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Reductive Capacity of Natural Reductants

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Reductive capacities of soil minerals and soil for Cr(VI) and chlorinated ethylenes were measured and characterized to provide basic knowledge for in-situ and ex-situ treatment using these natural reductants. The reductive capacities of iron-bearing sulfide (pyrite), hydroxide (green rust; GR_{SO4}), and oxide (magnetite) minerals for Cr(VI) and tetrachloroethylene (PCE) were 1−3 orders of magnitude greater than those of iron-bearing phyllosilicates (biotite, vermiculite, and montmorillonite). The reductive capacities of surface soil collected from the plains of central Texas were similar and slightly greater than those of iron-bearing phyllosilicates. The reductive capacity of iron-bearing soil minerals for Cr(VI) was roughly 3−16 times greater than that for PCE, implying that Cr(VI) is more susceptible to being reduced by soil minerals than is PCE. GR_{SO4} has the greatest reductive capacity for both Cr(VI) and PCE followed by magnetite, pyrite, biotite, montmorillonite, and vermiculite. This order was the same for both target compounds, which indicates that the relative reductive capacities of soil minerals are consistent. The reductive capacities of pyrite and GR_{SO4} for chlorinated ethylenes decreased in the order: trichloroethylene (TCE) > PCE > *cis*-dichloroethylene (c-DCE) > vinyl chloride (VC). Fe(II) content in soil minerals was directly proportional to the reductive capacity of soil minerals for Cr(VI) and PCE, suggesting that Fe(II) content is an important factor that significantly affects reductive transformations of target contaminants in natural systems.

Introduction

A number of anthropogenic chemicals that have contaminated soil and water resources are relatively susceptible to reductive transformation in natural environments (*1*−*3*). It has been shown that chlorinated solvents (*4*−*8*), organochlorine and carbamate pesticides (*3*, *9*−*14*), and nitroaromatic compounds (*15*−*18*) are reductively degraded in natural and artificially induced reducing environments. Inorganic contaminants such as chromium (*19*−*21*), arsenic (*22*, *23*), and nitrate (*24*, *25*) and nuclear wastes such as uranium (*26*) and plutonium (*27*) have also been reported to undergo reductive transformations.

Redox reactions play a crucial role in the mobility, transport, and fate of both inorganic and organic contaminants in natural and engineered systems because they can convert contaminants among different oxidation states that have different transport characteristics. For example, hexavalent chromium (Cr(VI)) can be converted to the less mobile and less toxic trivalent form (Cr(III)) by suboxic aquifer materials (*19*). PCE, one of the most common chlorinated solvents found in contaminated environments, can be reductively transformed by microbial processes to more toxic daughter compounds such as TCE, dichloroethylenes (DCEs), VC, or to harmless C_2 hydrocarbons (*28*). Many effective and cost-efficient remedial technologies have been developed that are based on redox chemistry. Natural attenuation and in-situ redox manipulation (*28*, *29*) are examples of attractive remediation techniques because they transform contaminants using natural reductants and indigenous microorganisms. The natural reductants can cause abiotic reductive degradation without extensive changes at the contaminated site. Some of the most abundant natural reductants are soil minerals that contain reduced forms of iron and sulfur. Such soil minerals can significantly increase the transformation rate of chlorinated organics in heterogeneous suspension with HS^- and Fe(II) and can also reductively transform organic and inorganic contaminants by themselves (*7*, *24*, *30*−*33*).

The term “reductive capacity” has been used in different ways to describe systems in which redox reactions occur. One approach is to define the reductive capacity analogously to the definition of buffer capacity, i.e., the derivative of the concentration of reductant with respect to E_h (*34*). As such, this definition measures the extent to which the redox potential is buffered in a system. An alternative is to define reductive capacity as the amount of an oxidant that can be reduced when sufficient time is given so that the reaction proceeds to its maximum extent. This definition is similar to that of reductive strength (*35*, *36*). However, this definition describes the potential amount of reduction achievable in a system and is attractive for use in remediation activities, so it is the definition that will be used in this paper.

Barcelona and Holm suggested that the oxidative and reductive capacity of soils could be related to the concentrations of labile chemicals in the soil (*37*). Heron et al. introduced Ti^{3+}−ethylenediaminetetraacetic acid extraction method for the determination of the oxidation capacity of aquifer sediments (*38*). Kozuh and Schara developed a method for rapid characterization of soil reductive capacity using electron paramagnetic resonance (EPR) spectroscopy (*39*). Fruchter et al. used the capability of reduced soil to consume oxygen as a measure of its reductive capacity with respect to chromium (*29*). Lee et al. developed a standard procedure to test the reductive capacity of soil for Cr(VI) by measuring the amount of Cr(VI) reduced per unit mass of soil (*40*). The reductive capacity of soil for Cr(VI) may provide an estimate of the reductive capacity of soil for other target contaminants. Knowing the reductive capacity of soil minerals for a variety of target contaminants would be useful for developing remedial technologies based on redox reactions by providing a means to estimate the potential for contaminant transformation. It could also improve understanding of transformation mechanisms, particularly identifying biotic and abiotic processes. However, no significant efforts have been made to measure and characterize the reductive capacity of soil minerals for various target contaminants. The objectives of this research were to measure and compare reductive capacities of natural reductants for different types of chemical compounds and to identify factors that significantly affect them. Six soil minerals (pyrite, GR_{SO4}, magnetite, biotite, vermiculite, and montmorillonite) and soil (Silawa soil) were chosen for study because of their importance in

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TABLE 1. Characteristics of Soil Minerals

soil minerals	formula	iron content[a] (Fe(II)/Fe(III), (mg/g))	surface area[b] (m^2/g)	pH_{pzc}	particle size (μm)
pyrite	FeS_2	94.8/120	27.8	1.2−2.5[c]	63−250
green rust (GR_{SO4})	$Fe^{II}{}_4Fe^{III}{}_2(OH)_{12}SO_4 \cdot yH_2O$	464/212	86.3	na[d]	<63
magnetite	Fe_3O_4	206/516	57.2	6.4−6.9[e]	<63
biotite	$K(Mg,Fe^{2+})_3(Si_3Al)O_{10}(OH)_2$	114/3.1	1.9	na	63−250
vermiculite	$Mg_{0.33}(Mg,Al,Fe^{3+})_3(Si_3Al)O_{10}(OH)_2$	14.2/42.5	26.7	na	63−250
montmorillonite	$Na_x[(Al_{2-x}Mg_x)Si_4O_{10}(OH)_2]$	1.2/6.3	488	2.5[f]	<63

[a] The extraction method is explained in analytical procedures. [b] Surface area measured by ethylene glycol monoethyl ether (EGME) method. [c] Ref *4*. [d] na, not available. [e] Ref *55*. [f] Ref *56*.

TABLE 2. Characteristics of Silawa Soil

Section A: Particle Size Distribution

	sand					sand total	silt	silt total	clay	clay total
size (mm)	2.0−1.0	1.0−0.5	0.5−0.25	0.25−0.10	0.10−0.05	2.0−0.05	0.02−0.002	0.05−0.002	<0.0002	<0.002
content (%)	0.3	0.6	15.5	46.0	18.7	81.1	5.5	12.2	3.7	6.7

Section B: Characteristics

surface area (m^2/g)[a]	organic carbon (%)	Fe(II) (mg/g)	Fe(III) (mg/g)	pH[b]
11.67	0.69	1.2	5.06	6.1

[a] Surface area measured by EGME method. [b] Ref *57*.

natural environments. Cr(VI) and a series of chlorinated ethylenes (PCE, TCE, c-DCE, and VC) were chosen as oxidants for this research.

Experimental Section

Anaerobic Environments. To simulate anaerobic conditions in natural reducing environments, all reagents and samples were prepared in an anaerobic chamber (Coy Laboratory Products Inc.) containing a mixed gas atmosphere (95% nitrogen and 5% hydrogen). A colorimetric redox indicator solution (resazurin, 89%, Aldrich) was used to ensure that anaerobic conditions were maintained (*8*). The solution is colorless when the redox potential is less than ∼218 mV at pH 9 but turns pink as the redox potential (oxygen level) increases (*41*). Aqueous solutions and chemicals sensitive to redox reaction were deoxygenated in an airlock (Coy Laboratory Products Inc.) and kept in the anaerobic chamber.

Chemicals. Hexavalent chromium and chlorinated organics used as target compounds were ACS or higher grades. These included K_2CrO_4 (99%, Sigma), PCE (99.9%, Sigma), TCE (99.6%, Sigma), c-DCE, (97.0%, Sigma), *trans*-dichloroethylene (t-DCE, 98%, Sigma), 1,1-dichloroethylene (1,1-DCE, 99.0%, Sigma), and VC (20,000 mg/L, Sigma). Ethane, ethylene, and acetylene (99.0%, 1.0%, and 1000 mg/L, respectively) were purchased from Scott Specialty Gases and used as standard gases for the analysis of non-chlorinated daughter products. Stock solutions (1 M) of PCE, TCE, c-DCE, and VC were prepared by diluting them in methanol (99.8%, HPLC grade, EM). Deaerated deionized water (ddw) was prepared by deoxygenating 18 $M\Omega \cdot cm$ deionized water with 99.99% nitrogen for 2 h and then by deoxygenating with the mixed gases in the anaerobic chamber for 12 h. A stock solution of dithionite (0.1 M) was prepared from $Na_2S_2O_4$ (88%, Sigma) and used within 2 days. A buffer solution (10 mM) was prepared from $NaHCO_3$ (100.3%, Sigma).

Preparation of Soil Minerals and Soil. Pyrite (Zacatecas, Mexico), biotite (Bancroft, Canada), and vermiculite (Transvaal, Africa) were purchased from Ward's (Rochester, NY), and montmorillonite (Gonzales, TX) was obtained from the Clay Minerals Society (Columbia, MO). Pyrite was ground with ceramic mortar and pestle, and biotite and vermiculite were ground with a grinder in the anaerobic chamber. Pyrite (30 g) was then washed with 30 mL of 1 M HCl twice for 2 min and rinsed with 60 mL of ddw several times until the pH of the supernatant was greater than 6.7 in order to remove oxidized material from its surface. Each 30-g portion of clay mineral (biotite, vermiculite, and montmorillonite) was pretreated with 200 mL of 0.1 M dithionite solution for 4 days and rinsed several times with 200 mL of ddw to remove residual dithionite. The pretreatment with dithionite provided a method of converting oxidized components of the minerals to their reduced forms so that the full reductive capacity of the soil minerals could be measured (*40*). GR_{SO4} was prepared by a method modified by Koch and Hansen (*25*). The dark blue-green precipitates synthesized were washed several times with ddw until no Fe(II) was detected in the supernatant. Magnetite was synthesized by modifying the method developed by Taylor et al. (*42*). The black precipitates formed were washed several times with ddw to remove Fe(II). The soil minerals were then freeze-dried, dry-sieved, and stored in the anaerobic chamber, except GR_{SO4} which was dried in the chamber. Two size fractions (63−250 and <63 μm) were used for this research.

Samples of a Silawa soil were collected from a ranch at Texas A&M University, College Station, TX. The soil is an alluvium of the Brazos River and is classified as siliceous, semi-active, thermic, and fine loamy sand (Alfisols) (*43*). The samples were dried in the air for 14 days and screened with a 0.425-mm sieve. The soil samples (120 g) were equilibrated with the anaerobic atmosphere for 2 days and reduced by 250 mL of 0.1 M dithionite solutions for 4 days (*40*). The pretreated soil samples were washed several times with ddw to remove residual dithionite (*40*) and were dried and stored in the anaerobic chamber. All soil minerals and soil prepared were used for experiments no later than 7 days after pretreatment and synthesis to preclude an aging effect (*4*) on reductive degradation of target compounds. Some characteristics of soil minerals and soil used for this research are summarized in Tables 1 and 2.

Experimental Procedures. Reductive capacities for Cr(VI) of soil minerals and soil were measured by modifying the basic procedure for measuring soil reductive capacity that was developed by Lee et al. (*40*). The effect of Cr(VI) contact time was investigated for soil minerals and soil used for this research. Amber borosilicate glass vials (nominally 20 mL, Kimble) with an open-top screw cap and three-layered septum system (2 mil PTFE film (Norton Performance Plastics Co.), lead foil (3M), and PTFE film lined rubber septum (Kimble)) were used as batch reactors for the measurement of reductive capacity. The reactor was originally designed to prevent oxidation of the sample by intrusion of oxygen from air and to minimize loss of volatile organic compounds by volatilization. It has been reported to keep anaerobic conditions for over 2 months (*43*). The recoveries of target compounds in controls in this research exceeded 98% at each sampling time. The vials were introduced into the anaerobic chamber and equilibrated with anaerobic atmosphere for 2 days to remove oxygen sorbed on their surfaces. Soil minerals and soil (1 g) were weighed and transferred to vials. An aliquot (10 mL) of Cr(VI) solution with 10 mM $NaHCO_3$ was then added to each vial while in the chamber. The mass ratio of solid to water was 0.1 (g/g). The concentration of Cr(VI) solution was approximately twice the expected reductive capacity of each soil mineral and soil. A 51.5 mM Cr(VI) solution was used to measure the reductive capacities of pyrite, green rust, and magnetite, and a 2.57 mM Cr(VI) solution was used to measure the reductive capacities of iron-bearing phyllosilicates and soil. The pH values of the soil mineral and soil suspensions were adjusted to 7 by adding H_2SO_4 and NaOH solutions (1.0 M). Control samples were prepared as the same manner without soil minerals and soil. The batch reactors were tightly capped, taken out of the anaerobic chamber, mounted on a tumbler, and then completely mixed at 7 rpm at room temperature (22 ± 0.5 °C). After contact with Cr(VI), the vials were introduced into the anaerobic chamber, and 0.142 g of Na_2SO_4 was added to result in 0.1 M sulfate. The vials were taken out of the chamber and completely mixed for 1 day to promote desorption of Cr(VI) from soil mineral and soil surfaces (*19*, *40*) and centrifuged at 2800*g* for 10 min. The supernatant was filtered through a 0.2-μm membrane filter (Whatman), and Cr(VI) concentration of filtered supernatant was measured colorimetrically. All soil mineral and soil samples and their controls were prepared in duplicate inside the anaerobic chamber.

Experiments were conducted to measure reductive capacities of soil minerals and soil for chlorinated ethylenes. Preliminary experiments were conducted to determine the contact time required to ensure complete reaction with the target organic. Batch experiments were then conducted to determine the extent of degradation of target organics and production of transformation products. All soil mineral and soil samples and controls (without soil minerals and soil) for these experiments were prepared in duplicate inside the anaerobic chamber. After equilibration of 20-mL amber vials with anaerobic atmosphere, weighed soil minerals and soil were transferred to vials and 10 mM $NaHCO_3$ solution was added, generally resulting in a mass solid/liquid ratio of 0.1. A mass ratio of 0.007 was used for GR_{SO4} because its reductive capacity was expected to be higher than those of other materials. The pH values of the suspensions were adjusted to 7 with H_2SO_4 and NaOH solutions (1.0 M). Batch evaluations started by spiking stock solutions of target organics to soil mineral and soil suspensions. Vials were rapidly capped, taken out of the anaerobic chamber, and mounted on the tumbler at 7 rpm for complete mixing. Target organics and transformation products sorbed on the solid phases and in aqueous solution were monitored at each sampling time.

Analytical Procedures. Both chromium (Cr(VI)) and iron (Fe(II) and total iron) were determined by spectroscopic analysis using a Hewlett-Packard (HP) 8452A diode-array spectrophotometer. Cr(VI) concentration in aqueous solution was measured using the colorimetric reagent, diphenylcarbazide, at a wavelength of 542 nm (*44*). Iron contents of soil minerals were measured after acid extraction with a colorimetric procedure using 1,10-phenanthroline at a wavelength of 562 nm (*45*, *46*). A 10% solution of hydroxylamine was added to the acid extractant to reduce Fe(III) to Fe(II) for the measurement of total iron content. The ferrozine method (*47*) was also used as an alternative method to measure Fe(II) and total iron concentrations in aqueous solution.

Target chlorinated ethylenes and their transformation products were measured by gas chromatographic analysis. PCE, TCE, DCEs, and VC were measured by a HP G1800A GCD system with a DB-VRX column (60 m × 0.25 mm i.d. × 1.8 μm film thickness, J&W Scientific) and an electron ionization mass spectrometer detector. The temperature of the injection port was 230 °C, and the temperature of detector was 300 °C. The oven temperature was isothermal at 80 °C for 8 min, increased to 160 °C at the rate of 20 °C/min, and then held for 2 min. Batch reactors were centrifuged to separate aqueous and solid phases at 2800*g* for 30 min. A 4-mL sample of supernatant was rapidly withdrawn with a 10-mL gastight syringe (Hamilton) and transferred to an 8-mL extraction vial (Kimble) with 2 mL of extractant (pentane with 0.22 mM toluene). Supernatant in the reactors was removed, and 10 mL of extractant was added to extract target organics and transformation products sorbed on soil minerals. Both vials for extraction were mounted on an orbital shaker and shaken for 30 min at 250 rpm. A 1-μL portion of extractant was automatically introduced into split/splitless injection port at a split ratio of 30:1.

Non-chlorinated transformation products were analyzed by a HP 6890 GC with a GS-alumina column (30 m × 0.53 mm i.d., J&W Scientific) and a flame ionization detector. The temperatures of split/splitless injection port and detector were both 150 °C, and the temperature of oven was isothermal at 100 °C. A 10-mL sample of supernatant was rapidly transferred with a 10-mL gastight syringe to a 20-mL amber vial. The vial was tightly capped after the addition of sample, shaken for 1 h at 250 rpm, and allowed to stand for 2 h in order to equilibrate the aqueous and gas phases. A gas-phase sample of 50−100 μL was withdrawn from the headspace with a 100-μL gastight syringe (Hamilton) and introduced into the injection port at a split ratio of 5:1. The concentrations of C_2 hydrocarbons in aqueous solution were calculated using dimensionless Henry's law constants at room temperature (20.4, ethane; 8.7, ethylene; 1.1, acetylene) (*48*, *49*).

Results and Discussion

Development of Test Methods. Optimal Cr(VI) contact time with soil minerals and Silawa soil was determined by measuring the reduction rate of Cr(VI) until it dropped to a level where it could not be statistically distinguished from zero. The optimal contact time for pyrite, GR_{SO4}, and magnetite to achieve maximum Cr(VI) reduction was 1 day and that for iron-bearing phyllosilicates (biotite, vermiculite, and montmorillonite) and Silawa soil was 4 days (see Figure S-1, Supporting Information). A Cr(VI) contact time of 4 days was chosen for all solids. Reductive capacity of soil minerals and soil for Cr(VI) was determined by dividing the difference between the equivalents of Cr(VI) originally added and that remaining after extraction by the mass of solids present. This approach assumes that all Cr(VI) that is removed was reduced to Cr(III).

The amounts of chlorinated organics reduced as functions of time were measured in preliminary experiments in which the concentrations of target organics were monitored in both aqueous and solid phases. Optimal contact times of target organics were determined by applying the same technique

TABLE 3. Optimal Contact Times of Target Organics and Distribution of Transformation Products Relative to Initial Target Compound in Pyrite and Green Rust (GR_{SO4}) Suspensions

type of minerals	target organics	contact time[a] (day)	transformation products	distribution[b] (%)
pyrite	PCE	40.6	TCE	4.0
			C_2H_2	28.0
			C_2H_4	6.0
	TCE	32.3	c-DCE	3.3
			C_2H_2	40.0
			C_2H_4	2.2
	c-DCE	39.4	C_2H_2	12.0
			C_2H_4	5.0
	VC	32.4	C_2H_4	31.7
			C_2H_6	5.9
green rust (GR_{SO4})	PCE	40.5	C_2H_2	5.6
			C_2H_4	0.7
	TCE	31.6	C_2H_2	8.5
			C_2H_4	1.0
	c-DCE	40.8	C_2H_2	1.1
			C_2H_4	7.1
			C_2H_6	1.6
	VC	40.8	C_2H_4	24.7
			C_2H_6	1.2

[a] All inference tests were conducted in the range of 95% confidence level under *t*-distribution. [b] Relative to initial target compound and based on the mass recovery (as %) of transformation products at optimal contact times.

described above. Batch experiments were then conducted to measure the concentrations of target organics and transformation products sorbed on solids and in aqueous solution at each optimal contact time, which were used to calculate the reductive capacity for target organics. Reductive capacity of soil minerals and soil for target organic was determined as the difference between the initial concentration of target organic and the sum of concentrations of target organic and all transformation products measured in aqueous solution and on solids at the optimal contact time, all expressed as electron equivalents relative to ethane (PCE, 10 equiv/mol; TCE, 8 equiv/mol; DCEs, 6 equiv/mol; VC, 4 equiv/mol; ethylene, 2 equiv/mol). The difference was divided by the mass of solids in batch reactors.

Table 3 summarizes the optimal contact times of target organics and transformation product distribution in pyrite and GR_{SO4} suspensions. The major transformation product was acetylene rather than DCEs and VC, which are more often found as products of biotic dechlorination. This suggests that the major transformation pathway may be reductive elimination. This result is consistent with the results of other abiotic reductive dechlorination studies by Sivavec and Horney (*30*) and Butler (*7*). TCE and c-DCE were observed as minor transformation products when PCE and TCE were degraded by pyrite, but they were not observed in experiments with green rust suspensions. Accumulation of DCEs and VC was not observed in either mineral suspension. The distribution of transformation products of c-DCE was different in each mineral suspension. More c-DCE was transformed to acetylene than ethylene in pyrite suspension (see Figure S-2, Supporting Information). However acetylene, ethylene, and ethane were evenly produced in green rust suspension. In the case of VC degradation, ethylene was the main transformation product with a low concentration of ethane observed.

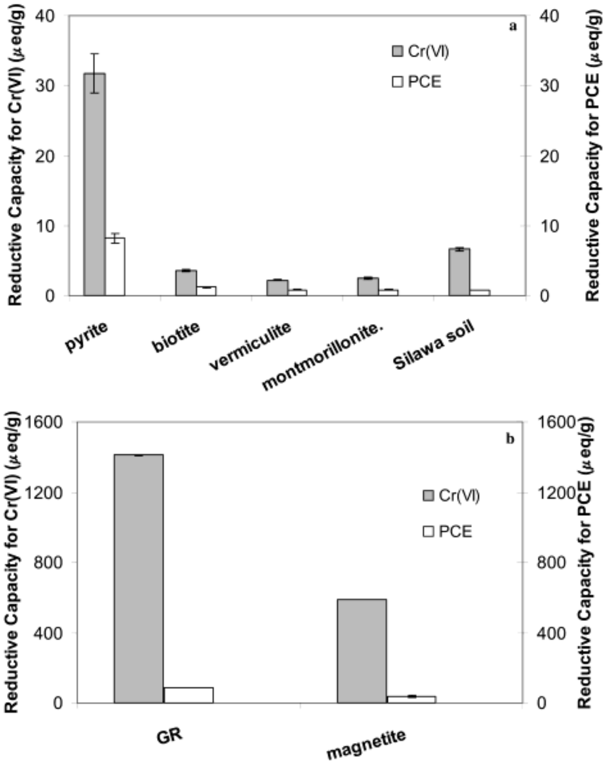

FIGURE 1. Reductive capacities of soil minerals and soil for target inorganic (Cr(VI)) and organic (PCE). Error bars represent the ranges of observed reductive capacities. Some error bars are not shown because of their small values.

Measurement of Reductive Capacity. The measured reductive capacities of soil minerals and soil for Cr(VI) and PCE are represented in Figure 1. The reductive capacities of GR_{SO4} and magnetite are shown with a different scale (Figure 1b) because their reductive capacities are substantially higher than others. Duplicate analyses for reductive capacity of soil minerals and Silawa soil for Cr(VI) are fairly consistent and reproducible as shown in Figure 1. The relative standard deviations (RSD) of the reductive capacities are less than 4.7%, except for pyrite (9.0%). This implies that the heterogeneity of soil minerals and soil does not significantly affect measurement of the reductive capacity for Cr(VI). Reductive capacities for Cr(VI) of pyrite, GR_{SO4}, and magnetite are roughly 1−3 orders of magnitude greater than those of iron-bearing phyllosilicates. This result may be due to the lower levels of iron in the phyllosilicates, which had 1−3 orders of magnitude less iron than iron-bearing sulfides, hydroxides, and oxides. Reductive capacity of pyrite for Cr(VI) was surprisingly low as compared to that of GR_{SO4} and magnetite. This is not compatible with other studies that have emphasized the reactivity of pyrite (*31*, *50*). This may be explained by the low content of Fe(II) and Fe(III) (94.8 and 120.3 mg/g, respectively) in the pyrite used for this experiment. The measured iron content of pyrite was less than 50% of the iron that should be present, which may be due to the incomplete dissolution of iron during the acid extraction. This suggests that there could be some iron in the pyrite that is not dissolved by acid and is unavailable for the reduction of Cr(VI). Although Fe(II) content in Silawa soil was 2 orders of magnitude lower than that in biotite, its reductive capacity (6.7 μequiv/g) was 1.9 times greater than that of biotite. This may be caused by high reactivity of reduced natural organic matter (NOM) in Silawa soil pretreated with dithionite. It has been reported that NOM acts as a redox catalyst in electron-transfer reaction and accelerates the reductive transformation of target contaminants in reducing environments (*15*, *16*, *51*).

The duplicate analyses for reductive capacity of soil minerals and Silawa soil for PCE were reasonably consistent and reproducible as shown in Figure 1. RSD of the measured reductive capacity for PCE was less than 8.8%, which is similar

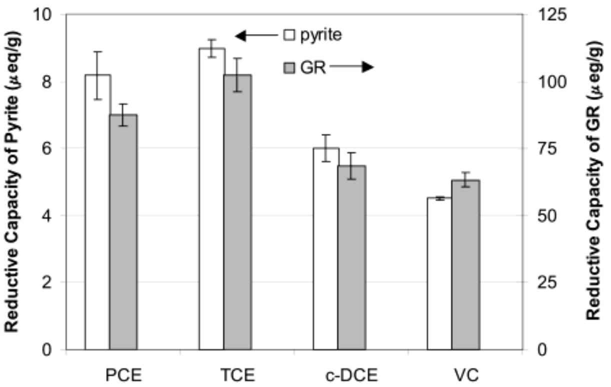

FIGURE 2. Reductive capacities of pyrite and GR_{SO4} for a series of chlorinated ethylenes. Error bars represent the ranges of observed reductive capacities.

to that for Cr(VI). Pyrite, GR_{SO4}, and magnetite have 1 or 2 orders of magnitude higher reductive capacity for PCE than iron-bearing phyllosilicates. Reductive capacity of pyrite for PCE was still lower than that of GR_{SO4} and magnetite. The reductive capacity of Silawa soil for PCE (0.80 μequiv/g) was similar to that of the iron-bearing phyllosilicates. The trends in these results are similar to those observed with Cr(VI) as target except that the reductive capacity of Silawa soil for PCE was about the same as that of iron-bearing phyllosilicates.

Discussion. Reductive capacities of soil minerals and soil for inorganic and organic contaminants can be compared in Figure 1 for the two targets. The reductive capacity of soil minerals for Cr(VI) was 3−16 times greater than that for PCE, which indicates that Cr(VI) is more susceptible to the reduction by soil minerals than PCE. GR_{SO4} has the greatest reductive capacity for Cr(VI) and PCE followed by magnetite, pyrite, biotite, montmorillonite, and vermiculite. A consistent relationship was observed for the relative reductive capacities of soil minerals for Cr(VI) and PCE. This suggests that the reductive capacities of soil minerals for either Cr(VI) or PCE could be used as representative values for representing the reducing power of soil minerals. The relationship between reductive capacities of soil minerals for Cr(VI) and PCE was examined so that one measurement could predict the other:

$$RC_{PCE} = 0.0622 \times RC_{Cr(VI)} \quad (r^2 = 0.993) \tag{1}$$

where RC_{PCE} and $RC_{Cr(VI)}$ represent reductive capacities of soil minerals for PCE and Cr(VI) in μequiv/g.

The reductive capacities of pyrite and GR_{SO4} for a series of chlorinated ethylenes (PCE, TCE, c-DCE, and VC) are compared in Figure 2. RSD of reductive capacities of duplicate pyrite and GR_{SO4} samples for target organics was less than 8.8%. The reductive capacity of GR_{SO4} for target organics was approximately 1 order of magnitude greater than that of pyrite. This may be due to the higher content of reactive compound (Fe(II)) in GR_{SO4}. Fe(II) content in GR_{SO4} was 5 times greater than that in natural pyrite. Pyrite and GR_{SO4} show a trend in the order of magnitude of reductive capacities for target organics. In both cases, the order of reductive capacities for target organics was TCE > PCE > c-DCE > VC. The reductive capacities of pyrite and GR_{SO4} for TCE were greater than those for PCE. This is very interesting because PCE is more highly oxidized than TCE; therefore, it would be more susceptible to reductive dechlorination than TCE (*52*). The similar trends in the higher susceptibility of TCE have been also observed in the reductive dechlorination kinetics of PCE and TCE by zerovalent metals (*53*) and iron sulfide (*54*).

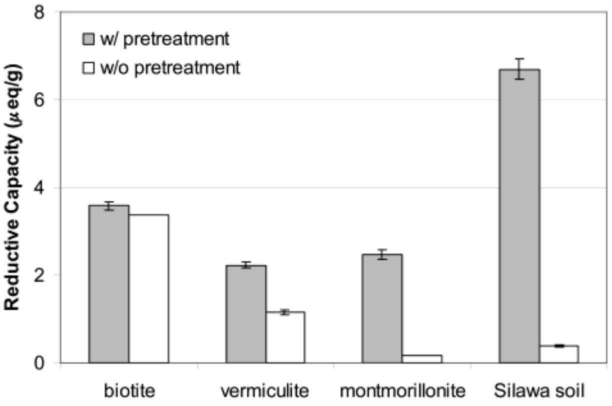

FIGURE 3. Reductive capacities for Cr(VI) for iron-bearing phyllosilicates and Silawa soil with and without dithionite pretreatment. Error bars represent the ranges of observed reductive capacities. Some error bars are not shown because of their small values.

Reductive capacities for Cr(VI) of iron-bearing phyllosilicates and Silawa soil with and without dithionite pretreatment are shown in Figure 3. Duplicate analyses for the reductive capacity without pretreatment were fairly reproducible with a RSD less than 4.8%. The reductive capacity of pretreated phyllosilicates and Silawa soil for Cr(VI) was greater than the reductive capacity of the same samples without pretreatment, but the extent of the difference varied among the solids. Pretreatment with dithionite increased the content of Fe(II) in biotite, vermiculite, montmorillonite, and Silawa soil (1.8, 12.7, 350, and 140% increase in Fe(II) content, respectively). However, it also resulted in slight dissolution (<10%) of structural Fe(II) in biotite, vermiculite, and Silawa soil. The relatively slight increase of Fe(II) content combined with the loss of Fe(II) could be a possible cause for the relatively small increase of reductive capacity of biotite and vermiculite after pretreatment. In contrast, the reductive capacity of pretreated montmorillonite and Silawa soil for Cr(VI) was 15.8 and 17.7 times greater than that of montmorillonite and Silawa soil without pretreatment, respectively. The content of Fe(II) in montmorillonite was quadrupled after dithionite pretreatment, and no dissolution of structural Fe(II) was observed. This may explain the robust increase of reductive capacity of montmorillonite after the pretreatment. Pretreated Silawa soil showed the greatest increase in reductive capacity, although the increase of Fe(II) content after pretreatment was smaller than that observed in montmorillonite and a slight loss of Fe(II) was observed. The large increase in reductive capacity after pretreatment may be due to the additional effect of reduced NOM. Except in biotite, most of the structural iron in phyllosilicates and soil was present as Fe(III), and this form was still dominant after the pretreatment. Less than 24% of initial Fe(III) was reduced to Fe(II) by the pretreatment, and the Fe(II) content stayed between 0.7 and 1.6 mg/g.

Figure 4 shows that the reductive capacities for PCE and Cr(VI) for different groups of soil minerals are directly proportional to Fe(II) contents, regardless of the soil mineral type. The correlation factors (*r*) of linear regression lines are significant in 95% confidence limit, indicating that Fe(II) content significantly affects the reductive capacity of soil minerals. The linear relationships between reductive capacity of all soil minerals and Fe(II) content are well-described by the following regression equations:

$$RC_{Cr(VI)} = 160.33 \times \{Fe(II)\} \quad (r^2 = 0.936) \tag{2}$$

$$RC_{PCE} = 10.00 \times \{Fe(II)\} \quad (r^2 = 0.9332) \tag{3}$$

where {Fe(II)} is Fe(II) content in soil minerals in mequiv/g. However, the slopes indicate that only 16% of the Fe(II) is able to reduce Cr(VI) and that only 1% of the Fe(II) is able

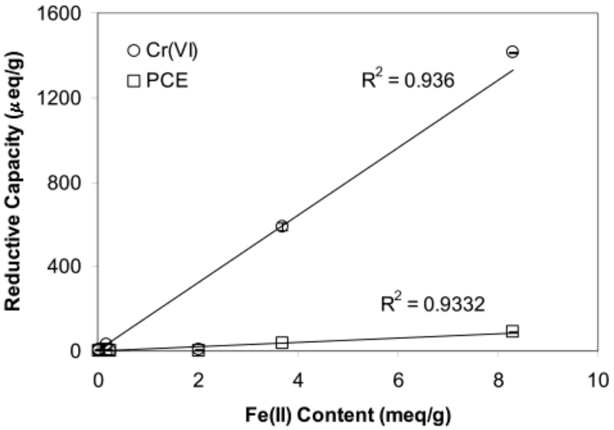

FIGURE 4. Linear relationship between the reductive capacity of iron-bearing soil minerals and Fe(II) content. Some error bars are not shown because of their small values.

to reduce PCE. This result suggests that all Fe(II) in the soil minerals cannot be used for the reduction of target compounds and that the reactivities of Fe(II) sites are different and specific to the target compounds. The reductive capacities of soil minerals predicted by these regression equations are in good accordance with the measured reductive capacities of soil minerals except for those of biotite and vermiculite. The measured reductive capacities of biotite and vermiculite were overestimated by at least 1 order of magnitude by the regression equations. This indicates that Fe(II) in these minerals may not be as reactive as that in other soil minerals tested. The correlation between the reductive capacity of soil mineral and Fe(II) content observed in this research suggests that Fe(II) is an important and reactive compound in soil minerals for the reductive transformation of target compounds. It would provide an approximate estimation to predict and evaluate the potentials of natural reductants that could be applied to the remedial technologies such as natural attenuation and in-situ redox manipulation.

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Supporting Information Available

Two graphs showing the effect of Cr(VI) contact time on the reduction of Cr(VI) and reductive transformation of c-DCE by pyrite. This material is available free of charge via the Internet at http://pubs.acs.org.

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