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Chromium availability in ultramafic soils from New Caledonia

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Abstract

The sources and potential availability of chromium (Cr) on soils formed on ultramafic rocks were investigated with mineralogical studies and selective chemical extractions. Soil solutions were collected in the field (i) along a soil toposequence under natural vegetation with ceramic cups; (ii) under grass in a mandarin trees plantation with tension-free tube lysimeters. On selected soil solutions, the Cr(VI) was determined colorimetrically with the *s*-diphenylcarbazide method and total Cr by ICP-AES and speciation of Cr(VI) was performed with the MINEQL+ V 4.5 software. The main mineralogical sources of Cr were Cr-substituted goethite and chromite. Up to 90 mg kg^{-1} of Cr was extracted by KH_2PO_4, whereas KCl extractable Cr was very low, indicating that exchangeable Cr was mainly in the highly toxic Cr(VI) form in these soils. Under natural vegetation, the Cr concentrations in the soil solutions remained relatively low (< 20 μg l^{-1}) due to the high retention of the Cr(VI) anions by Fe-oxides. The Cr concentrations were larger in well aerated colluvial soils, where high levels of Mn-oxides are able to oxidize Cr(III) to Cr(VI), than in piedmont soil where the Mn-oxide content is lower, or in alluvial soils from the lowlands, where waterlogging occurs. Cr concentrations reached 700 μg l^{-1} in the field that was fertilized with high amount of phosphorus, due to the exchange of Cr(VI) with phosphate. In such conditions, toxicity phenomena for crops can be expected.

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1. Introduction

Chromium (Cr) content in soils and rocks ranges generally from 0 to 200 mg kg^{-1} (Bourrelier and Berthelin, 1998). However, in soils developed on ultramafic rocks, Cr contents up to 10 000 mg kg^{-1} have been reported (Stueber and Goles, 1967; Schwertmann and Latham, 1986). Ecosystems developed on ultramafic rocks have been mainly investigated for their botanical and ecological interest (Baker et al., 1992; Brooks, 1987; Jaffré, 1980; Jaffré et al., 1997; Proctor and Woodell, 1975; Roberts and Proctor, 1992; Whittaker et al., 1954). In New Caledonia, where the outcrops of ultramafic rocks cover 5500 km^2, accounting for about one-third of the Grande Terre, these areas are of agronomic interest. Most of the studies on metal bioavailability in these soils have been conducted on nickel (Ni) (Becquer et al., 1995; L'Huillier and Edighoffer, 1996), whereas Cr behaviour has been poorly investigated. One of the main reasons is that Cr of geogenic origin occurs in soils and rocks mostly as chromite which is extremely insoluble. The second reason is that the plant uptake of Cr is generally very low (Jaffré, 1980), unlike to Ni that can be taken up by native vegetation as well as by crops (Jaffré, 1980; L'Huillier and Edighoffer, 1996).

Cr has different degrees of toxicity depending on its oxidation state: the Cr(III), mainly present at soil pH as CrOH^{2+}, is rather benign and being easily adsorbed in soils, whereas the Cr(VI), present as HCrO$_4^-$, is highly toxic and soluble (Fendorf, 1995). The chemistry of Cr in soils and in natural waters, particularly the conversions between its two oxidation states, has been described by Fendorf (1995), who explain that Cr(III) can only be oxidized to Cr(VI) by manganese oxides, while Cr(VI) is reduced to Cr(III) by organic matter, Fe(II) and sulfites. Some studies indicated that Cr is mobile within ultramafic soils. Soane and Saunder (1959) found appreciable quantities of Cr on cation exchange resins inserted in serpentine soils from Rhodesia. Gasser et al. (1994) found concentrations from 0.1 to 3.2 μM l^{-1} in serpentinitic soils from the Swiss Alps. However, Anderson et al. (1973), who extracted soil solution by centrifugation on a range of ultramafic soils, reported low Cr concentrations ranging between 0.2 and 0.4 μM l^{-1}.

Different studies have shown the high toxicity of Cr(VI) to plants. Turner and Rust (1971) showed that 0.5 mg l^{-1} Cr(VI) in nutrient medium of soybean decreases the yield and the element concentrations of plants for different macro- and micro-nutrients. Bini Maleci et al. (1999) also showed a marked reduction of root and leaf lengths of two species of *Calendula* with 1 mg l^{-1} Cr(VI). Sharma et al. (1995) showed that the grain yield and different metabolic activities were severely affected on wheat by the supply of 0.05 mM of Cr(VI).

Thus, the aim of the present work was to determine the speciation and the availability of Cr in the ultramafic soils from New Caledonia. Mineralogical and chemical extraction studies were combined with in situ soil solution collections to determine the Cr sources and predict the fate and the potential toxicity of Cr for crops growing on these soils.

2. Material and methods

2.1. Study area and soils characteristics

The study was carried out on the Ouénarou station (E166°44′–S22°8′) in the south of the Grande Terre, New Caledonia. The area corresponded to the piedmont and valleys of the massifs that could be used for agriculture. Climate is characterised by annual precipitation of approximately 3000 mm with a wet season occurring from December to August.

The soils are Geric Ferralsols (FAO, 1998) comprising upslope sedentary soils grading progressively downwards towards colluvial and, later on, alluvial soils, all deriving from weathered peridotites. Different types of soil, essentially related to the topographic position in the landscape, have been distinguished along a soil toposequence: highly weathered and strongly desaturated soils on the piedmont (OUE 1); colluvio-alluvial soils with some poorly weathered silicates (OUE 3); alluvial soils subject to temporary waterlogging on terraces

(OUE 4). Their main features are described elsewhere (Becquer et al., 1995, 2001) and some of their chemical characteristics are presented in Table 1.

2.2. Chemical analysis

Extractions of exchangeable Cr(III) and Cr(VI) were performed with 1 M KCl and 0.1 M KH_2PO_4 (Bartlett and James, 1996), respectively, by shaking 1 g of soil with 25 ml of reactant for 1 h at 20 °C.

A modification of the dithionite–citrate–bicarbonate (DCB) deferrification method from Holmgren (1967) is used for Cr associated to Fe-oxides (Becquer et al., 2001). Strong acid extractable Cr contents were determined by diacid digestion (2:1 HNO_3:HCl ratio) in a microwave oven. Then, all the samples were centrifuged at $48\,000 \times g$ for 20 min and the supernatant analysed for Cr by ICP-AES (Jobin Yvon 238).

2.3. Mineralogical study

X-Ray diffraction (XRD) analyses were performed on selected horizons of each profile on the deferrified clay fraction (<2 μm) and on the sand + silt fraction (2–2000 μm). The soil samples were also observed by transmission electron microscopy (TEM) (Phillips CM 20). The finely powdered soil samples were suspended in ethanol under ultrasonication. A drop of suspension was then evaporated on a carbon-coated copper grid, and the preparation was observed with TEM at an accelerating voltage of 200 kV. EDXS analysis of selected particles were carried out using an energy dispersive analysis of X-ray spectrometer mounted on the Phillips CM 20 TEM.

2.4. Soil solution collection

Soil water samples were collected with ceramic cups samplers (SDEC, France, Catalog no. SPS2xx4BM3) under natural vegetation in plots located in the three soil types studied. After cleaning with 1 M HCl and washing with ultrapure water, the samplers were inserted into the soil at two depths (0.1 and 0.4 m) with eight replicates per depth. Soil solution samples were taken at approximately 2-week intervals during the wet season, from April to August 2000 and from January to April 2001. The samples were acidified to approximately pH 2 with pure HNO_3 in the field and stored in the fridge before analysis by ICP-AES for their Cr content.

Cr sorption on the sampler was evaluated. After cleaning as indicated previously, the samplers were placed in duplicate in bechers containing a solution of approximately 100 μg l^{-1} of Cr (96 μg l^{-1} of Cr(III) as $Cr(NO_3)_3$ or 108 μg l^{-1} of Cr(VI) as K_2CrO_4). Then, approximately 800–1000 ml of Cr solutions were drawn through the porous sampler with a vacuum by sub-samples of 100–150 ml and analysed for Cr as previously. The Cr concentrations after extraction through the ceramic cup are presented in Fig. 1. The curves showed that the sorption of Cr(III) was practically total showing that the ceramic cups are unsuitable to monitor the Cr(III) concentration in the soil solutions. On the other hand, the Cr(VI) sorption on the ceramic is practically nil except for the first sampling, where 20–40% of the Cr(VI) was sorbed.

Soil solutions were also collected with tension-free tube lysimeters between November 2000 and June 2001 in a field located in the colluvio-alluvial area with a soil similar to OUE 3. The field is planted with mandarin trees and the rows between the trees, as well as the lysimeters, are covered by grass. As phosphorus availability is very limited in this soil (L'Huillier et al., 1998), it had received high inputs of phosphorus (P) fertilizers (6 t P_2O_5 ha^{-1}), calcium carbonate (2 t CaO ha^{-1}) and compost (20 t ha^{-1}) before tree plantation, 4 years before the soil solution collection. Phosphorus was mixed with the soil to two different depths (30 and 60 cm). Water is supplied by drip irrigation. The soil solutions were collected in duplicate at 60-cm depth. Then, the two treatments are noted P30/C60 and P60/C60 for P incorporated at 30 and 60 cm, respectively, and for the soil solutions collected at 60 cm. On selected soil solutions ($n = 78$), the Cr(VI) was determined colorimetrically with the *s*-diphenylcarbazide (DPC) method (Bart-

Table 1
Main physical and chemical properties of the soils

Sample origin	Profile	Horizon	Depth of sampling (cm)	pH		Organic matter		EB				EA	ECEC	Strong acid extractable concentration					
				H_2O	KCl	C ($g\,kg^{-1}$)	N	Ca^{2+} ($cmol\,kg^{-1}$)	Mg^{2+}	K^+	Na^+			SiO_2 ($g\,kg^{-1}$)	Al_2O_3	Fe_2O_3	MnO_2	NiO	Cr_2O_3
Piedmont	OUE 1	OUE 1–1	0–5	4.6	5.1	36.2	1.62	0.5	0.4	0.1	0.1	0.05	1.7	22	107	623	6	8	31
		OUE 1–4	38–57	4.8	5.8	2.4	0.16	0.1	0.1	0.0	0.0	0.04	0.2	17	103	648	9	9	30
Colluvial	OUE 3	OUE 3–1	0–4	5.1	5.1	76.3	2.37	9.9	2.4	0.5	0.2	0.07	14.4	91	70	539	8	12	27
		OUE 3–4	40–51	5.0	6.1	11.9	0.71	0.2	0.6	0.1	0.0	0.03	1.1	75	72	521	7	11	28
Alluvio-colluvial	OUE 4	OUE 4–2	4–9	4.6	4.7	25.4	1.35	0.2	0.5	0.1	0.0	0.03	1.4	73	63	563	7	12	20
		OUE 4–3	26–39	5.0	6.2	9.6	0.51	0.1	0.2	0.0	0.0	0.05	0.5	42	95	579	9	10	32

EB, exchangeable bases; EA, exchangeable acidity ($Al^{3+}+H^+$); ECEC, effective cation exchange capacity measured in 0.5 M NH_4Cl.
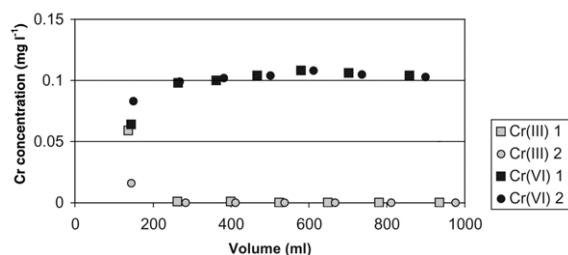
Fig. 1. Laboratory test on the Cr sorption by the ceramic cup sampler: the concentrations of an initial concentration of 0.1 mg l^{-1} of either Cr(III) or Cr(VI) were recorded after passing of an increasing volume of the solution through the sampler.

lett and James, 1996) and total Cr by ICP-AES as described previously.

3. Results

3.1. Chemical extractions

The strong acid extraction of soil samples (Table 2) showed that the amounts of Cr reached 13 700–21 900 mg kg^{-1}. The amounts of metals extracted by KCl were very low with regard to the content of Cr extracted by strong acids, and reached only 6.5 mg kg^{-1} at maximum in OUE 4–3. However, up to 90 mg kg^{-1} of Cr was extracted by KH_2PO_4 (Table 2). The extraction yield was lower in surface horizons than in deeper ones. The DCB dissolution indicated that an average of 40% of Cr was associated with Fe-oxides (Table 2).

3.2. Mineralogical studies

The XRD of the sand + silt fractions showed the presence of spinels. As magnetite could be also present, chromite was not determined with certainty. Nevertheless, TEM observations and EDXS analysis revealed the presence of chromite (Fig. 2), but it was rare and not detected in all the observed samples. EDXS analysis of goethite particles indicated Cr content ranging from 0.4 to 7.9% (atomic) with a mean of 2.2% (Fig. 2). Some differences in Cr content of goethite have been observed depending on the position of the soil sample in the profile and the landscape and on the goethite types (Becquer et al., submitted

for publication). These contents and the mineral association are in good agreement with those expected from the DCB extractions.

3.3. Soil solution

3.3.1. Cr concentrations in the soil of the toposequence

Soil solutions collected with the ceramic cups contained only Cr(VI), as Cr(III) is sorbed either in the soil or on the cups (Fig. 1). For 2000, the concentrations of Cr averaged 4.6, 15.1 and 13.1 $\mu g\ l^{-1}$ at 0.1 m deep for OUE 1, OUE 3 and OUE 4, respectively (Table 3). The concentrations at 0.4 m were slightly higher (significant at $P = 0.05$) or not significantly different than those at 0.1 m for OUE 1 and OUE 3, respectively. However, Cr concentration was substantially lower at 0.4 m than 0.1 m (significant at $P = 0.001$) for OUE 4. The average Cr concentrations decreased progressively with time (Fig. 3). They were 4 times lower for OUE 1 and 2 times lower for OUE 3 and OUE 4 at the end of the sampling period than at the beginning. The same trends were observed at 0.1 and 0.4 m. For 2001, the concentrations of Cr were systematically lower than those of 2000. The average Cr concentrations were lower than 5 $\mu g\ l^{-1}$ except for OUE 3, where they reached 10 and 7.3 $\mu g\ l^{-1}$ at 0.1 and 0.4 m deep, respectively (Table 3).

3.3.2. Cr concentrations in the cultivated soil

The Cr concentrations of the soil solutions collected with the lysimeters averaged 190 and 555 $\mu g\ l^{-1}$ for treatments P30/C60, P60/C60, respectively, with maximum concentrations reach-

Table 2
Extractable concentrations of Cr of the soils

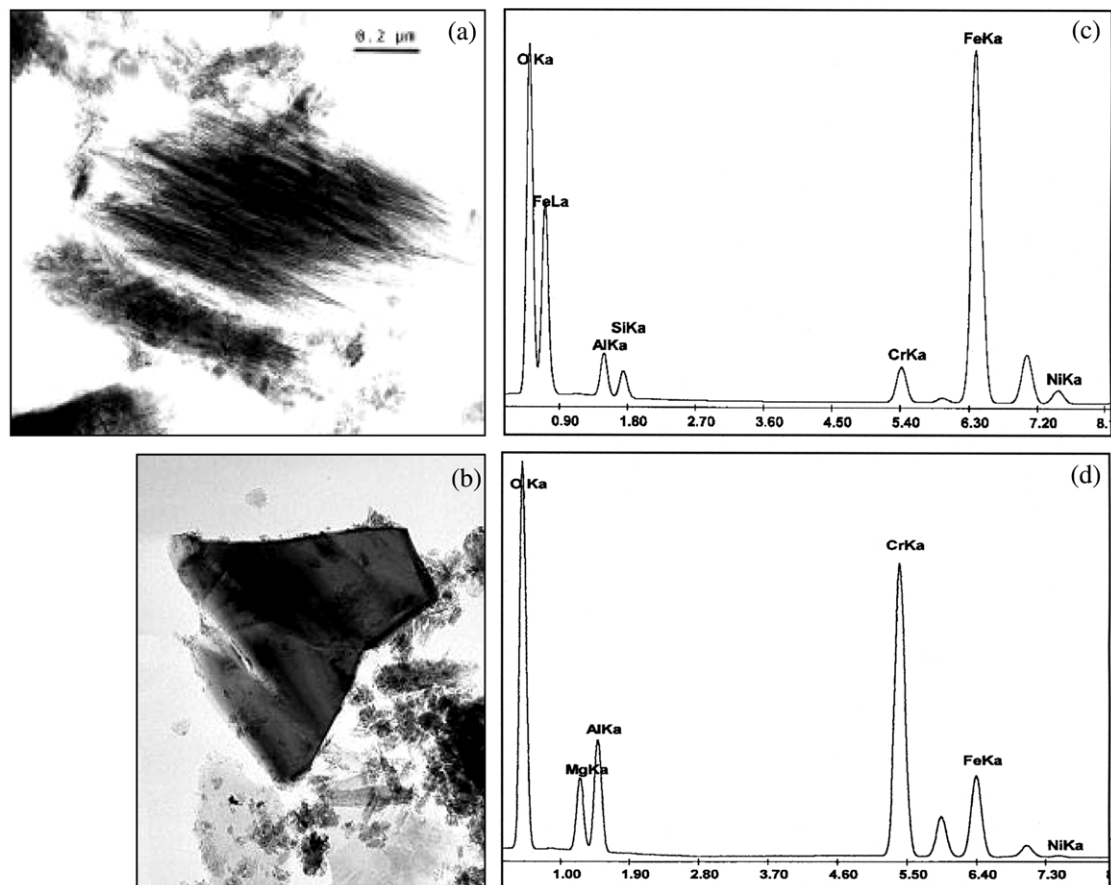| Profile	Horizon	KCl	KH_2PO_4	CBD	Strong acid
		mg kg^{-1}			
OUE 1	OUE 1–1	0.0	8.2	3466	21 210
	OUE 1–4	4.0	82.8	8904	20 530
OUE 3	OUE 3–1	0.0	4.2	6602	18 470
	OUE 3–4	6.5	73.0	7560	19 160
OUE 4	OUE 4–2	2.5	12.6	9072	13 680
	OUE 4–3	5.5	45.8	8120	21 890

Fig. 2. TEM observations (a, b) and EDX spectra (c, d) of a Cr-rich goethite (a, c) and of chromite (b, d).

Table 3
Mean ($\pm$ standard deviation) concentrations of Cr in the soil solutions collected at 0.1 and 0.4 m under natural vegetation during 2000 and 2001

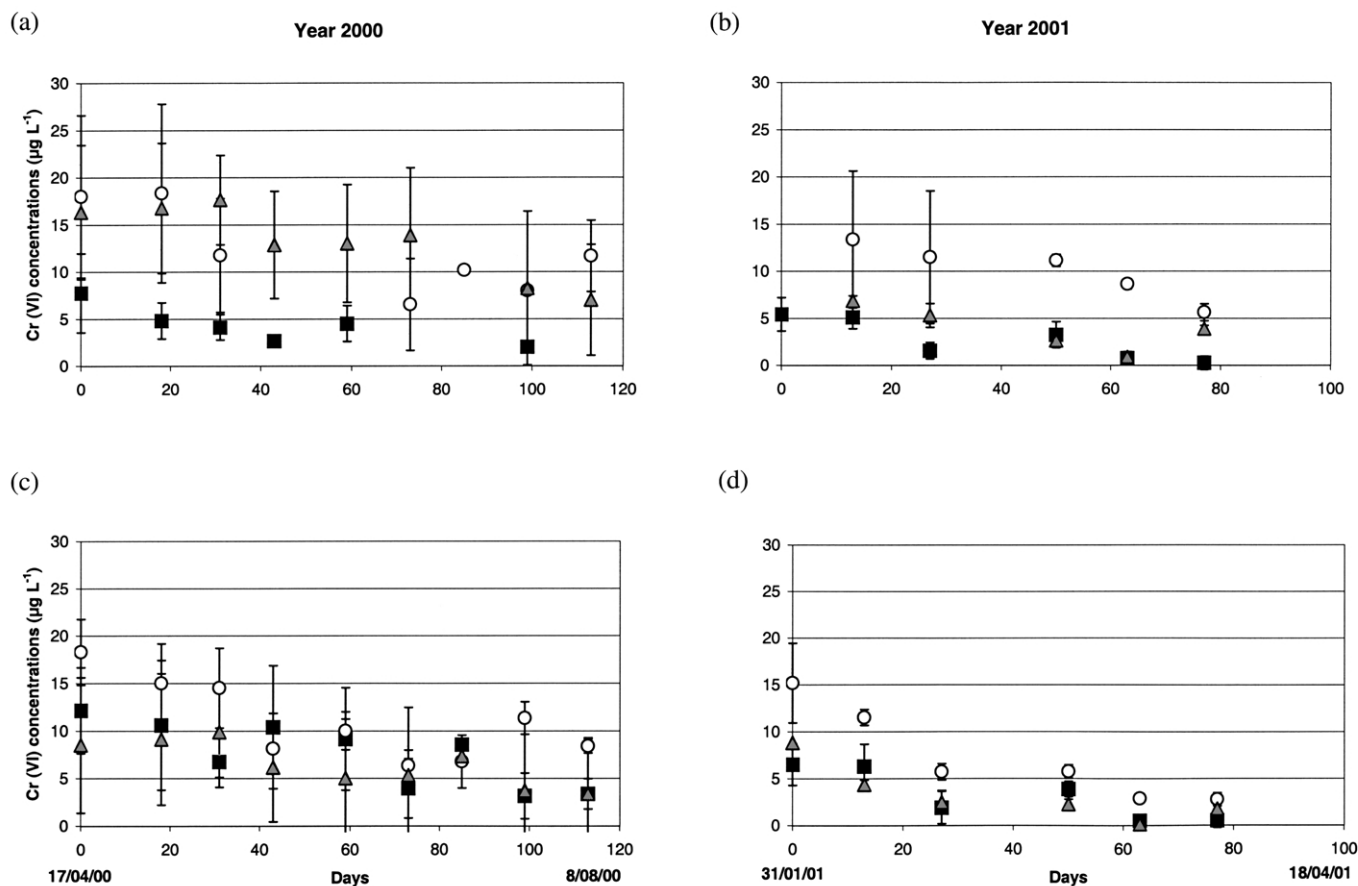| Depth m	Profile	Sample number μg l^{-1}	Mean	Standard deviation	Sample number	Mean	Standard deviation
		2000			2001		
0.1	OUE 1	32	4.64	3.19	48	2.72	2.33
	OUE 3	31	15.10	10.28	48	10.04	5.10
	OUE 4	56	13.06	7.21	40	3.91	2.20
0.4	OUE 1	54	7.23	5.15	48	3.27	2.93
	OUE 3	49	12.13	4.95	40	7.30	4.94
	OUE 4	66	6.62	3.51	48	3.29	3.30

Fig. 3. Time evolution of Cr(VI) concentrations measured at 10 (a, b) and 40 (c, d) cm depth in the rainy seasons of 2000 (a, c) and 2001 (b, d) for three locations (OUE 1, OUE 3 and OUE 4) situated along a soil toposequence under natural vegetation.
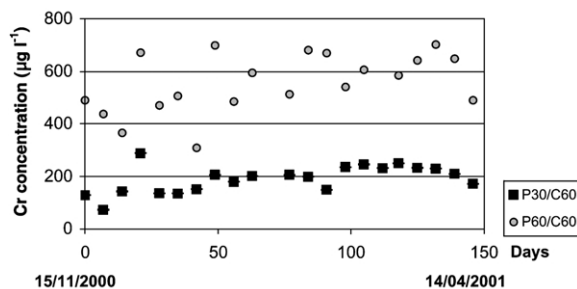
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Fig. 4. Time evolution of Cr concentrations measured at 60 cm depth during the rainy seasons of 2000–2001 in a field highly fertilized with phosphorus (in P30/C60 treatment, P was incorporated to 30 cm depth, and in P60/C60 treatment, P was incorporated to 60 cm depth).

ing 700 $\mu g\,l^{-1}$ for P60/C60 (Fig. 4). The Cr concentrations of these soil solutions collected under a field fertilized with high amount of P are therefore 10–50 times higher than those collected under natural vegetation (OUE 3). The determinations with the DPC method showed that all the Cr was in the Cr(VI) form. Speciation of Cr(VI) performed with the MINEQL+ V 4.5 software (Schecher and McAvoy, 1998) showed that more than 99% of the Cr(VI) was in the CrO_4^{2-} and $HCrO_4^-$ forms, the proportion between the two species depending on the pH of the soil solution (Fig. 5).

4. Discussion

4.1. Cr sources

The larger effectiveness of KH_2PO_4 over KCl indicated that exchangeable Cr was mainly under the anionic form of Cr(VI). The lower levels of exchangeable Cr in surface horizons than in deeper ones were in good agreement with the lower Anionic Exchange Capacity measured in A horizons than in Bo (Becquer et al., 2001) and the greater sorption capacity of Bo horizons for phosphorus (Dubus et al., 1998). In the deep horizons, the KH_2PO_4 extractable Cr(VI) decreased markedly from the piedmont soil (OUE 1) to the alluvio-colluvial soil (OUE 4). As the colluvio-alluvial soils (OUE 3 and OUE 4) are richer in organic matter and OUE 4 is subjected to temporarily waterlogging leading to Fe(II) production,

reduction of Cr(VI) to Cr(III) is thought to occur in this conditions (Fendorf, 1995) and can partly explain the decrease of Cr concentrations.

A large part of Cr was associated with Fe-oxides in these soils as noticed earlier (Nalovic and Quantin, 1972; Schwertmann and Latham, 1986) and in such mineral phases, Cr substitute isomorphically for Fe (Schwertmann et al., 1989). These compounds are poorly solubilized except in waterlogged conditions, where Fe reduction due to ferri-reducing bacteria occurs (Quantin et al., 2001). In such conditions, Cr solubilisation was not observed in batch experiments (Quantin et al., 2001), but the amount of Cr associated with poorly crystallised Fe-oxides increase (Quantin et al., 2002b) indicating a redistribution of Cr species into the solid phase to more labile species. Cr that was not associated to Fe-oxides was mainly present in chromite and therefore unavailable.

4.2. Cr availability in the soil solutions

Soil solution analysis allows direct analysis of the medium surrounding the roots. Sampling methods display various limitations, because the element concentrations may vary substantially according to the extraction procedures (Dahlgren, 1993). For ceramic cup samplers, the retention of significant quantities of trace metals occurs on certain sampling devices (McGuire et al., 1992; Wenzel and Wieshammer, 1995). Cr(III) sorption occurring on the sample devices used decreased the concentrations of Cr measured in the soil solution. The tube lysimeters are more suitable to the collection of both Cr(III) and Cr(VI) species. However, the concentration of the toxic Cr(VI) was not affected by the suction cups.

Cr concentrations in the soil solutions collected under natural vegetation were of the same order than those reported in other studies for ultramafic soils (Anderson et al., 1973; Proctor et al., 1981). Gasser et al. (1994) found Cr concentrations ranging from 0.1 to 3.2 $\mu M\,l^{-1}$ in soil solution collected with tension-free lysimeter. However, they worked on serpentinic soils with a lot of coarse fragments of rocks and they noticed that only 28% of Cr was present in dissolved form in their samples, the remaining being in colloidal form.
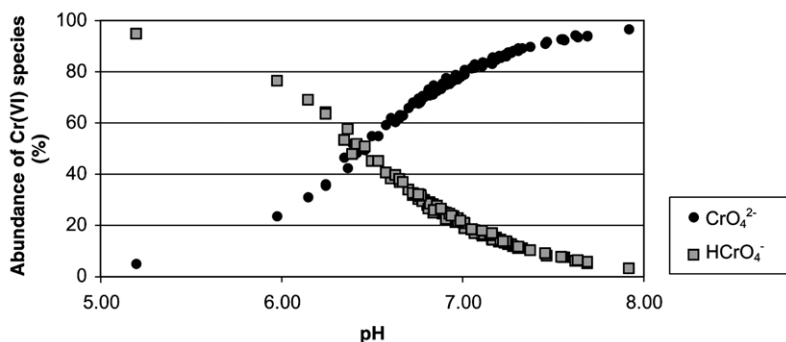
Fig. 5. Abundance of Cr(VI) species in the soil solutions collected in the field calculated with MINEQL+.

The decrease of the Cr concentration during the wet season has considerable environmental importance. During the dry season, the oxidation of Cr(III) to Cr(VI) is expected to occur. Mn-oxides, which have been proved to be the only naturally occurring oxidant of Cr(III) (Fendorf, 1995), were observed by TEM in OUE 4 (Quantin et al., 2002a). Although these compounds were not detected with XRD or TEM in the other profiles, they are thought to occur as expected from hydroxylamine extractions (Becquer et al., submitted for publication) and to lead to the oxidation of Cr(III). Cr(VI) accumulates on Fe-oxides, accounting for the flux of Cr(VI) which takes place at the beginning of the next wet season. During the wetting phase, the redox potential decreases and Cr(VI) can be reduced by both organic material and Fe^{2+}. This leads to the decreasing of Cr(VI) in the soil solution. However, the rate of the chromate reduction has been proved to be generally low, especially when the soil pH is over 4.5 (Eary and Rai, 1991). In OUE 4, particularly in the deep horizon OUE 4–3 where waterlogging occurs, the Cr(VI) concentration decreased more sharply than in the other horizons. In OUE 1, the Cr(VI) concentration remained lower than in colluvio-alluvial soils although waterlogging is not suspected to occur. The amount of Mn-oxides extracted by hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) was substantially lower than in other profiles with contents of 840 to 2200–3000 mg kg^{-1} in OUE 1 and OUE 3–OUE 4, respectively (Becquer et al., submitted for publication). Therefore, the Cr(III) oxidation remained probably low in OUE 1.

Whereas under natural vegetation the Cr concentrations remained relatively low, under highly P fertilized crops, the Cr(VI) concentrations can be over 500 µg l^{-1}. Cr concentration in soil solutions is substantially increased after the input of phosphorus fertilizers. Due to its anionic nature, Cr(VI) has a high affinity for iron oxides and XAFS studies show that Cr(VI) forms an inner-sphere complex on goethite (Fendorf, 1995). However, the greater retention strength of phosphate over Cr(VI) (Bartlett and Kimble, 1976) leaded to its desorption from the goethite after P fertilizer inputs. The Cr concentrations were significantly lower in the P30/C60 treatment. The inputs of P can desorb the anionic Cr(VI) sorbed on the iron oxide surfaces and then to increase the Cr concentrations in the soil solutions. However, when the incorporation of P is only made on the top 30 cm of the soil, the soluble Cr(VI) can be readsorbed between 30 and 60 cm depth leading to the decrease of Cr concentration.

Under highly P fertilized crops, the Cr(VI) concentrations can be over 500 µg l^{-1}. Different studies have shown that 0.25–1 mg l^{-1} Cr(VI) in nutrient culture decrease the yield, the macro- and micro-nutrients uptake and different metabolic activities of plants (Turner and Rust, 1971; Sharma et al., 1995; Bini Maleci et al., 1999). In these soils, the very high fixation of phosphorus (Dubus et al., 1998) imposes high phosphorus inputs to prevent yield limitations for crops (L'Huillier et al., 1998). However, the leaching of Cr(VI) after these inputs has most probably a harmful effect on crops and may have major environmental consequences.

5. Conclusion

Despite the presence of a large part of Cr in highly insoluble solid phases such as chromite and Cr-substituted goethite, Cr was also present in the soil solutions collected under natural vegetation. The most available fraction was the exchangeable Cr in the highly toxic anionic form Cr(VI). However, its retention on the Fe-oxides limited its concentration below $15–20$ $\mu g\,l^{-1}$. Under crops, the phosphorus fertilizer inputs increased its solubility and Cr concentrations reached 700 $\mu g\,l^{-1}$. In these conditions, toxicity phenomena for crops are expected. The potential risk varied according to the position of the soils in the landscape, to their physico-chemical characteristics and to the prevailing edaphic conditions. Cr availability was larger in well-aerated colluvial soils whereas in alluvial soils, where waterlogging occurs, the Cr contents in the soil solutions was limited.

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