Field availability and mobility of metals in Ferralsols developed on ultramafic rock of Niquelândia, Brazil

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Abstract
Ultramafic (UM) rocks are defined as igneous rocks that contain more than 90% of mafic minerals. Soils derived from ultramafic rock are generally nutrient-deficient and have concomitant high concentrations of potentially phytotoxic trace elements (Ni, Cr, Co, Mn). Consequently, to assess the dynamics of nutrients and metals in the ultramafic complex of Niquelândia (Brazil), soil solutions have been sampled in soils characterized by high Cr(VI) availability. The metal contents in surficial water have also been analyzed to investigate the metals’ leaching and mobility. Soil solutions featured low nutrient contents, a large Ca:Mg imbalance, and high Ni and Cr concentrations. Chromium was present in its toxic dissolved form (Cr(VI)) in the soil and surficial solutions. Metals concentrations were often above the toxic limit for biota and were therefore able to affect soil functioning. Ni behavior in the topsoil appeared to be primarily controlled by organic matter, while Cr was more likely to be released from Fe-oxides by anionic exchange. This result agreed with the Cr(VI) lability assessed using isotopic exchange kinetics in a companion study. In these serpentinic tropical soils, the highly leached Fe-oxide horizons appear to play a large role in the sequestration and diffuse leaching of labile Cr(VI) and Ni, respectively, in the deeper part of soil profiles and the topsoil. At the catchment scale, surficial solutions results suggest that metals may be exported to surrounding ecosystems that are not adapted to these metals.

KEYWORDS: chromium; nickel; soil solution; runoff; serpentine syndrome; metal toxicity.

INTRODUCTION
Ecosystems developed on ultramafic (UM) rocks have long been known as unique (1). Serpentinitic or ultramafic substrates are harsh environments for biota due to their low levels of nutrients (N, P, and K), the imbalance between calcium (Ca) and magnesium (Mg), and the presence of metals, such as nickel (Ni), chromium (Cr) and cobalt (Co) (Whittaker 1954, Brooks 1987, Kazakou et al. 2008, Péčživiat et al. 2018). These chemical characteristics have contributed greatly to the consideration of certain ultramafic ecosystems as “hot spots” of biodiversity (Myers et al. 2000). Moreover, the chemical characteristics of UM ecosystems explain the major ecological traits of these environments, which are often called the serpentine syndrome:

• low plant productivity;
• a high degree of endemism;
• vegetation types distinct from those of neighboring areas;
• the presence of certain “hyperaccumulators” of metals (Ni) (Jaffré et al. 1976, Proctor and Nagy 1992, Reeves et al. 2007, Kazakou et al. 2008, Anacker 2014, Bini et al. 2017, Kanellopoulos et al. 2015, Ratï et al. 2018, 2019).

These features are magnified in tropical areas where strong leaching conditions have led to the formation of deep lateritic profiles.

Tropical soils developed in ultramafic rock have been widely studied due to their edaphic particularities and lateritic Ni mining. However, most of the research has focused on the solid component, including subjects such as soil characteristics, mineral compositions, metal solid speciation behavior, and more recently, Ni isotopic compositions (Quantin et al. 2002, Oze et al. 2004, Becquer et al. 2006, Fandeur et al. 2009, Dublet et al. 2012, Ratï et al. 2015, Hseu et al. 2017). During the past few decades, the availability of Ni and hexavalent Cr has been highlighted by laboratory investigations of tropical soils developed in ultramafic rock from New Caledonia (Quantin et al. 2002, Becquer et al. 2003, Becquer et al. 2006). Metal concentrations in “ultramafic” soil solutions remain incompletely and poorly documented (Anderson et al. 1973, Johnston and Proctor 1981, Gasser et al. 1994), particularly under tropical conditions. However, a recent investigation of soil solutions from New Caledonia has shown significant concentrations of metals in toxic forms, i.e. free-ion species (Becquer et al. 2010). The concentration, speciation and availability of Cr...
have been studied in soils of the Niquelândia ultramafic mas-
sif in Brazil. The high availability of Cr in its most toxic form,
*i.e.*, hexavalent Cr (Cr(VI)), has been quantified using several
laboratory approaches, that is, chemical extractions, kinetics
and XANES isotopic exchange (Garnier et al. 2006, Garnier
et al. 2009a, Garnier et al. 2013).

Metals, such as Co, Cr, Mn, and Ni, are known to be poten-
tially toxic in soils, even at low concentrations, and may lead
to major limitations to root and leaf development and even
the death of non-adapted organisms. The phytotoxicity of
such metals depends on their mobility, uptake, and biological
impact (Anderson et al. 1973, Sharma et al. 1995, L’Huillier
and Edighoffer 1996, Samantary 2002, Becquer et al. 2010).
Therefore, in addition to their concentrations, the phytoto-
xicity of metals in soil solutions is controlled by speciation,
complexation with organic and/or inorganic components,
ionic strength, pH, and exposure duration. Moreover, the
uptake of metals by roots and microorganisms is complex
and depends on bio-physico-chemical interactions in the
solid-solution-biota continuum (Alexander 2000, Zayed
and Terry 2003).

A large spatiotemporal variability in soil solution compo-
sition is expected with regard to different edaphic conditions.
Thus, soil solution sampling under field conditions, with native
biota and seasonal climate variations, is complementary to lab-
oratory approaches that study potential metal availability, fate,
and toxicity. Field approaches and large datasets that describe
the spatial and temporal variations in soil solution composi-
tion are essential and required to identify the main processes
that control the release and mobility of both nutrients and
metals concentrations.

Due to the relatively high metals concentrations of UM
bedrock (Ni, Co, and Cr), weathering products can repre-
sent an important source of metals for surface and ground-
water. Nonetheless, in UM complexes, few authors have pre-
viously reported natural transfers of trace elements (Weng
et al. 1994, Robles-Camacho and Armienta 2000, McClain
and Maher 2016). In the Putah Creek watershed (California
Coast Range Mountains, USA), riverine Cr concentrations
and speciation in ultramafic catchments are governed by the
balance between ultramafic rock weathering and elemen-
tal cycling along water flow paths, mainly by the availabil-
ity of electron donors and acceptors (*e.g.*, Fe(II), organics,
Mn(III/IV)-oxides) (Mcclain and Maher 2016). However,
the uptake of metals by roots and microorganisms is complex
and depends on bio-physico-chemical interactions in the
solid-solution-biota continuum (Alexander 2000, Zayed
and Terry 2003).

**MATERIALS AND METHODS**

**Site and materials**

The study area is located in the ultramafic complex of
Niquelândia, Goiás, Brazil (S14°18’–E48°23’). The regional
climate is tropical humid; the region experiences an annual
average temperature of 20°C and receives rainfall amount-
ing to 1,500 mm. Two contrasting seasons are present: a
wet and hot season occurs from November to April, and a
dry season occurs from May to October. The vegetation,
which is dominated by herbaceous plants and bushes, is sim-
ilar to “Campo limpo” (Cerrado), a portion of the Brazilian
Savanna dominated by grasses and herbaceous subshrubs.
Several Ni-hyperaccumulating plants have been found in the
ultramafic complex and have been described by Reeves et al.
(2007), such as *Justicia Lanstyakii*, *Heliotropium aff salicoide*,
and *Cnidoscolus aff urens*.

Two Geric Ferralsols (NIQII and NIQIII; WRB, 2006)
located on the footslope of a toposequence representative of
the Niquelândia massif and previously described by Garnier
et al. (2006, 2009b) were selected for this study due to their
high Cr(VI) lability (Garnier et al. 2006, 2009b, 2013).

The studied soils (NIQII and III) come from the massif
consists of a hilly landscape controlled by a level of silcrust
(a hardened accumulation of silica) and containing eroded
backslope and footslope composed of debris stripped from the
entire landscape (Fig. 1). The weathering profiles are charac-
terized by the presence of a relatively thick upper Fe-rich zone
overlying a saprolite containing Mg-Ni clay silicates (“gar-
ierite”) in contact with the ultramafic bedrock (Garnier
et al. 2009b). The mineralogy of the soils is dominated by iron oxides
(goethite and haematite); other accessory minerals are also
present, such as chromite and quartz (Garnier et al. 2009b).
These soils are particularly rich in Fe, with more than 400 g
kg⁻¹, and feature high concentrations of “trace” metals, such as
Ni and Cr (3,156–6,252 and 5,687–9,268 mg kg⁻¹, respec-
tively) (Suppl. Tab.). The organic C content ranges between
20 and 22 g kg⁻¹ in the surface horizons and decreases rapidly
with depth (Suppl. Tab.).
Water sampling

Soil solutions were collected from plots under natural vegetation developed on the Ferralsols NIQ II and NIQ III (Fig. 1). Ceramic cup samplers (No. 653X02B1 M3, Soilmoisture Equipment Corp., Goleta, CA, USA) were used. Studies that have tested the metal sorption in these ceramic cups have shown that they are suitable for monitoring metal concentrations in soil solutions, with the exception of Cr(III) (Becquer et al. 2003, Becquer et al. 2010). After cleaning with 1.10⁻³ M HCl and rinsing the ceramics with ultrapure water four times, the samplers were carefully inserted into the soil at depths of 20, 70, and 150 cm for NIQ II and 20 and 150 cm for NIQ III. For each ceramic cup, a soil hole has been previously opened using a soil sampler. Six replicates were collected at each depth. The soil solutions were sampled approximately every 2 weeks between December 2006 and June 2007 (i.e., during the rainy season until water was no longer extractable) and again in February 2008. It was possible to collect soil solutions at 20 cm depth until April 2007, and deeper samples could be collected until June 2007. Typically, 50 to more than 500 ml of solution was collected at each sampling location and depth, depending on the seasonal period, but sometimes no water could be extracted because the soil was dry. After pH measurement, the soil solutions were filtered using cellulose membranes (0.22 μm) and separated into three aliquots in the field. The first aliquot was acidified with pure HNO₃ for cation analysis and stored at 4°C. Cations were measured using ICP-AES (Varian Liberty 200 at UPS-GEOPS Laboratory). As Cr(III) is known to sorb onto the ceramic cups, the Cr measured in the soil solutions was expected to be hexavalent (Becquer et al. 2010). Nevertheless, a few hours after sampling, the Cr valence was verified in the second aliquot using the 1,5-diphenylcarbazide (DPC) method described by Bartlett and James (1996). Inorganic anions were analyzed in the second aliquot using anionic chromatography ( Dionex ICS1000 at UPS Laboratory) equipped with an IonPac AS14 (Dionex) column and conductivity detection. The eluent was 3.5 mM Na₂CO₃ and 1.0 mM NaHCO₃ under isocratic conditions with a flow rate of 1.2 ml min⁻¹. The third aliquot was also stored at 4°C until analyses of anions and dissolved organic carbon (DOC) were performed. DOC concentrations were determined using a TOC-Vsh Shimadzu analyzer, calibrated using potassium hydrogen phthalate (Fisher Scientific, Analytical Reagent grade) with an accuracy of 0.01 mmol L⁻¹. Uncertainties were lower than 5%, and the detection limits calculated for ICP-AES, DPC, and ionic chromatography were 0.001, 0.002, and 0.002 mmol L⁻¹, respectively. A water internal standard was used to check the validity and reproducibility of each water analysis (less than 5% using the same instrument). As it was not possible to measure it in the field, the alkalinity of the samples was calculated as the difference between the cation and anion concentrations.

Rainwater (collected twice on 01/29/2007 and 03/14/2007) and water from the nearby stream draining the studied catchment area were both analyzed. The stream water was regularly collected at the spring and at its outlet at the ultramafic complex boundary 8 and 7 times in 2007, respectively (Fig. 1). These samples were analyzed using the same procedures as those applied to the soil solutions. Rain infiltration is highly efficient and rapid in both of the studied Ferralsols, as observed by Reatto et al. (2007). Nevertheless, runoff has occasionally been observed in the field during rainstorms. Thus, runoff solution samples (n = 3) were taken from temporary streams on the footslope uphill of NIQ II during three heavy rain events. The same methodologies have been used to analyze the concentrations of cations, Cr(VI), anions, and DOC of surface samples.

In both soil solutions and surface waters, chromium has been found entirely in the hexavalent form due to the total concentrations (Cr₄tot = Cr(III)+Cr(VI)) determined via ICP-AES and Cr(VI) determined via DPC having been statistically equivalent (p > 0.70).
Simplified Pourbaix diagrams were generated from the average water compositions and physicochemical parameters of the surface waters collected during the experiment. This was performed using the Act2 module of the Geochemist Workbench (GWB) 14 software.

Since colloidal particles have been proven to play a key role in metal mobility in solutions of soils developed on ultramafic rock (Gasser et al. 1994, Zelano et al. 2013, Bolaños-Benítez et al. 2018), a special investigation was conducted using all solutions sampled during the sampling of February 2008, including runoff waters. A size fractionation approach was performed on soil and surface solutions using the frontal cascade filtration technique (Patel-Sorrentino et al. 2007, Garnier et al. 2011). In the field, solutions were successively filtered at nominal cut-offs of 0.22 μm, 0.025 μm, and 10 kDa, leading to the collection of four θ fractions (unfiltered, θ₁; 0.22 > θ₁ > 0.025 μm; 0.025 > θ₂ > 10 kDa; 10 kDa > θ₂). The first filtration was performed using a syringe filter holder, and the 0.025 μm and 10 kDa filtrations were performed under N₂ pressure with acetate membranes and polyethersulfone Millipore membranes, respectively, in a 47 mm filter holder.

RESULTS

Soil solution

The pH of the soil solutions was slightly acidic, ranging from 5.60 ± 0.15 to 6.10 ± 0.08, and increased slightly with depth in both soils (Tab. 1). At a depth of 20 cm, the pH was low (pH 5.60–5.70) at the beginning of the rainy season (Dec. 2006 – Jan. 2007) and subsequently increased. At deeper levels, the pH fluctuations were smaller, and the pH remained close to pH 6.00 during the entire sampling period (Fig. 2).

Cations concentrations in soils solutions were always low, ranging from 4.7 to 58.0 μmol L⁻¹ (Tab. 1), with Silicon (Si) as the most abundant element, followed by cations Mg, Ca, and Na.

Table 1. pH and Mg, Ca, Na, Si, Cr, Ni, and Mn mean concentration of the soil solutions from NIQ II and NIQ III and the surfaces water. (All the water were filtered at 0.2 μm; d.l. detection limit; X ± Y mean ± SD; min / max value minimum and maximum observed). The K, Al, and Fe content of all solutions filtered were always below detection limit (< d.l.).

| Depth cm | pH  | Mg  | Ca  | Na   | Si  | Cr  | Ni  | Mn  | NO₃⁻ | SO₄²⁻ | Cl⁻ | DOC mg L⁻¹ | number of samples |
|----------|-----|-----|-----|------|-----|-----|-----|-----|------|-------|-----|-------------|------------------|
|          | 20  |     |     |      |     |     |     |     |      |       |     |             |                  |
| Soil NIQ II | 5.7 ± 0.15 | 28.1 ± 4.7 | 18.5 ± 4.7 | 58 ± 0.9 | 1.2 ± 0.6 | < d.l. | 89.2 ± 58.1 | 8.2 ± 5.6 | 31.2 ± 25 | 9.9 ± 0.3 | 40 / 10* |
|           | 5.4 / 6.05 | 0.3 / 13.3 | 38.4 / 74.1 | 1.1 / 2.6 | 1.1 / 3.2 | < d.l. | 3.6 / 201 | 3.7 / 21 | 5.8 / 122 |         |          |
| Soil NIQ III | 6.00 ± 0.05 | 9.8 ± 0.05 | 10.1 ± 0.05 | 6.1 ± 0.05 | 52.5 ± 0.05 | 1.7 ± 0.8 | < d.l. | 18.2 ± 17 | 6.1 ± 3.1 | 19.4 ± 35 | 11.6 ± 2.0 |
|           | 5.85 / 6.09 | 0.3 / 17.9 | 39.7 / 75.4 | 0.3 / 3.9 | 0.21 / 1.5 | < d.l. | 2.3 / 204 | 2.7 / 78 | 6.8 / 78 |         |          |
| Soil spring | 6.00 ± 0.06 | 9.8 ± 0.06 | 9.7 ± 0.06 | 7.6 ± 0.06 | 39.6 ± 0.06 | 1.2 ± 0.7 | < d.l. | 12.6 ± 4.7 | 4.0 ± 2.5 | 8.4 ± 4.2 | 10.7 ± 3.0 |
|           | 5.9 / 6.15 | 0.3 / 8.1 | 32.5 / 67.4 | 0.3 / 3.9 | 0.07 / 0.7 | < d.l. | 5.5 / 70 | 2.3 / 9.1 | 3.7 / 25 |         |          |
| Surface water outlet | 5.85 ± 0.16 | 22.6 ± 0.16 | 20.1 ± 0.16 | 3.0 ± 0.16 | 56.4 ± 1.1 | 0.5 ± 0.7 | < d.l. | 65.5 ± 0.7 | 17.7 ± 8.2 | 7.0 ± 2.6 | 7.4 ± 4.1 |
|           | 5.6 / 6.1 | 0.3 / 8.1 | 39.6 / 67.4 | 0.3 / 3.9 | 0.07 / 0.7 | < d.l. | 2.0 / 36 | 2.5 / 44 | 2.8 / 9.2 |         |          |
| Surface water runoff | 6.05 ± 0.08 | 7.2 ± 0.08 | 9.5 ± 0.08 | 5.3 ± 0.08 | 54.2 ± 1.0 | 0.8 ± 0.5 | < d.l. | 16.3 ± 0.7 | 11.8 ± 7.9 | 4.2 ± 8.2 | 11.2 ± 2.2 |
|           | 5.85 / 6.2 | 0.3 / 8.1 | 36.4 / 69.6 | 0.3 / 3.9 | 0.07 / 0.7 | < d.l. | 8.5 / 68 | 3.3 / 17 | 6.7 / 31 |         |          |

*Number of analyses of dissolved organic carbon.
Figure 2. Mean pH of the soil's solutions from NIQ II-20, 70 and 150 and from NIQ III-20 and 150 (20, 70, and 15 refer of the sampling depth in cm).

Figure 3. Si, Ca, and Cr concentrations for all NIQ II-20, 70, and 150 ceramics cups (Si a, b and c; Ca d, e and f; Cr g, h and i), in μmol L⁻¹ from December 2006 to June 2007; (● soils solution of February 2008) (20, 70, and 15 refer of the sampling depth in cm).

(Tab. 1 and Fig. 3). In NIQ II, Si concentrations decreased with depth, whereas they were homogeneous in the NIQ III solutions (Tab. 2). Calcium concentrations decreased with depth from 18.5 ± 10.0 to 9.7 ± 5.2 μmol L⁻¹ in NIQ II and from 20.1 ± 10.8 to 9.5 ± 6.2 μmol L⁻¹ in NIQ III (Tab. 1). Mg concentrations at 20 cm were slightly higher than those of Ca for both soils and ranged from 28.1 ± 14.6 to 22.6 ± 12.6 μmol L⁻¹ in both NIQ II and NIQ III; the values in both soils decreased considerably with depth (Tab. 1). The Ca:Mg ratios ranged from 0.65 to 0.88 at a 20 cm depth and increased to 1 and 1.32 in the deeper parts of the profiles.
Table 2. Mean Ca:Mg ratios of leaching topsoil solutions (C.P. Ceramic Cup).

| Date of sampling | C.P.1 | C.P.2 | C.P.3 | C.P.4 | C.P.5 | C.P.6 |
|------------------|-------|-------|-------|-------|-------|-------|
| 12/19/06         | 0.6   | 1.1   | 0.9   | 1     | 1     | 1.5   |
| 01/17/07         | 1     | 1.2   | 1.3   | 2.1   | 1.5   | 2.6   |
| 01/31/07         |       | 2.8   | 1.5   | 2.6   |       |       |
| 02/15/07         |       |       |       |       |       |       |
| 02/24/07         |       |       |       |       |       |       |
| 03/15/07         |       |       |       |       |       |       |
| 03/30/07         |       |       |       |       |       |       |
| 04/18/07         |       |       |       |       |       |       |
| 05/10/07         |       |       |       |       |       |       |
| 02/25/08         |       |       |       |       |       |       |

The variability of the Ca:Mg ratio at 20 cm depth was particularly high (Tab. 2). Finally, the concentrations of Na were very low and variable, ranging between 3 and 7.6 µmol L⁻¹, and the concentrations of K were below the quantification limit (Tab. 1).

The dominant inorganic anions were NO₃⁻ and, to a lesser extent, SO₄²⁻ and Cl⁻ (Tab. 2). In soil solutions, the concentration of anions, particularly NO₃⁻, decreased below 20 cm. The concentrations of other anions, such as H₂PO₄⁻, were always below the detection limit. The DOC concentration in the soil solution was homogeneous in both soil profiles and ranged between 7.4 ± 4.1 and 11.6 ± 2.0 mg L⁻¹.

Metal concentrations in the soil solutions were more variable among the soil profiles and during the seasonal cycle. Iron, Al, and Mn concentrations were below the detection limits throughout the sampling period (Tab. 1). Mean Ni concentrations varied from 0.15 ± 0.2 to 1.2 ± 0.8 µmol L⁻¹ (Tab. 1) and decreased drastically with depth for NIQ II, but increased slightly with depth in NIQ III. Ni concentrations were heterogeneous both spatially and temporally, particularly in NIQ III. For example, in the ceramic cup at 20 cm depth and at 150 cm depth in NIQ III, the Ni content was always particularly high compared to the others, indicating significant lateral variability. Hexavalent chromium concentrations in the soil solutions were relatively high, reaching 3.9 µmol L⁻¹ in December 2006 (Tab. 1). In NIQ II, Cr(VI) concentrations tended to increase between 20 to 70 cm and decrease slightly below, with a higher concentration observed at 70 cm, whereas the Cr(VI) concentrations in NIQ III remained homogeneous with depth (approximately 1.0 µmol L⁻¹) (Tab. 1). Over time, Cr(VI) concentrations tended to decrease from December 2006 to January 2007, followed by a long-term increase from January to June 2007 (as shown for NIQ II at 20 and 70 cm depth in Figure 3).

Surface waters

The pH of the rainwater was acidic (pH = 4.8 ± 0.05), and the ion concentrations were below the detection limits of the ICP-AES and the ion chromatograph.

The pH of the water at the spring was neutral (7.25 ± 0.12), and the pH was higher at the outlet (8.00 ± 0.05). In surface waters, Si and Mg concentrations were dramatically higher than in the soil solutions and increased between the spring and the outlet, from 254 to 383 and 275 to 308 µmol L⁻¹, respectively (Tab. 1). Finally, the Ca and Na concentrations were equivalent to those measured in the soil solutions.

The stream solution was free of Fe and Al, but traces of Mn were present (0.3 ± 0.5 µmol L⁻¹) (Tab. 1). The Ni concentrations at the spring and outlet were in the same range as the soil concentrations (0.7–1 µmol L⁻¹), whereas the concentrations of Cr, which occurred as Cr(VI), were lower, with values of 0.5 and 0.4 µmol L⁻¹ for the spring and outlet, respectively.

Elemental concentrations in the runoff waters filtrated at 0.22 µm were lower than those observed in the stream solutions. Si was the dominant element, with a concentration of 12.3 ± 3.1 µmol L⁻¹. Importantly, the Cr(VI), Ni, and Mn concentrations were significant, with values of 0.8 ± 0.4, 0.2 ± 0.1, and 1.6 ± 0.2 µmol L⁻¹, respectively (Tab. 1).

Filtration fractionation

More than 20 samples collected in February 2008 were analyzed following the filtration fractionation protocol, and the results are presented in Table 3. The concentrations of Cr, Ni, Ca, Mg, and Si in the different subsamples (unfiltered, θₙ; 0.22 > θₙ > 0.025 µm; 0.025 > θₙ > 10 kDa; 10 kDa > θₙ) of both the soil and stream solutions were in the same range within the limits of analytical error (Tab. 3). The concentrations of Fe and Al in all soil solution fractions were always below the detection limits in all subsamples. However, in the runoff water, the Fe concentration was particularly high (3,253 µmol L⁻¹) in the unfiltered water, whereas it was below the detection limit after filtration (Tab. 3). To a lesser extent, the concentrations of Mn, Cr, and Ni in the unfiltered runoff water also sharply decreased after filtration at 0.22 µm: only 30% of the Mn, 7% of the Cr, and 1% of the Ni remained after the 0.22 µm filtration. The concentrations in all filtered fractions remained equivalent, at approximately 1.8, 1.0, and 0.2 µmol L⁻¹ for Mn, Cr, and Ni, respectively. Therefore, metals are present in the runoff samples associated with Fe colloids > 0.22 µm and as free ions. Finally, the Si concentration in the unfiltered
The chemical composition exhibited high variability, in agreement with the fact that several parameters control the content and speciation of soil solutions over time (e.g., local mineralogy, vegetation and biological activities, as well as water content and saturation).

Silica dominated the solution composition. In such slightly acidic solutions, aqueous Si species occurred predominantly in the form of neutral species, primarily $H_4SiO_4^{0+}$ (Gérard et al. 2008). The concentrations remained relatively constant throughout the soil profiles during both the rainy and dry seasons. Silica appears to be only slightly affected by edaphic conditions or biological processes (Fig. 3). Moreover, the concentrations observed are consistent with the solubility of quartz ($\log[H_4SiO_4^{0+}]$ of -4.4 to -4) (Maitat et al. 2000, Wonisch et al. 2008). The results also indicate that the Si buffering capacity of these soils is large, in agreement with the soil mineralogy and the presence of quartz as the only silicate minerals in both the bulk and fine fractions (Garnier et al. 2009b).

Ca and Na concentrations were in the same range as those reported by Lilienfein et al. (2000) in soil solutions from Brazilian savanna oxisols, highlighting the high degree of weathering of these Ferralsols. However, Mg concentrations were slightly higher in the Niquelândia soil solutions, which is explained by the UM nature of the parent material. Mg and Ca concentrations were in the same range as those reported by other studies on ultramafic soils (Proctor 1970,
Anderson et al. 1973, Johnston and Proctor 1981, Gasser et al. 1994) but lower than those reported by Becquer et al. (2010). The chemical discrepancies between the topsoil and deeper horizons suggest that for different soil processes; the higher nutrient content in the topsoil solutions is associated with nutrient recycling. Nutrient cycling appears to be located at the surface and is likely related to plant development (Lucas et al. 1993). The rapid mineralization of organic matter likely promotes this feature and is emphasized by the large decrease in NO₃⁻ with depth. Moreover, given the presence of Mg-rich plants (Reeves et al. 2007) and consequently Mg-enriched litter in the topsoil, Mg concentrations are 3-fold higher in the topsoil than in deeper horizons.

Ca:Mg molar ratios measured in the soil solutions were extremely low (0.65 to 1.32), as were the total and extractable Ca:Mg molar ratios measured in the soil matrix (data not shown). This imbalance has already been considered to be a specific feature of ultramafic soils (Whittaker 1954). Here, the ratio was lower than the values reported by Johnston and Proctor (1981), who studied less-developed “ultramafic” soils. In quite similar soils in New-Caledonia, Becquer et al. (2010) showed that the Mg:Ca molar ratio was close to unity. In a vegetation survey of the Brazilian ultramafic massifs, Reeves et al. (2007) showed that leaves from plants growing in the soils of these massifs have a low Ca:Mg ratio, which ranges from 0.26 to 2.26. Moreover, this study noted the presence of plants that are particularly rich in Ca or Mg in those soils and contain 12,910 and 28,270 mg kg⁻¹ of Ca and Mg, respectively (Reeves et al. 2007). Given the composition of the soil solutions and the ratio in plant tissues, it appears that the plants of the Niquelândia massif can concentrate Ca relative to Mg or vice versa. The data obtained in this study (Tab. 2) demonstrates that the Ca:Mg ratio varies spatially and temporally; thus, variations in Ca and Mg in soil solutions can explain the large variations in the concentrations of these elements observed in plants.

Hexavalent chromium always represents more than 95% of the total Cr quantified by ICP-AES in surface waters. Even if the sampling method is not suitable for Cr(III) sampling (Becquer et al. 2010), given the slightly acidic pH and the large amount of iron oxides present in the soils (Garnier et al. 2009b), the Cr(III) is expected to be entirely sorbed (Fischer et al. 2007) and consequently not mobile (Kotas and Stasicka 2000). The Cr(VI) concentrations remained high throughout the complete hydrological cycle (Fig. 3), and the field results confirm the high Cr(VI) lability measured in the laboratory by KH₂PO₄-extraction, Isotope Exchange Kinetic (IEK) and XANES (Garnier et al. 2006, 2009a, 2013). Cr(VI) was present in “truly” dissolved forms, as shown by the filtration fractionation (Tab. 3). Cr speciation is in agreement with other results obtained from tropical UM soils by Becquer et al. (2003, 2010) (Suppl. Fig.). Gasser et al. (1994) found that the Cr in soil solution was primarily (65–75%) present in colloidal form. These results, being obtained from a poorly weathered serpentine soil developed under a cold mountain climate where the dominant pedogenetic process was cryofractionation, leading to the production of rock fragments and low chemical weathering, cannot be compared to presents results obtained in highly leached soils. The vertical distribution of Cr(VI) concentrations over the hydrological cycle agreed with the distribution of Cr(VI) availability in both the NIQ II and NIQ III profiles, as assessed via IEK (Garnier et al. 2009a). Moreover, Garnier et al. (2009a) also identified a high correlation between the granulometric clay content and Cr(VI) availability. An increase in the sorption of oxyanions onto Fe-oxides, consistent with the pH increase with depth, may also significantly influence Cr(VI) mobility. Finally, the presence of organic matter can explain the lower concentrations of Cr(VI) in topsoil solutions compared to mineral horizons, as it can reduce Cr(VI) into Cr(III) in topsoil, which is subsequently immobilized in its trivalent form. However, given the contrasting effects of the various components or properties of the soils, no simple relationship exists between Cr concentrations in soil solutions and other soil properties, e.g., pH, and organic matter and iron oxide contents.

Cr(VI) concentrations in soil solutions were higher than toxicity standards, such as recommended levels for irrigation water (< 0.15 μmol L⁻¹) or freshwater life (< 0.02 μmol L⁻¹) (Pawlisz et al. 1997, WHO 1998). Therefore, Cr(VI) probably contributes to the endemism seen within the study region, i.e., one of the features of the serpentine syndrome (Reeves et al. 2007). However, unlike Ni, the content of Cr in all analyzed plant leaves was low (Reeves, personal communication). Thus, Cr seems not to be absorbed by plants and stored in roots, as observed by Shanker et al. (2005). However, due to the high toxicity of Cr(VI) even at low concentrations, Cr must have an indirect effect on the biota, and the ecosystem has likely acquired a tolerance capacity.

Ni concentrations in solutions were of the same order of magnitude as those observed in a New Caledonian UM outcrop (Becquer et al. 2010). However, the local variability in Ni concentrations was large. In NIQ II, the Ni concentrations were larger in the topsoil than in the deeper horizons, whereas the concentrations were homogeneous in NIQ III, except for local anomalies. Ni concentrations can be analyzed using the profile structures of both soils, which were presented in a previous study (Garnier et al. 2009b). NIQ II presents a superficial horizon with a larger content of organic matter and deeper horizons rich in iron oxides. In the surface horizons, it is thought that the high Ni content in the soil solutions is controlled by organic matter or litterfall mineralization in the topsoil. Litter-fall from Ni-hyperaccumulating plants (Reeves et al. 2007) contributes to the addition of Ni to the surface horizon. This feature is in agreement with the solid speciation of Ni in these soils, with high contents of Ni associated with organic matter (between 100 and 400 mg kg⁻¹, Garnier 2008). In deeper horizons, the slight increase in the content of iron oxides, associated with the decrease in the organic matter content and the increase of pH, promotes Ni sorption on goethite (Fischer et al. 2007) (Suppl. Fig.). Otherwise, the local variability in Ni concentrations in the NIQ III solutions collected at the same depth (from the detection limit to 2.8 μmol L⁻¹) could be related to local-scale mineralogical variability. The presence of relics composed of weathered Ni-smectite in the upper part of
the NIQ III profile may locally increase Ni availability and mobility. This finding is in good agreement with the results of Becquer et al. (2010), who showed a lower availability of Ni in a highly weathered, iron-rich soil in a mountain piedmont (OUE1) relative to a colluvio-alluvial soil containing some poorly weathered silicates (OUE3). Nickel concentrations in the soil solutions also often exceed the toxic threshold for freshwater given in the WHO (1998) guidelines for drinking water quality or for biota reported by L’Huilier and Edighoffer (1996) and Becquer et al. (2010). However, Ca$^{2+}$ and Mg$^{2+}$ are known to alleviate the phytotoxicity of Ni (Proctor and McGowan 1976, Gabrielli and Pandolfini 1984, Robertson 1985), and their presence may limit Ni toxicity.

The serpentine syndrome has been proposed and is related to a low level of nutrients (N, P, and K), a Ca:Mg imbalance, as well as the presence of metals that can decrease fertility (Whittaker 1954, Brooks 1987, Bini et al. 2017). Nutrient contents were not lower than those observed in other oxisols of the Cerrado region (Lilienfein et al. 2000), i.e., high leached soils. However, Ca:Mg ratios were low in the topsoil, and both Ni and Cr(VI) are highly labile. At a minimum, the present results are in agreement with two of the three serpentine syndrome conditions, i.e., the low Ca:Mg ratio and the presence of labile metals, leading to limited fertility of the ultramafic outcrop area of Niquelândia. This limitation likely contributes to the high degree of endemism observed in the ultramafic massif. Rapid recycling of nutrients and Ni, i.e., via uptake of the elements released by the mineralization of litter, appears to occur, thereby limiting the leaching of essential elements. This feature confers greater fertility through the enhanced availability of nutrients, which mitigates one of the typical traits of areas with ultramafic substrates. This feature also produces higher Ni concentrations in the topsoil solutions. The present results suggest that, in deep, leached soils developed in ultramafic rock, the (hyper)accumulation of Ni by plants and the recycling of Ni-rich organic matter can indirectly contribute to maintaining high Ni concentrations in the topsoil and thus contribute to the high degree of endemism on the outcrop. Similar features seem to occur at Mg concentrations that can maintain higher Mg bioavailability relative to Ca in topsoil. Both features are in agreement with the ecological traits of these environments, as reflected by the serpentine syndrome.

**Metal mobility**

The pH value of the spring water (7.25) was higher than the values observed in the soil solutions (6.05), likely due to hydrolysis processes in the deeper part of the profiles, i.e., the saprolite, where Ni-bearing clays and weatherable primary minerals are abundant. In surface water, cation concentrations decrease in the order Mg$^{2+} >$ Ca$^{2+} >$ Na$^+ >$ K$^+$, and the Ca/Mg ratio for all water samples was lower than 1, due to the low Ca concentration in ultramafic bedrocks, similar to the findings of Kaprara et al. (2015) for UM water in Greece and Mcclain and Maher (2016) in the United States. The elevated Mg and Si concentrations in the stream solutions in relation to the soil solutions underline this feature. The large content of Mg and Ca may be balanced by alkalinity (not measured), which agrees with the alkaline pH. These findings are in good agreement with those of McClain and Maher (2016) and with the solubility of the main silicate minerals in the soil and the saprolite, i.e., UM rock-solution equilibrium. The Mg, Ca, and Si concentrations were lower than those reported by McClain and Maher (2016), whereas those of Cr (considering both Cr(VI) and Cr(VI) + Cr(III) reported) and Ni are higher. On the one hand, the Si concentrations in the soil, which are nearly 40 to 100 μM$^{-1}$, are closely related to the solubility product of quartz, which is close to a Log[H$_4$SiO$_4$°] value of -4.4 to -4 (Maitat et al. 2000, Wönsch et al. 2008). In turn, the Si concentrations in the spring and the outlet, which are nearly 300 μM$^{-1}$, are much higher due to the lower resistance to weathering of the olivine or serpentine encountered in the deeper parts of the profiles.

Particular attention was given to the composition of the solutions collected during February 2008 to verify the presence of colloids and their role as metal-bearing phases, as observed by Gasser et al. (1994) for soils developed on ultramafic rock in the Davos region. For a given element, lower concentrations in one of two different size fractions indicate the presence of a particulate form of this element. This finding, as well as variations in the ratios between certain elements among different size fractions, can be used to determine the impact, if any, of different components on metals and colloid formation (Garnier et al. 2011). The presence of Cr(VI) and Ni in the filtered solutions, even at 10 kDa, in both soil and surface waters from the stream and runoff, proves that these elements are mobile at the catchment scale in “truly” dissolved forms. More than 66% of the Ni and 92% of the Cr(VI) in the soil solutions, as well as all of the Ni and Cr(VI) in the stream, were present in dissolved form, the remainder being in colloidal forms. The Ni concentration in the spring was close to the soil concentrations, and the concentration decreased slightly, whereas the Cr concentration in the spring was lower than the soil concentrations and remained constant along the watercourse. The behavior of Ni and Cr(VI) is very different than that of Si and Mg. Unlike those of the latter species, the concentrations of Ni and Cr(VI) in the soil solutions did not increase after passing through the saprolite. This difference in Ni and Cr dynamics from the soil to the spring with regards to Si and Mg can be explained by different mechanisms, including:

- dilution by soil solutions that are relatively poor in Cr or Ni (in less developed soils);
- weathering and precipitation of different kinds of metal-bearing phases;
- sorption/desorption mechanisms operating between Ni, which occurs as cations, and Cr(VI), which occurs as oxyanions, and the surface charges of minerals;
- the reduction of Cr to a less mobile form, i.e., Cr(III).

The adsorption of Ni on goethite, which forms quickly during weathering of UM primary minerals, appears to be a key factor. Indeed, the increase beyond pH 7 in the saprolite leads to the total sorption of Ni in goethite (Fischer et al. 2007). Therefore, soil solutions coming from the highly weathered upper part of the soil profile are the main source of mobile
nickel in the environment. For Cr(VI), the increase in pH in the saprolite should decrease the retention of Cr(VI) anions by goethite (Garnier et al. 2009a). According to Dai et al. (2009), free Cr(III) ions and [CrOH]2+ are the forms of Cr(III) that oxidize to Cr(VI) most readily. However, these Cr species disappear beyond pH 7. Therefore, the production of Cr(VI) would be limited in the saprolite, unlike the weathered soil. Soil solutions coming from the highly weathered upper part of the soil profile are also the main source of mobile Cr(VI) in the environment.

Runoff waters filtered at 0.22 μm were entirely free of Fe and Al, whereas the unfiltered samples featured high concentrations of Fe, showing that Fe was mobile as a particulate material. This observation is in agreement with in situ observations during rainstorms, in which oxide particles were mobilized at the catchment scale in this area, where UM rocks outcrop. In the sample tubes, these particles (> 0.22 μm) remained dispersed in the runoff waters for several months. Thus, despite being larger in size than the typical cut-off for colloids, this fraction behaved as a colloidal fraction. A XANES measurement on this fraction has revealed that a portion of the Cr was present in its hexavalent form in this fraction (Garnier et al. 2013). This fraction, the > 0.22 μm fraction, involved metal transfer on the outcrop in “colluvial” transport from the hill to the footslope, as already discussed by Garnier et al. (2009b), as well as to the surrounding ecosystems. This fraction is also rich in Al, Mn, Ni, and Cr, and this colloidal transport and mobility may promote metal dispersion, thereby acting as a vector of metal mobility.

CONCLUSION

This investigation of soil solutions and surface waters from the Niquelândia ultramafic massif improves our understanding of the unique qualities of this ultramafic area and the serpentine syndrome. The low Ca:Mg ratio in the soil solutions was consistent with both the ultramafic features and the Mg-rich vegetation. Moreover, Cr, mainly in its hexavalent form, and Ni occurred in the topsoil solutions as “truly” dissolved ions. Cr(VI) concentrations remained high, and no change in the oxidation state was observed in the soil solutions through a complete hydrological cycle. These metals’ lability, coupled with the large Ca:Mg imbalance, contribute to the biodiversity selectivity within the outcrop area of these UM rocks, highlighting once again the close relationship between the serpentine syndrome and the availability of metals in soils.

Niquelândia UM soils might constitute a source of labile metals, mainly Ni and Cr(VI), which are partly exported to surrounding areas of the ultramafic massif. Two main environmental dispersal forms of metals have been: “truly” dissolved metals and colloidal transfer of Ni and Cr associated with Fe-oxides. The highly weathered upper parts of the soil are more likely to be the source of mobile, “truly” dissolved Ni and Cr, whereas saprolite can act as a sink of metals. Colloidal transfer of Fe-oxides and associated metals occurs during intense rain events. However, this metal’s mobility may have an impact on the surrounding ecosystems, particularly for plants and microorganisms not adapted to these metals.

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