Abiotic reductive dechlorination of chlorinated ethylenes by soil

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Abstract

Abiotic reductive dechlorination of chlorinated ethylenes by soil in anaerobic environments was characterized to improve knowledge of the behavior of chlorinated ethylenes in natural systems, including systems modified to promote attenuation of contaminants. Target organics in the soil suspension reached sorption equilibrium in 2 days and the sorption isotherm of target organics was properly described by the linear sorption model. A modified Langmuir-Hinshelwood model was developed to describe the kinetics of reductive dechlorination of target organics by soil. The rate constants for the reductive dechlorination of chlorinated ethylenes at the reactive surfaces of reduced soils were found in the range between 0.055 (±8.9%) and 2.60 (±3.2%) day⁻¹. The main transformation products in reduced soil suspensions were C₂ hydrocarbons. No chlorinated intermediates were observed at concentrations above detection limits. Five cycles of reduction of the soil followed by oxidation of the soil with trichloroethylene (TCE) did not affect the removal of TCE. The removal was affected by the reductants used and increased in the order: Fe(II) < dithionite < Fe(II) + dithionite.

Keywords: Chlorinated organics, Natural attenuation, Redox manipulation, Waste site cleanup

1. Introduction

Reductive dechlorination of chlorinated organics in natural environments by microorganisms (Holliger and Schumacher, 1994; Gossett, 1996; McCarty, 1996) and specific natural reductants such as transition metal coenzymes (Assaf-anid et al., 1994; Chiu and Reinhard, 1995; Burris et al., 1996), reduced natural organic matter (NOM) (Curtis and Reinhard, 1994), and iron-bearing soil minerals (Kriegman-King, 1993; Butler and Hayes, 1999; Lee and Batchelor, 2000) has been extensively investigated. Some research has been conducted to investigate the reactivity of whole soils and sediments for the reductive dehalogenation of
halogenated organics. It has been reported that selected halogenated ethanes (e.g., hexachloroethane (HCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), 1,2-diiodoethane (1,2-DIA), and 1,2-dibromoethane (1,2-DBA)) were degraded via vicinal dehalogenation in anoxic sediments and the dehalogenation kinetics by the sediments followed a pseudo-first-order rate law (Jafvert and Wolfe, 1987). The degradation kinetics of a set of halogenated aliphatic compounds in anaerobic sediment slurries has been investigated (Peijnenburg et al., 1998) and quantitative structure-activity relationships have been developed for predicting the reductive dehalogenation rate constants of halogenated aromatic and aliphatic compounds in anoxic sediments (Peijnenburg et al., 1992; Rorije et al., 1997). Lately, it has been reported that sediments which have been reduced by dithionite effectively dechlorinated trichloroethylene (TCE) via reductive elimination and that the main transformation products were acetylene, ethylene, and ethane (Szecsody et al., 2000). Little research has been conducted to characterize the reductive dechlorination of chlorinated ethylenes by soil that supports development of methods to predict fate and transport of these compounds in natural environments and development of remedial technologies. This may be due to the low reductive capacity of soils for the reductive dechlorination of chlorinated ethylenes. Although they are low, they can be significant, particularly over long periods of time.

The goal of experiments described in this research was to characterize abiotic reductive dechlorination of chlorinated ethylenes by soil. Because many components in soil are not in their reduced forms, various treatment techniques were investigated to convert them to reduced states. Experiments were conducted to evaluate the effects of reductant type and reaction time of soil with reductant on the reductive capacity of the soil. The equilibrium aspect of sorption of chlorinated ethylenes on soil was investigated as well as the kinetics of dechlorination by the reduced soils. Lastly, the effect of reductant type on the effectiveness of batch regeneration was
evaluated by repeating the dechlorination kinetic experiments with soils that had been sequentially oxidized and reduced for up to five times.

2. Materials and methods

2.1. Materials

Chemical reagents and soil samples were prepared in an anaerobic chamber (Coy Laboratory Products Inc.) containing an atmosphere of 95% N₂ and 5% H₂. Chlorinated ethylenes used as target organics and transformation products for this research were ACS (American Chemical Society) or higher grades and used as received. Stock target organic solutions were prepared by diluting target organics in methanol. Hexane was used as an extractant and 1,2-dibromopropane was used as an internal standard for gas chromatograph (GC) analysis. Deaerated deionized water (ddw) was prepared by deoxygenating ultra-pure water (18 MΩ cm) with nitrogen for 2 hrs and then with the atmosphere in anaerobic chamber for 12 hrs. It was used to prepare all solutions.

Soil samples were collected from the top 20 to 40 cm near College Station, Texas and were brought to the laboratory without any efforts to maintain the original redox state. This soil is an alluvium of the Brazos River and is classified as Silawa loamy sand (Hwang, 2000). Soil samples were air dried and screened through a 0.425-mm sieve. X-ray diffraction (XRD) analysis (Rigaku automated diffractometer using Cu Kα radiation, 0° to 70° 2θ, scan speed of 1° 20 min⁻¹) showed the presence of mica (10, 5Å), kaolinite (7.1, 3.56 Å), and quartz (4.26, 3.34 Å). The composition of the clay fraction was semi-quantitatively estimated as including 20 – 25% quartz, 40 – 50% kaolinite, and 30 – 40% mica. The silt and sand fractions include quartz with small
amount of feldspar. Particle size distribution and important physicochemical characteristics of the soil are summarized in Tables 1 and 2.

To characterize degradation kinetics by reduced soil, samples (120 g) were treated with Fe(II) (250 mL, 0.6 M, 2 days), dithionite (250 mL, 0.1 M, 2 days), and sequential addition of both reducing agents. The treated soil samples were washed several times with ddw to remove residual Fe(II) and dithionite and were dried and stored in the anaerobic chamber. Treatment with dithionite increases Fe(II) concentration in the soils as well as their ability to reduce chromate (Lee et al., 2000; Lee and Batchelor, 2003) (Table 2). The soil samples were used for experiments no more than 7 days after treatment to preclude a potential aging effect on reductive degradation kinetics.

2.2. Experimental procedures
Batch tests were conducted by transferring soil (5 g) to 20-mL amber vials and adding 20 mL of reducing solution (Fe(II), dithionite) at room temperature (22 ± 0.5 °C) in an anaerobic chamber. pH of the soil suspension was kept at 11.2 by the high concentration of K₂CO₃ during the dithionite treatment, while pH was maintained at 3.2 during treatment with Fe(II). Vials were tightly sealed with open-top cap and a three-layered septum system (Teflon film + lead foil + Teflon lined rubber septum) (Lee and Batchelor, 2002a; Lee and Batchelor, 2002b; Lee and Batchelor, 2003). Then they were taken out of the anaerobic chamber and shaken at 250 rpm for 1, 2, 4, and 11 days. After this, vials were centrifuged at 1400g for 30 minutes, they were transferred to the anaerobic chamber, the supernatant was decanted, and the soil sample was washed with ddw several times to remove Fe(II) and dithionite remaining on the soil surfaces. Tris buffer (23.4 mL) was then added to keep the pH of soil suspension at 7.2 and 10 μL of 0.76 M TCE stock solution was spiked to the soil suspension. Vials were rapidly capped, taken out of
anaerobic chamber, and mounted on the tumbler to completely mix the soil suspension at 7 rpm for 8 and 20 days.

Sorption experiments were conducted in a system that was similar to the one used for reduction experiments (5 g soil, 20-mL vial, Tris buffer at mass ratio of 0.21 for pH 7.2, three-layered septum). Different initial concentrations of four target organics were prepared in the range of 4.0 – 140.0 mg L\(^{-1}\) to measure the sorption isotherm. Vials were mixed at 7 rpm at room temperature for 10 days before analysis. Linear sorption coefficients were determined by linear least squares regression.

The same batch reactor system was used to characterize degradation kinetics of chlorinated ethylenes by soil that had been treated by Fe(II) or dithionite. Initial concentrations of 43 mg L\(^{-1}\) (PCE), 42 mg L\(^{-1}\) (TCE), 42 mg L\(^{-1}\) (c-DCE), and 41 mg L\(^{-1}\) (VC) were used with vials for all conditions and controls. Concentrations of target organics and transformation products were determined in aqueous and solid phases (reactor wall + septum liner + soil surface) at each sampling time.

Batch experiments were conducted to evaluate the effect of reductant type on the effectiveness of regeneration of soil. Soil samples (8.5 g) were treated with Fe(II), dithionite, and a combination of Fe(II) and dithionite and then transferred to heavy duty glass centrifuge tubes (nominal volume: 35 mL, Kimex) in the anaerobic chamber. Tris buffer solution was added to keep pH of soil suspension 7.2 throughout the experiments. This resulted in a solid/solution mass ratio of 0.21. A volume (10 \(\mu\)L) of 1.34 M TCE stock solution was spiked to triplicate soil suspensions and controls. The tubes were rapidly sealed with an open-top cap and the three-layered septum system, taken out of anaerobic chamber, and completely mixed using the tumbler at 7 rpm under room temperature. After 10 days, tubes were centrifuged at 1400g for 30 minutes and exact amount of supernatants were transferred to extraction vials and extracted with hexanes.
The extracts were analyzed to determine concentrations of target organic compound and transformation products in aqueous solution. Supernatants were then removed from the tubes and the soil samples were extracted with hexane (10 mL) to measure and remove target organic and transformation products sorbed onto soils. Extractants were removed from the tubes and the soils in the tubes were dried in the air for 2 days. The soil samples were treated with reductants again and the experiments were repeated for 5 cycles.

2.3. Analytical procedures

Target chlorinated ethylenes and their transformation products (PCE, TCE, and 1,1-DCE) were measured after extraction by gas chromatography (Hewlett-Packard 5890 GC-ECD, combination of DB-5 and DB-5MS column (J&W Scientific), injector at 220 °C, detector at 240 °C, oven initially at 80 °C for 2 min, increased to 110 °C at 5 °C min⁻¹, and then held for 2 min, injection volume of 1 µL, split ratio of 35:1). Aqueous samples (50 µL) were extracted with 1 mL extractant (hexane with 0.025 mM 1,2-DBP). Soil samples were separated from the aqueous phase and were extracted with 10 mL extractant on an orbital shaker. Other compounds (c-DCE, t-DCE, VC) were analyzed by a headspace procedure (HP 6890 GC-FID, DB-VRX column (J&W Scientific), injector at 220 °C, detector at 240 °C, oven isothermal at 80 °C for 7 min, injection volume of 50 – 100 µL, split ratio of 5:1). A 10-mL sample of supernatant was rapidly transferred to a 20-mL vial and allowed to equilibrate for 2 hrs at room temperature before a sample of the gas phase was analyzed. The concentrations in aqueous solution were calculated using dimensionless Henry’s law constants (0.14 (c-DCE), 0.35 (t-DCE), and 1.01 (VC)) (Mackay and Shiu, 1981; Gossett, 1987).

Acetylene, ethylene, and ethane were analyzed by a similar headspace procedure (HP 6890 GC-FID, GS-Alumina column (J&W Scientific), oven isothermal at 100 °C, injector and
detector at 150 °C, sample volume of 50 – 100 μL, split ratio of 5:1). The formation of chloride was monitored by ion chromatograph (Dionex 500, AS9-HC column, 10 mM Na₂CO₃ eluent, flow rate of 1 mL min⁻¹). A 2-mL sample of supernatant was filtered with 0.2 μm membrane filter 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

The behavior of target organics by reductive degradation in suspensions of soil was similar to that observed in suspensions of iron-bearing soil minerals (Lee and Batchelor, 2002a; Lee and Batchelor, 2002b). The concentrations of target organics rapidly decreased in early times and then slowly decreased in both suspensions. This was assumed to be caused by reactive chemical compounds (e.g., iron-bearing soil minerals and NOMs) in soil having a finite capacity for the reductive dechlorination of target organics. Therefore, the modified Langmuir-Hinshelwood model that was developed to describe dechlorination kinetics by iron-bearing soil minerals (Lee and Batchelor, 2002a; Lee and Batchelor, 2002b) was applied to describe reductive dechlorination by soil. This model assumes that the rate of dechlorination is proportional to the concentration of the target compound sorbed onto active sites and to the concentration of active sites. The concentration of active sites is represented as the concentration of reductive capacity and it decreases over time as the active sites are consumed by the reaction. The reductive capacity is expressed as the concentration of target organic that could be reduced by the soil if given an infinite amount of time. The concentration of target organic sorbed onto active sites is described by a Langmuir model. These assumptions and the assumption of phase equilibria among water, gas and solids lead to the following mathematical model for the batch reactors:
\[
\frac{dC_{CE}}{dt} = -\frac{(k/p_{CE})\left[C_{RC}^0 - p_{CE}\left(C_{CE}^0 - C_{CE}\right)\right]}{1/K + C_{CE}}
\]  \tag{1}

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

\[k_s = \frac{C_s}{C_{aq}} = \frac{qS}{C_{aq}} = k_p S\]  \tag{3}

where \(C_{CE}\) is the concentration of target organic (chlorinated ethylene) in aqueous solution, \(k\) is the rate constant for the decay of target organic at the reactive sites, \(C_{RC}^0\) is the initial reductive capacity of soil for the target organic, \(C_{CE}^0\) is the initial concentration of target organic in aqueous solution, \(K\) is the sorption coefficient of target organic, \(p_{CE}\) is the partitioning factor for the effect of partitioning of target organics onto aqueous (dissolution), gas (volatilization), and solid phases (sorption) assuming instantaneous equilibrium among the three phases, \(H_{CE}\) is the dimensionless Henry’s law constant for target organics, \(V_g\) and \(V_{aq}\) are the volumes of gas and aqueous phases, \(k_s\) is the non-soil solid phase partitioning coefficient of target organics, \(C_s\) is the amount of target organic in the non-soil solid phase (primarily the septum) per unit aqueous phase volume, \(C_{aq}\) is the concentration of target organics in aqueous phase, \(q\) is the mass of target organics sorbed per unit mass of soil, \(S\) is the soil concentration, and \(k_p\) is the partitioning coefficient of target organics. The kinetic parameters (\(k\), \(K\), and \(C_{RC}^0\)) were estimated by an optimization procedure using MATLAB® (MathWorks Inc.) that solves the differential equation numerically and calculates the sum of squares for the parameters repeatedly to find its minimum value.
3. Results and discussion

3.1. Evaluation of reductant type and reaction time with reductant on soil reactivity

Figure 1 shows the effects of reductant type, previous reaction time of soil with reductant, and reaction time with TCE on the recovery of TCE (C/C₀) in the soil suspensions. The recoveries of TCE in dithionite-treated soil suspension were 1.05 – 1.12 times lower than the recoveries in Fe(II)-treated soil suspension, indicating that dithionite is a more effective reductant than Fe(II) for Silawa soil. The recoveries at the TCE contact time of 23 days were slightly lower than those at the contact time of 8 days; however, the differences were small (less than 5%). The reaction times of the soil with the reductant needed to reach the minimum values of recoveries were slightly different, but were generally near 2 days. This indicates that at least 2 days are required to fully and effectively reduce Silawa soil with Fe(II) and dithionite.

3.2. Sorption equilibria of chlorinated ethylenes on soil

A preliminary kinetic experiment showed that sorption equilibria occurred within 1 or 2 days of contact, but isotherm experiments were conducted with 10 days contact to insure equilibrium. Sorption isotherms of chlorinated ethylenes on the Silawa soil are shown in Fig. 2. The amount of chlorinated ethylenes sorbed onto Silawa soil (q) was calculated using equation (4) which takes into account the partitioning of chlorinated ethylenes to gaseous, aqueous, and non-soil solid phases in the experimental system (Hwang, 2000).

\[
q = \frac{M_{CE} - C_{eq}(V_{aq} + H_{CE}V_g + k_sV_{aq})}{M_{soil}} \quad (4)
\]
where $M_{CE}$ and $M_{soil}$ are the mass of chlorinated ethylenes spiked and mass of soil, respectively. $C_{eq}$ is the equilibrium concentration of chlorinated ethylenes in the aqueous solution. Values for linear partition coefficients ($k_p$), organic carbon partition coefficients ($k_{oc}$), and the $R^2$ values for the linear regressions are shown in Table 3. The $R^2$ values stayed between 0.92 and 1, indicating the linear sorption model adequately described the partitioning of chlorinated ethylenes to the soil. The $k_{oc}$ values were calculated using the fraction of organic matter in Silawa soil (0.0069) and they are similar to those reported in the literature (Karickhoff et al., 1979; Garbarini and Lion, 1986; Mouvet et al., 1993).

3.3. Degradation kinetics of chlorinated ethylenes by reduced soil

Figure 3 shows the recoveries ($C/C_0$) of chlorinated ethylenes in reduced soil suspensions and controls. The recoveries in controls after 10 days were similar to those observed during sorption experiments. The slight decrease of target organic recoveries after 10 days (controls) may be caused by the intrinsic reductive capacity of Silawa soil for chlorinated ethylenes. This soil suspension had a Fe(II) content that is equivalent to 2.6 times the stoichiometric amount required to fully reduce the initial concentration of PCE to ethylene. However, there was little evidence that target organics were being degraded in controls, because most of them were recovered when the solid phase of the control reactors was extracted. In contrast, target organics in reduced soil suspensions tended to be transformed to $C_2$ hydrocarbons and chloride as well as being sorbed. Quantitative measurements of chlorinated transformation products were conducted at each sampling time, but no chlorinated intermediates (e.g. TCE, DCEs, and VC) were observed in systems spiked with PCE at concentrations above detection limits (TCE: 0.11 mg L$^{-1}$, c-DCE: 0.20 mg L$^{-1}$, t-DCE: 0.080 mg L$^{-1}$, 1,1-DCE: 0.23 mg L$^{-1}$, and VC: 0.26 mg L$^{-1}$). Qualitative gas chromatographic analyses were conducted after 10 and 40 days to investigate if non-chlorinated products ($C_2$ hydrocarbons) were being produced during the decay of chlorinated
ethylenes. Acetylene was observed after 10 and 40 days in systems spiked with PCE, TCE, and c-DCE when soils were treated with Fe(II) and dithionite. Ethylene was also observed in systems spiked with TCE and VC. Ethane was observed only with the soil treated by dithionite and spiked with VC and only after 10 days. These observations are consistent with a reductive elimination pathway for dechlorination of PCE, TCE, and c-DCE (PCE $\rightarrow$ dichloroacetylene $\rightarrow$ chloroacetylene $\rightarrow$ acetylene) (Butler and Hayes, 1999; Lee and Batchelor, 2000; Lee and Batchelor, 2002a; Lee and Batchelor, 2002b) and a hydrogenolysis pathway for dechlorination of VC (VC $\rightarrow$ ethylene). Further evidence of degradation of target organics in systems with reduced soils is that chloride was observed in all of the reduced soil suspensions after 10 and 40 days, but it was not observed in any controls.

Each curve in Fig. 3 is a prediction of recoveries made by the kinetic model. The model is based on the assumption that phase equilibrium is maintained in the soil suspensions as indicated by equation (2). This assumption is reasonable because the sorption kinetics of target organics was observed to be much faster (1-2 days) than the reductive degradation kinetics of target organics in this study. Additionally, it has been reported that equilibrium for sorption of hydrophobic organics onto soils is usually achieved in less than one hour and frequently in a few minutes (Voice and Weber, 1983).

Table 4 shows partitioning factors and kinetic parameters obtained in this study. Specific initial reductive capacities were calculated by dividing the initial reductive capacity by soil concentration. The rate constants and specific initial reductive capacities for the dithionite-treated soil were greater than for the Fe(II)-treated soil, indicating that dithionite-treated soil is more reactive. The rate constants increased in the order: VC, c-DCE, TCE, and PCE. Redox-active compounds in soil (NOMs, iron-bearing soil minerals, and Fe and Mn surface species sorbed on
soil minerals and soil) can be converted to reduced forms by treatment with Fe(II) and dithionite. The reactivity of these reduced may be different depending on the type of reductant used during treatment. Fe(II) can both reduce redox-active compounds that exist in the soil and produce more redox-active compounds by providing additional sorbed Fe(II) or soil minerals containing Fe(II). Dithionite can both reduce the redox-active compounds that exist in soil and produce more redox-active compounds by forming iron sulfides and reduced sulfur species sorbed on soil surfaces. The compounds resulting from treatment with dithionite seem to have more reducing power than those resulting from treatment with Fe(II). Experiments to identify and quantify the different types of reactive compounds resulting from treatment with Fe(II) and dithionite need to be conducted to verify these assumptions.

Table 4 also shows the maximum concentrations of target organics that potentially could be treated in a reduced soil zone. These were estimated using the specific initial reductive capacity of reduced soils and typical soil conditions (e.g., porosity = 0.45 and bulk density = 1.35 g cm\(^{-3}\)). The half-lives for these dechlorination reactions under typical soil conditions were also estimated to be between 2.5 and 245 days. These are lower than many half-lives reported for chlorinated organics in aquifer systems assumed to be controlled by biotic dechlorination (Wiedemeier et al., 1998). This indicates that abiotic processes may be important in such systems, particularly when microbial processes help regenerate redox-active compounds in soil by producing reductants such as Fe(II) and reduced organic compounds.

3.4. Evaluation of the effect of reductant type on effectiveness of batch regeneration

Experiments were conducted to determine if Silawa soil could maintain its original reductive capacity after being repeatedly cycled between its reduced and oxidized states. Such ability would be important if soils were to be used as a permeable reactive barrier to dechlorinate groundwater. Figure 4 shows the variations of TCE recoveries in soil suspensions reduced in
three different ways over 5 cycles of reduction/oxidation. TCE was allowed to contact the soils for 10 days in each cycle, so the total reaction time shown in Fig. 4 for the fifth cycle is 50 days. The symbols shown in the figure are measured values and the solid lines are linear (soil samples treated with reducing agents) and polynomial (control) regression fits. The recovery of TCE in controls stayed between 77 – 80% of initial TCE concentration in fourth cycle and increased approximately to 90% in the fifth cycle. The TCE that was not recovered from aqueous solution in the controls was probably lost to sorption. The increased recovery at the fifth cycle may be caused by the loss of soil during the washing procedure that resulted in less TCE being sorbed. Statistical inference tests about slopes showed that the hypothesis that the slopes were zero could not be rejected at the 95% confidence level. The soils reduced with any of the three reductants were very stable in removing TCE through the five cycles so that they might be able to be cycled for a higher number of times. The recoveries of TCE by the reduced soils decreased in the order: Fe(II) > dithionite > Fe(II) + dithionite. The highest reactivity (lowest recovery) observed for the soil treated with the combination of both reductants may be caused by increased levels of Fe(II) in the soil and/or possible formation of reactive iron sulfides. Black precipitates were observed after the treatment of soil with the combination of reductants and may be iron sulfides.

4. Conclusions

The results described in this research showed that the Silawa soil treated with reducing agents can reductively dechlorinate a series of chlorinated ethylenes. The soil treated with dithionite showed better removal of target organics than the soil treated with Fe(II).

Recoveries of target organics in controls stayed between 57 and 93% of initial target organic concentrations, which indicates that the sorption of chlorinated ethylenes onto the soil significantly affects the removal of chlorinated organics in the soil suspensions. The modified
Langmuir-Hinshelwood kinetic model was able to adequately describe the dynamics of reductive dechlorination of target organics in reduced soil suspensions. The rate constants for the reductive degradation of target organics by the soil treated with dithionite were greater than those by the soil treated with Fe(II), indicating that the soil treated with dithionite is more reactive for the reductive degradation of chlorinated ethylenes. The main transformation products in the reductive degradation of chlorinated ethylenes by the reduced soils were acetylene, ethylene, and ethane. Chlorinated intermediates were not observed at concentrations above detection limits. Formation of chloride was observed in all reduced soil suspensions, but not in controls. These results indicate that chlorinated ethylenes are reductively dechlorinated to non-chlorinated products by the reduced soils as well as being sorbed.

The recovery of TCE by the soils treated with three different reducing agents was constant during five cycles of reduction/oxidation. The recoveries of TCE by the reduced soils decreased in the order: Fe(II) > dithionite > Fe(II) + dithionite, so the removal increased in the reverse order. The highest removal (lowest recovery) was observed with the soil treated with the combination of both reductants. This could be caused by increased levels of Fe(II) in the soil and/or possible formation of reactive iron sulfides.

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dechlorination mechanism. PNNL-13178, Pacific Northwest National Laboratory, Richland, WA, USA.


Figure captions

Fig. 1. The effects of reductant type, reaction time of soil with reductant, and TCE contact time on the recovery \((C/C_0)\) of TCE in 0.21 g g\(^{-1}\) Silawa soil suspensions at pH 7.2. The soil was treated with 0.6 M Fe(II) and 0.1 M dithionite.

Fig. 2. Sorption isotherms of chlorinated ethylenes on Silawa soil. Experiments were conducted in soil suspensions (0.21 g g\(^{-1}\)) at pH 7.2. Concentration range of chlorinated ethylenes spiked to the suspensions was 4.0 – 140.0 mg L\(^{-1}\). The solid lines are fitted by a linear sorption model.

Fig. 3. Decay of chlorinated ethylenes in suspensions of Silawa soil (0.21 g g\(^{-1}\), treated with 0.6 M Fe(II) and 0.1 M dithionite) at initial pH 7.2. Initial concentration of chlorinated ethylenes: 43.1 mg L\(^{-1}\) (PCE), 42.5 mg L\(^{-1}\) (TCE), 41.7 mg L\(^{-1}\) (c-DCE), and 41.2 mg L\(^{-1}\) (VC). The solid curves represent predicted values by the kinetic model.

Fig. 4. The recovery of TCE (52.6 mg L\(^{-1}\)) in suspensions of Silawa soil (0.21 g g\(^{-1}\), treated with 0.6 M Fe(II), 0.1 M dithionite, and the combination of both reductants) at initial pH 7.2 during the fifth cycle. The solid lines represent regression lines fit to a linear model for soil samples treated with reductants and to a polynomial model for controls.
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Table 1. Particle size distribution\textsuperscript{a} of Silawa soil

<table>
<thead>
<tr>
<th>size and content</th>
<th>sand</th>
<th>silt</th>
<th>clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>size (mm)</td>
<td>2.0-1.0</td>
<td>0.5-0.25</td>
<td>0.10-0.05</td>
</tr>
<tr>
<td>content (%)</td>
<td>0.3-0.6</td>
<td>15.5-46.0</td>
<td>18.7-81.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The distribution of particle size was analyzed by the pipette method (SSSA, 1986).
Table 2. Characteristics of Silawa soil

<table>
<thead>
<tr>
<th>Surface area(a) (m(^2) g(^{-1}))</th>
<th>Organic carbon(b) (%)</th>
<th>Fe(II)(c) (mg g(^{-1}))</th>
<th>Fe(III)(c) (mg g(^{-1}))</th>
<th>Reductive capacity for Cr(VI)(d) (μeq g(^{-1}))</th>
<th>pH(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.0 (11.7)(f)</td>
<td>0.69</td>
<td>0.5 (1.2)(f)</td>
<td>5.76 (5.06)(f)</td>
<td>0.38 (6.69)(f)</td>
<td>6.1</td>
</tr>
</tbody>
</table>

\(a\) Specific surface areas of soil minerals and soil were measured by the ethylene glycol monoethyl ether (EGME) method (SSSA, 1986).

\(b\) Organic carbon content was determined by dry combustion method (SSSA, 1996).

\(c\) Fe(II) and total iron in soil were measured by modified 1, 10-phenanthroline method (Amonette and Templeton, 1998). A reducing agent (10% hydroxylamine) was added to measure total iron. Fe(III) in soil was determined by subtracting Fe(II) from total iron.

\(d\) Reductive capacities of soil for Cr(VI) were measured by a standard method developed by Lee et al. (Lee et al., 2000).

\(e\) Standard soil analysis method was used to measure the pH of the soil. Deionized water was added to the soil (mass ratio = 1:1) and equilibrated for 1 day (SSSA, 1996).

\(f\) Values in parentheses have been measured after pretreatment of soil with dithionite.

Table 3. Partition coefficients and \(R^2\) values for linear regressions

<table>
<thead>
<tr>
<th>Target organic</th>
<th>(k_p) (L kg(^{-1}))</th>
<th>(k_{oc}) (L kg(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>1.73</td>
<td>250</td>
<td>0.998</td>
</tr>
<tr>
<td>TCE</td>
<td>0.91</td>
<td>130</td>
<td>0.990</td>
</tr>
<tr>
<td>c-DCE</td>
<td>0.61</td>
<td>89</td>
<td>0.915</td>
</tr>
<tr>
<td>VC</td>
<td>0.49</td>
<td>66</td>
<td>0.926</td>
</tr>
</tbody>
</table>
Table 4. Partitioning factor and kinetic parameters of chlorinated ethylenes in the soil suspensions

<table>
<thead>
<tr>
<th>reductant</th>
<th>target organic</th>
<th>p&lt;sub&gt;CE&lt;/sub&gt;</th>
<th>K&lt;sup&gt;c&lt;/sup&gt; (mM&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>C&lt;sup&gt;0&lt;/sup&gt;RC (mM)</th>
<th>k&lt;sup&gt;d&lt;/sup&gt; (day&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>R&lt;sup&gt;2b&lt;/sup&gt; (%)</th>
<th>S&lt;sub&gt;R&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; (µmol g&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>C&lt;sub&gt;E&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>PCE</td>
<td>1.38</td>
<td>3.36 (±4.1%)</td>
<td>0.073 (±5.2%)</td>
<td>2.26 (±4.7%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.972</td>
<td>0.348</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>TCE</td>
<td>1.21</td>
<td>1.89 (±8.2%)</td>
<td>0.058 (±8.2%)</td>
<td>1.42 (±11%)</td>
<td>0.833</td>
<td>0.276</td>
<td>0.829</td>
</tr>
<tr>
<td></td>
<td>c-DCE</td>
<td>1.14</td>
<td>1.49 (±11.3%)</td>
<td>0.033 (±9.1%)</td>
<td>1.18 (±16%)</td>
<td>0.806</td>
<td>0.157</td>
<td>0.471</td>
</tr>
<tr>
<td></td>
<td>VC</td>
<td>1.13</td>
<td>0.30 (±9.4%)</td>
<td>0.057 (±10%)</td>
<td>0.055 (±8.9%)</td>
<td>0.912</td>
<td>0.271</td>
<td>0.814</td>
</tr>
<tr>
<td>dithionite</td>
<td>PCE</td>
<td>1.39</td>
<td>4.02 (±3.3%)</td>
<td>0.075 (±4.8%)</td>
<td>2.60 (±3.2%)</td>
<td>0.982</td>
<td>0.357</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>TCE</td>
<td>1.21</td>
<td>3.58 (±7.1%)</td>
<td>0.059 (±6.1%)</td>
<td>1.57 (±6.7%)</td>
<td>0.956</td>
<td>0.281</td>
<td>0.843</td>
</tr>
<tr>
<td></td>
<td>c-DCE</td>
<td>1.15</td>
<td>1.32 (±10.7%)</td>
<td>0.036 (±8.4%)</td>
<td>1.30 (±12.6%)</td>
<td>0.816</td>
<td>0.171</td>
<td>0.514</td>
</tr>
<tr>
<td></td>
<td>VC</td>
<td>1.13</td>
<td>0.31 (±8.1%)</td>
<td>0.083 (±11%)</td>
<td>0.15 (±11%)</td>
<td>0.851</td>
<td>0.395</td>
<td>1.19</td>
</tr>
</tbody>
</table>

<sup>a</sup> Uncertainties represent 95% confidence intervals expressed in %.
<sup>b</sup> R<sup>2</sup> values of non-linear regression for kinetic parameters.
<sup>c</sup> Specific initial reductive capacity of soil for target organic (S<sub>R</sub>) = C<sup>0</sup>RC / soil concentration.
<sup>d</sup> Equivalent concentration of target organic (C<sub>E</sub>) that could be reduced at porosity = 0.45 and bulk density of soil = 1.35 g cm<sup>-3</sup>.