Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing phyllosilicates

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Abstract

Abiotic reductive dechlorination of chlorinated ethylenes (tetrachloroethylene (PCE), trichloroethylene (TCE), cis-dichloroethylene (c-DCE), and vinylchloride (VC)) by iron-bearing phyllosilicates (biotite, vermiculite, and montmorillonite) was characterized to obtain better understanding of the behavior of these contaminants in systems undergoing remediation by natural attenuation and redox manipulation. Batch experiments were conducted to evaluate dechlorination kinetics and some experiments were conducted with addition of Fe(II) to simulate impact of microbial iron reduction. A modified Langmuir-Hinshelwood kinetic model adequately described reductive dechlorination kinetics of target organics by the iron-bearing phyllosilicates. The rate constants stayed between 0.08 (±10.4%) and 0.401 (±8.1%) day\(^{-1}\) and the specific initial reductive capacity of iron-bearing phyllosilicates for chlorinated ethylenes stayed between 0.177 (±6.1%) and 1.06 (±7.1% \(\mu\)M g\(^{-1}\)). The rate constants for the reductive dechlorination of TCE at reactive biotite surface increased as pH (5.5 – 8.5) and concentration of sorbed Fe(II) (0 – 0.15 mM g\(^{-1}\)) increased. The appropriateness of the model is supported by the fact that the rate constants were independent of solid concentration (0.0085 – 0.17 g g\(^{-1}\)) and initial TCE concentration (0.15 – 0.60 mM). Biotite had the greatest rate constant among the phyllosilicates both with and without Fe(II) addition. The rate constants were increased by a factor of 1.4 – 2.5 by Fe(II) addition. Between 1.8 to 36% of chlorinated ethylenes removed were partitioned to the phyllosilicates. Chloride was produced as a product of degradation and no chlorinated intermediates were observed throughout the experiment.

Keywords: Chlorinated organics, Iron-bearing soil minerals, Abiotic reductive transformation, Natural attenuation, Groundwater remediation
1. Introduction

Chlorinated organics are common aquifer and soil contaminants susceptible to reductive dechlorination in reducing environments. Research has been conducted to characterize abiotic reductive dechlorination of these contaminants by reactive soil minerals. Iron sulfides and polysulfides (pyrite, marcasite, troilite, and mackinawite) have been reported to reductively dechlorinate chlorinated ethylenes and ethanes (Kriegman-King and Reinhard, 1994; Sivavec and Horney, 1997; Butler and Hayes, 1999; Lee and Batchelor, 2002a). Surface Fe(II) or sulfide species are assumed responsible for these reactions (Kriegman-King and Reinhard, 1994; Sivavec and Horney, 1997). A mixed Fe(II)/Fe(III) hydroxide called sulfate green rust (GR\textsubscript{SO\textsubscript{4}}) has been shown to reductively transform chlorinated organics (Erbs et al., 1999; Lee and Batchelor, 2000; Lee and Batchelor, 2002b). The addition of Cu\textsuperscript{2+} to suspensions of GR\textsubscript{SO\textsubscript{4}} has enhanced the dechlorination rates of chlorinated ethanes (O'Loughlin and Burris, 2000). A mixed Fe(II)/Fe(III) oxide (magnetite) has been reported to dechlorinate chlorinated ethylenes at relatively slower rates (Sivavec and Horney, 1997; Lee and Batchelor, 2000; Lee and Batchelor, 2002a). Addition of Fe(II) to the suspension of this soil mineral has been observed to accelerate the dechlorination kinetics of the chlorinated ethylenes, which indicates a potential link between abiotic dechlorination and biotic processes that could produce Fe(II) (Lee and Batchelor, 2000).

Iron-bearing phyllosilicates (biotite and vermiculite) in the presence of sulfide have been shown to reductively dechlorinate 10\% of the carbon tetrachloride that was added. This reaction is caused by electron transfer from Fe(II) in phyllosilicates, from sulfide adsorbed onto the phyllosilicates, and from secondary iron sulfides produced by sulfide and dissolved Fe(II) (Kriegman-King and Reinhard, 1992). An iron-bearing phyllosilicate (ferruginous smectite) pretreated with dithionite has been reported to reduce trichloroacetonitrile and chloropicrin (Cervini-Silva et al., 2001). It has been assumed that the reduced structural iron in smectite
serves as a bulk reductant and the association of the contaminants with the surface and/or surface-bound water is responsible for the reductive dechlorination (Cervini-Silva et al., 2001). The effects of concentrations of dithionite and clay minerals (ferruginous smectite and montmorillonite) on abiotic transformation of tetrachloroethylene (PCE) have been studied by Nzengung et al. (2001). Increased concentrations of dithionite and clay minerals did not necessarily enhance the abiotic transformation of PCE. The reductive capacity of iron-bearing phyllosilicates (biotite, vermiculite, and montmorillonite) for chromium (Cr(VI)) and PCE has been measured and compared to that of pyrite, GR$_{SO_4}$, and magnetite (Lee and Batchelor, 2003). Iron-bearing phyllosilicates are some of the most abundant soil components in natural soils and sediments. Therefore, they could significantly affect the fate and transport of chlorinated organics in natural environments. However, little research has been conducted to quantify the kinetics of degradation of chlorinated organics in systems containing iron-bearing phyllosilicates so that it could be used to predict the fate and transport of chlorinated organics. This is probably due to the low reductive capacities for chlorinated organics that have been reported to date. The research presented here was performed to describe the reductive dechlorination of chlorinated ethylenes by iron-bearing phyllosilicates with and without Fe(II) addition. The goals of this research were: 1) to characterize the reductive dechlorination of chlorinated ethylenes by iron-bearing phyllosilicates in order to evaluate a major degradation mechanism in natural reducing environments, 2) to obtain basic kinetic data in order to better understand the processes of natural attenuation and in situ redox manipulation, and 3) to identify the influence of geoenvironmental factors on the dechlorination kinetics of chlorinated ethylenes.
2. Materials and methods

2.1. Materials

All chemical reagents and soil mineral samples were prepared in an anaerobic chamber (Coy Laboratory Products Inc.) containing 95% N\textsubscript{2} and 5% H\textsubscript{2}. Descriptions of procedures used to insure anaerobic conditions in this study can be found elsewhere (Lee and Batchelor, 2002a; Lee and Batchelor, 2003). Stock target organic solutions were prepared by diluting pure target organics in methanol (99.8%, HPLC grade, EM). These targets included: PCE (99.9%, Sigma), trichloroethylene (TCE, 99.6%, Sigma), \textit{cis}-dichloroethylene (\textit{c}-DCE, 97.0%, Sigma), and vinyl chloride (VC, 20,000 mg L\textsuperscript{-1}, Sigma). Deaerated deionized water (ddw) was prepared by deoxygenating 18 M\Omega cm deionized water with 99.99% nitrogen and then by purging with the mixed gases in the anaerobic chamber. Fe(II) and dithionite stock solutions (0.5 M and 0.1 M, respectively) were prepared by adding exact amounts of FeSO\textsubscript{4}.7H\textsubscript{2}SO\textsubscript{4} (102.8%, Sigma) and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} (88%, Sigma) into ddw and they were used within 2 days. A 10 mM NaHCO\textsubscript{3} solution was prepared by adding an exact amount of NaHCO\textsubscript{3} (100.3%, Sigma) to ddw. Acid and base solutions were prepared by diluting H\textsubscript{2}SO\textsubscript{4} (95.7%, Sigma) and NaOH (97.0%, EM) with ddw. Biological buffers (0.05 M, Sigma) prepared with ddw and used for identifying the effect of pH on degradation kinetics include: 2-[N-Morpholino]ethanesulfonic acid, 3-[N-Morpholino]propanesulfonic acid, and mixture of Tris[hydroxymethyl]aminomethane and Tris[hydroxymethyl]aminomethane hydrochloride (Tris). These buffers were evaluated in the reactor systems without phyllosilicates or iron and found to not result in any degradation of target organics.

Biotite (Bancroft, Canada), vermiculite (Transvaal, South Africa), and montmorillonite (Gonzales, TX) were ground and sieved in the anaerobic chamber. Each portion (30 g) was pretreated with 200 mL of 0.1 M dithionite solution for 4 days to reduce oxidized soil mineral
surfaces and rinsed several times with 200 mL ddw to remove residual dithionite. The phyllosilicates were then freeze-dried, dry-sieved, and stored in the anaerobic chamber. Specific size fractions of biotite and vermiculite (63 – 250 μm) as well as montmorillonite (< 63 μm) were used in this research. The identity and purity of the phyllosilicates used in this study was confirmed by X-ray diffraction (XRD) and some measured properties of the phyllosilicates (e.g., iron content, surface area, and reductive capacity) were previously described in detail (Lee, 2001; Lee and Batchelor, 2003).

2.2. Experimental procedures

Batch kinetic experiments were conducted in amber borosilicate glass vials (nominally 20 mL, Kimble) with an open-top cap and three-layered septum system (PTFE tape, lead foil, PTFE-lined rubber septum). After equilibration with the anaerobic atmosphere for 2 days, exact amounts of phyllosilicates were transferred to the vials and they were filled with 10 mM NaHCO₃ solution. In order to evaluate the effect of Fe(II), sufficient stock Fe(II) solution (0.5 M) was spiked to some suspensions to result in Fe(II) concentration of 4.28 mM. The suspensions were adjusted to pH 7 by adding 1 M acid or base solutions. The mass ratio of solid to water was 0.085 resulting in different surface area concentrations of biotite (163 m² L⁻¹), vermiculite (2,230 m² L⁻¹), and montmorillonite (42,000 m² L⁻¹). The average head space volume in the filled vials was 0.6 mL, which would allow less than 1.5% of TCE partitioning to the head space, assuming a dimensionless Henry’s law constant (Gossett, 1987) of 0.359 at 22 °C and no sorption. The phyllosilicate suspensions were spiked with stock solutions to achieve initial concentrations of 0.19 mM PCE, 0.25 mM TCE, 0.41 mM c-DCE (cis-dichloroethylene), and 0.64 mM VC. The vials were rapidly capped, taken out of the anaerobic chamber, mounted on the tumbler, and
completely mixed at 7 rpm at room temperature (22 ± 0.5 °C). Control samples were prepared by following the same procedure described above except that phyllosilicates were not added. The controls were intended to investigate the possible loss of target organics due to volatilization and sorption as well as to determine if FeCO$_3$(s) would form when Fe(II) was added. All phyllosilicate samples and controls were prepared in duplicate. Target organics and their transformation products in aqueous solutions and on the phyllosilicates were measured at each sampling time.

Based on the results of batch kinetic experiments, biotite was chosen as a representative iron-bearing phyllosilicate and TCE was chosen as a target organic to investigate the effects of pH, solid concentration, target organic concentration, and sorbed Fe(II) on dechlorination kinetics. For a batch experiment where pH was an experimental parameter, biological buffers were added to vials containing biotite to keep pH values of the suspension constant throughout the experiment. The pH range investigated was 5.5 to 8.5. The mass ratio of the suspension was 0.085. To identify the effect of solid concentration, exact amounts of biotite were added to vials at mass ratios of 0.0085 to 0.17 and the suspension pH was kept constant at 8.1 by 0.05 M Tris buffer solution. The experiment started by spiking 10 μL of 0.76 M TCE stock solution to biotite suspensions under different experimental conditions and completely mixing on the tumbler (7 rpm) at room temperature. To investigate the effect of target organic concentration, biotite suspensions with mass ratio of 0.085 at pH 8.1 were spiked with 5 to 20 μL TCE stock solutions resulting in TCE concentrations of 0.15, 0.30, 0.45, and 0.60 mM. The effect of sorbed Fe(II) was investigated by spiking 0 to 200 μL of 0.5 M Fe(II) stock solution to biotite suspension with mass ratio of 0.085 and equilibrating the suspension for 2 days. The amount of sorbed Fe(II) on biotite was then determined by subtracting aqueous Fe(II) concentration from initial Fe(II)
concentration. TCE stock solution was spiked to the suspension resulting in the initial concentration of 0.3 mM and suspension pH was kept constant at 8.1 by Tris buffer. Controls were prepared in a similar way as described above. The phyllosilicates samples and controls were also prepared in duplicate. The concentration of target organic in aqueous solution was monitored at each sampling time.

2.3. Analytical procedures

Target chlorinated ethylenes and their chlorinated transformation products, except c-DCE, t-DCE (trans-dichloroethylene), and VC, were measured by a Hewlett Packard (HP) 5890 gas chromatograph (GC) with an electron capture detector (ECD) and a combination of DB-5 column (30 m × 0.25 mm i.d. × 0.25 µm film thickness, J&W Scientific) and DB-5MS column (30 m × 0.25 mm i.d. × 0.25 µm film thickness, J&W Scientific). The temperatures of injector and detector were 220 °C and 240 °C, respectively. The oven temperature was programmed to be isothermal at 80 °C for 2 min, increased to 110 °C at the rate of 5 °C min⁻¹, and then held for 2 min. After batch reactors were centrifuged to separate aqueous and solid phases, 50 µL of supernatant was transferred to 2 mL target vials (National Scientific Co.) containing 1 mL extractant (hexane with 0.025 mM 1,2-DBP). Supernatant in the reactors was removed and 10 mL extractant was added to extract target organics and transformation products sorbed on phyllosilicates. Both were extracted on an orbital shaker and a 1-µL sample of each extractant was automatically introduced into split/splitless injector at a split ratio of 35:1. Because responses of the ECD for c-DCE, t-DCE, and VC were weak, a HP 6890 GC with a DB-VRX column (60 m × 0.25 mm i.d. × 1.8 µm film thickness, J&W Scientific) and a flame ionization detector (FID) was used to measure these compounds. The temperatures of split/splitless injector
and detector were 220 °C and 240 °C, respectively. The oven temperature was programmed to be isothermal at 80 °C for 7 min. A 10-mL sample of supernatant was rapidly transferred to a 20 mL vial. The vial was tightly sealed and shaken for 1 hr at 250 rpm to equilibrate the aqueous and gas phases and stood for 2 hrs at room temperature. Gas-phase samples (50 – 100 µL) were withdrawn from the headspace with a 100 µL gas-tight syringe (Hamilton) and introduced into the injector at a split ratio of 5:1. The concentrations of c-DCE, t-DCE, and VC in aqueous solution were calculated using dimensionless Henry’s law constants at room temperature (0.14 (c-DCE), 0.35 (t-DCE), and 1.01 (VC)) (Mackay and Shiu, 1981; Gossett, 1987).

Acetylene, ethylene, and ethane were identified by a HP 6890 GC with a FID and a GS-Alumina column (30 m × 0.53 mm i.d., J&W Scientific). The temperatures of split/splitless injector and detector were both 150 °C and the temperature of oven was isothermal at 100 °C. The headspace sampling described above was also conducted for the analysis of C₂ hydrocarbons. A gas phase sample (50 – 100 µL) from the headspace was manually introduced to the injector at a split ratio of 5:1.

Chloride concentrations were determined by an ion chromatograph (IC, Dionex 500) equipped with AS9-HC column (250 mm × 4 mm i.d., Dionex) and conductivity detector. A 10 mM Na₂CO₃ solution was used as an eluent and the flow rate was 1 mL min⁻¹. A sample (2.5 mL) of suspension or supernatant was filtered with 0.2 µm membrane filter (Whatman) and the filtrate with or without dilution was automatically injected into the column through a 10 µL sample loop.
2.4. Treatment of kinetic data

Behavior of chlorinated ethylenes during reductive dechlorination by iron-bearing phyllosilicates was similar to that observed in experiments with pyrite, green rust, and magnetite suspensions (Lee and Batchelor, 2002a, 2002b). The concentration of target organic compounds rapidly decreased at first and then decreased more slowly or not at all. This behavior can be described by recognizing that the phyllosilicates have a limited reductive capacity and that it was being consumed by reaction with target organics during the experiment (Lee and Batchelor, 2003). A modified Langmuir-Hinshelwood kinetic model (Lee and Batchelor, 2002a, 2002b) that considers the effect of reductive capacity was used to describe kinetics of reductive dechlorination by iron-bearing phyllosilicates. This model assumes that the rate of dechlorination is proportional to the concentration of target adsorbed onto active sites and that a Langmuir isotherm describes adsorption equilibrium. The maximum adsorption capacity is equal to the concentration of reductive capacity (concentration of active sites) and the change in concentration of reductive capacity at any time is equal to the change in concentration of target organic. The model also assumes that target organics partition rapidly to the gas and solid phases, so that they can be assumed to be in phase equilibrium.

\[
\frac{dC_{CE}}{dt} = -\frac{k}{p_{CE}} \left( C_{RC}^0 - p_{CE} \left( C_{CE}^0 - C_{CE} \right) \right) C_{CE} \left( \frac{1}{K + C_{CE}} \right) \tag{1}
\]

\[
p_{CE} = (1 + H_{CE} \frac{V_g}{V_{aq}} + k_s) \tag{2}
\]

\[
C_{RC}^0 = M_R S_R \tag{3}
\]
where $C_{\text{CE}}$ is the aqueous concentration of target organic; $k$ is the rate constant for the decay of target organic at the reactive sites; $C_{\text{RC}}^0$ is the initial concentration of reductive capacity of soil mineral for the target organic and represents the maximum concentration of target organic that can be reduced by the soil mineral in its initial condition; $C_{\text{CE}}^0$ is the aqueous concentration of target organic at time equal to zero; $K$ is the sorption coefficient of target organic; $p_{\text{CE}}$ is the partitioning factor to explain the effect of partitioning of chlorinated ethylenes onto aqueous, gas, and solid phases; $H_{\text{CE}}$ is the dimensionless Henry’s law constant for chlorinated ethylenes; $V_g$ and $V_{\text{aq}}$ are the volumes of gas and aqueous phases; $k_s$ is the partition coefficient of chlorinated ethylenes to solid phase; $M_R$ is the concentration of phyllosilicate; and $S_R$ is the specific initial reductive capacity of phyllosilicate. The kinetic parameters ($k$, $K$, and $C_{\text{RC}}^0$) were estimated by an optimization procedure using MATLAB® (MathWorks Inc.) that solves the differential equation numerically and calculates the sum of squares repeatedly to find its minimum value by adjusting the values of the parameters using the Levenburg-Marquardt algorithm.

3. Results and discussion

3.1. Partitioning of chlorinated ethylenes in iron-bearing phyllosilicate suspensions

The concentrations of target organics in controls with and without Fe(II) addition rapidly decreased and reached constant concentrations (95 to 98% and 96 to 99% of initial target organics, respectively) after the first sampling time (3.7 days for PCE and TCE and 2.5 days for $c$-DCE and VC). This behavior was believed to be caused by the partitioning of target organics to solid phase (reactor wall + PTFE liner) because most of the target organics lost in controls was recovered by an extraction of the reactor after decanting the aqueous solution. The solid phase (phyllosilicates + reactor wall + PTFE liner) partitioning coefficients of chlorinated ethylenes in
iron-bearing phyllosilicates suspensions were calculated by averaging the measured $k_s$ values at sampling times for each experiment. In contrast to the solid phase partitioning coefficients of chlorinated ethylenes in pyrite, GR$_{SO_4}$, and magnetite suspensions (Lee and Batchelor, 2002a, 2002b), the partitioning coefficients in the phyllosilicate suspensions were 1.2 to 3.4 times greater than those in controls without phyllosilicates, which indicates that a substantial amount (16.7 to 70.6%) of target organics lost from solution were partitioned to the iron-bearing phyllosilicate surfaces. Partitioning of most target organics to montmorillonite was greater than that to biotite and vermiculite by one to two orders of magnitude, which was probably due to the greater surface area of montmorillonite. The solid phase partitioning coefficients of target organics in iron-bearing phyllosilicate suspensions with Fe(II) were 1.1 to 2.9 times greater than the coefficients for systems without Fe(II). This may be partly caused by increased polarization of hydrating water molecules (i.e., perturbation of hydrating water molecules) due to the increase of Fe(II) content of soil minerals (Cervini-Silva et al., 2001) that was caused by Fe(II) addition. A thin layer of precipitates was found in some controls with Fe(II) after 60 days. No significant difference in aqueous and sorbed concentrations of target organics was observed between the controls with and without the precipitates. The thin layer of precipitates is assumed to be siderite (FeCO$_3$) but no analytical effort was made to identify the precipitates.

3.2. Reductive dechlorination of chlorinated ethylenes by iron-bearing phyllosilicates

Figure 1 shows the reductive dechlorination of PCE in iron-bearing phyllosilicate suspensions with and without Fe(II) addition. The aqueous concentrations of target organics in Fig. 1 are represented as relative organic chlorine concentrations, which were calculated by dividing the concentration of organic chlorine at each sampling time (C) by the initial concentration of organic chlorine for that compound ($C_{0,\text{chlorine}}$). The lines in this figure are from
the modified Langmuir-Hinshelwood kinetic model and show the ability of the model to describe measured concentrations over time. Table 1 reports values of the parameters used by the kinetic model. The rate constants for the reductive dechlorination of target organics at the reactive biotite surfaces both with and without Fe(II) addition were 1.5 to 5 times greater than those at the surfaces of vermiculite and montmorillonite. This result may be due to the higher content of sites on biotite that contain Fe(II). The Fe(II) content of biotite is 8 and 97.5 times higher than that of vermiculite and montmorillonite, respectively (Lee, 2001; Lee and Batchelor, 2003). The addition of Fe(II) to iron-bearing phyllosilicate suspensions increased the rate constants of target organics by 1.4 to 2.5 times. This enhanced reactivity may be caused by the regeneration of active sites on the phyllosilicates resulting from reaction with Fe(II) or by the reactivity of Fe(II) that binds to the phyllosilicate surfaces. Surface charge of phyllosilicates is negative because the pH of phyllosilicate suspensions is higher than pH_{PZC} (point of zero charge) of the phyllosilicates. Therefore, Fe(II) added into the soil mineral suspensions can be electrostatically bonded onto the phyllosilicate surfaces and form reactive Fe(II) surface sites.

The rate constants for phyllosilicates were 1.8 to 20 times smaller than those for pyrite and GR_{SO4} (Lee and Batchelor, 2002a, 2002b). The difference of rate constants among soil minerals may be due to different intrinsic reactivity of active sites or to different concentrations of active sites on each soil mineral. Fe(II) is expected to be a part of all active sites and the Fe(II) contents of iron-bearing phyllosilicates are 4 to 400 times lower than those of GR_{SO4} (Lee, 2001; Lee and Batchelor, 2003). Although the addition of Fe(II) to iron-bearing phyllosilicate suspensions increased the dechlorination rates, the rate constants with Fe(II) addition were still 1.2 to 12.7 times smaller than those for pyrite and GR_{SO4} (Lee and Batchelor, 2002a, 2002b).

Abiotic reductive dechlorination of c-DCE (0.41 mM) and VC (0.64 mM) by iron-bearing phyllosilicates with and without Fe(II) addition removed 8.8 to 15.3% and 3.7 to 12% of initial
target organics, respectively, over a 30 day period. For comparison, biological degradation of 1,2-dichloroethylene (1.4 - 80 μM) and VC (57 μM) by Fe(III)-reducing and methanogenic bacteria has been reported as removing 4 to 14% of initial target organics in 37 days (Bradley and Chapelle, 1997). This indicates that the extent of removal of c-DCE and VC by iron-bearing phyllosilicates can be similar to those by microorganisms, even when the initial concentrations are higher in the abiotic system. This result suggests that abiotic reductive dechlorination of c-DCE and VC may be important processes that act in combination with biodegradation during natural attenuation of contaminated groundwater when the aquifer materials contain iron-bearing phyllosilicates.

3.3. Recovery and transformation products

Figure 2 shows typical results for removal of a target organic (PCE) and production of chloride in iron-bearing phyllosilicate suspension (biotite) with and without Fe(II) addition. The concentrations of target organic and chloride measured in the suspension are also represented as relative organic chlorine concentrations. The maximum removals of target organics in biotite, vermiculite, and montmorillonite suspensions were 14 to 16%, 6 to 12%, and 4 to 11% of initial concentrations of target organics after 100 days, respectively. Chloride recoveries were calculated by dividing the chloride concentrations produced in the phyllosilicate suspensions by initial organic chlorine concentrations of target organics. They were 22 to 27%, 12 to 44%, and 18 to 37% of the target organic removal, which indicates that target organics were partially dechlorinated. It has been reported that PCE is slowly adsorbed on smectite pretreated with dithionite, but that it is not dechlorinated over a period of 20 hours (Cervini-Silva et al., 2001). The concentrations of target organics in controls stayed between 89 to 97% of the initial values and the recovery of total chlorine (organic chlorine + chloride) in the phyllosilicates suspensions
stayed at 87 to 96% (with Fe(II)) and 88 to 97% (without Fe(II)) over 100 days. The incompleteness of total chlorine mass balance may be due to unrecovered chloride sorbed on the solid phase and to volatilization of target organics during sample preparation. Addition of Fe(II) increased removals of target organics by factors of 1.3 to 2.3, as well as increasing the percentages of chloride produced in the phyllosilicate suspensions by factors of 1.4 to 3.8.

Chloride was produced as a transformation product during degradation of target organics by iron-bearing phyllosilicates with and without Fe(II) addition. In contrast to the chlorinated intermediates observed in abiotic reductive transformation of PCE by clay minerals with dithionite addition (Nzengung et al., 2001), none of the chlorinated intermediates that would be expected in a sequential hydrogenolysis pathway were observed at concentrations above detection limits (TCE: 0.8 μM, c-DCE: 2.06 μM, t-DCE: 8.3 μM, 1,1-dichloroethylene: 2.4 μM, and VC: 16 μM). This indicates that most of the chlorinated ethylenes studied (PCE, TCE, and c-DCE) are primarily transformed to non-chlorinated compounds such as acetylene, ethylene, and ethane via reductive elimination. The formation of these C₂ hydrocarbons was identified during the reactions but they were not quantified in this study. Acetylene was observed in the phyllosilicate suspensions with PCE, TCE, and c-DCE and ethylene was observed in the phyllosilicate suspensions with TCE, only when Fe(II) was added. Stable chlorinated intermediates are not normally observed in reductive elimination pathways for the reductive degradation of chlorinated ethylenes (Sivavec and Horney, 1997; Butler and Hayes, 1999; Lee and Batchelor, 2002a, 2002b). Ethylene, but not acetylene, was observed in the phyllosilicate suspensions spiked with VC. Ethane was only observed in the phyllosilicate suspensions with Fe(II). VC is dechlorinated via the hydrogenolysis pathway, because the reductive elimination pathway is not possible. These results indicate that the transformation products in abiotic
degradation of chlorinated ethenyes by iron-bearing phyllosilicates may vary with types of phyllosilicate, target organic, and reducing agent and experimental conditions.

3.4. Factors affecting dechlorination kinetics

Table 2 shows values of rate constants and other kinetic parameters observed at various geoenvironmental conditions.

3.4.1. Influence of pH

The specific initial reductive capacity of biotite for TCE increased with increasing suspension pH and the sorption coefficient was independent of pH. Increasing pH increased the dechlorination rates of TCE in biotite suspension with and without Fe(II) addition. This result may be caused by the increase of reactive surface complexes on biotite due to the decrease of surface charge as the pH of biotite suspension increased. The decrease of surface charge could promote the formation of deprotonated surface complexes that are more reactive than protonated surface complexes (Butler and Hayes, 1998; Lee and Batchelor, 2002b). The pH_{pzc} of Al-OH, Fe-OH, and Mg-OH edge sites have been reported to be between pH 7 and pH 10 (Davis and Hem, 1989; Sposito, 1989; Alloway, 1995). The pH dependence on the rate constants for the reductive dechlorination of TCE at reactive biotite surfaces with and without Fe(II) addition is shown in Fig. 3. The rate constants for the reductive dechlorination of TCE with and without Fe(II) addition increased with increasing pH. The rate constants without Fe(II) were 1.4 to 2.8 times smaller than those with Fe(II) addition. Additional Fe(II) could increase the rate constants by sorbing to the biotite surface at higher pH and forming surface complexes and/or precipitates that are reactive.
3.4.2. Influence of solid concentration

The rate constants were independent of mass ratio in the range of 0.0085 to 0.17, whether Fe(II) was added or not. However, the rate constants with Fe(II) addition were approximately 1.6 times greater than those without Fe(II) addition. Higher rate constants would imply that additional Fe(II) might be producing a higher concentration of reactive surface sites or increasing the reactivity of existing sites. The specific initial reductive capacity was independent of mass ratio. A constant value of specific initial reductive capacity was calculated as 0.23 μM g\(^{-1}\) by a linear regression between initial reductive capacities of biotite samples and their mass ratios in suspension. The addition of Fe(II) into the biotite suspensions increased specific initial reductive capacity of biotite by factors of 1.2 to 4. The increase of mass ratio in biotite suspension with Fe(II) addition increased dechlorination rates of TCE by a factor of 4.9 and the addition of Fe(II) to biotite suspension increased the dechlorination rates of TCE by factors of 1.2 to 4.0. This result may be caused by the increase of reductive capacity of biotite due to the increased number of reactive sites and/or regeneration of Fe(III) surface sites to Fe(II).

3.4.3. Influence of target organic concentration

The rate constants for the reductive dechlorination of TCE appeared to be independent of initial TCE concentration in biotite suspensions with and without Fe(II) addition. The rate constants with Fe(II) addition were approximately 1.6 times greater than those without Fe(II), which may be caused by the change of reactivity of biotite due to the formation of different type of reactive surface sites by Fe(II) addition. The specific initial reductive capacities (Table 2) decreased slightly with increasing initial TCE concentration, but sorption coefficients did not change significantly. The dechlorination rates of TCE with and without Fe(II) addition increased with increasing initial TCE concentration by a factor of 2.1 and 1.9, respectively. These results
may be due to the finite numbers of reactive sites on biotite (i.e., limited reductive capacity of biotite) that could play an important role for the reductive dechlorination of TCE under the different initial TCE concentrations.

3.4.4. Influence of sorbed Fe(II)

The amount of Fe(II) sorbed to biotite was calculated and its effects on specific initial reductive capacity are shown in Fig. 4a. The specific initial reductive capacity of biotite increased slightly with increasing amounts of Fe(II) adsorbed, which indicates that sorbed Fe(II) is reactive. Figure 4b shows the effect of the amount of sorbed Fe(II) on the rate constant for the reductive dechlorination of TCE. The rate constant increased with increasing concentration of sorbed Fe(II) with the maximum value being 1.6 times the value without Fe(II) addition. This increase could be caused by Fe(II) increasing the reactivity of existing sites or by forming new sites with higher activity due to surface complexation and precipitation. The biggest change in rate constant is observed when comparing the result with no Fe(II) addition to the result with the lowest amount of Fe(II) sorbed. This suggests that the effect of Fe(II) addition is to first convert existing sites to more active forms. However, the slight increase observed with increase in sorbed Fe(II) indicates that there are some additional sites being formed resulting in increased activity.

3.5. Application of kinetic rate constant

Kinetics of degradation in the field will be different than those observed in these experiments because the concentration of active sites per volume of water will be different. However, the laboratory results can be used to estimate observed first-order rate constants that would be observed in a saturated soil in the field. An initial pseudo-first-order rate constant ($k_1$) can be calculated from the modified Langmuir-Hinshelwood kinetic model
where \( r_{\text{decay}} \) is the decay rate of target organic and \( C_{RC} \) is the concentration of reductive capacity for target organics. The concentration of initial reductive capacity (\( C_{RC}^0 \)) can be calculated using the specific initial reductive capacity (\( S_R \)) from Table 1 and the ratio of phyllosilicate in the soil per volume of water. The latter variable can be calculated with the following assumptions: 20% of soil mass is due to phyllosilicate, bulk density = 1.4 kg L\(^{-1}\), and porosity = 0.40. These assumptions lead to biotite providing iron at a concentration near the average for soils (2.6%). Less than the average iron concentration would be provided by vermiculite and montmorillonite. A partitioning factor for PCE of 4.66 can be calculated by assuming a soil organic fraction of 0.005 and an organic carbon partition coefficient of 206 L kg\(^{-1}\). These assumptions result in the values shown in Table 3 for estimated first-order rate constants for degradation of PCE in the field. These values are not intended to be predictive, but to provide an order-of-magnitude estimate of the effect of phyllosilicates on chlorinated organics. The half-lives calculated indicate that abiotic reductive dechlorination is fast enough to be a significant contributor to reported degradation on chlorinated solvents in groundwater systems.
4. Conclusions

The potential importance of reductive dechlorination by iron-bearing phyllosilicates in affecting the fate of chlorinated organics in natural environments was demonstrated by experiments in which a series of chlorinated ethylenes were dechlorinated in systems with and without addition of Fe(II). Partitioning of chlorinated ethylenes to surfaces of iron-bearing phyllosilicates was another important process, accounting for 1.8 to 36% of the chlorinated ethylenes removed after 100 days. A kinetic model based on the modified Langmuir-Hinshelwood kinetics was able to describe dechlorination kinetics in this system. Reductive dechlorination by iron-bearing phyllosilicates resulted in similar removals of c-DCE and VC as observed for Fe(III)-reducing and methanogenic bacteria. This indicates that abiotic reductive dechlorination by iron-bearing soil minerals may be as important as biotic processes in some systems and could be more important in systems where biotic processes are inhibited by toxic compounds. Chloride and C₂ hydrocarbons were observed as transformation products for the reductive dechlorination of chlorinated ethylenes by iron-bearing phyllosilicates. No chlorinated intermediates were observed at concentrations above detection limits. This suggests that PCE, TCE, and c-DCE may be reductively dechlorinated to non-chlorinated compounds via a reductive elimination pathway and that VC may be dechlorinated via a hydrogenolysis pathway. The rate constants for the reductive dechlorination of TCE at reactive biotite surfaces increased with increasing suspension pH. The effect of pH may be caused by the higher pH shifting the distribution of Fe(II) surface complexes and precipitates to more active forms. The rate constants also increased as Fe(II) concentration adsorbed on biotite surface increased, which implies that Fe(II) surface complex groups and precipitates on biotite are effective in reductive dechlorination of TCE in biotite suspension with Fe(II) addition. Estimated half-lives for PCE in a typical soil indicate that abiotic reductive dechlorination is potentially fast enough to describe removals of
chlorinated organics during natural attenuation. The results obtained from this research could be applied to develop remedial technologies to treat contaminated ground water plume and used to better understand natural attenuation and redox manipulation process.

Acknowledgements

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References


Lee W., 2001. Abiotic Reductive Dechlorination of Chlorinated Ethylenes by Soil Minerals and Soil. PhD dissertation, Texas A&M University, College Station, TX, USA.


**Figure captions**

Fig. 1. Reductive dechlorination of PCE (0.19 mM) in iron-bearing phyllosilicate suspensions (0.085 g g\(^{-1}\)) with and without Fe(II) addition (4.28 mM). Curves represent kinetic model predictions based on the parameters in Table 1.

Fig. 2. Reductive dechlorination of PCE and production of chloride in the presence of biotite with and without Fe(II) addition (4.28 mM).

Fig. 3. Rate constants as a function of pH for the reductive dechlorination of TCE (0.3 mM) in biotite suspension (0.085 g g\(^{-1}\)) with and without Fe(II) addition (4.28 mM). Error bars represent 95% confidence intervals. Some error bars are smaller than the symbols.

Fig. 4. (a) Fe(II) concentration added and specific initial reductive capacity as a function of sorbed Fe(II) concentration. Error bars for \(S_R\) represent 95% confidence intervals. (b) Rate constants as a function of Fe(II) concentration adsorbed on biotite for the reductive dechlorination of TCE (0.3 mM) in biotite suspension (0.085 g g\(^{-1}\)) at pH 8.1. Error bars for \(k\) and sorbed Fe(II) concentration represent 95% confidence intervals.
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Table 1. Kinetic parameters, recoveries of chloride and total chlorine, and percentage of target organic remaining for the reductive dechlorination of chlorinated ethylenes\(^a\) by iron-bearing phyllosilicates\(^b\) with and without Fe(II) addition\(^c\) at the last sampling time.

<table>
<thead>
<tr>
<th>soil minerals</th>
<th>target organics (last sampling time)</th>
<th>(S_R) (µM g(^-1))</th>
<th>(K) (mM(^{-1}))</th>
<th>(k) (day(^{-1}))</th>
<th>(R^2)</th>
<th>product recovery and target organic remaining (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>biotite</td>
<td>PCE (98.8 day)</td>
<td>0.400 (±5.3%)(^d)</td>
<td>1.6 (±6.1%)</td>
<td>0.401 (±8.1%)</td>
<td>0.906</td>
<td>chloride: 4.1 / 16.0* PCE: 83.6 / 75.8* total: 87.7 / 91.8* chlorides: 3.8 / 12.4* TCE: 84.1 / 78.6* total: 87.9 / 91.0* chloride: 3.9 / 10.8* TCE: 85.6 / 80.0* total: 89.5 / 90.8* chloride: 3.0 / 17.6*</td>
</tr>
<tr>
<td></td>
<td>TCE (98.8 day)</td>
<td>0.565 (±3.7%)*</td>
<td>0.802 (±2.8%)(^*)</td>
<td>0.601 (±5.1%)*</td>
<td>0.969</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c-DCE (98.6 day)</td>
<td>0.482 (±7%)</td>
<td>1.0 (±3.5%)</td>
<td>0.4 (±5.7%)</td>
<td>0.954</td>
<td></td>
</tr>
<tr>
<td></td>
<td>VC (98.6 day)</td>
<td>0.647 (±4.0%)*</td>
<td>0.615 (±2.7%)(^*)</td>
<td>0.572 (±3.9%)*</td>
<td>0.973</td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vermiculite</td>
<td>PCE (89 day)</td>
<td>0.177 (±6.1%)(^d)</td>
<td>0.7 (±7.2%)</td>
<td>0.08 (±10.4%)</td>
<td>0.878</td>
<td>chloride: 2.0 / 5.0* PCE: 92.8 / 89.6* total: 94.8 / 94.6* chlorides: 2.4 / 5* TCE: 94.5 / 90.6* total: 96.9 / 95.6* chloride: 1.8 / 4.5* TCE: 89.5 / 84.4* total: 91.3 / 88.9* chloride: 1.4 / 3.0* TCE: 87.9 / 83.9* total: 89.3 / 86.9*</td>
</tr>
<tr>
<td></td>
<td>TCE (89 day)</td>
<td>0.282 (±10.1%)*</td>
<td>1.0 (±9.8%)</td>
<td>0.125 (±15.2%)</td>
<td>0.807</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c-DCE (89 day)</td>
<td>0.188 (±7.9%)</td>
<td>0.803 (±6.8%)(^*)</td>
<td>0.08 (±16.2%)</td>
<td>0.817</td>
<td></td>
</tr>
<tr>
<td></td>
<td>VC (89 day)</td>
<td>0.294 (±10.7%)*</td>
<td>0.803 (±6.8%)(^*)</td>
<td>0.08 (±16.2%)</td>
<td>0.806</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>montmorillon</td>
<td>PCE (100.6 day)</td>
<td>0.635 (±2.7%)(^d)</td>
<td>0.775 (±3.2%)</td>
<td>0.162 (±4.1%)</td>
<td>0.976</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TCE (100.6 day)</td>
<td>0.871 (±2.5%)*</td>
<td>0.775 (±3.2%)</td>
<td>0.162 (±4.1%)</td>
<td>0.988</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c-DCE (100.6 day)</td>
<td>1.01 (±11.4%)*</td>
<td>0.502 (±6.3%)</td>
<td>0.355 (±12.6%)</td>
<td>0.965</td>
<td></td>
</tr>
<tr>
<td></td>
<td>VC (100.6 day)</td>
<td>1.41 (±12.4%)*</td>
<td>0.502 (±12.1%)*</td>
<td>0.537 (±20.4%)</td>
<td>0.989</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Initial concentrations of target organics were 0.19 (PCE), 0.25 (TCE), 0.41 (c-DCE), and 0.64 mM (VC). pH of soil mineral suspension was controlled at 7.0.

\(^b\) Mass ratios of solid to water were 0.085 g g\(^{-1}\).

\(^c\) Fe(II) concentration: 4.28 mM.

\(^d\) Uncertainties represent 95% confidence intervals. The uncertainties are calculated by multiplying standard errors of estimated kinetic parameters by \(t\)-values.

\(^e\) Total is recovery of total chlorine in the phyllosilicate suspension with and without Fe(II) at the last sampling time.

\(^f\) \(R^2\) values of non-linear regression for kinetic parameters.

\(*\) Samples with Fe(II) addition.
Table 2. Kinetic parameters as functions of pH, solid concentration, initial target organic concentration, and sorbed Fe(II) concentration.

<table>
<thead>
<tr>
<th>pH</th>
<th>mass ratio (g g(^{-1}))</th>
<th>C(^{\text{in}}) TCE (mM)</th>
<th>Fe(II)(^{b}) (mM)</th>
<th>(S_R) ((\mu)M g(^{-1}))</th>
<th>K (mM(^{-1}))</th>
<th>k (day(^{-1}))</th>
<th>(R^2) (%)(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.164 (±7.2%)(^c)</td>
<td>1.00 (±5.4%)</td>
<td>0.15 (±3.5%)</td>
<td>91.9</td>
</tr>
<tr>
<td>6.0</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.259 (±3.6%)*</td>
<td>0.615 (±6.8%)*</td>
<td>0.35 (±3.6%)*</td>
<td>93.7*</td>
</tr>
<tr>
<td>7.0</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.188 (±5.6%)</td>
<td>0.989 (±3.4%)</td>
<td>0.16 (±2.9%)</td>
<td>95.2</td>
</tr>
<tr>
<td>8.0</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.318 (±4.7%)*</td>
<td>0.612 (±2.1%)*</td>
<td>0.45 (±2.0%)*</td>
<td>98.3*</td>
</tr>
<tr>
<td>8.1</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.200 (±6.4%)</td>
<td>0.961 (±4.7%)</td>
<td>0.38 (±1.6%)</td>
<td>93.2</td>
</tr>
<tr>
<td>8.2</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.353 (±3.4%)*</td>
<td>0.615 (±3.1%)*</td>
<td>0.53 (±1.8%)*</td>
<td>95.7*</td>
</tr>
<tr>
<td>8.3</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.259 (±8.5%)</td>
<td>1.00 (±6.0%)</td>
<td>0.44 (±2.7%)</td>
<td>90.1</td>
</tr>
<tr>
<td>8.4</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.400 (±5.5%)*</td>
<td>0.615 (±4.7%)*</td>
<td>0.70 (±3.0%)*</td>
<td>94.2*</td>
</tr>
<tr>
<td>8.5</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.271 (±3.6%)</td>
<td>0.975 (±7.3%)</td>
<td>0.95 (±3.3%)</td>
<td>89.8</td>
</tr>
<tr>
<td>8.6</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.435 (±9.1%)*</td>
<td>0.616 (±8.4%)*</td>
<td>1.59 (±4.4%)*</td>
<td>88.7*</td>
</tr>
<tr>
<td>8.7</td>
<td>0.0085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.222 (±7.2%)</td>
<td>1.00 (±3.9%)</td>
<td>0.43 (±2.2%)</td>
<td>93.4</td>
</tr>
<tr>
<td>8.8</td>
<td>0.043</td>
<td>0.3</td>
<td>4.28</td>
<td>0.889 (±6.3%)*</td>
<td>0.615 (±3.1%)*</td>
<td>0.70 (±1.9%)*</td>
<td>94.7*</td>
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<tr>
<td>8.9</td>
<td>0.128</td>
<td>0.3</td>
<td>4.28</td>
<td>0.233 (±7.8%)</td>
<td>1.00 (±3.6%)</td>
<td>0.42 (±1.5%)</td>
<td>94.7</td>
</tr>
<tr>
<td>9.0</td>
<td>0.17</td>
<td>0.3</td>
<td>4.28</td>
<td>0.297 (±10%)*</td>
<td>0.615 (±6.7%)*</td>
<td>0.71 (±2.5%)*</td>
<td>85.7*</td>
</tr>
<tr>
<td>9.1</td>
<td>0.085</td>
<td>0.15</td>
<td>4.28</td>
<td>0.194 (±8.5%)*</td>
<td>1.01 (±6.0%)</td>
<td>0.45 (±2.6%)</td>
<td>90.8</td>
</tr>
<tr>
<td>9.2</td>
<td>0.085</td>
<td>0.45</td>
<td>4.28</td>
<td>0.259 (±9.2%)*</td>
<td>0.620 (±4.6%)*</td>
<td>0.72 (±2.6%)*</td>
<td>93.2*</td>
</tr>
<tr>
<td>9.3</td>
<td>0.085</td>
<td>0.6</td>
<td>4.28</td>
<td>0.459 (±9.7%)*</td>
<td>0.603 (±7.9%)*</td>
<td>0.69 (±7.1%)*</td>
<td>88.2*</td>
</tr>
<tr>
<td>9.4</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.200 (±6.5%)</td>
<td>1.02 (±3.8%)</td>
<td>0.43 (±4.5%)</td>
<td>94.3</td>
</tr>
<tr>
<td>9.5</td>
<td>0.085</td>
<td>0.6</td>
<td>4.28</td>
<td>0.329 (±9.9%)*</td>
<td>0.615 (±4.7%)*</td>
<td>0.71 (±2.1%)*</td>
<td>92.1*</td>
</tr>
<tr>
<td>9.6</td>
<td>0.085</td>
<td>0.3</td>
<td>4.28</td>
<td>0.188 (±3.7%)*</td>
<td>1.00 (±2.1%)</td>
<td>0.45 (±2.6%)</td>
<td>96.7</td>
</tr>
<tr>
<td>9.7</td>
<td>0.085</td>
<td>0.3</td>
<td>1.07</td>
<td>0.294 (±4.0%)*</td>
<td>0.615 (±3.0%)*</td>
<td>0.70 (±1.9%)*</td>
<td>98.2*</td>
</tr>
<tr>
<td>9.8</td>
<td>0.085</td>
<td>0.3</td>
<td>2.14</td>
<td>0.353 (±4.6%)*</td>
<td>0.615 (±4.1%)*</td>
<td>0.64 (±2.7%)*</td>
<td>94*</td>
</tr>
<tr>
<td>9.9</td>
<td>0.085</td>
<td>0.3</td>
<td>3.21</td>
<td>0.365 (±7.6%)*</td>
<td>0.615 (±5.0%)*</td>
<td>0.65 (±3.2%)*</td>
<td>90.3*</td>
</tr>
</tbody>
</table>

\(a\) Initial concentration of TCE (mM).
\(b\) Concentration of Fe(II) added to iron-bearing phyllosilicate suspension.
\(c\) Uncertainties of kinetic parameters represent 95% confidence intervals.
\(d\) \(R^2\) values of non-linear regression for kinetic parameters.
* Soil mineral samples with Fe(II) addition.
Table 3. Kinetic results for the reductive dechlorination of PCE extrapolated to field conditions

<table>
<thead>
<tr>
<th>phyllosilicates</th>
<th>$k_1$ (day$^{-1}$)</th>
<th>half-life (day)</th>
<th>$C^0_{RC}$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>biotite</td>
<td>0.030</td>
<td>23</td>
<td>0.28</td>
</tr>
<tr>
<td>vermiculite</td>
<td>0.0024</td>
<td>290</td>
<td>0.12</td>
</tr>
<tr>
<td>montmorillonite</td>
<td>0.010</td>
<td>69</td>
<td>0.19</td>
</tr>
</tbody>
</table>