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Reduction Kinetics of Hexavalent Chromium in Soils and Its Correlation with Soil Properties

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The toxicity of chromium (Cr) to biota is related to its chemical forms and consequently to the redox conditions of soils. Hexavalent Cr [Cr(VI)] may undergo natural attenuation through reduction processes. In this study, the reduction kinetics of Cr(VI) in seven soils and its relationships with soil properties were investigated with laboratory incubation experiments. The results indicate that the reduction of Cr(VI) can be described by a first-order reaction. The reduction rates of Cr(VI) in the seven soils decreased in the order: Udic Ferrisols > Stagnic Anthrosols > Calcaric Regosols > Mollisol > Typic Haplustalf > Periudic Argosols > Ustic Cambosols. Simple correlation analysis revealed that the reduction of Cr(VI) in soils was positively related to organic matter content, dissolved organic matter content, Fe(II) content, clay fraction, and to the diversity index of the bacterial community but negatively correlated with easily reducible Mn content. Using stepwise regression, the reduction of Cr(VI) in soil could be quantitatively predicted by the measurement of dissolved organic matter content, Fe(II) content, pH, and soil particle size distribution, with a fitting level of 95.5%. The results indicated that the reduction of Cr(VI) in natural soils is not controlled by a single soil property but is the result of the combined effects of dissolved organic matter, Fe(II), pH, and soil particle size distribution.

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Chromium (Cr) is a natural element in the earth's crust and occurs in soils at concentrations of 10 to 150 mg kg^{-1} (Adriano, 2001). Anthropogenic sources, including ore refining, electroplating industry, tanning, paper making, steel production, and automobile manufacturing, contribute greatly to Cr pollution in the environment (Zayed and Terry, 2003). The lack of appropriate disposal facilities has led to severe Cr pollution in water and soils throughout the world (Loyaux-Lawniczak et al., 2001).

In the natural environment, the most stable forms of Cr are trivalent Cr [Cr(III)] and hexavalent Cr [Cr(VI)] (Rai et al., 1987). Trivalent Cr is generally considered nonbioavailable due to its low solubility in water at a normal pH range (4–9) (Rai et al., 1987). Trivalent Cr is an essential trace element for mammals (Dayan and Paine, 2001). In contrast, Cr(VI) exists as the following highly soluble oxyanionic species: CrO_4^{2-} (chromate), $HCrO_4^-$ (bichromate), and $Cr_2O_7^{2-}$ (dichromate) (Kozuh et al., 2000). Hexavalent Cr is highly toxic and is a known human carcinogen (Costa and Klein, 2006). The chemistry of naturally occurring Cr and its compounds added to the soil is important because it influences plant uptake and animal and human nutrition.

Reduction of Cr(VI) to Cr(III) is an effective means of Cr immobilization in soil (Banks et al., 2006). The reduction-oxidation of Cr depends largely on soil properties, such as organic matter (OM) (Banks et al., 2006), Fe(II)-bearing minerals (Buerge and Hug, 1997), Mn(II) (Li et al., 2007), Mn(IV) oxides (Kozuh et al., 2000), and pH (Kozuh et al., 2000). Bioreduction of Cr(VI) can occur directly as a result of microbial metabolism (enzymatic) or indirectly, mediated by a bacterial metabolite (such as H_2S) (Losi et al., 1994). However, the influence of soil properties on Cr(VI) reduction is not fully understood due to the lack of systematic studies.

The present work evaluated the influence of soil properties (OM, dissolved organic matter [DOM], Fe(II), Mn(II), easily reducible Mn [Mn(ER)], pH, particle size distribution (PSD), cation exchange capacity [CEC], and diversity of soil bacterial community) on Cr(VI) reduction in soils simultaneously by

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Abbreviations:CEC, cation exchange capacity; DGGE, denaturing gradient gel electrophoresis; DOM, dissolved organic matter; Mn(ER), easily reducible Mn; PSD, particle size distribution; OM, organic matter.

simple correlation and stepwise multiple regression analysis. The objectives of this study were (i) to investigate the kinetics of Cr(VI) reduction in representative soils under controlled soil moisture and temperature in the laboratory, (ii) to determine the relative importance of direct and indirect effects of soil physicochemical and biological properties on Cr(VI) reduction, and (iii) to establish a model for predicting Cr(VI) reduction in soils based on key soil properties.

Materials and Methods

Soil Samples

Seven representative soils were used in this study: Udic Ferrisols, Typic Haplustalf, Periudic Argosols, Calcaric Regosols, Stagnic Anthrosols, Mollisol, and Ustic Cambosols, respectively collected (0–20 cm in depth) from Guilin City (104°40′–119°45′E, 24°18′–25°41′N), Zhanjiang City (110°08′–110°77′E, 20°33′–21°62′N), Huzhou City (119°68′–120°43′E, 30°53′–31°02′N), Ya'an City (102°37′–103°12′E, 29°23′–30°37′N), Jiaxing City (120°7′–121°02′E, 30°5′–30°77′N), Ha'erbing City (126°32′–129°55′E, 44°92′–46°32′N), and Qufu City (116°51′–117°13′E, 35°29′–35°49′N), China. Before the incubation study, soil samples were analyzed for total Cr (Shentu et al., 2008), Cr(VI) (James et al., 1995), pH (Chaturvedi and Sankar, 2006), CEC (Hendershot and Duquette, 1986), OM content (Rashid et al., 2001), DOM content (Jones and Willett, 2006), PSD (Day, 1965), and microbial community structure (described below). The soil samples were analyzed for Fe(II) content (Schnell et al., 1998), Mn(II) content (Schnell et al., 1998), and Mn(ER) content (Jarvis, 1984) and were conducted under the same conditions as for the Cr(VI) reduction experiments except for the absence of Cr(VI).

Microbial Community Analysis

Soil DNAs from approximately 0.5 g of soil were extracted using an Ultra High Purity DNA Isolation Kit for Soil (MoBio Laboratories). The resolution of extracts in a 1% agarose gel containing ethidium bromide (0.3 μg mL^{-1}) was used to estimate the DNA quantity and quality. The V3 region of 16S rDNA was amplified using the primer 357F (5′-CCTACGGGAGGCAGCAG-3′) with a GC clamp (5′-CGCCCGCCGCGCGCGGCG-GGCGGGGCGGGGGCACGGGGGG-3′) attached to the 5′ end and primer 518R (5′-ATTACCGCGGCTGCTGG-3′) (Muyzer et al., 1993). Polymerase chain reaction analyses were performed following the method of Nakatsu et al. (2005). The product was purified using a TIANgel Midi Purification Kit (TIANGEN) and applied to denaturing gradient gel electrophoresis (DGGE) (Bio-Rad Laboratories, Inc.).

Approximately 400 ng of purified polymerase chain reaction product was loaded onto an 8% (w/v) polyacrylamide gel, with denaturing gradients ranging from 20 to 50% (100% denaturant contains 7 mol L^{-1} urea and 40% formamide). Denaturing gradient gel electrophoresis was conducted in 1× TAE buffer (pH 8.0) at 60°C for 5 h at a constant voltage of 200 V. After electrophoresis, gels were stained with SYBR GREEN I (Sigma) for 30 min following the manufacturer's instructions. Cluster analysis of DGGE band patterns was performed using the Neighbor Joining cluster method with Quantity One image analysis software (Version 4.62, Bio-Rad). The Shannon index was used to estimate soil bacterial diversity based on the intensity and number of bands using the following equation:

$$\text{Shannon index} = -\Sigma(n_i/N)\ln(n_i/N)$$

where n_i is the peak height of the band i, i is the number of bands in each DGGE gel profile, and N is the sum of peak heights in a given DGGE gel profile.

Incubation Experiments

A spiking solution was prepared by dissolving $K_2Cr_2O_7$ (purity >98%) (Aldrich Chemical Co.) in ultrapure water to give a concentration of 1 g Cr(VI) L^{-1}. Fresh soil samples (100 g oven-dry basis) were spiked with 10 mL of the spiking solution and mixed thoroughly, giving an initial concentration of 100 mg Cr(VI) kg^{-1} soil. The soil samples were incubated at 25°C in the incubator (14D-78532) and kept under constant moisture throughout the experiment by periodic watering. Portions of moist soil (5 g, oven-dry basis) were sampled for the determination of Cr(VI) and Fe(II) at 1, 3, 7, 14, 21, and 28 d after addition. The watering and sampling processes were conducted inside an anaerobic glove box (Coy Scientific Products) (Guha et al., 2003; Wang et al., 2008). The soil samples were stored in sealed plastic containers at 4°C immediately after collection and until analysis (Hopp et al., 2008). Three replicate samples were used for each soil analysis.

Determination of Hexavalent Chromium

Extraction and analysis of soil samples for Cr(VI) were conducted based on modified USEPA Method 3060A (James et al., 1995). Fresh soils (2.5 g) were digested with 50 mL 0.28 mol L^{-1} Na_2CO_3/0.5 mol L^{-1} NaOH in a 250-mL digestion vessel. The solutions were heated at 95°C for 60 min with continuous stirring. After cooling, the digested suspension was filtered, and the filter cake was washed twice with 5 mL digesting solution. The filtrates were acidified with nitric acid to a pH of 7 to 8 and then diluted to 100 mL with deionized water. The concentrations of Cr in the solutions were analyzed using an Inductively Coupled Plasma Optical Emission Spectrometer (iCAP 6300, Thermo Fisher). Experiments on Cr(VI) recovery were performed by adding known concentrations of Cr(VI) standards (10 and 100 mg kg^{-1}) to Cr(VI)-free soil. The recovery of spiked Cr(VI) was 93.5 ± 2.9% and 96.3 ± 4.7%, respectively.

Statistical Analysis

Means of data were compared by LSD tests at the 5% significance level. Reduction data for Cr(VI) (time course for ln[Cr(VI)]) were described by a linear model ($C = C_0 - Kt$, where C is concentration after time t, C_0 is the apparent initial concentration, and K is the rate constant). Linear correlations between K and all measured properties were tested using Pearson's r with a $P < 0.05$ significance threshold. Stepwise multiple linear regression analysis was used to identify the significant soil variables, which could be used to fit a model of estimating Cr reduction rate. In correlation and regression analysis, all parameters except pH and Shannon index were Log_{10} transformed to ensure homogeneity of variances. All statistical

Table 1. Physical, chemical, and biological characteristics of the soils.

Soil	Periudic Argosols	Udic Ferrisols	Calcaric Regosols	Stagnic Anthrosols	Mollisol	Typic Haplustalf	Ustic Cambosols
Chromium							
Total Cr, mg kg^{-1}	30.17	68.53	58.02	56.80	65.54	63.22	35.76
Cr(VI), mg kg^{-1}	0.23	0.46	0.22	0.35	0.53	0.34	0.21
Chemical characteristics†							
pH	5.37	5.03	8.25	6.49	7.23	4.56	7.80
OM, g kg^{-1}	11.56	19.08	21.80	21.40	32.19	10.28	7.54
DOM, mg kg^{-1}	86.94	207.7	155.4	167.7	246.2	96.71	75.16
CEC, cmol$_c$ (+) kg^{-1}	12.63	17.33	25.47	20.20	34.00	8.33	15.80
Fe(II), mg kg^{-1}	34.33	71.19	30.20	49.11	32.51	27.49	27.59
Mn(II), mg kg^{-1}	54.89	15.85	76.44	38.85	12.71	40.85	2.95
Mn(ER), mg kg^{-1}	133.7	2.64	263.6	230.6	109.2	308.6	139.6
Soil texture							
Sand, %	24.8	10.6	31.6	11.4	20.6	37.4	21.6
Silt, %	58.2	39.8	44.0	73.0	60.2	40.8	65.4
Clay, %	17.0	49.6	24.4	15.6	19.2	21.8	13.0
Microbial characteristic							
Shannon index	2.00	2.36	1.88	2.02	1.76	1.82	1.51

† CEC, cation exchange capacity; DOM, dissolved organic matter; Mn(ER), easily reducible Mn; OM, organic matter.

calculations were performed using SPSS 18.0 for Windows (CoHort Software) (SPSS, 2010).

Results

Soil Properties

There were significant differences in properties influencing the reduction of Cr(VI) among the seven soils (Table 1). The concentrations of Cr(VI) in all the studied soils were very low, ranging from 0.21 mg kg^{-1} for the Ustic Cambosols to 0.53 mg kg^{-1} for the Mollisol, whereas total Cr concentrations (background value) in the soils ranged from 30.17 to 68.53 mg kg^{-1}.

Soil pH ranged from 4.56 for the Typic Haplustalf to 8.25 for the Calcaric Regosols (i.e., strong acid to mild alkaline), total OM content ranged from 7.54 g kg^{-1} for the Ustic Cambosols to 32.19 g kg^{-1} for the Mollisol, DOM content ranged from 75.16 mg kg^{-1} for the Ustic Cambosols to 246.2 mg kg^{-1} for the Mollisol, and CEC ranged from 8.33 cmol kg^{-1} for the Typic Haplustalf to 34.00 cmol kg^{-1} for the Mollisol. The Fe(II), Mn(II), and Mn(ER) contents were the lowest in the Typic Haplustalf (27.49 mg kg^{-1}), Ustic Cambosols (2.95 mg kg^{-1}), and Udic Ferrisols (2.64 mg kg^{-1}), respectively. The highest values were found in the Udic Ferrisols (71.19 mg kg^{-1}), Calcaric Regosols (76.44 mg kg^{-1}), and Typic Haplustalf (308.6 mg kg^{-1}), respectively. The clay and silt fractions of all soils were relatively high, ranging from 13.0% for the Ustic Cambosols to 49.6% for the Udic Ferrisols and from 39.8% for the Udic Ferrisols to 73.0% for the Stagnic Anthrosols, respectively.

Denaturing gradient gel electrophoresis profiles of the soil bacterial community profiles are shown in Fig. 1. The Shannon index was used to interpret the diversity of bacterial communities. The Ustic Cambosols had the lowest Shannon index (1.51), and Udic Ferrisols had the highest Shannon index (2.36).

Reduction Processes of Hexavalent Chromium in Soil

Extractable Cr(VI) in soil decreased significantly with increasing incubation time (Fig. 2A). The reduction of Cr(VI) was rapid at the beginning (1–3 d after application) and slower thereafter. Three days after the application of Cr(VI), 7.0 to 72.3% of applied Cr(VI) was reduced. At the end of the

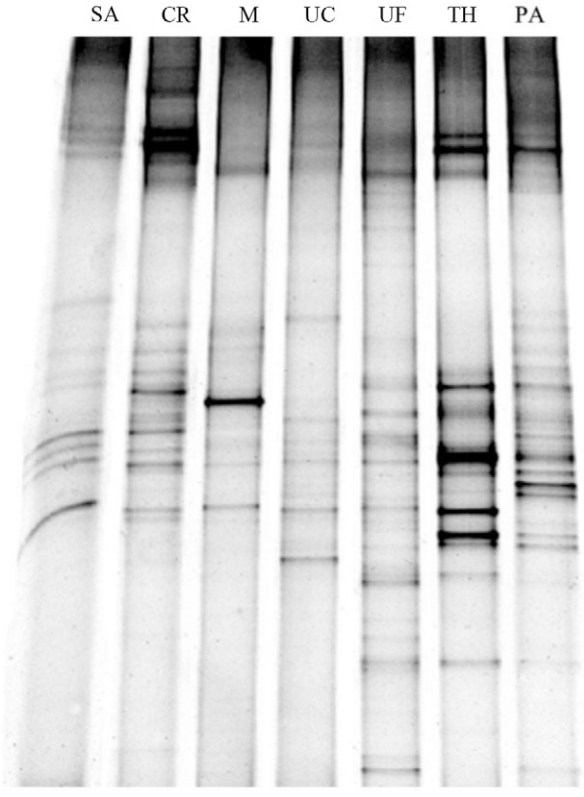

Fig. 1. Denaturing gradient gel electrophoresis profiles of the soil bacterial 16S rRNA fragments amplified with the primer set 357F-GC/518R. CR, Calcaric Regosols; M, Mollisol; PA, Periudic Argosols; SA, Stagnic Anthrosols; TH, Typic Haplustalf; UC, Ustic Cambosols; UF, Udic Ferrisols.

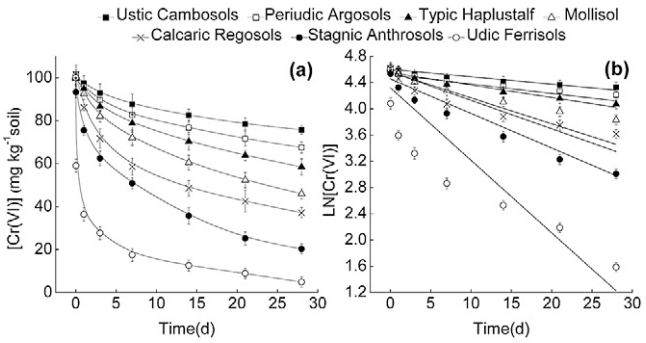

Fig. 2. Time courses for hexavalent chromium [Cr(VI)] after addition of 100 mg kg^{-1} Cr(VI) to seven soils. (a) Dissolved Cr(VI). (b) First-order plots of ln[Cr(VI)]. The slope of the lines is equal to the first-order rate constant. Vertical scales are different.

incubation experiment (28 d), the extractable residues of spiked Cr(VI) in the soils fell to 4.9 to 75.8% of the applied amount. The percentage of Cr(VI) reduced in soil after 28 d incubation varied substantially among the soils and decreased in the following order: Udic Ferrisols (95.1%) > Stagnic Anthrosols (79.7%) > Calcaric Regosols (62.8%) > Mollisol (50.0%) > Typic Haplustalf (41.5%) > Periudic Argosols (32.4%) > Ustic Cambosols (24.2%).

The reduction kinetic curves (plots of ln(C) [Cr(VI)] versus time) are shown in Fig. 2B, and their linearity seems to indicate that the Cr(VI) reduction in the soils follows a first-order reaction. The decreasing trend of extractable Cr(VI) over time could be well described by the kinetic equations, with correlation coefficients ranging from 0.76 to 0.98 (P < 0.01) (Table 2). The first-order constants (C_0, K) summarized in Table 2 were determined from the least-square linear regression of first-order plots of lnC [Cr(VI)] as a function of time (C_0 refers to apparent initial concentration, and K refers to rate constant). The reduction rate for Cr(VI) among all soils conformed to an order of Udic Ferrisols > Stagnic Anthrosols > Calcaric Regosols > Mollisol > Typic Haplustalf > Periudic Argosols > Ustic Cambosols.

Table 2. Fitted linear regressions of time courses for ln(C) [Cr(VI)] in the form of $C = C_0 - Kt$, where C refers to concentration after time t, C_0 refers to apparent initial concentration, and K refers to rate constant.

Soil	C_0	K	R^2	P value
Ustic Cambosols	4.60	0.01131	0.9578	0.000**
Periudic Argosols	4.53	0.01433	0.7933	0.002**
Typic Haplustalf	4.55	0.01897	0.9604	0.000**
Mollisol	4.56	0.03942	0.9081	0.000**
Calcaric Regosols	4.56	0.04335	0.9385	0.000**
Stagnic Anthrosols	4.46	0.05263	0.9766	0.000**
Udic Ferrisols	4.32	0.11056	0.7610	0.003**

** Significant at the 0.01 probability level.

The Relationship between Hexavalent Chromium Reduction and Soil Properties

Simple correlation analysis was performed to obtain a measure of the effect of different soil properties on Cr(VI) reduction, and the correlation coefficients for Cr(VI) reduction rate constant (K) and soil parameters are summarized in Table 3. The coefficients showed a significant (P < 0.01) positive correlation between Cr(VI) reduction and DOM; a significant (P < 0.05) positive correlation between Cr(VI) reduction and total OM, Fe(II), clay fraction, and Shannon index; and a negative (P < 0.05) correlation between Cr(VI) reduction and Mn(ER). Values for pH, CEC, Mn(II), sand, and silt fractions did not yield strong correlations with the Cr(VI) reduction trend.

Further evaluation of the relationship between the Cr(VI) reduction kinetics and soil properties was conducted using stepwise regression analysis (Table 4). According to correlation analysis and previous studies (Eary and Rai, 1987; Kozuh et al., 2000), five independent variables (DOM, Fe(II), clay content, pH, and Shannon index) were included in the multiple regression analysis. Out of the five variables measured, four were extracted by stepwise multiple regression as being significant. The extracted variables included DOM, Fe(II), pH, and clay fractions. Both coefficients of multiple correlation and partial regression reached at least the 0.05 statistically significant level.

Table 3. Pearson coefficients of linear correlation between hexavalent chromium reduction rate constant (K) from first-order reaction and selected soil physical, chemical, and biological characteristics.†

	pH	OM‡	DOM‡	CEC‡	Fe(II)	Mn(II)	Mn(ER)‡	Sand	Silt	Clay	SI‡
OM	0.233										
DOM	0.110	0.949**									
CEC	0.713	0.802*	0.734								
Fe(II)	−0.382	0.384	0.551	0.144							
Mn(II)	−0.270	0.305	0.126	−0.121	0.054						
Mn(ER)	0.355	−0.316	−0.559	−0.152	−0.887**	0.193					
Sand	0.099	−0.349	−0.501	−0.324	−0.878**	0.274	0.733				
Silt	0.420	−0.008	−0.124	0.305	−0.133	−0.347	0.370	−0.308			
Clay	−0.409	0.346	0.531	0.030	0.656	0.199	−0.826*	−0.289	−0.804*		
SI	−0.564	0.383	0.482	−0.029	0.883**	0.450	−0.763*	−0.568	−0.428	0.777*	
K‡	−0.086	0.762*	0.879**	0.481	0.801*	0.223	−0.761*	−0.635	−0.330	0.756*	0.756*

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

† Selected soil physical, chemical, and microbial characteristics (except pH and Shannon index) were Log_{10} transformed to ensure homogeneity of variances.

‡ CEC, cation exchange capacity; DOM, dissolved organic matter; Mn(ER), easily reducible Mn; OM, organic matter; SI, Shannon index; K, hexavalent chromium reduction rate constant.

Table 4. Stepwise regression models for predicting hexavalent chromium reduction rate based on soil characteristics.

Stepwise regression model	*F* value†	*T* value of the partial regression coefficient	
K = −5.656 + 0.882DOM + 0.881Fe(II) + 0.530clay content + 0.031pH	10.630* (0.955)†	DOM‡	7.254** (0.854)
		Fe(II)	5.654* (0.772)
		clay content	4.262* (0.678)
		pH	3.403* (0.515)

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

† Values in parentheses are R^2 values.

‡ Dissolved organic matter.

Discussion

Although the incubation conditions were the same, the contrasting reduction rates of Cr(VI) were observed in the different soils studied. As shown in Table 1, pH, OM, DOM, CEC, Fe(II), Mn(II), Mn(ER), PSD, and Shannon index differed considerably among the soils. Thus, the variations in reduction of Cr(VI) during the incubation period might be ascribed to the differences in the composition and properties of the tested soils.

The results of stepwise regression were distinctly different from those obtained with simple correlation analysis. The parameter of Shannon index, which showed a significant correlation with Cr(VI) reduction in simple correlation analysis, could not be screened into the stepwise regression equations. The reduction of Cr(VI) may influence the diversity of the soil bacterial community (Nakatsu et al., 2005), and the change of soil bacterial community may influence soil DOM content (Ogawa et al., 2001) and consequent reduction of Cr(VI) (Nakayasu et al., 1999); therefore, the reduction of Cr(VI) in soils was strongly correlated with the diversity index of soil bacterial community. Despite its strong correlation with Cr(VI) reduction, the contribution of Shannon index may be limited compared with the overall influence of soil on Cr(VI) reduction. Camargo et al. (2003) reported that chromium-resistant bacteria isolated from soils contaminated with dichromate can be used to remove toxic Cr(VI) from contaminated environments by reducing Cr(VI) to Cr(III). Therefore, it is supposed that chromium-resistant bacteria or chromium-reducing bacteria could be stimulated in response to the addition of Cr(VI) in soil, and, only in this case, the contribution of soil bacterial community on Cr(VI) reduction might be significant. pH, which is weakly related to Cr(VI) reduction in the simple correlations, showed a significant correlation with Cr(VI) reduction in the stepwise multiple regression. This disparity may be attributed to the combined effects of DOM, Fe(II), pH, and PSD on Cr(VI) reduction.

This hypothesis was confirmed by the results of path analysis (Table 5), which provides the values of direct and indirect path coefficients to indicate the relative importance of each soil property. Although the values of the indirect path coefficients were generally lower than those of the direct path, some of them were quite high, especially when it comes to the value of the pH→Fe(II)→Cr(VI) reduction rate. The values of clay content→DOM content→Cr(VI) reduction rate, clay content→Fe(II)→Cr(VI) reduction rate, and pH→clay content→Cr(VI) reduction rate were close to those of direct path coefficients (Table 5). The data elucidated the strong combination of pH together with Fe(II) and of clay fractions together with DOM, Fe(II), and pH to describe the reduction rate of Cr(VI). Therefore, it is reasonable to conclude that the reduction of Cr(VI) in soil is not controlled by a single soil property but is the result of the collective effects of many involved factors.

On the basis of the discussion above, we concluded that the reduction of Cr(VI) in natural soils is a complex process that is controlled by the combined effects of soil properties such as DOM, Fe(II), pH, and soil PSD. This finding is in agreement with previous reports (Banks et al., 2006; Buerge and Hug, 1997; Graham and Bouwer, 2010; Han et al., 2004; Kozuh et al., 2000; Li et al., 2007; Nakayasu et al., 1999; Qafoku et al., 2009). Dissolved organic matter, the most bioavailable fraction of soil OM, has been identified to facilitate the reduction of Cr(VI) to Cr(III) in soils (Jardine et al., 1999; Nakayasu et al., 1999). The hydroquinone groups of DOM were regarded as the major source of electron donor for the reduction of Cr(VI) to Cr(III) in soils (Elovitz and Fish, 1995). Also, the dissolved organic carbon fractions provide the energy source for the soil microorganisms involved in the reduction of Cr [i.e., Cr(VI) to Cr(III)] (Jardine et al., 1999). Regardless of the pH-dependent mechanisms, Cr(VI) reduction increased with increasing soil dissolved organic carbon (Bolan et al., 2003).

In addition to OM, Fe(II) is the most common reductant involved in the reduction of Cr(VI) in soil (James and Bartlett, 1983). The reaction between Cr(VI) and Fe(II) was evidenced by the simultaneous decreases of Cr(VI) and Fe(II) in soil (Fig. 2 and 3). Mineral phases that contain significant amounts of Fe(II), such as magnetite (Fe_3O_4), pyrite (FeS_2), and biotite (black mica), are known to reduce Cr(VI) (Peterson et al., 1997). Particulate Fe oxyhydroxides act as electron donors and release Fe(II) in the presence of organic ligands, and Fe(II) then reduces Cr(VI) to Cr(III) (Kozuh et al., 2000). Trivalent Cr can substitute for Fe(III); the resulting Cr(III) is likely to be incorporated into Fe(III) oxyhydroxides (Fendorf, 1995). Buerge and Hug (1998) have reported that Fe(II) promotes Cr(VI) reduction by natural organic material as a redox catalyst.

Table 5. The path coefficients of Equation K of the stepwise regression model.

	DOM†	Fe(II)	Clay content	pH
DOM	(0.502)‡	0.211	0.153	0.014
Fe(II)	0.277	(0.383)	0.189	−0.048
Clay content	0.264	0.250	(0.290)	−0.051
pH	0.055	−0.146	−0.119	(0.125)

† Dissolved organic matter.

‡ The data in the parentheses represent the direct effect, and the data outside the parentheses represent the indirect effect.

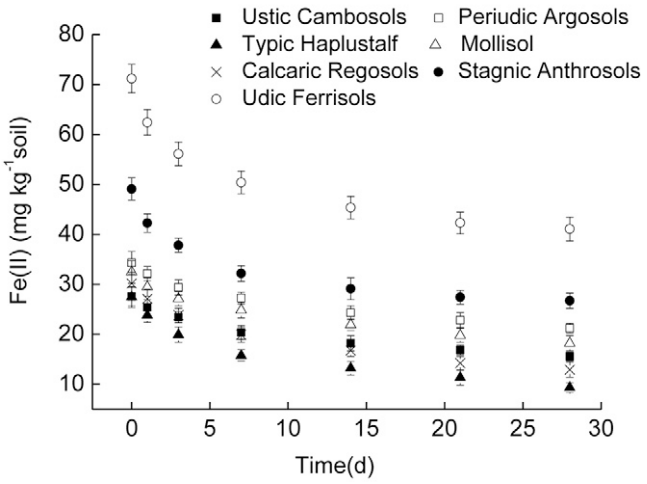

Fig. 3. Time courses for Fe(II) after addition of 100 mg kg^{-1} hexavalent Cr to seven soils.

pH level plays an important role in the environmental behavior of Cr(VI) by affecting the distribution of the Cr(VI) species. pH may enhance adsorption of $HCrO_4^-$ or increase rates of electron transfer for adsorbed $HCrO_4^-$ relative to adsorbed CrO_4^{2-}. Rates of Cr(VI) reduction by various organic reductants increase with decreasing pH due to increased protonation level of Cr(VI) species (Elovitz and Fish, 1994; Wittbrodt and Palmer, 1995). Previous researches have suggested that the enhanced rates of Cr(VI) reduction by Fe(II)-bearing minerals at a low pH are related to enhanced rates of minerals dissolution and to the reaction of Cr(VI) with dissolved Fe(II) (Eary and Rai, 1989).

Soil particles consist of different minerals with different chemical formulae, supplying the sites for most chemical, physical, and biological activities (Buffle and De Vitre, 1994). Although very few studies have reported the contribution of soil PSD to Cr(VI) reduction, Loyaux-Lawniczak et al. (2001) noted that the clay particles can be considered as the Cr-Fe–bearing phase in the finest fraction, suggesting the reaction between Cr(VI) and Fe(II) took place in the clay fraction, as evidenced by the strong combination of clay fractions together with Fe(II) in path analysis. Also, because clay content was correlated with Shannon index and reduction rate of Cr(VI) in this study, the functional groups on the surfaces of clay particles might enrich the diversity of the soil microbial community, thus promoting the reduction of Cr(VI). Kwok and Loh (2003) reported that the small particles, especially the clay fraction, resulted in large surface area-to-mass ratios to supply the sites for microbial activities.

The above results indicate that DOM, Fe(II), pH, and PSD have combined effects on Cr(VI) reduction kinetics. The Cr(VI) chemical characteristics and soil properties contribute to the complexity of Cr(VI) behavior in the soil system. Although the mechanistic understanding of the reduction processes of Cr(VI) is essential, the combination of correlation analysis and stepwise regressions provides a powerful analytical tool. Using the stepwise regression models obtained, Cr(VI) reduction could be well predicted by DOM, Fe(II), pH, and PSD, accounting for 95.5% of variance in the reduction rate of Cr(VI) in the soils. This demonstrates the reliability of the model. Therefore, this model may be useful for predicting Cr(VI) reduction in soil.

Conclusions

Hexavalent Cr may undergo natural attenuation through reduction processes. The reduction of Cr(VI) in the soils followed a first-order reaction. The reduction rates of Cr(VI) were strongly correlated with OM, DOM, Fe(II), Mn(ER), clay content, and the diversity index of the bacterial community. To quantify the reduction of Cr(VI) in natural soils, the effects of DOM, Fe(II), pH, and PSD—particularly their combined effects—need to be considered. The empirical model obtained from the stepwise regression analysis confirmed the findings of several investigators on the effects that soil properties exert on Cr(VI) environmental behavior in natural soils. Using this model, Cr(VI) reduction in the soils could be quantitatively predicted.

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