane) in this study differs from observations in several studies using zerovalent iron, where higher coupling hydrocarbon species accounted for only a trace fraction of the chlorinated ethene or acetylene transformation products in the presence of zerovalent iron (Arnold and Roberts, 2000; Elsner et al., 2008). A notable exception is a study by Gao et al. (2015), where up to 50% of the TCE that was dechlorinated resulted in generation of coupling products from ball milled zerovalent iron. Ball milled zerovalent iron has a much higher abundance of iron oxides present on the surface compared to native zerovalent iron (Li et al., 2009), thus the presence of iron oxide mixtures may facilitate the formation of coupling products. In rock containing ferrous minerals, propane accounted for approximately 20 to 25% of abiotically dechlorinated TCE in ferrous mineral containing rock (Schaefer et al., 2015), thus ferrous oxide and hydroxide minerals present in natural solids may have a greater propensity to from these higher coupling compounds than unoxidized zerovalent iron.

Lowry and Reinhard (2001) observed a substantial increase in coupling reactions when hydrogen levels were decreased below approximately 100 µM in hydrodechlorination reactions between TCE and Pd catalysts. Hydrogen levels measured in Soils 1 and 2 at the end of the experiments were below the analytical detection limit of 0.082 µM in the bulk water phase (based on headspace sampling and Henry's Law). Thus, limited availability of hydrogen in the natural clay systems may have allowed coupling reactions to further outcompete hydrogenation reactions at the natural ferrous mineral surfaces, although bulk water hydrogen levels may not have been representative of hydrogen levels near the active mineral surfaces. Others (Schrick et al., 2002; Fennelly and Roberts, 1998) showed substantial generation of alkane and alkene coupling products using bimetalic iron particles, suggesting that coupling reactions may be enhanced in the presence of bimetalic mineral surfaces. The mineralogy for Soils 1 and 2 is complex and consists of multiple minerals; thus, these soil multi-metallic mineral surfaces may facilitate coupling reactions.

3.3 PCE Removal Rates as a Function of Temperature

Figure S6 shows the mole fraction of PCE abiotically transformed for Soil 2 based on the sum of the dechlorination transformation products generated in Figure 1. Results show that PCE removal in Soil 2 was greatest at 55° C, and that only a small (<0.1%) fraction of PCE was removed over the duration of the experiments. The fractional molar PCE removal for Soil 2 (Figure S6) is approximately two orders of magnitude greater than the fractional molar PCE removal for Soil 1 at 55° C (Figure S5).

Due to the presence of the vapor phase (approximately 8 mL) in the vials, Henry's Law partitioning of the PCE occurred between the water and gas phases. To determine the true kinetics of PCE dechlorination, properly accounting for a reduction in the observed rate due to water-gas partitioning of PCE, the following mass balance was employed for PCE in the vials:

$$\frac{\partial C_w}{\partial t} = \frac{k_{bulk}}{R_e} C_w \qquad \text{Eq. 2}$$

$$k_{bulk} = -k\left(\frac{\rho k_m}{\varepsilon_w}\right) \qquad \text{Eq. 3}$$

$$R_e = \frac{\varepsilon_v H_{PCE} + \varepsilon_w}{\varepsilon_w} \qquad \text{Eq. 4}$$

where C_w is the PCE concentration in the aqueous phase, t is time, k_{bulk} is the bulk first-order abiotic dechlorination rate constant, R_e accounts for the reduction in observed rate due to gas-liquid partitioning, k is the intrinsic first-order abiotic dechlorination rate constant, ρ is the bulk soil density, k_m is the PCE linear sorption coefficient on to the reactive mineral surfaces, and H_{PCE} is the dimensionless Henry's Law constant, which is a function of temperature with values of 0.76, 1.6, and 4.1 at 20, 35, and 55° C experiments, respectively (Sander, 1999). PCE sorption to the bulk soil was minimal, as determined by parallel experiments performed at 20° C comparing PCE loss in the vials with and without soil present, so a soil sorption term is omitted from Eq. 4. Since the trace adsorption of PCE to the reactive minerals cannot be independently determined, the reaction rate constant is assessed in terms of k_{bulk} rather than k. Equation 4 was solved for each temperature in the Soil 2 experiments, with R_e values of 1.2, 1.5, and 2.9 for the 20, 35, and 55° C experiments, respectively; these R_e values account for observed reduction in the dechlorination reaction rate due to PCE partitioning into the vapor phase. First order kinetics were assumed, consistent with several pervious abiotic dechlorination studies with ferrous minerals (Butler et al., 2013; He et al., 2015; Schaefer et al., 2015). Measured PCE dechlorination products were used to determine the mass of PCE removed.

The regressed values of k_{bulk} are provided in Table 3. Regression results indicate that the data are well described by the first-order model, and that k_{bulk} increases with temperature. It is noted that a zero-order model also would have well-described the experimental data, but previous studies have suggested that ferrous mineral enhanced dechlorination is a first-order process (Schaefer et al., 2013; He et al., 2015). The correction for leakage at 55° C (Eq. 1) resulted in less than a 35% change in the regressed first-order rate constants.

To further assess dechlorination reaction kinetics in Soil 2, Eqs. 2 through 4 were applied to the formation of the individual transformation products generated (i.e., acetylene, ethene, butane, and propane). For assessment purposes, acetylene and ethene were lumped together, as ethene is an immediate hydrogenation product of acetylene. Figure 2 shows the contribution of each of the gases on the fractional removal of PCE, and how first order kinetics provide a reasonable prediction of the data for each of the gases. Figure 3 shows the regressed rate constants as a function of inverse temperature for the generated gases. The Arrhenius equation is used to further assess kinetics:

$$k_{bulk}=A\ \exp\left[\frac{-E}{RT}\right] \qquad \text{Eq. 5}$$

where E is the activation energy, T is temperature (K), R is the gas constant, and A is a pre-exponential factor. Figure 2 shows that the generation of acetylene+ethene is well described by Eq. 5. The activation energy of 91 kJ/mol (via regression of Eq. 5) is substantially greater than the dechlorination activation energies of 32 to 45 kJ/mole observed for zerovalent iron (Su and Puls, 1999; Lien and Zhang, 2007), likely causing the ferrous minerals present in the natural soils examined to be far less reactive towards chlorinated ethenes than Fe^0. While Eq. 5 describes the temperature effects on acetylene/ethene generation, it does not accurately describe the generation of the coupling products butane and propane as a function of temperature, and subsequently the overall PCE dechlorination kinetics (first order rate constants were over-predicted by Eq. 5 by up to a factor of 3.5). The failure of the Arrhenius expression as defined in Eq. 5 has been noted when recombination and free radical reactions occur (Gardiner Jr., 1977; Upadhyay, 2006). The coupling reactions that generate butane and propane from PCE (C-C bond formation) are combination-type reactions and are likely radical induced via a reductive process (Lowry and Reinhard, 2001; Schrick et al., 2002; Shang et al., 2017). For such reactions, modified forms of the Arrhenius equation have been developed that show the non-linear functionality similar to that shown for the coupling product data in Figure 3

(Upadhyay, 2006). A more detailed mechanistic kinetic interpretation of these coupling reactions as a function of temperature is beyond the scope of this study.

Alternate explanations for the observed butane and propane formation kinetics, and deviation from the Arrhenius expression in Eq. 5, also are possible, but are less likely than the explanation provided above. For example, increased PCE adsorption with increasing temperature could result in the non-linear coupling products behavior shown in Figure 3, as this would cause the magnitude or the slope to increase with increasing temperature due to the enhanced PCE attachment to mineral surfaces. However, previous studies have suggested that chlorinated ethene sorption to mineral surfaces is slightly exothermic (Goss and Eisenreich, 1996; Werth and Reinhard, 1997), and thus PCE is expected to adsorb less as temperature increases, which would cause the opposite deviation from non-linearity shown for the coupling products in Figure 3. In addition, such PCE sorption behavior would likely impact all gaseous products, not just the coupling products. Thus, the deviation of the coupling product generation from the Arrhenius model (Eq. 5) is likely not due to sorption effects.

It is also plausible, but unlikely, that diffusional mass transfer within small clay pores was the cause of the observed k_{bulk} deviation from the Arrhenius equation (Eq. 5) at 55° C. The aqueous PCE diffusion coefficient increases by approximately a factor of 2 between 20 and 55° C (Cussler. 1994). Heating can alter the pore structure of the clays (Romero et al., 2001), which can further enhance the diffusion coefficient with temperature. If the active mineral sites were located in micropores, the increase in temperature at 55° C may also have facilitated the activation-driven diffusion processes in the micropores (Werth et al., 2000). These mass transfer effects would all lead to an increase in the magnitude of the slope with increasing temperature, consistent with the coupling product trend in Figure 3, if mass transfer to mineral surfaces played a role in controlling the observed dechlorination kinetics. However, such mechanisms would impact all gaseous products, not just the coupling products, unless the mineral sites responsible for coupling reactions were different from those responsible for the other (acetylene and ethene) products, with only the minerals responsible for coupling products located within clay micropores.

3.4 TCE Dechlorination in Soil 3

Results for Soil 3 are provided in Table 3 and Figure S7. Although TCE was used for Soil 3, previous studies showed that the observed dechlorination rate constant for TCE is within a factor of 2 of that observed for PCE (Lee and Batchelor, 2002a,b). Thus, it is reasonable to expect that TCE dechlorination behavior in natural solids is within a factor of 2 (with respect to k_{bulk}) as PCE, so comparison among the 3 soils is warranted. Acetylene was the only observed dechlorination product for Soil 3, indicating that the dechlorination mechanism was abiotic despite not gamma-irradiating the soil. The absence of higher coupling products for Soil 3 is not readily explained. Because previous studies have shown that coupling product formation proceeds via (chloro)acetylene (Elsner et al., 2008), it is unlikely that the presence of acetylene and absence of butane is attributable to the use of TCE (rather than PCE) as the parent compound in the Soil 3 experiments. Rather, the difference in dechlorination daughter product composition is likely due to the complexities associated with the mineral phase and mineral distribution in the soil; this is discussed further below.

3.5 Mineral Impacts on Abiotic Dechlorination

The values for k_{bulk} in Table 3 do not appear to be correlated to magnetic susceptibility, although previous studies have been careful to note that magnetic susceptibility is only appropriate as an indicator of abiotic dechlorination when the magnetic susceptibility is controlled by magnetite (USEPA, 2009; Weidemeier et al., 2017), which is not the case for the soils used in this current study; this current study is consistent with that assessment. Soil 1, which has a magnetic susceptibility approximately 15-times greater than the other soils, did not exhibit any measureable abiotic dechlorination at 20 and 35° C, and approximately 2 orders of magnitude less abiotic dechlorination than Soils 2 and 3 at 55°. Ferrous mineral content appeared to be a better indicator for abiotic dechlorination among these 3 soils, as Soils 2 and 3 had elevated ferrous mineral contents and measureable abiotic dechlorination. Riebeckite and/or chlorite likely are the ferrous minerals responsible for the observed abiotic dechlorination in Soils 2 and 3, while illite likely is the ferrous mineral responsible for the limited abiotic dechlorination in Soil 1.

Riebeckite minerals (Wittenham Gorge, Australia, and Longvale Quarry, California) were purchased from the Mineralogical Research Co. (San Jose, CA), and chlorite minerals (Green Fine Grained Chlorite Schist Metamorphic Rock) were purchased from American Educational Products (Cat# 5241-01A) to test, using the same methodology used for the soils, if these minerals facilitated the abiotic dechlorination of PCE. No generation of PCE transformation products was observed in these mineral tests. However, the minerals used were dry and stored under aerobic conditions for an unknown period of time prior to the laboratory dechlorination testing, so the mineral surfaces may have become oxidized, and the tested riebeckite and chlorite minerals may not have been representative of the minerals present in the clays. Ferrous mineral analysis performed on the chlorite showed that the ferrous mineral content was only 31 mg/kg, indicating that the chlorite mineral tested was not representative of the ferrous-rich chlorite that is likely present in Soils 2 and 3. Hence, further work is needed to unambiguously determine the ferrous iron minerals responsible for abiotic PCE reduction.

The 20° C data show that Soil 3 had a much greater k_{bulk} than Soil 2, despite the fact that Soil 2 had a greater ferrous mineral content. Because the XRD data show that the ferrous minerals in Soil 3 are present at equal or greater quantities in Soil 2, it is speculated that either the specific nature of the individual ferrous minerals, the local pH near the surface of the clay minerals, and/or the pore scale distribution of the minerals are the cause of the increased abiotic dechlorination activity and lack of coupling products observed in Soil 3. It has been shown that abiotic dechlorination activity for chlorinated ethenes can increase with pH (Lee and Batchelor, 2002b). Thus, the elevated pH for Soil 3 may have facilitated enhanced abiotic dechlorination despite the fact that the ferrous mineral content was slightly less than that of Soil 2. The elevated pH for Soil 3 may also have contributed to the transformation product distribution, as previous studies using FeS have suggested that elevated pH results in an increase in the fractional conversion of TCE to acetylene (Butler and Hayes, 2001).

The clay mineralogy also may have played a role in the observed difference between Soils 2 and 3. Soil 3 has a much smaller clay content and a much higher coarse-grained fraction than Soils 1 and 2. Additional mineral testing showed that >90% of the ferrous mineral content was associated with the silt and clay fraction of Soil 3, and an additional batch test performed on the sand component of Soil 3 showed that no measurable abiotic dechlorination was observed in the sandy material associated with Soil 3. Thus, the difference in behavior with respect to ferrous iron and dechlorination are likely associated with the fine grained particles in Soils 2 and 3. For Soil 3, chlorite is the primary clay mineral by mass, which likely accounts for an appreciable fraction of the ferrous mineral content. For Soil 2, illite is the primary clay by mass, which is typically much more deficient in ferrous iron than chlorite. Mass transfer limited access to the (presumably) ferrous-rich chlorite clay by intermingled illite clay in Soil 2 serves as a plausible explanation for the lower k_{bulk} in Soil 2 than in Soil 3. Alternately, Soil 2 contains kaolinite, which is a known weathering/oxidation product of chlorite (Jackson, 1963). Ferrous-rich chlorite clays in Soil 2 could be bounded by kaolinite, which would also potentially serve as a means to limit the dechlorination reaction via diffusional mass transfer.

3.6 Environmental Implications

The solid:liquid ratio in the experimental vials was substantially less than those encountered for in situ soils. The term ρ/ε_w in Equation 3, assuming a bulk clay density of 1.8 g/cm^3 and a water porosity of 0.4 under typical field conditions, would be approximately 24-times greater than in the vials, resulting in values of k_{bulk} that are 24-times larger than those measured in this study (Table 3). At 20^{o} C, assuming first-order kinetics and the k_{bulk} for in situ conditions in Table 3, 315 years would be required for PCE concentrations to decrease by 90% via abiotic dechlorination alone in Soil 2. This estimated timeframe assumes that the dechlorination rate constant remains constant, which previous studies in rock have shown may be a reasonable assumption for a time scale of decades (Schaefer et al., 2015). At 55° C, 20 years would be required for PCE concentrations to decrease by 90% via abiotic dechlorination alone. Thus, for Soils 1 and 2, mild heating is not expected to result in treatment timeframes that are economically attractive.

For Soil 3, assuming the TCE bulk rate constant for in situ conditions in Table 3, 48 years would be required for TCE concentrations to decrease by 90% via abiotic dechlorination alone. Thus, these rates would likely be an important to include in conceptual site models incorporating natural attenuation process. If heating to 55° C also were to increase the dechlorination bulk rate constant of TCE in Soil 3 by 20-times, then the time needed for TCE concentrations to decrease by 90% under solid:liquid ratios typical of field conditions at 55° C would be 3.2 years. Similarly, using the same assumption for DCE with a bulk dechlorination rate constant of 0.0015 day^{-1} measured at 20° C for a shallow sandy sediment containing magnetite (Ferrey et al., 2004), heating to 55° C would result in 90% DCE removal in approximately 76 days. Thus, there is reasonable potential that mild heating of natural sediments with high intrinsic rates of ferrous mineral induced dechlorination reactions can be used for cost-effective remediation.

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Supporting Materials available.

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Tables

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 (^{o}C)
Soil 1	Biotic	None	20, 35, 50
	Biotic	PCE	20, 35, 50
	Abiotic	PCE	20, 35, 50
Soil 2	Abiotic	None	20, 55
	Abiotic	PCE	20, 35, 55
Soil 3	Biotic	None	20
	Biotic	TCE	20

Table 2. Mineral properties for Soils 1 through 3.XRD, magnetic susceptibility, ferrous content, and sieve results are provided. Only minerals with at least 1% content are shown.

Property	**Soil 1**[1]	**Soil 2**	**Soil 3**
% Mineral Content (XRD analysis)	Dickite (26%); Kaolinite (26%); Antigorite (25%); Quartz (12%); Illite/mica (8.5%); Hematite (1.8%)	Albite (30%); Quartz (23%); Illite/Mica (11%); Orthoclase (7.4%); Chlorite (6.7%); Dolomite (6.4%); Riebeckite (5.8%); Goethite (4.7%); Kaolinite (2.3%); Illite/Smectite (1.8%)	Quartz (46%); Albite (25%); Orthoclase (6.1%); Chlorite (3.8%); Illite/Smectite (2.9%); Calcite (2.0%); Riebeckite (1.2%)
% Clay	44	78	17
% Silt	50	21	44
% Sand & Gravel	6	1	39
Magnetic Susceptibility (m^3/kg)	1.1 x 10^{-5}/ 1.1 x 10^{-5}	6.7 x 10^{-7}	7.7 x 10^{-7}
Ferrous mineral content (mg/kg)	3.8 / 4.5	4200	1800
pH[2]	4.9	7.2	9.7

[1] replicate values are shown for the magnetic susceptibility and ferrous mineral content, and the average value of two samples is shown for the XRD

[2] pH sample collected from the aqueous phase in the vials. pH varied by less than 0.5 units among the temperature conditions.

Table 3. Regressed first order PCE or TCE bulk rate constants (k_{bulk} in Eq. 2) for Soils 1 through 3. Due to the limited amount of transformation and scatter in the data, first order rate constant were not calculated for the 20 and 35 C conditions for Soil 1. The calculated k_{bulk} scaled for *in situ* soil conditions, which are based on the rate constants observed for Soil 2, also are provided for each temperature. The ± values indicate the 95% confidence intervals. NA=not applicable.

Temperature (^{o}C)	**k_{bulk} (day^{-1})**	**R^2**
	Soil 1 - PCE	
Observed in Vials (regression results)		
55	$1.7 \pm 0.84 \times 10^{-7}$	0.75
	Soil 2 - PCE	
Observed in Vials (regression results)		
20	$8.3 \pm 0.82 \times 10^{-7}$	0.98
35	$10 \pm 1.8 \times 10^{-7}$	0.94
55	$134 \pm 7.8 \times 10^{-7}$	0.99
Average Value Scaled for in situ Soil:Water Ratio		
20	2.0×10^{-5}	NA
35	2.4×10^{-5}	NA
55	32×10^{-5}	NA
	Soil 3 - TCE	
Observed in Vials (regression results)		
20	$45 \pm 0.10 \times 10^{-7}$	0.99
Average Value Scaled for in situ Soil:Water Ratio		
20	11×10^{-5}	NA

FIGURES

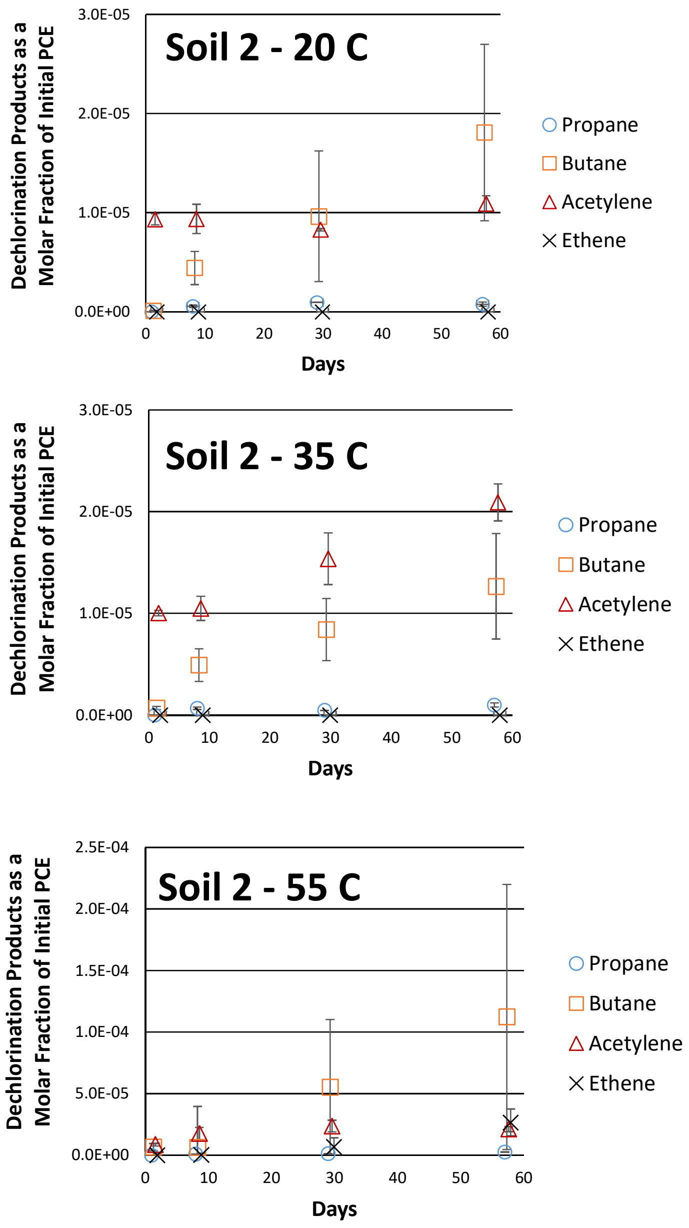

Figure 1. Reduced gas PCE dechlorination products as a molar fraction of the initial PCE added to the vials (moles dechlorination product / moles initial PCE). Results are shown for Soil 2 at 20° C (top), 35° C (middle) and 55° C (bottom) under Abiotic conditions. Values were calculated by subtracting the concentration measured in the samples that were not spiked with PCE from the concentration measured in the PCE-spiked samples. Average values are shown. Error bars represent the 95% confidence interval. The y-axis scale was increased for the 55° C condition. Data are plotted with a slight off-set to improve the clarity of the error bars.

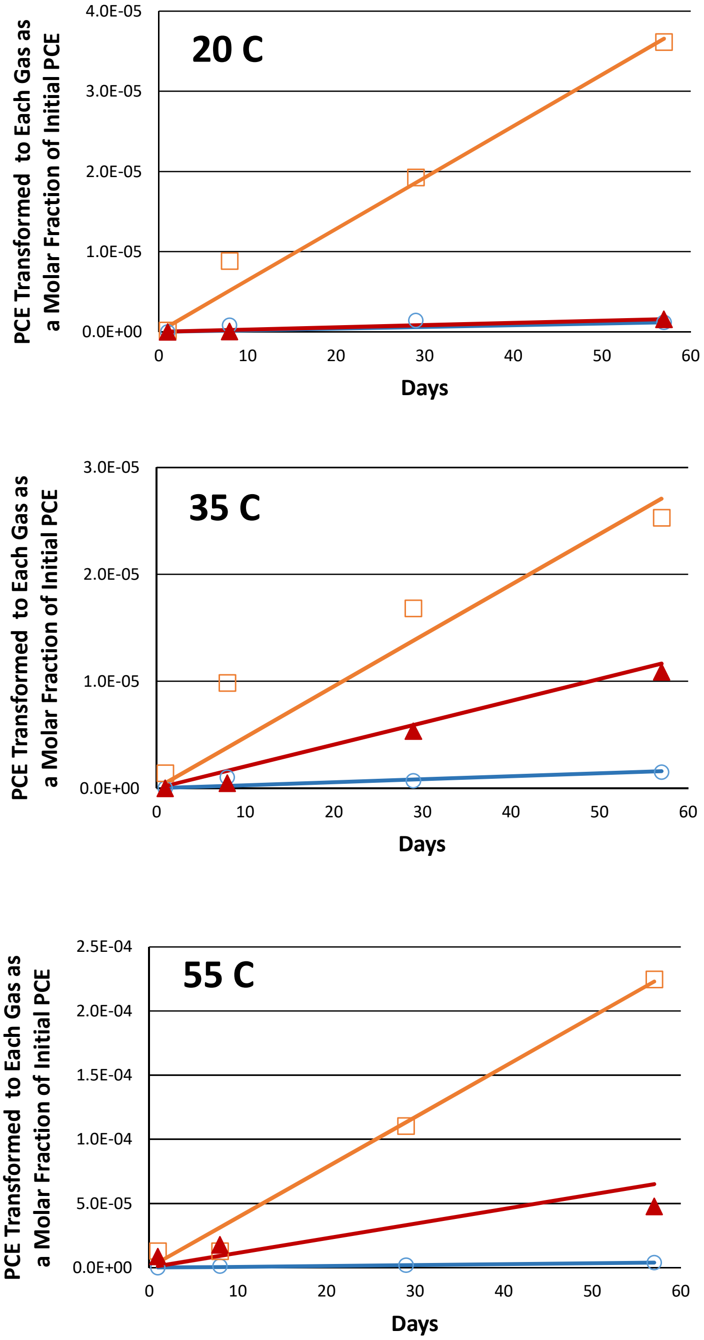

Figure 2. Contribution of each gas (□=butane, ▲=acetylene+ethene, ○=propane) in Soil 2 to the cumulative PCE dechlorination calculated based on the generation of reduced gas daughter products at each temperature, and plotted as the fraction of PCE transformed. Averages of the triplicate samples are shown. Lines represent the first-order kinetic model (Eqs. 2-4) applied to the individual gases.

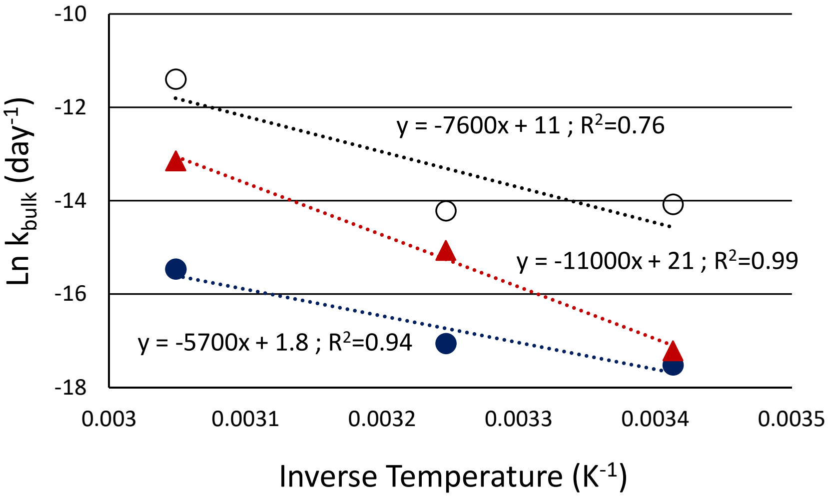

Figure 3. Values of k_{bulk} for generation of butane (○), propane (●), and acetylene+ethene (▲) as a function of temperature. The dashed lines represent the regression of the Arrhenius equation to the data.

Graphical Abstract