Environ. Sci. Technol. **2000**, *34,* 112−119

Reduction and Oxidation Processes of Chromium in Soils

N. KOŽUH,*,† J. ŠTUPAR,† AND B. GORENC‡

Jožef Stefan Institute, Jamova 39, P.O. Box 100, 1111 Ljubljana, Slovenia, and Department of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, 1000 Ljubljana, Slovenia

The kinetics of reduction and oxidation of soluble chromium in various soils (peat, clay, sand, and luvi-chromic cambisols) were studied at constant soil moisture and constant temperature. A total of 1500 g of each soil was incubated with different concentrations of aqueous solutions of $K_2Cr_2O_7$ or $CrCl_3$ [1−1000 μg (g of dry soil)$^{-1}$]. The total exchangeable chromium and Cr(VI) were analyzed in soil extracts over a period of up to 10 days. The parameters influencing the reduction and oxidation of soluble chromium were studied. Reduction of soluble chromium was observed in all the soils examined. It depends mostly on the content of organic matter, on the concentration of the added chromium, and on the pH of the soil. Up to 3 days of the experiment, the reaction was found to be first-order with respect to Cr(VI). Oxidation of soluble chromium was observed especially in soils high in manganese(IV) oxides and low in organic matter. The oxidation of added soluble chromium did not occur in peat soil. The results indicate that the oxidation and reduction of soluble chromium added to soils depends on the soil structure and on the reduction/oxidation conditions in the particular soil.

Introduction

The most stable oxidation states of chromium in the environment are Cr(III) and Cr(VI). The concentration and toxicity of soluble chromium and its mobility in aquatic and terrestrial environments depend on its oxidation state. The chemistry of naturally occurring chromium and various chromium compounds added to the soil is important as it influences plant uptake and animal and human nutrition.

Cr(VI) is more toxic and generally more mobile than Cr(III). Since under alkaline to slightly acidic conditions Cr(VI) compounds, i.e., CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$, are not strongly absorbed by many soils, they can be very mobile in surface environments. On the other hand, under these conditions Cr(III) readily precipitates as $Cr(OH)_3$ or as the solid solution $Fe_xCr_{1-x}(OH)_3$. It can also be chelated by organic molecules that are adsorbed to mineral surfaces (*1, 2*).

Cr(VI) can be reduced to Cr(III) in soils by redox reactions with aqueous inorganic species, electron transfer at mineral surfaces, reactions with nonhumic organic substances such as carbohydrates and proteins, or reduction by soil humic substances. The latter, which constitute the majority of the organic fraction in most soils, represent a significant reservoir of electron donors for Cr(VI) reduction.

Eary and Rai (*3*) reported on a rapid quantitative, stoichiometric reduction of aqueous Cr(VI) by aqueous Fe(II) in the pH range of 2.0−10.0, even in oxygenated solutions. At pH values higher than 10.0 and in alkaline phosphate solutions, the competitive oxidation of aqueous Fe(II) with dissolved oxygen results in a nonstoichiometric reduction of aqueous Cr(VI). However, another study showed that the reduction of Cr(VI) by organic matter and Fe(II) was equivalent with respect to total reduction capacity (*4*).

Several investigators (*5, 6*) have reported that Cr(VI) can be reduced in most soil systems, especially in soils high in organic matter. The presence of the organic matter spontaneously reduces Cr(VI) to Cr(III), even at pH values around and above neutrality. In addition to organic matter, Fe(II) and HS^- ions are the most common reductants involved in the reduction of Cr(VI) in aquatic and terrestrial environments (*6*).

On the basis of field and laboratory experiments, Kieber and Helz (*7*) proposed an indirect photoreduction of chromium adsorbed on clay particles by photoproduced Fe(II). Sunlight acts on the particulate iron oxyhydroxides, which act as electron donors and release Fe(II) in the presence of organic ligands. Fe(II) then reduces Cr(VI) to Cr(III).

The Fe(II,III)-mediated photochemical reduction of Cr(VI) was investigated in a laboratory study with oxalate and citrate at pH values from 3 to 7 by Hug et al. (*8*). They suggested that Fe(II,III) acts as a photocatalyst by transferring electrons from oxalate to Cr(VI) in a photocatalytic cycle. In this cycle, iron(III) oxide absorbs light whereby Fe(II) and radicals are produced. Fe(II) is reoxidized by Cr(VI), and Fe(III) recomplexes with oxalate. This reaction runs in a cycle until all the oxalate or Cr(VI) is consumed.

Buerge and Hug (*9*) have determined rate constants for Cr(VI) reduction by a series of Fe(II)−organic complexes. The authors extracted dissolved organic matter from the organic horizon of a forested Spodosol and found that the presence of organic ligands leads to soluble Cr(III) and Fe(III) complexes. It was concluded that the Cr(VI) reduction that has been observed in field studies is probably the result of the synergistic properties of Fe(II) and organic compounds. Fe(II) promotes Cr(VI) reduction by natural organic material by acting as a redox catalyst.

Wittbrodt and Plamer (*10, 11*) studied the rate of Cr(VI) reduction by a soil fulvic acid (SFA) (*10*) and by soil humic substances (SHS) (*11*) in aqueous solutions, where the temperature, ionic strength, background electrolyte, and concentration of Fe(III) and Cr(III) were independently varied. Rate experiments were conducted with an excess concentration of SFA and SHS with respect to Cr(VI). The rates of reduction were not significantly altered by changes in either ionic strength or background electrolyte. The presence of Cr(III) slightly inhibited the rate of reduction by SHS but not that by SFA. The latter effectively reduced Cr(VI) in aqueous solution in the 1−7 pH range. Cr(VI) reduction rate increased strongly with decreasing pH as well as with increasing concentrations of SFA and Cr(VI). The rate of reduction was found to be nonlinear and could not be described by either a simple first- or second-order rate equation (*11*). Only a small fraction of the SFA was oxidized during their experiments (<5%). The reduction of Cr(VI) by SFA and SHS increased with the addition of Fe(III). Fe was first reduced by the SHS and then oxidized by the Cr(VI) as a part of the redox cycle.

* Corresponding author present address: Institute of Physiology, Pharmacology, and Toxicology, Veterinary Faculty, Gergičeva 60, 1115 Ljubljana, Slovenia. Telephone: +386 61 1779 136; fax: +386 61 332 243; e-mail: KOZUHNE@mail.vf.uni-lj.si.

† Jožef Stefan Institute.

‡ University of Ljubljana.

10.1021/es981162m CCC: $19.00
Published on Web 11/25/1999

TABLE 1. Characteristics of the Investigated Soils

soil type	moisture (%)	pH of soil	TOC[a] (%)	SOM[b] (%)	soil particle diameter (μm)	exchangeable Cr (μg g^{-1})	total Cr (μg g^{-1})	exchangeable manganese(IV) oxides (μg g^{-1})
clay	22.0	7.3	1.52	6.8×10^{-5}	50−2, 53% <2, 17%	<5.0	57.7	399
peat	50.2	7.0	41.1	4.3×10^{-4}	most of particles <2	<5.0	57.3	60
sand	13.0	7.4	3.0	1.7×10^{-4}	most of particles 20−50 and <2	<2.5	48.8	150
cambisols	24.4	5.4	0.22	4.6×10^{-5}	2−20, 32% <2, 61%	<5.0	144	234

[a] Total organic carbon (TOC) determined by Walkley-Black method (*25*). [b] SOM, soluble organic matter.

Deng and Stone (*12, 13*) studied the catalytic effect of various oxide surfaces, i.e., TiO_2, Al_2O_3, and FeOOH, on the reduction of Cr(VI) by a number of low molecular weight organic compounds in the pH range from 3 to 7. It was suggested that a surface-catalyzed Cr(VI) reduction may occur in soils, sediments, aquifers, and other aquatic environments rich in mineral surfaces. Hydrous aluminum and Fe(III) are widespread in surface environments and, therefore, act as potential catalysts for the reduction of Cr(VI) by organic reductants.

Elovitz and Fish (*14*) studied the kinetics of the reduction of Cr(VI) to Cr(III) by substituted phenols in aqueous solution. They observed that, at fixed pH, the reaction was first-order with respect to both the concentration of phenol reductant and the total concentration of monomeric Cr(VI). In the pH range from 5 to 1, the reaction rates increased as much as 4 orders of magnitude.

Cary et al. (*15*) found out that the reduction of Cr(VI) is more rapid in acid than in alkaline soils and that soluble Cr(III) is rapidly transformed to its insoluble forms. It is characteristic of the formation of Cr(III) by reduction of Cr(VI) that it is partially adsorbed or precipitated in various soil mineral fractions or complexed as high molecular weight humic acid complexes (*16, 17*).

On the other hand, the oxidation of Cr(III) in soils is also possible especially in soil high in manganese(IV) oxides. The oxidation of aqueous Cr(III) by common naturally occurring forms of manganese oxide has been studied extensively (*18*−*20*). The concentration of aqueous Cr(III), pH, and available active surface were the main parameters controlling the degree of oxidation. The experiments performed by Eary and Rai (*20*) indicated that the extent of Cr(III) oxidation may be limited by the adsorption of anionic Cr(VI) in acidic solutions and by the adsorption and precipitation of various $Cr(OH)_x$ species in neutral to alkaline solutions. Beside the oxidation of aqueous Cr(III) added to soil, many investigators (*6, 1, 2, 21*) reported the complexation of Cr(III) with organic compounds present in the soil. This process may limit the extent of Cr(III) oxidation.

The aim of present work was to investigate the kinetics of aqueous Cr(VI) reduction in various soils (peat, clay, luvichromic cambisols, and sand) at constant soil moisture and temperature under laboratory conditions. The oxidation of aqueous Cr(III) was also investigated, and the reductive and oxidative capacity of soils for chromium were determined. The essential parameters influencing both processes were studied and discused in detail.

Experimental Section

Instrumentation. A Varian AA 575 atomic absorption spectrophotometer with an HGA Perkin-Elmer graphite furnace and a Varian AA 5 flame atomic absorption spectrophotometer were employed for the determination of total exchangeable chromium and Cr(VI) in soil extracts. A Varian Cary model 1650 spectrophotometer adjusted to a wavelength of 540 nm was used for the determination of Cr(VI) by the 1,5-diphenylcarbazide spectrophotometric method (*18, 22*).

An ion-pairing RP-HPLC equipped with a Merck-Hitachi 6200 intelligent pump, a 150 × 4.6 mm i.d in-house packed column (LiChrosorb RP-C_{18}, 5 μm particles), and a Rheodyne injector with a laboratory-built 5 cm^3 loop was used for the separation of the Cr(VI) in low concentration levels (<30 ng cm^{-3}) (*22*).

Soil extractions were performed in 38 cm^3 polyurethane tubes, with phase separation obtained by centrifugation using a Heraeus Sepatech Biofuge 17S.

A Dohrmann TOC analyzer (high temperature, combustion oxidation method) was used for the determination of soluble TOC in soil extracts (*23, 24*).

Reagents. Merck suprapure acids and doubly distilled water were used for preparing samples and standard solutions. All other chemicals were of analytical-reagent grade. Standard Cr(VI) (potassium dichromate) and Cr(III) [chromium(III) chloride] stock solutions (Cr, 1000 μg cm^{-3}) were used. KH_2PO_4 and Na_2HPO_4 was used for the buffer solution (0.15 mol dm^{-3}, pH 5.0−7.0) to extract the exchangeable chromium in soils.

Physicochemical Characteristics of Soils. To study the redox processes of chromium in soils, four typical soils [clay, peat, sand, and luvi-chromic cambisols (cambisols)] were collected from A horizon at different locations and were classified according to pedological parameters, i.e., texture, organic matter content, and total soluble carbon content.

Samples were stored in 30 dm^3 plastic vessels under atmospheric conditions. Several physical and chemical parameters were measured in these soils in parallel with the experiments. The results are summarized in Table 1. The parameters shown provide a wide variation of values between soils and are essential for determining the oxidation/reduction properties of soils. The original pH of the cambisols is around neutral values. The low pH value of the cambisols studied (5.4) originates from the rain washing of soil particles. The concentration of exchangeable chromium in all of the soils was below the detection limit (Table 1). The concentration of total chromium in soils was found to be from 48.8 μg g^{-1} in sand soil to 144 μg g^{-1} in cambisols. It is bound in sparingly soluble fractions of soils; therefore, it could not affect the analysis of the added soluble chromium.

Determination of Physicochemical Characteristics of Soils. Samples (25−30 g) of soil were dried at 60 °C for 12 h, and the moisture content (at the time of the sampling) was calculated from the weight loss. The pH was determined in a suspension of 10 g of soil in 10 cm^3 of water. The soil texture was determined by employing the sedimentary technique (*25*).

The Walkley-Black method (*25*) was introduced to determine the total organic carbon in soils. Total water-soluble organic carbon was determined in water soil extracts (50 g of moist soil with 50 cm^3 of distilled water) (*23, 24*) by employing a TOC analyzer (high temperature, combustion oxidation method). The total chromium and manganese in soil were determined by flame atomic absorption spectrometry after HNO_3, $HClO_4$, and HF digestion (*28*).

Determination of the Exchangeable Chromium and Chromium(VI). A total of 2.00 g of moist Cr-treated soil samples were shaken for 30 min with 20 cm^3 of 0.15 mol dm^{-3} KH_2PO_4/Na_2HPO_4 buffer solution, centrifuged for 20 min at 10 000 rpm and decanted. The pH of the KH_2PO_4/Na_2HPO_4 extractant was adjusted to the pH of the particular soil. Samples were then filtered through cellulose nitrate membrane filters (pore size 0.1 μm), and the concentration of exchangeable chromium was determined by flame or electrothermal atomic absorption spectrometry (*22*). Extractions were performed in duplicate at room temperature (295 $\pm$ 2 K). The phosphate buffer extraction procedure was found to be an appropriate method for determining exchangeable chromium in soils (*18, 22*).

Aliquots of these soil extracts were used for the determination of Cr(VI). Three different analytical techniques were employed for the determination of Cr(VI) in phosphate soil extracts: 1,5-diphenylcarbazide spectrophotometry (*18, 22*), ion-pairing reversed-phase high-performance liquid chromatography (RP-HPLC) combined with electrothermal atomic absorption spectrometry (ETAAS) (*22*), and extraction of Cr(VI)−HCl complex into methyl isobutyl ketone (MIBK) at 277 K by measuring of Cr(VI) in the organic phase immediately after the extraction by flame atomic absorption spectrometry (FAAS) (*27*).

Spectrophotometry was applicable for the determination of Cr(VI) in phosphate soil extracts in concentrations above 30 ng cm^{-3} (LOD = 30 ng cm^{-3}). RP-HPLC-ETAAS was used for determining Cr(VI) at very low concentrations (LOD = 0.3 ng cm^{-3}), while the extraction of Cr(VI)−HCl complex into MIBK at 277 K was appropriate for the determination of low concentrations of Cr(VI) in cambisols. RP-HPLC-ETAAS was found experimentally to be unsuitable for determining Cr(VI) in cambisols due to their low pH.

Determination of Exchangeable Mn(II) and Easily Reducible Mn(IV) in Soils. Ammonium acetate buffer solutions (1 mol dm^{-3}) at various pH values and Mg and Ca salts with and without hydroquinone (*18, 29*) have been proposed for determining exchangeable Mn(II) and easily reducible Mn(IV) in soils. The $MgSO_4$−hydroquinone extraction proposed by Bartlett and James (*18*) was used for determining easily reducible Mn(IV). It is the oxidized form of manganese involved in the oxidation of chromium in soils.

Two parallel extractions were performed. For the determination of extractable Mn(II) and easily exchangeable Mn(IV), 2.00 g of moist soil was shaken for 1 h with 20 cm^3 of extractant containing $MgSO_4$ (1 mol dm^{-3}) and hydroquinone (0.02 mol dm^{-3}) (1:1). The exchangeable Mn(II) was determined in a parallel extraction using 20 cm^3 of $MgSO_4$ (1 mol dm^{-3}) as an extractant. After centrifugation, extracts were filtered through 0.45-μm membrane filters. The concentration of manganese was measured by FAAS (N_2O−acetylene flame). The concentration of easily reducible Mn(IV) is given by the difference between the concentration of the manganese in both extracts.

Experiment Design. A total of 1500 g each of four moist soils (clay, peat, sand, and cambisols) was mixed with 200 cm^3 of an appropriate amount of aqueous solution of $CrCl_3$ or $K_2Cr_2O_7$, such that the final concentrations of added chromium in these soils were between 1.0 and 1000 μg g^{-1}. Duplicate samples were mixed using a plastic-coated metal mechanical stirring device to obtain a homogeneous thick paste. The latter was placed in a 2.0 dm^3 shallow plastic container to achieve rapid evaporation of excess water and left at constant temperature. The moisture of the soils was kept constant throughout the experiment by periodical watering. The 2.00-g samples of moist soil were taken for the determination of total exchangeable chromium and Cr(VI) over a time span of 1−10 days after addition.

Results and Discussion

Reduction Processes of Cr(VI) in Soils. *The Kinetics of Reduction of Cr(VI) in Soils.* The kinetics of reduction of soluble Cr(VI) added to the soil were studied in the peat, clay, sand, and cambisols. The concentrations of added Cr(VI) were 1, 10, 25, and 50 μg (g of dry soil)$^{-1}$. The results are presented in Figure 1. The reduction of soluble Cr(VI) was observed in all four soils investigated. The reactions are characterized by a nonlinear loss of the added soluble Cr(VI) with time. The decrease of the concentration of soluble Cr(VI) was rapid at the beginning (1−3 days after application) and much slower in the following days. The change of the reduction rate was probably due to the oxidation of a larger fraction of the most reactive organic matter. Another possible explanation could be the complexation of the organic matter with Cr(III) formed by reduction. Cr(III) could also form various $Cr(OH)_x$ species [in pH range of 3.8−11.5 (*30*)], which would occupy the organic matter and thus decrease its accessibility for further reduction of Cr(VI). Our observations correlate well with the results of Wittbrodt and Palmer (*10, 11*), who proposed that trivalent cations could affect the rate of reduction by binding portions of the humic materials into a complex, thus making them more resistant to oxidation (*11*).

The shape of the plots of ln (c/c_o) [Cr(VI)] versus time for the first 3 days of the experiment in Figure 2, panels A and B, and their linearity seems to indicate that the Cr(VI) reduction follows first-order reaction with respect to Cr(VI). From Figure 2A,B, it is also evident that after first 3 days of the experiment the overall data are not in agreement with first-order kinetics and need additional detailed investigations. The reaction rate of the reduction of Cr(VI) in soils depends on the concentration of several substances (electron donors). With respect to the concentrations of the added Cr(VI), the concentrations of these substances are sufficiently high and effectively constant during the reduction. The concentration of Cr(VI) changed appreciably during the reaction performed at constant moisture and temperature. Therefore, the reduction of Cr(VI) in soils up to 3 days of the experiment could be described as a pseudo-first-order reaction (*31*). Our findings are in good agreement with the results of other investigators (*29, 32*). Masscheleyn et al. (*29*) found that Cr(VI) removal from the soil was a first-order process and that in soils a with high reductive ability most of the Cr(VI), especially in low concentrations, was reduced after the first day.

The initial first-order rate constants for Cr(VI) (k_{exp}) summarized in Table 2 were determined from the least-squares linear regression of first-order plots of ln c/c_o [Cr(VI)] as a function of time. Since the initial rate of reduction is the highest in the peat soil and the lowest in the sand soil, it follows that it depends on the soil organic matter content and on the concentration of added soluble Cr(VI). The latter effect is especially pronounced for the soils low in organic matter content, i.e., clay, cambisols. On the other hand, the initial rate of reduction in the sand soil was found to be independent of the concentration of the added soluble Cr(VI).

On the basis of the results presented in Figure 1, it can be further concluded that, at higher concentrations of added soluble Cr(VI) (25, 50 μg g^{-1}) and especially in soils low in organic matter, the maximum concentration of the reduced Cr(VI) was achieved after 3 days. The concentration of soluble Cr(VI) in these soils remains practically constant.

Reduction Mechanisms of the Soluble Cr(VI) in Soils. On the basis of the experiments presented in Figure 1, the mechanism of reduction of the added soluble Cr(VI) in soils could not be explained. It can be only concluded that the reduction takes place rapidly in soils high in organic matter.

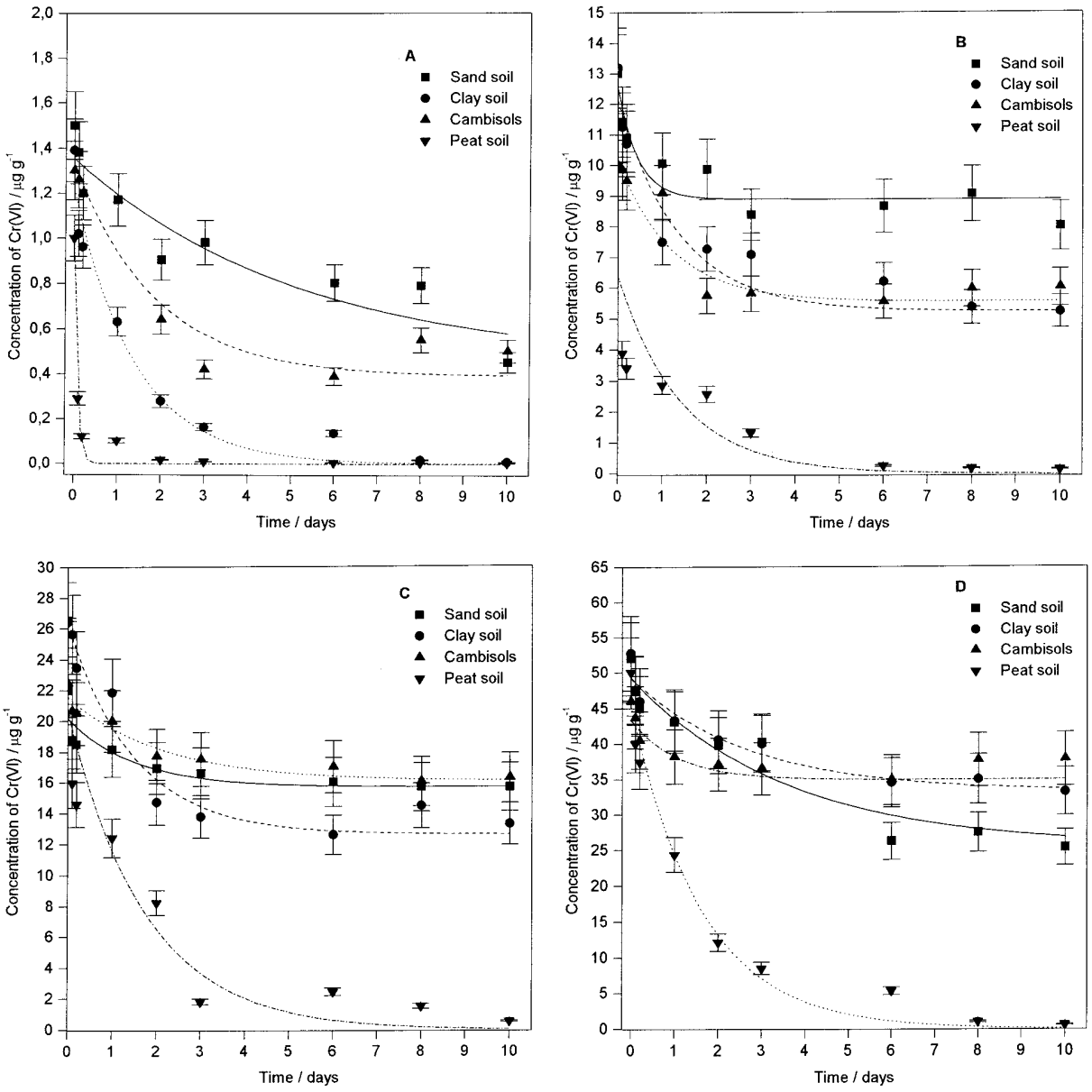

FIGURE 1. Kinetics of reduction of soluble Cr(VI) added in different concentrations in various soils: A, 1 μg g^{-1} Cr(VI) added; B, 10 μg g^{-1} Cr(VI) added; C, 25 μg g^{-1} Cr(VI) added; D, 50 μg g^{-1} Cr(VI) added.

To explain the mechanism of reduction of the soluble Cr(VI) with organic matter, soluble organic matter was extracted from the peat and clay soil. To these extracts, the soluble Cr(VI) was added in concentrations between 0.5 and 10.0 μg cm^{-3}, and the reduction was followed for up to 10 days. In these experiments, the concentration of soluble organic matter exceeded the concentration of the added soluble Cr(VI). The results are presented in Table 3. Reduction of the soluble Cr(VI) by the soluble organic matter extracted from the peat and the clay soil was not observed even after 10 days of the experiment. Slight changes in concentration of Cr(VI) were observed in the peat soil but these results were within the range of experimental error. From the data in Table 3, we can conclude that the reduction of Cr(VI) with dissolved organic matter is a slow process and can be observed only after an extended time of the experiment (more than 10 days). Our observations are in accordance with those published by Wittbrodt et al. (*10*), who reported that the reduction of Cr(VI) by dissolved organic compounds at pH values from 4.0 to 8.0 is a slow process, occurring in a time scale of days at micromolar concentrations. Deng and Stone (*13*) reported that at pH 3.5−6.5 no reduction of 20 μM of Cr(VI) in homogeneous 200 μM oxalate was observed even after 400 days. However, 30% reduction occurred in the presence of TiO_2 at pH 4.7 [surface-catalyzed Cr(VI) reduction (*12*, *13*)]. We propose that the reduction of soluble Cr(VI) probably requires the involvement of available solid organic matter in the soil. It could depend primarily on the amount of organic matter and on its accessibility to Cr(VI), although the rates of Cr(VI) reduction are highly dependent on the specific organic compound. To test these hypotheses, the cambisols was mixed with an appropriate amount of organic matter (humus—the natural peat soil with over 80% of organic matter), so that the final amount of the organic matter was approximately 10%. Then 10 μg of soluble Cr(VI) g^{-1} was added, and the reduction was followed at constant moisture and temperature for up to 10 days. In a parallel experiment, the cambisols mixed with humus was treated with 100 μg of Fe(III) (g of dry soil)$^{-1}$ to test the dependence on the accessibility of organic matter for the reduction of Cr(VI).

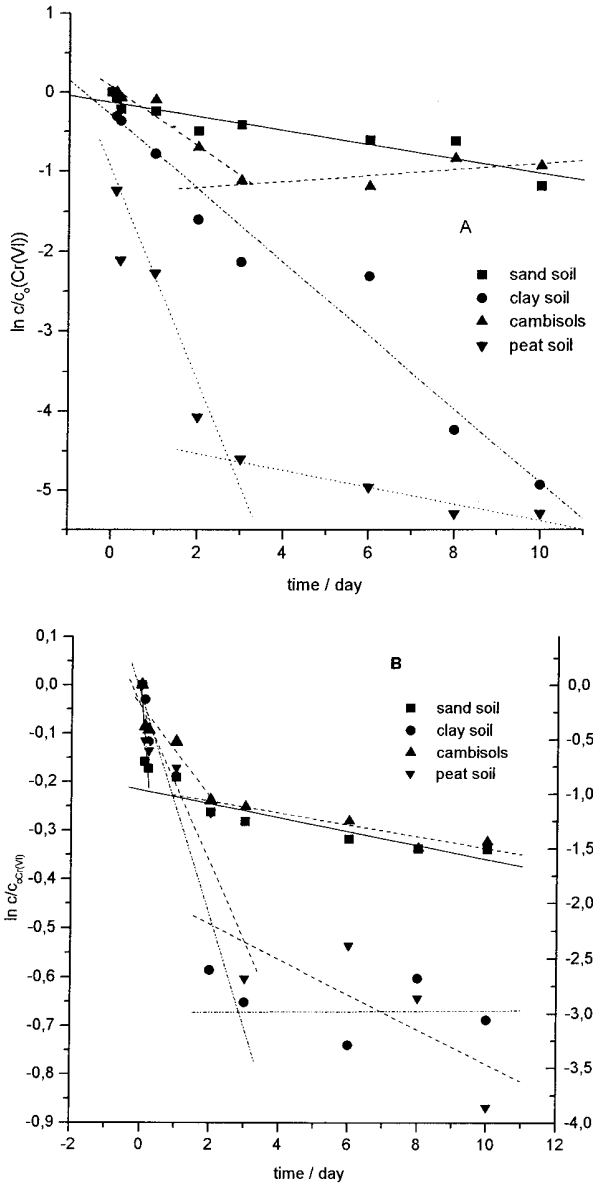

FIGURE 2. First-order plots of ln [relative Cr(VI) concentration] versus time for the reduction of Cr(VI) in various soils. The slope of the lines is equal to the first-order rate constants (k_{exp}): A, 1 μg g^{-1} Cr(VI) added; B, 25 μg g^{-1} added (peat soil ploted to the right axis).

TABLE 2. Initial First-Order Rate Constants ($k_{expR(concn\ of\ Cr(VI))}$) for the Reduction of Different Concentrations (μg g^{-1}) of Added Cr(VI) in Various Soils

soil type	k_{expR1} (s^{-1})	k_{expR10} (s^{-1})	k_{expR25} (s^{-1})	k_{expR50} (s^{-1})
peat	2.6×10^{-5}	7.5×10^{-5}	8.8×10^{-6}	6.3×10^{-6}
clay	6.1×10^{-6}	6.5×10^{-6}	4.2×10^{-6}	1.0×10^{-6}
sand	1.0×10^{-6}	1.2×10^{-6}	1.0×10^{-6}	1.1×10^{-6}
cambisols	4.1×10^{-6}	3.5×10^{-6}	1.4×10^{-6}	1.7×10^{-6}

These results are presented in Figure 3. The reduction of soluble Cr(VI) added to the cambisols was found to be faster in the cambisols mixed with humus than in both the cambisols mixed with humus and treated with Fe(III) and in natural cambisols. After 10 days, all the added Cr(VI) was reduced in the cambisols mixed with humus. Thus, the reductive capacity of that soil was much higher as compared to other two soils. The addition of the organic matter to the cambisols increases the reductive capacity of the soil for

TABLE 3. Reduction of Soluble Cr(VI) with Soluble Organic Matter Extracted from Peat and Clay Soils

soil type	SOM[a] (μg cm^{-3})	added Cr(VI) (μg cm^{-3})	Cr(VI) after 4 h (μg cm^{-3})	Cr(VI) after 1 d (μg cm^{-3})	Cr(VI) after 4 d (μg cm^{-3})	Cr(VI) after 10 d (μg cm^{-3})
clay	6.85	0.50	0.53	0.53	0.52	0.53
		1.00	1.00	0.98	0.96	1.04
		5.00	5.34	5.28	4.48	4.88
peat	43.3	0.50	0.52	0.50	0.50	0.48
		1.00	1.01	1.01	0.94	0.54
		10.0	10.8	9.71	8.87	9.97

[a] SOM, soluble organic matter extracted from clay and peat soil [24 h extraction of 50 g of soils with 50 cm^3 of water (v/w = 1) (*34, 35*)].

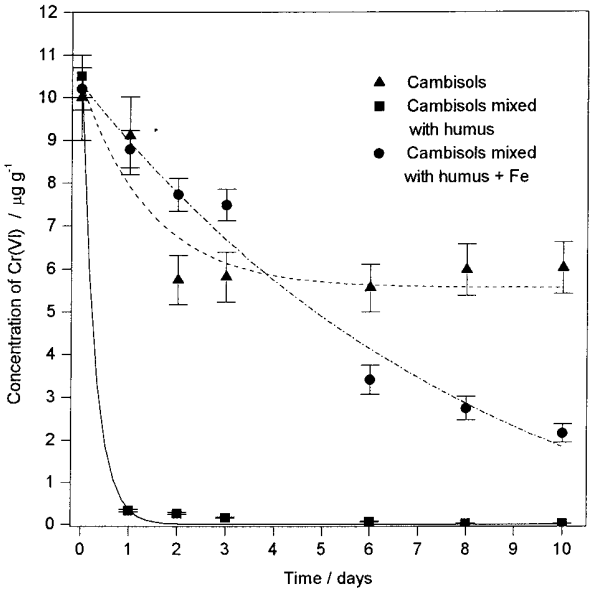

FIGURE 3. Kinetics of reduction of soluble Cr(VI) (10 μg g^{-1}) added to the cambisols.

Cr(VI). On the other hand, added Fe(III) should form iron-(III) (oxy)hydroxides species, which could block active organic sites. This could decrease the reductive capacity of the soil and inhibit the reduction of soluble Cr(VI) (9). Another explanation would include the binding of chromate to the Fe(III) precipitates independent of whether it coats the organic matter. If the discrete phases of Fe(III) precipitates are forming, then a competitive adsorption reaction would be established. Cr(VI) could be preferentially adsorbed on the iron(III) (oxy)hydroxides, and reduction of Cr(VI) would be diminished.

It is generally known that Cr(III) forms various $Cr(OH)_x$ species in the pH range from 3.8 to 11.5 (30). These species could be formed in the soil after Cr(VI) reduction. They could block active organic sites and decrease the accessibility of the organic matter for further reduction of Cr(VI). However, the reduction process could be decreased or even stopped at higher concentrations of added soluble Cr(VI).

The Reductive Capacity of Soils. The amount of reduced Cr(VI) (μg g^{-1}) in a particular soil represents the capacity of the soil for the reduction of soluble Cr(VI). It could be graphically determined from the experimental curves (Figure 1) or calculated by the Walkley-Black method (18) that is founded on the chromate oxidation equivalent to the soil organic matter.

The reductive capacity is highest in the peat soil and lowest in the cambisols (Figure 1). Therefore, it depends mostly on the content of organic matter. The comparison between the

TABLE 4. Comparison between the Amount of Organic Matter Present in Soils and the Reductive Capacity of Soils for Cr(VI)

soil type	organic matter (%)	OM/Cr(VI)	soluble organic carbon (%)	reductive capacity of soil for Cr(VI)	
				graphically (μg g^{-1})	calculated (μg g^{-1})
peat	41.1	188	4.3×10^{-3}	>1000	385
clay	1.52	7	6.6×10^{-4}	12−14	14.2
sand	3.01	14	1.7×10^{-3}	30−32	28.3
cambisols	0.22	1	4.6×10^{-4}	2−3	2.1

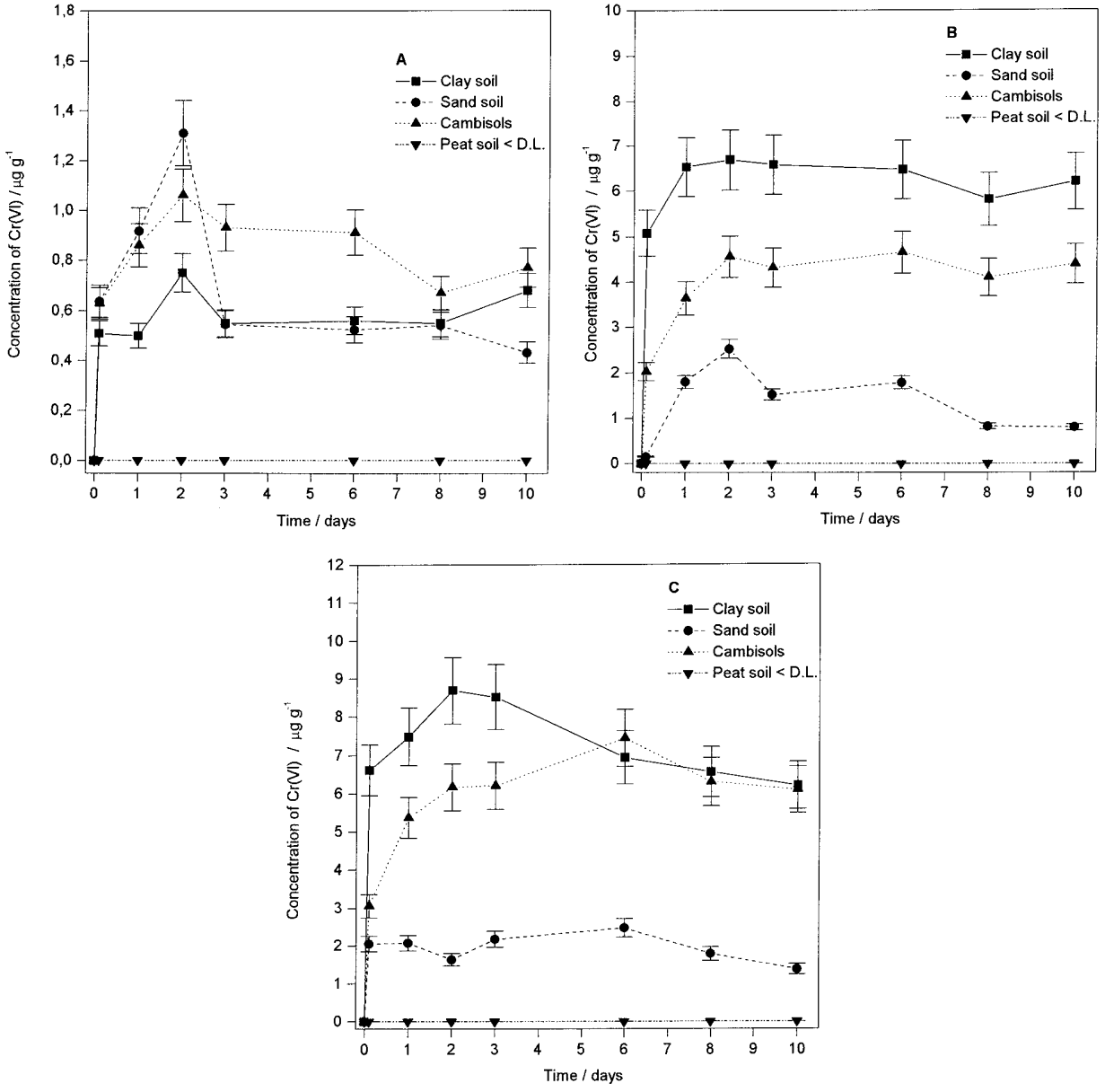

FIGURE 4. Kinetics of oxidation of soluble Cr(III) added in different concentrations in various soils: A, 10 μg g^{-1} Cr(III) added; B, 100 μg g^{-1} Cr(III) added; C, 500 μg g^{-1} Cr(III) added.

amount of the organic matter and the reductive capacity of soils for soluble Cr(VI) determined graphically from the experimental curves and calculated from the Walkley-Black method is presented in Table 4. Since it was not possible to determine the reductive capacity for the soluble Cr(VI) in the peat soil with addition up to 50 μg g^{-1} Cr(VI), higher amounts of Cr(VI) were added (up to 1000 μg g^{-1}), and the reductive capacity was then calculated. The data from Table 4 indicate, for all the soils investigated, good agreement between the graphically determined and the calculated reductive capacity of the soil. The exception is the peat soil, where the calculated reductive capacity is lower as compared to that determined graphically. The reason for that may originate from a different preparation of samples for the two methods. When a Walkley-Black method was employed, the soil samples were sterilized and sieved through 2-mm pore size sieve. Most of the organic debris was therefore removed from the samples. In the natural soils on the other hand, various organic substances produced during the organic debris decomposition represent a significant reservoir of

electron donors for Cr(VI) reduction (21).

As seen from Table 4, the peat soil has the highest reductive capacity for the soluble Cr(VI) (>1000 μg g^{-1}), and the cambisols has the lowest (2−3 μg g^{-1}). The data also show that the reductive capacity of soils for soluble Cr(VI) depends mostly on the amount of the organic matter present in the particular soil.

Oxidation Processes of Cr(III) in Soils. The Oxidation of Cr(III) in Various Soils. On the contrary to the reduction processes of chromium in soils, the oxidation processes take place generally in soils high in manganese(IV,III) oxides and low in organic matter content (18−20). The oxidation of aqueous Cr(III) to Cr(VI) in soils normally does not occur in such a wide range as the reduction of aqueous Cr(VI). Masscheleyn et al. (29) found that in wetland soil the reduction of Cr(VI) dominates over possible oxidation of Cr-(III). Cr(III) in natural soils exists bound in various sparingly soluble fractions or complexed by organic matter as Cr(III)−organic complexes. When aqueous Cr(III) is added, it could be oxidized to Cr(VI) under the particular conditions. Milačič et al. (33) found a possible oxidation of chromium in tannery waste-amended sand and clay soils 5 months after addition. The concentration of soluble chromium and Cr(VI) decreased on further continuation of the experiment, since chromium was redistributed to more sparingly soluble fractions.

Possible oxidation of soluble Cr(III) added to soils was studied in peat, sand, clay, and the cambisols. A total of 10, 100, and 500 μg of Cr(III) (g of dry soil)$^{-1}$ were added to the soils, and oxidation was followed at constant moisture and temperature over a period of up to 10 days. The results are presented in Figure 4. The oxidation of soluble Cr(III) occurred in all the soils with the exception of the peat soil. In the latter, oxidation was not observed even at 500 μg g^{-1} of the added soluble Cr(III). Our results agree very well with those published by Milačič et al. (33), who observed the oxidation of chromium in all the tannery waste-amended soils, the exception being the peat soil with a high content of organic matter and a low content of manganese(IV) oxides. As seen from Figure 4, the concentration of oxidized Cr(III) achieved its maximum within 2 days after addition and then slightly decreased with time. This phenomenon was found to be pronounced particularly at low concentrations of added soluble Cr(III) (10 μg g^{-1}). A slight decrease in the concentration of oxidized Cr(III) 2−3 days after application is the consequence of competition between the oxidation and reduction processes of chromium in soils. It was particularly significant in the sand soil, which has a higher amount of organic matter than clay and cambisols. The concentration of added soluble Cr(III) decreased quickly after addition. The concentrations of the total soluble chromium were found to be similar to those of Cr(VI). The added soluble Cr(III) was probably complexed as Cr(III)−organic complexes or adsorbed and precipitated as $Cr(OH)_x$ species (16, 17).

The Oxidative Capacity of Soils. The amount of oxidized Cr(III) (μg g^{-1}) in the particular soil represents the oxidative capacity of the soil. On the basis of the data in Figure 3, the oxidation capacity of soils for soluble Cr(III) could be determined graphically. It was found to be highest for clay soil and lowest for sand soil. The data presented in Tables 4 and 5 indicate that the degree of chromium oxidation is proportional to the concentration of manganese(IV) oxides, but it also depends on the reductive capacity of soils.

Soils high in manganese(IV) oxides and low in organic matter have a high oxidative capacity for the oxidation of soluble Cr(III). On the contrary, soils high in organic matter and low in manganese(IV) oxides have a high reductive capacity for the reduction of soluble Cr(VI). In all the soils examined, the reductive capacity for soluble chromium was higher than the oxidative capacity; the exception being the cambisols with a high content of manganese(IV) oxides and a low content of organic matter.

TABLE 5. Parameters That Influence the Oxidation of Soluble Cr(III) in Soils

soil type	soil pH	oxidative capacity of soil for Cr(III) (μg g^{-1})	exchangeable manganese(IV) oxides (μg g^{-1})	organic matter (%)
clay	7.30	8.69	399	1.52
peat	6.95	<0.05	60.0	41.1
sand	7.37	3.48	150	3.01
cambisols	5.39	7.44	234	0.22

Environmental Significance

Our experiments confirm that the reduction and oxidation of soluble chromium can occur in all the natural soils. In all the soils the reduction of Cr(VI) dominates over possible oxidation of Cr(III). Up to 3 days of the experiment, a first-order reaction with respect to Cr(VI) was found. The reduction and oxidation of chromium depend mostly on the soil composition, i.e., content of the electron donors [organic matter, Fe(II), HS^-], manganese(IV) oxides, and texture of the soil, as well as on the conditions in the soil, i.e., moisture, pH, and temperature. Soluble Cr(III) added to the soil is either quickly complexed with organic substances or adsorbed and precipitated as $Cr(OH)_x$ species (16, 17). Soils that are low in organic matter and high in manganese(IV) oxides deserve special attention. These types of soil might be well able to oxidize chromium despite the fact that this process was generally found to be very slow (18, 32).

Acknowledgments

This work was supported by the Ministry of Science and Technology of Slovenia and the U.S. Environmental Protection Agency (Project JF 908). The authors thank Miss Katarina Adamič of the Jožef Stefan Institute for technical assistance in soil samples analysis. The authors also thank Marko Zupan for providing some soil samples and for their physical characterization and Prof. Roger Pain for critical reading of the manuscript.

Supporting Information Available

Two figures and text showing the kinetics of reduction and oxidation of soluble Cr in various soils (3 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) James, B. R.; Bartlett, R. J. J. Environ. Qual. 1983, 12, 173−176.
(2) James, B. R.; Bartlett, R. J. J. Environ. Qual. 1983, 12, 169−172.
(3) Eary, L. E.; Rai, D. Environ. Sci. Technol. 1988, 22, 972−977.
(4) Eary, L. E.; Rai, D. Soil Sci. Soc. Am. J. 1991, 55 (3), 676−683.
(5) Bartlett, R. J.; Kimble, J. M. J. Environ. Qual. 1976, 3, 379−383.
(6) James, B. R.; Bartlett, R. J. J. Environ. Qual. 1983, 12, 177−191.
(7) Kieber, R. J.; Helz, G. R. Environ. Sci. Technol. 1992, 26, 307−312.
(8) Hug, S. H.; Laubscher, H. U.; James, B. R. Environ. Sci. Technol. 1997, 31, 160−170.
(9) Buerge, I. J.; Hug, S. J. Environ. Sci. Technol. 1998, 32, 2092−2099.
(10) Wittbrodt, P. R.; Palmer, C. D. Environ. Sci. Technol. 1995, 29, 255−263.
(11) Wittbrodt, P. R.; Palmer, C. D. Environ. Sci. Technol. 1996, 30, 2470−2477.
(12) Deng, B.; Stone, A. T. Environ. Sci. Technol. 1996, 30, 2484−2494.
(13) Deng, B.; Stone, A. T. Environ. Sci. Technol. 1996, 30, 463−472.
(14) Elovitz, M. S.; Fish, W. Environ. Sci. Technol. 1994, 28, 2161−2169.
(15) Cary, E. E.; Allaway, W. H.; Olson, O. E. J. Agric. Food Chem. 1977, 25, 305−309.

(16) Bartlett, R. J. Environ. Health Perspect. 1991, 92, 17−24.
(17) Grove, J. H.; Ellis, B. G. Soil. Sci. Soc. Am. J. 1980, 44, 243−246.
(18) Bartlett, R. J.; James, B. R. J. Environ. Qual. 1979, 8, 31−35.
(19) Fendorf, S. E.; Zasoski, R. J. Environ,. Sci. Technol. 1992, 26, 79−85.
(20) Eary, L. E.; Rai, D. Environ. Sci. Technol. 1987, 21, 1187−1193.
(21) Adriano, D. C. Trace Elements in the Terrestrial Environment; Springer-Verlag: New York, 1986; pp 156−180.
(22) Milačič, R.; Štupar, J.; Kožuh, N.; Korošin, J. Analyst 1992, 117, 125−130.
(23) Novak, J. M.; Bretsch, P. M.; Mills, G. L. J. Environ. Qual. 1992, 21, 144−147.
(24) Giusquani, P. L.; Gigliotti, G.; Businelli, D. J. Environ. Qual. 1992, 21, 330−335.
(25) Jackson, M. L. Soil Chemical Analysis; Prentice-Hall: Englewood Cliffs, NJ, 1958; pp 205−226.
(26) Ajlec, R.; Čop, M.; Štupar, J. Analyst 1988, 113, 585−595.
(27) Milačič, R.; Štupar, J.; Kožuh, N.; Korošin, J.; Glazer, I. J. Am. Leather Chem. Assoc. 1992, 87, 221−234.
(28) Hathaway, J. A. Sci. Total Environ. 1989, 86, 181−190.
(29) Masscheleyn, P. H.; Pardue, J. H.; DeLaune, R. D.; Patric, W. H., Jr. Environ. Sci. Technol. 1992, 26, 1217−1226.
(30) Rai, D.; Eary L. E.; Zachara, J. M. Soil Total Environ. 1989, 86, 15−23.
(31) Espenson, J. H. Chemical Kinetics and Reaction Mechanisms; McGraw-Hill: New York, 1981; pp 12−41.
(32) Bohn, H. L.; McNeal, B. L.; O'Connor, G. A. Soil Chemistry; John Wiley: New York, 1985; pp 56−266.
(33) Milačič, R.; Štupar, J. Environ. Sci. Techol. 1995, 29, 506−514.
(34) Novak, J. M.; Bertsch, P. M.; Mills, G. L. J. Environ. Qual. 1992, 21, 144−147.
(35) Giusquani, P. L.; Gigliotti, G.; Businelli, D. J. Environ. Qual. 1992, 21, 330−335.

Received for review November 10, 1998. Revised manuscript received October 4, 1999. Accepted October 14, 1999.

ES981162M