

Assessing chromate availability in tropical ultramafic soils using isotopic exchange kinetics

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Received: 14 October 2008 / Accepted: 27 January 2009 / Published online: 21 February 2009
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Abstract

Background, aim, and scope The presence of labile chromate in the soils is an environmental problem because of its high toxicity. The isotopic exchange kinetics (IEK) methods have been shown to be a useful tool to measure the phytoavailability of major (P, K) and trace elements (Cd, Zn, Ni, Pb) in soils. This study focused on the potential of applying IEK for chromate to characterize its availability in two tropical ultramafic Ferralsols.

Materials and methods Two Ferralsols (NIQ II and NIQ III) of the ultramafic complex of Niquelândia (Goias, Brazil), known to have a high content of extractable chromate, were investigated. We adapted IEK for chromate in order to distinguish different pools of available chromate according to their rate of exchange kinetic.

Results The extractable Cr(III) ranged from 9 to 132 mg kg⁻¹, whereas extractable Cr(VI) ranged from 64 to 1,014 mg kg⁻¹. The intensity factor, i.e., concentration of soluble Cr, ranged from 78 to 231 μg L⁻¹ in profile NIQ II and from 6 to 141 μg L⁻¹ in profile NIQ III. The highest

concentrations were found in both topsoils and in the NIQ II-5 horizon. Most of the Cr(VI) was labile in short ($E_{0-1 \text{ min}}$) or medium-term ($E_{1 \text{ min}-24 \text{ h}}$) in both soils. The $E_{0-1 \text{ min}}$ and $E_{1 \text{ min}-24 \text{ h}}$ represented 39 to 83% of labile Cr(VI) in NIQ II and 69 to 80% in NIQ III. A high quantity of Cr(VI) was thus extremely labile and highly available, particularly in NIQ II. Moreover, both soils had a high buffering capacity of soluble Cr(VI) by labile pools.

Discussion The Cr(VI) availability is large and varied significantly among the soil profiles. The r_1/R parameter has long been considered as an indicator of the soil “fixing capacity” for ions like P. The values of r_1/R for Cr(VI) measured on the two studied soils are among the lowest ever reported for any element, especially in the organic matter-poor and iron oxide-rich horizons (r_1/R in the 0.001–0.003 range). But, considering the high proportion of labile Cr(VI) in these soils, it is more appropriate to relate r_1/R to the buffer capacity. The latter was extremely high and probably due to labile Cr(VI) retained in its majority by low-energy bonds on the surface of colloids. The quantity of readily labile Cr ($E_{0-1 \text{ min}}$) was significantly correlated ($r=0.96$, $p<0.01$) with the quantity of Cr associated to amorphous or poorly crystallized Fe-oxides. Thus, amorphous Fe oxides control the Cr availability in these Ferralsols. The correlation between E parameters and clay content has to be carefully considered. Indeed, these soils contain mainly fine and discrete clay-sized Fe oxides, particularly goethite. Despite different data supporting the idea of the formation of inner-sphere surface complexes of chromate on goethite, the high quantity of readily labile Cr(VI) and the high buffer capacity observed for these soils are consistent with low-energy bonds on the surface of colloids in agreement with the formation of outer-sphere complexes.

Conclusions The two studied Ferralsols contain a large quantity of labile Cr(VI), which is controlled by amorphous

Responsible editor: Chengrong Chen

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Fe oxides and pH. IEK for chromate allows distinguishing different pools of available chromate according to their rate of exchange kinetic. The buffer capacity of these soils is extremely high and probably with a majority of low-energy bonds on the surface of colloids. The study highlighted a high chromate availability in those soils and, consequently, potential chromate toxicity on soils organisms.

Recommendations and perspectives IEK could be a powerful tool to quantify chromate availability in soils. Our attempt to apply the IEK for chromate seems to be a success and the IEK for Cr consequently seems to have future. However, the robustness and the limit of the IEK for chromate have to be examined in more detail for a large diversity of soils.

Keywords Availability · Brazil · Chromate · Isotopic exchange · Lability · Metal · Serpentinic soils · Toxicity · Ultramafic soils

1 Background, aim, and scope

The presence of metals and the low concentrations of nutrients like N, P, K and Ca are generally thought to be responsible for the low fertility of ultramafic soils (Proctor and Woodell 1975), which support an endemic and metalliferous vegetation adapted to the metal stress. Despite high Cr concentrations in ultramafic rocks, Cr availability is generally low since the soil Cr-bearing minerals are extremely insoluble and very slowly weathered.

Chromium is commonly present in ultramafic soils either as Cr(III) or Cr(VI). Cr(VI) is a strong oxidizing agent and thus highly toxic, whereas Cr(III) is a micronutrient and a non-hazardous species (Fendorf 1995). Moreover, chromate is known to be mutagenic, teratogenic, and carcinogenic (Nieboer and Shaw 1988). Thus, aqueous chromate, even at a low concentration, is highly toxic for plants and organisms. Cr availability in ultramafic soils is generally low (Shanker et al. 2005), but unexpectedly high levels of KH_2PO_4 -extractable Cr, up to 960 mg kg^{-1} of Cr(VI), have been reported in Niquelândia soils (Goiás, Brazil) (Garnier et al. 2006).

Only a fraction of an element (nutrient, metal or organic contaminant) is available for organisms and is therefore potentially toxic (Alexander 2000; Young et al. 2005). Availability is governed by three concepts: intensity (the free ion activity in the soil solution), quantity (the ion amount potentially released from the soil matrix into the soil solution), and the buffering capacity (the capacity of the soil matrix to maintain the concentration of the target element constant in the soil solution; Beckett 1964; Echevarria et al. 1998). Up to the present time, no unique method exists to assess metal availability to soil organisms.

Some are direct like plant and ecotoxicological tests (Morel 1996) and indirect like chemical extractions (Kotas and Stasicka 2000), diffusion gradient in a thin-film (Zhang et al. 1998) and isotopic exchange kinetics approaches (Echevarria et al. 1998). The last have been shown to be useful tools to measure the phytoavailability of major (P, K) and trace elements (Cd, Zn, Ni, Pb) in soils (Fardeau 1996; Gray et al. 2004; Sinaj et al. 1999; Tiller et al. 1972; Tongtavee et al. 2005) and also for invertebrates (Scheifler et al. 2003). Isotopic dilution was used for Cr to investigate the Cr(VI) concentration in contaminated soils (Szulczewski et al. 1997) and to compare the Cr(III) sorption evaluated by EDTA and isotopic dilution (Gäbler et al. 2007). Isotopic exchange kinetics (IEK) allows one to distinguish different pools of available elements according to their rate of exchange kinetics and, thus, to have more knowledge on the bonding of the exchangeable elements with the bearing phase (Echevarria et al. 2006). Furthermore, it has been shown that plants take up major elements and metals predominantly from the isotopically exchangeable pool (Fardeau 1996; Gérard et al. 2000; Hamon et al. 1997).

Thus, the objectives of the research reported here are (a) to characterize the chromate availability by isotopic exchange kinetics in two Cr-rich ultramafic Ferralsols, which contain different proportions of exchangeable Cr (VI), and (b) to relate the availability data derived from IEK to soil mineralogy and Cr speciation in order to validate their use for chromate.

2 Materials and methods

2.1 Sampling and soil analyses

Two Ferralsols were selected along a soil toposequence representative of the Niquelândia ultramafic massif (Garnier et al. 2006). Pits were opened and horizons sampled (NIQ II-1 to 5 and NIQ III-1 to 5, 1 to 5 denoted the horizons). Samples were dried at 40°C , sieved to $<2 \text{ mm}$ and sterilized by γ -irradiation (6 kGy) before analysis. Elemental analyses were performed after the total dissolution of approx. 250 mg of finely crushed samples by a mixture of HF, HClO_4 , HNO_3 , and HCl. Extractions of elements associated with the amorphous or poorly crystallized Fe-oxides (Fe_a ; Cr_a) and with the well crystallized Fe-oxides (Fe_c ; Cr_c) have been performed according to Garnier et al. (2006). Major and trace elements were quantified by ICP-OES. Extractable Cr(III) and Cr(VI) were determined after extraction with 1 M KCl and 0.1 M KH_2PO_4 , respectively (Bartlett and James 1996). In the filtered extracts ($<0.2 \mu\text{m}$), the total Cr (corresponding to Cr(III)+Cr(VI)) was measured by ICP-OES and Cr(VI) was determined by colorimetry with the diphenylcarbazide complex (DPC) method. In

this way, it was verified that the Cr extracted by KH_2PO_4 was exclusively Cr(VI).

2.2 Isotopic exchange kinetics

2.2.1 Rationale: theoretical considerations before extending the use of IEK to chromate

The isotopic exchange kinetics method was adapted from the procedure developed for PO_4^{3-} (Fardeau 1993) to study the chromate availability in soils using $^{51}\text{CrO}_4^{2-}$ as a tracer. The use of the IEK concepts on a new element requires that some hypotheses and conditions be fulfilled. Firstly, the isotope used as a tracer must behave identically to the chemical species under study. The redox transformation of Cr during the time frame of the kinetics can therefore be neglected. This key parameter is assumed to be true as (a) soils were γ -irradiated before the experiment; (b) the oxidation is limited, as demonstrated by Oze et al. (2007) in a New Caledonia soil similar to the Niquelândia ones, and, at equilibrium, the reduction is then also limited. Secondly, the quantity of isotope added must be negligible compared to the amount of chromate in the soil solution. Finally, the compartment into which the tracer is added must behave homogeneously in terms of exchange properties. In this case, the assumption made is that all chromate ions from the soil solution have the same behavior in terms of isotopic exchange properties (Collins et al. 2006; Hamon et al. 2004). According to the Cr Eh–pH diagram and the pH range of soils, HCrO_4^- represents 70 to 95% and CrO_4^{2-} 5 to 30% of the stable forms of Cr(VI) which can be present (Kotas and Stasicka 2000) and were defined hereafter as Cr(VI). We also assume that the tracer added will partition similarly to natural Cr(VI) between HCrO_4^- and CrO_4^{2-} forms. If these hypotheses are verified, the decrease in the activity of the tracer in the soil solution can be attributed solely to steady-state exchanges between labile pools on the soil solid phase and the soluble pool. The method therefore allows for an evaluation of the three parameters that characterize the availability of a given element in soils (Echevarria et al. 1998): intensity, quantity, and capacity

The specific activity of CrO_4^{2-} ions in solution was followed with IEK and extrapolated to longer times as validated for Ni, Zn, and Cd (Echevarria et al. 1998; Gray et al. 2004; Sinaj et al. 1999). Since the soil-solution system is under steady state conditions, the concentration of Cr(VI) in the soil solution remains constant throughout the entire experiment (verified initially in soil solution mixtures over time). Therefore, the monitoring of the radioactivity in the soil solution (r_t in kBq kg^{-1}) is sufficient to quantify the labile compartments in the solid phase (E_t in mg kg^{-1}). The equation describing the decrease of r_t over time developed

by Fardeau (1993) and successfully utilized for Cd, Ni, and Zn was applied to chromate (Eq. 1):

$$r_t/R = r_1/R \times \left[t + (r_1/R)^{\frac{1}{n}} \right]^{-n} + r_\infty/R \quad (1)$$

where R is the total radioactivity introduced at time $t=0$ (in kBq kg^{-1}), r_t is the radioactivity in the soil solution system at time $t=1$ min, r_∞ is the radioactivity after an infinite time of exchange and n is a parameter which describes the rate of net transfer of the tracer from the solution to the solid phase of the soil for $t>1$ min. The ratio r_∞/R is the maximal possible dilution of the isotope in the soil:solution system and corresponds to the dilution of the total radioactivity added into total Cr(VI) in the soil solid phase, Cr(VI)_T , then (Eq. 2):

$$r_t/R = r_1/R \times \left[t + (r_1/R)^{\frac{1}{n}} \right]^{-n} + \text{Cr(VI)}_S/\text{Cr(VI)}_T \quad (2)$$

where Cr(VI)_S (in mg kg^{-1}) is the amount of chromate in the soil solution per kg of soil. According to the principles of isotope dilution, the labile compartment of chromate for a time comprised between 0 min and t minutes is given by Eq. 3:

$$E_t = \frac{\text{Cr(VI)}_S}{\frac{r_t}{R}} \quad (3)$$

The capacity factor (CF), i.e., the capacity of the solid phase to maintain the chromate concentration in the soil solution, was estimated by computing the ratio of the most instantaneously labile compartment of chromate on the concentration of chromate in solution (i.e., $E_{1 \text{ min}} \times 1,000/C_{\text{Cr(VI)}}$). It is the best available estimate of the capacity factor and is consistent in terms of units with a distribution coefficient, K_d (1 kg^{-1}). Actually, according to Eq. 3, the capacity factor is the inverse of r_1/R . Therefore, the buffer capacity or capacity factor of a soil towards a given element is described by the r_1/R value. The higher the buffer capacity, the lower the r_1/R value. The n value describes the evolution of isotopic exchange for higher times and is influenced by two phenomena: (1) diffusion-limited isotopic exchange and (2) slow chemical processes at surfaces. n values have never exceeded 0.5 for any element so far, which is consistent with Crank's equations in $t^{1/2}$ that describe solute diffusion kinetics. The higher the n value, the more important the diffusion effects in isotopic exchange.

2.2.2 Experimental

One ml of a $^{51}\text{CrO}_4^{2-}$ (1.6 kBq ml^{-1}) was injected in soil suspensions (10 g/100 ml deionized water, five replicates) after mixing on an end-over-end shaker for 17 h, i.e., until

the Cr concentration in solution (C_{Cr}) was constant. After 1, 4, 10, and 40 min, aliquots were sampled with a syringe and immediately filtered (cellulose nitrate, 0.2 μ m). C_{Cr} , i.e., the sum of Cr(III) and Cr(VI), was measured in the filtered solution by ICP-MS and the speciation of Cr determined using DPC. The measurement of Cr(VI) by DPC confirmed that the KH_2PO_4 -extracted Cr was exclusively Cr(VI) and also that a significant part of the KCl-extracted Cr, assumed to be Cr(III), was in fact Cr(VI). Fe concentration in solution was determined by ICP-MS and found negligible, indicating the absence of any colloidal-Fe in suspension. Radioactive Cr(VI) in the soil solution aliquots was measured at different times by using γ counting. The maximal dilution of $^{51}Cr(VI)$ was considered as the ratio between the concentration of the ionic species in the solution and its total concentration in the solid phase (i.e., $Cr(VI)_s/Cr(VI)_T$). Because most Cr in soils is present as Cr(III), a large part is not involved in the isotopic exchange of Cr(VI). Thus, the total concentration of Cr(VI) in the solid phase $Cr(VI)_T$ involved in IEK was estimated by the KH_2PO_4 -extractable Cr(VI).

2.3 Statistical analysis

Pearson correlation matrix was calculated for all soil characteristics with Statistical Analysis System SAS 9.1.

3 Results

3.1 Soil parameters and Cr speciation in soil

Soil horizons were slightly acidic and pH values decreased with depth (Table 1). The ΔpH was negative in surface horizons and became positive in deeper ones for both soils, indicating that positive charges prevail in the lower horizons. The organic carbon content ranged from 1.5 to 22 mg kg^{-1} , and decreased with depth. Soils are loamy, with a higher clay proportion in profile NIQ II. The mineralogy of the two soils was dominated by goethite and haematite (data not shown), with the presence of chromite, and quartz, particularly in NIQ II-5. Soils were free from clay minerals and the clay fraction contained only Fe oxides and quartz. Fe content ranged from 271 to 513 g kg^{-1} . Fe (75–98%) was associated with well-crystallized Fe oxides (Fe_o , see Table 1). Total Cr (Cr_T) ranged from 5,690 to 9,270 mg kg^{-1} and nickel from 3,150 to 6,252 mg kg^{-1} . Most of the Cr was associated to the well-crystallized Fe oxides (about 53–78%) (see Table 1).

The extractable Cr(III) ranged from 0.1 to 1.9% Cr_{tot} , whereas extractable Cr(VI) ranged from 1.1 to 10.9% Cr_{tot} (Table 2). This labile Cr was thus mainly present in the anionic Cr(VI) form, which can form labile complexes with

Table 1 Main physical and chemical characteristics of the soil horizons

Depth cm	Particle size distribution			Org. C $g\ kg^{-1}$	pH	ΔpH	Total elements				Selective sequential extractions						
	Clay $g\ kg^{-1}$	Silt	Sand				Fe $g\ kg^{-1}$	Al	Mg	Mn	Cr $mg\ kg^{-1}$	Ni	Co	$Fe_o\ mg\ kg^{-1}$	Fe_r	Cr_a	Cr_r
NIQ II-1	20	49	31	20.7	5.23	-0.21	427	20.2	2.38	6.91	6.217	3,945	829	3,935	323,122	88	3,131
NIQ II-2	20	50	30	14.8	5.43	0.15	431	20.9	2.25	6.92	6,986	3,704	830	4,060	328,860	153	3,873
NIQ II-3	34	43	23	5.3	6.07	0.23	466	21.8	2.22	8.21	9,268	4,048	627	3,135	382,310	270	4,760
NIQ II-4	43	35	22	4.0	6.15	0.43	513	15.0	3.62	6.16	5,687	6,252	513	1,919	423,511	344	6,284
NIQ II-5	26	45	29	1.5	6.23	0.37	271	5.6	1.85	3.78	6,553	4,119	380	813	233,551	201	3,101
NIQ III-1	18	46	36	22.1	5.27	-0.43	413	25.8	1.90	6.72	6,135	3,710	881	4,195	359,332	60	3,626
NIQ III-2	21	47	32	7.8	5.38	0.49	430	30.6	1.88	5.96	6,925	3,650	807	5,477	378,244	199	3,869
NIQ III-3	27	44	29	5.2	5.51	0.63	448	28.7	1.52	5.69	7,611	3,383	652	6,097	428,341	234	4,430
NIQ III-4	38	36	26	2.8	5.48	0.56	467	32.9	1.47	5.83	7,048	3,513	683	5,023	417,658	210	4,360
NIQ III-5	38	36	26	1.5	5.48	0.86	469	39.1	1.34	4.79	8,557	3,156	517	4,591	444,279	201	4,596

Table 2 Extractable concentrations of Cr of the soils and percentages of Cr(III) and Cr(VI) on Cr total

	Cr _{tot}	Cr(III)–KCl		Cr(VI)–KH ₂ PO ₄	
	mg kg ⁻¹	mg kg ⁻¹	%Cr _t	mg kg ⁻¹	%Cr _t
NIQ II-1	6,597	11	0.16	116	1.76
NIQ II-2	6,217	30	0.48	270	4.34
NIQ II-3	6,986	77	1.11	708	10.14
NIQ II-4	9,268	132	1.42	1,014	10.94
NIQ II-5	5,687	106	1.87	593	10.43
NIQ III-1	6,135	9	0.14	64	1.04
NIQ III-2	6,925	39	0.56	343	4.95
NIQ III-3	7,611	63	0.82	466	6.12
NIQ III-4	7,048	53	0.75	430	6.10
NIQ III-5	8,557	64	0.75	463	5.41

Fe oxide surfaces and can be displaced by phosphate (Bartlett and James 1996). Cr(VI) extracted by KH₂PO₄ was highly correlated to Cr_a ($r=0.88, p<0.01$, Fig. 1a), Cr_r ($r=0.76, p<0.01$), and pH_{H₂O} and pH_{KCl} ($r=0.87$ and 0.87 , respectively, $p<0.01$, Fig. 1b). Obviously, there was no correlation with total Cr.

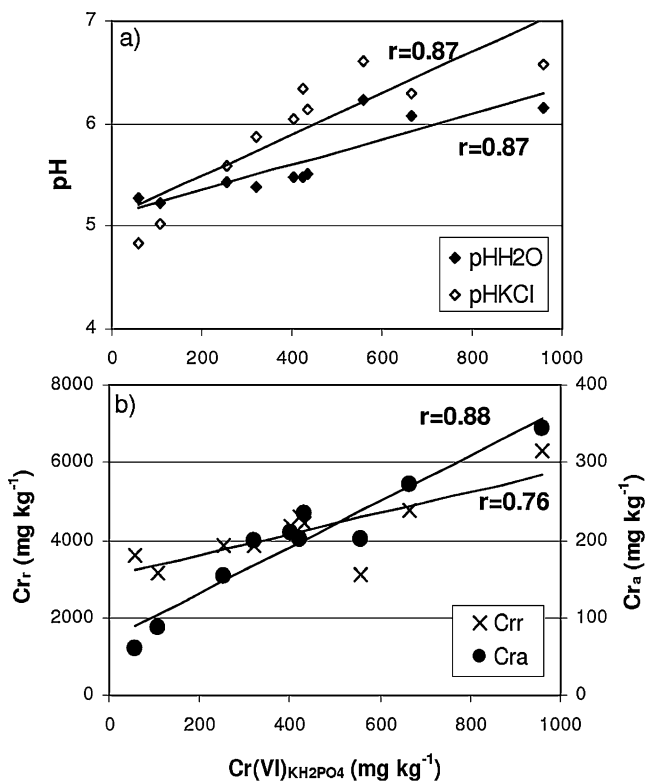


Fig. 1 Content of Cr(VI) extracted by KH₂PO₄ in function of pH_{H₂O} and pH_{KCl} of soils (a) and in function of Cr associated to amorphous Fe-oxides (Cr_a) and well crystallized Fe-oxides (Cr_r) (b)

3.2 Assessment of chromium availability by IEK

The *n* parameter, corresponding to the decrease of radioactivity for exchange times larger than 1 min, varied from 0.15 to 0.37 (Table 3). These values are close to those obtained for PO₄³⁻ of 0.1 to 0.4 (Frossard et al. 1994), Cd 0.19–0.50 (Gérard et al. 2000; Gray et al. 2004), Ni 0.11–0.39 (Echevarria et al. 2006) and Zn 0.13–0.27 (Sinaj et al. 1999).

The Cr(VI) availability varied significantly among the soil profiles (Fig. 2). The intensity factor (*C*_{Cr}) ranged from 78 to 231 μg L⁻¹ in NIQ II and from 6 to 141 μg L⁻¹ in NIQ III (see Table 3). The highest concentrations were found in the topsoils and in NIQ II-5. Some of these values were well above the reported concentrations for natural water or soil solutions (Becquer et al. 2003, Robles-Camacho and Armienta 2000).

Most of the Cr(VI) was labile and short (*E*_{0–1 min}) or medium-term (*E*_{1 min–24 h}) in both soils (see Fig. 2). Indeed, *E*_{0–1 min} ranged from 24 to 336 mg kg⁻¹ Cr(VI) and 18 to 204 mg kg⁻¹ Cr(VI) in NIQ II and NIQ III, respectively. *E*_{1 min–24 h} ranged from 64 to 244 mg kg⁻¹ Cr(VI) in NIQ II and from 23 to 205 mg kg⁻¹ Cr(VI) in NIQ III. The *E*_{0–1 min} and *E*_{1 min–24 h} represented 39 to 83% of labile Cr(VI) in NIQ II and 69% to 80% in NIQ III. A high quantity of Cr(VI) was thus extremely labile and highly available, particularly in NIQ II, and both soils had a high potential to replenish the soil solution with Cr(VI).

The labile Cr over a short time (*E*_{0–1 min}) and medium time (*E*_{0–24 h}) were significantly correlated with pH_{H₂O} ($p<0.05$, Fig. 3) and pH_{KCl} ($p<0.05$, see Fig. 3) and highly correlated with the clay content ($p<0.01$, Fig. 3). The *E*_{0–1 min} and *E*_{0–24 h} were also highly correlated with Cr_a ($p<0.01$, see Fig. 3) and Cr_r ($p<0.01$, see Fig. 3). Thus, pH, Fe-oxides, and the clay-size particles control Cr(VI) dynamics in the soils studied.

Table 3 Kinetic parameters for the soil profiles NIQ II and NIQ III

	<i>r</i> (1)/ <i>R</i>	<i>n</i>	<i>C</i> _{Cr} μg l ⁻¹	CF l kg ⁻¹
NIQ II-1	0.034±0.004	0.366±0.060	104	231
NIQ II-2	0.028±0.013	0.179±0.042	93	372
NIQ II-3	0.002±0.000	0.193±0.063	87	2,669
NIQ II-4	0.002±0.000	0.149±0.109	78	4,312
NIQ II-5	0.028±0.013	0.179±0.042	231	364
NIQ III-1	0.052±0.008	0.240±0.037	141	131
NIQ III-2	0.003±0.001	0.259±0.088	46	2,130
NIQ III-3	0.002±0.000	0.271±0.091	40	3,108
NIQ III-4	0.001±0.000	0.189±0.082	39	5,241
NIQ III-5	0.001±0.000	0.313±0.100	6	14,527

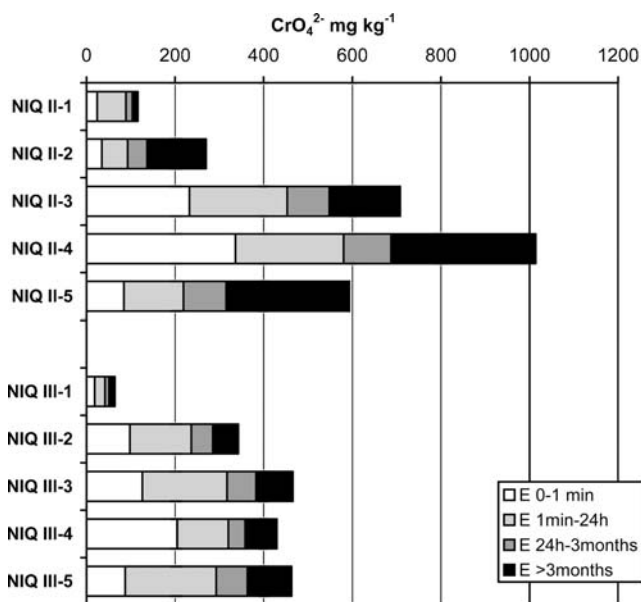


Fig. 2 Distribution of CrO_4^{2-} in the different isotopically exchangeable pools for the two profiles

4 Discussion

The r_1/R parameter has long been considered as an indicator of the soil ‘fixing capacity’ for ions like P (Fardeau 1993). Actually, the binding energy of surface ions that exchange with the radioactive isotopes is very likely to be inversely proportional to the r_1/R value according to both the sorption data published and the reported IEK parameters. The more rapidly and intensely

the radiotracer is taken from the solution, the weaker the bonds. The term “fixing capacity” is then likely to bring confusion, so that it would be better to qualify this as the ‘buffer capacity’ from the soil surfaces, with higher values (i.e., >0.1) characterizing unbuffered systems, lower values (i.e., <0.1) characterizing buffered systems and much lower values (i.e., <0.01) characterizing strongly buffered systems. The values of r_1/R for Cr(VI) measured on the two studied soils are among the lowest ever reported for any element, especially in the organic matter-poor and iron oxide-rich horizons (r_1/R in the 0.001–0.003 range). Then, the buffer capacity of these soils is extremely high, particularly in oxide- and clay-rich horizons, and probably with a majority of low-energy bonds on the surface of colloids. These high values, particularly in the NIQ II profile, highlight the high potential replenishment of soil solution by the fine particles of the soil matrix.

The n parameter can be linked to slow interaction processes with solid phases (sorption/desorption, precipitation/dissolution, surface complexation), but more specifically to diffusion-limited surface sorption inside the soil matrix. In general, chromate ions do not seem to differ from phosphate. In the case of soil NIQ II, it is clear that the presence of a well-developed microstructure of the soil colloids in the upper organo-mineral horizon leads to much higher diffusion of the isotope than in mineral horizons. In the other soil, the mineralogy and discontinuity may probably explain the complexity of the pattern of n values within the soil profile.

The relatively high Cr concentrations in solution mean there is no strong limitation for plant root uptake of Cr and,

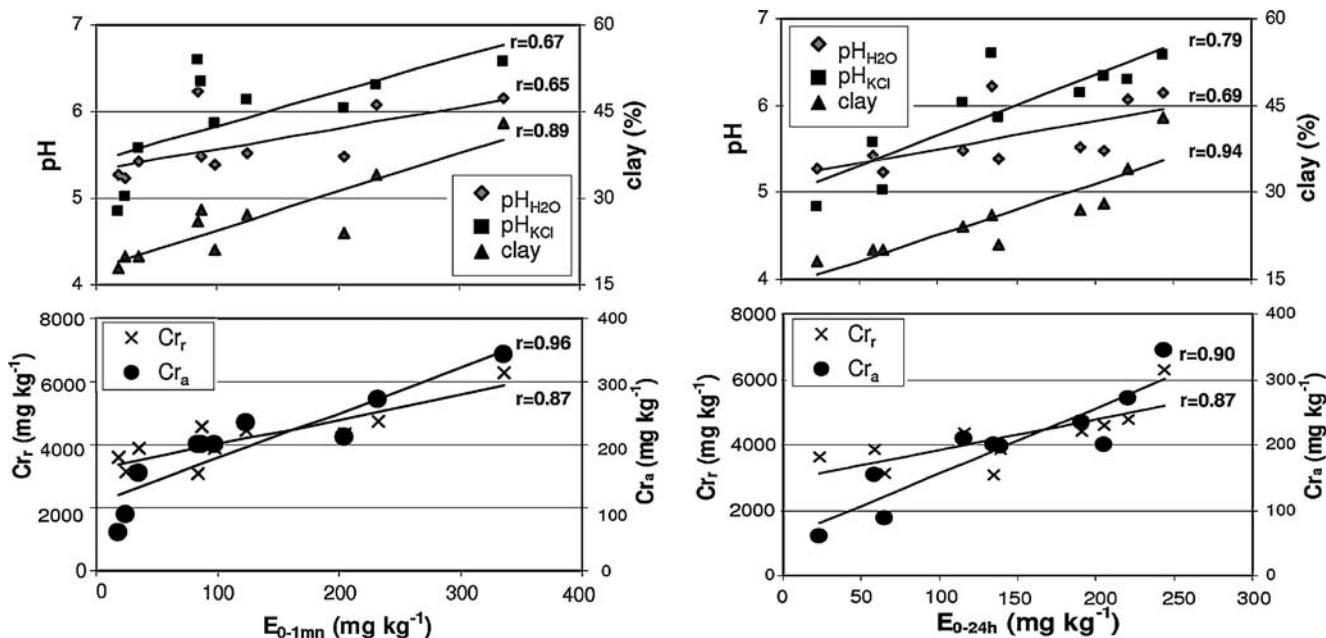


Fig. 3 Relationships between $E_{0-1\text{min}}$, $E_{0-24\text{h}}$ and $\text{pH}_{\text{H}_2\text{O}}$, pH_{KCl} , clay content, Cr_a and Cr_r

thus, for its potential transfer into the plant and phytotoxicity. The quantity of readily labile Cr ($E_{0-1 \text{ min}}$) is significantly correlated with the quantity of Cr associated to amorphous or poorly crystallized Fe-oxides. This correlation increases when considering the sum of $E_{0-1 \text{ min}}$ and $E_{1 \text{ min}-24 \text{ h}}$, i.e., $E_{0-24 \text{ h}}$ ($r=0.96$, $p<0.01$). $E_{0-1 \text{ min}}$ and $E_{0-24 \text{ h}}$ are also significantly correlated to Cr_r and clay content (see Fig. 3). This kind of correlation has already been reported for Ni (Chardot et al. 2007). Thus, amorphous Fe oxides control the Cr availability in these Ferralsols. Moreover, the pH dependance of the most labile fractions of Cr(VI) is explained by the close relationships between oxide surface protonation and Cr(VI) sorption. When pH increases, oxide surfaces deprotonate and, thus, the Cr(VI) sorption decreases. As a consequence, $E_{0-1 \text{ min}}$ increases. This was previously highlighted on these soils by Garnier et al. (2006). The correlation between E parameters and clay content has to be carefully considered. Indeed, the clay fraction contains mainly fine and discrete clay-sized Fe oxides, which show a high surface area, up to $200 \text{ m}^2 \text{ g}^{-1}$ (Cornell and Schwertmann 1996), and can control the sorption of chromate and other anions. Geric Ferralsols from New Caledonia, particularly rich in Al and Fe-oxides, are able to sorb $8,000\text{--}8,300 \text{ mg P kg}^{-1}$ (Dubus and Becquer 2001), and goethite is reported to retain $2.6 \text{ mmol P m}^{-2}$ (Cornell and Schwertmann 1996). Using these data, we can estimate that only 2–3% of the iron oxide surfaces would be covered by labile chromate.

Despite the different data supporting the idea of the inner-sphere surface complexes formation of chromate on goethite (Fendorf et al. 1997), the high quantity of readily labile Cr(VI) and the high buffer capacity observed for these soils are consistent with low-energy bonds on the surface of colloids in agreement with the formation of outer-sphere complexes.

5 Conclusions

The chromate availability in these soils is large and controlled by the amorphous Fe-oxides, particularly those from the clay-size fraction. This may have an impact on vegetation biodiversity and Cr-tolerant species are probably growing on these soils. The high Cr concentrations in solution mean there is no limitation for its potential transfer to plants. The high buffer capacity and quantity of readily labile Cr(VI) of both soils suggest that chromate forms low-energy bonds on the surface of colloids. Finally, IEK for chromate allows one to distinguish different pools of available chromate according to their rate of exchange kinetics. The very labile pool of chromate is particularly high in these two Ferralsols. This compartment is the most important from the ecotoxicological point of view. More-

over, this was the first successful attempt to adapt the use of Isotopic Exchange Kinetic methods to Cr(VI) ever reported.

6 Recommendations and perspectives

The difficulty in assessing the total fraction of available chromate in the soil solid phase (here, phosphate extractable chromate) is introducing limitations in the accuracy of the method because the extrapolation of the power function (see Eq. 1) requires it. However, the IEK method provides a good estimation of the reactivity of chromate in the soil and of the quantities of chromate retained by the solid phase. One could argue why we did not calculate a single E -value at so-called equilibrium but, according to both the detection limit of ^{51}Cr in the solution samples and the intensity of isotopic exchange (very low r_1/R values), it was impossible to reach the 2- to 6-day equilibrium E value often used (Young et al. 2000) for other elements. Therefore, the extrapolation of the kinetics after 40 min was the only tool available, but this has some limitations in terms of the accuracy on the quantity factors and the error increases when one assesses long-term exchangeable pools. The robustness and the limit of IEK for chromate now have to be examined in more detail. Thus, it has to be performed with a wider range of Cr-rich soils, particularly on soils with a different Cr(VI)-fixing capacity. However, our results were consistent and correlated with soil key parameters, suggesting that IEK could be a powerful tool to quantify chromate availability in soils. Our attempt to apply the IEK for chromate is a success and, consequently, the IEK for Cr has a future.

Acknowledgments This work was supported by a grant awarded to J. Garnier by the French Ministry of National Education and Research and by the CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil) under contract No 475124/2006-5. The authors thank Dr. V. Ettler (Charles Univ. Prague) for ICP-MS analysis, Pr E. Guimarães (Univ. Brasilia) and P. Pradel (UMR IDES) for XRD analysis, and Dr. J.-M. Garnier for his useful comments and manuscript improvement. We also thank the Votorantim Niquel, for field access facilities, and Embrapa Cerrados, Planaltina (DF), Brazil, for laboratory support.

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