Speciation and Availability of Cr, Ni and Co IN Serpentine Soils of Ranau, Sabah

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Abstract: Problem statement: Serpentine soils are known as a geogenic source of heavy metal pollution because they are anomalously rich in chromium, nickel and cobalt. **Approach:** However, only that portion of these metals which is available in the ecosystem and incorporates in the bio-transformation processes, is dangerous for the environment. Availability of Cr, Ni and Co depends on their speciation into the different fractions of a soil and corresponds with their chemical binding forms. Soil is a combination of several reactive fractions which have the ability to interact physically and chemically with heavy metals and changes their existence form in the soil. **Results:** Thus, understanding the geochemical form and distribution of metals in different fractions of soil is fundamental for predicting the availability and potential toxicity of them under natural condition. **Conclusion:** This study set out with the aim of fractionation of Cr, Ni and Co in serpentine soils of Ranau in Sabah state of Malaysia. Selective Sequential Extraction analysis (SSE) was combined with X-ray diffraction of soil powders to find the mineralogical source and mobility of Cr, Ni and Co in serpentine soils.

Key words: Serpentine soil, Cr, Ni and Co, speciation, availability, ranau

INTRODUCTION

Serpentinites are essentially metamorphic rocks which originate from hydrothermal alteration of ultramafic rocks along convergent continental margins.

Serpentinized ultramafic rocks are very poor in silica (less than 45% SiO_2) and macronutrient elements. On the opposite, they are characterized by large amounts of iron and magnesium. Serpentinites are also naturally enriched in heavy metals (Morrison *et al.*, 2009). As a general rule, the sidrophile elements such as cobalt, chromium and, nickel are strongly elevated in serpentinized ultramafic rocks because of the substitution of cations (Fe, Mn and Mg) by Cr, Ni and Co in octahedral sheets of the primary serpentine minerals. While decomposition of serpentine rocks during weathering or pedogenesis process, certain minerals inherit from the parent rocks and some secondary new mineral form. Thus, the formed soil contains a mixture of variable proportions of minerals which range from primary minerals to secondary phyllosilicates and lastly to Mn and Fe oxides, especially in tropical regions (Dissanayake and Chandrajith, 2009). Serpentine originated soils are exceptionally rich in heavy metals notably chromium, nickel and cobalt (Siebecker, 2010) which can cause an adverse effect on the environment if they get available. Therefore, serpentine soils are

considered a source of geogenic pollution by numerous researchers (Caillaud *et al.*, 2009). However, many evidences indicate that even though the heavy metal content in soils is an essential factor for assessing environmental pollution, the ecotoxicological risk does not control by total heavy metal concentration. In the other word, overall level of metal presence in soil is an insufficient criterion to evaluate the environmental impact because it provides no information regarding the potential mobility and bioavailability of metals (Iizuka *et al.*, 2011).

Metal availability influence by its origin, physiochemical and mineralogical properties and edaphic characters of soil (Bani *et al.*, 2012). The primary factor limiting the availability of the contaminant in the subsurface environment is their association with the solid subsurface. Thus, understanding the geochemical form and speciation of metals in soil is fundamental for predicting the availability and potential toxicity of heavy metals under natural condition (Garnier *et al.*, 2009). Metal speciation is defined as the identification and quantification of the different and defined forms, species or phases in which an element occurs. It reveals the way that metal is distributed among its different chemical forms and physical phases. The chemical speciation also focuses upon the quantitative distribution of an element between the chemical forms and the oxidation states. The term chemical

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fractionation emphasizes the concept of subdividing the total content of a metal and it is frequently used intermittently with chemical speciation. The knowledge of chemical heavy metal speciation in soils is essential to understand their chemical and biological interactions and transport mechanisms.

Metal cations in the soil are divided into the following recognizable chemical pools; pool A (the water soluble), pool B (the easily exchangeable pool), pool C (completed, adsorbed and exchangeable only by other cations with higher affinities), pool D (Co-precipitated with metal oxides) and pool E (held in the primary minerals). The water soluble, exchangeable and completed pools are believed to be in reversible equilibrium with one another. Pool C is the most significant source for plant uptake of metal cations. The co-precipitated pool D is not able to be the immediate source of bio-available ions because the equilibrium between this pool and the pools A, B and C is established very slowly and over a long period of time. The advantage of the chemical pool concept is the monitoring of the heavy metals availability related to their successive pools. The successive pools represent a decreasing degree of availability that ranging from ions in the soil solution to ions in the soil crystal lattice.

Thus, based on the affinity of heavy metals to bind among different soil fractions they are classified into five groups: (i) Adsorptive and exchangeable (ii) contained in carbonate phase, (iii) bound to reducible phases (Fe and Mn oxides), (iv) occluded with organic matter and sulfides and (v) residual or lattice metals (Kierczak *et al.*, 2008). Chemical Selective Sequential Extraction (SSE) of soil is a one of the most useful technique which frequently employs to determine metal distribution within soil solid fractions. Sequential extraction procedures provide information about the differentiation of the relative binding strength of metals on the solid phase and about their potential reactivity under different physio-chemical environmental conditions. SSE includes progressively using of appropriate reagents to destroy the binding agents between the target metal and the specific soil fraction and release heavy metals selectively from their structural context (Iizuka *et al.*, 2011). Regents of each step extraction are chosen depends on their specificity towards particular forms. Successive extraction permits metal species to be detected. It is assumed that metals in water soluble and exchangeable fractions are readily mobilized in the environment whereas the metals in the residual fractions are tightly bound and would not be expected to be available under natural conditions. Among the large variety of proposed extraction schemes for soils and sediments, the sequential extraction method of (Silveira *et al.*, 2006) has been

followed in the current study. This method is especially adapted for tropical soils.

MATERIALS AND METHODS

Study Area: The selected study site is Ranau in North West of Sabah Malaysia. It is about 80 miles far from Kota Kinabalu between the latitudes of N5° 57'-N6° 02' and longitudes of E116° 40'-E116°45' (Fig. 1). Since decades, special attention is devoted to the Sabah region because it contains several large and extended and numerous smaller bodies of serpentinized ultramafic formations. Ultramafic series of Ranau are broadened in about 16 square miles (Hutchison, 2005), but not all parts are accessible because of the dense forest and rugged nature.

Sample preparation and analysis: Soil samples developed on serpentinites were collected from the superficial parts (less than 10 cm thick) after clearing debris and vegetations. Samples were air-dried, pulverized and grinded to pass through a 2 mm plastic sieve to obtain the most desirable soil fraction size.

The number of 5 soil samples was subjected for mineralogical study and 2 of them were chosen for SSE analysis.

In order to identify the constituent minerals of the soil, X-Ray Diffraction (XRD) technique was performed using a D8 advance Bruker AXS diffractometer with wave length 1.5406 A° (0.15406 nm), housed at the Faculty of Science AND Technology UKM. X-ray diffractogramms were collected on powder samples within the 2θ range [5°-60°], with 0.02o/0.1s step. In this case, the ideal specimen is a statistically infinite amount of randomly oriented powder with crystallite size less than 10 μm, mounted in a manner in which there is no preferred crystallite orientation.

The Selective Sequential Extraction analysis (SSE) was accomplished for the purpose of heavy metal speciation in the studied soils. The SSE has been limited to the heavy metals of chromium, nickel and cobalt. Soil specimens were weighted in 1gr portions and were placed in 50 mL centrifuge tubes to be extracted by different reagents in stepwise fashion. Extraction was carried out in duplicate to provide the precision of measurement. The accuracy of extraction was checked by comparing the extracted and the total content of each metal in samples. According to Tessier *et al.* (1979), the experiment is considered acceptable if the difference between the total concentration measured by single analysis and the sum of element amounts extracted by sequential extraction be lower than 20%.
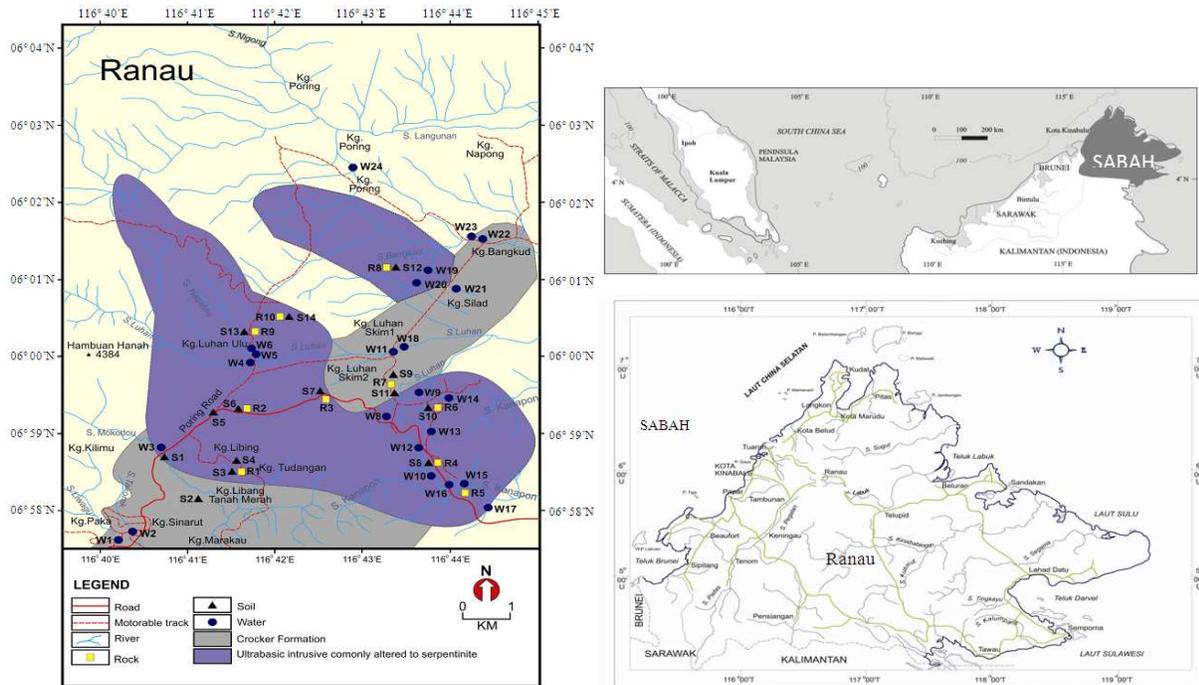
Fig. 1: The map of Sabah state, the location of Ranau area and the sampling stations

The following operationally defined fractions were determined by SSE analysis:

- Fraction 1-Soluble- Exchangeable 15 mL 0.1 M Calcium hydrochloride dehydrate $(CaCl_2)$ was applied to each 1gr soil sample. Extraction was accomplished by shaking tubes for 2 h at room temperature
- Fraction 2-Surface adsorbed Each soil was reacted with 30 mL Sodium acetate 1M (NaOAc) adjusted to pH 5.0 with Glacial acetic acid (HOAc). The slurry was shaken for 5 h at room temperature
- Fraction 3-Organic matter the residue from the fraction 2 was treated by 5 mL Sodium hypochlorite (NaOCl) adjusted to pH 8.5 with drops of concentrated HCl. The mixture was heated to 90-95°C in a water bath for 30 min
- Fraction 4-Oxide and Hydroxide This extraction stage is divided into three phases
- Mn-Oxide Following the optimization of fraction 3, 30 mL hydroxyl amine hydrochloride at pH 2.0 (adjusted with HCl) was added to the residual soil. Samples were shaken continuously for 30 min at the room temperature
- Poor crystalline Fe oxide the residue from the previous extraction was mixed with 30 mL 0.2 M Oxalic acid +0.2 M NH_4 Oxalate adjusted to pH 3 with NH_4OH. The slurry was shaken in a dark room temperature for 2 h.

- Crystalline Fe oxide 40 mL 6 M Hydrochloric acid (HCl) was added to the residue soil and was shaken continuously at the room temperature for 24 h
- Fraction 5-Residual Following optimizing fraction 3, the residue was oven-dried at 105°C, pulverized and mixed 0.1 gr of the residue was treated by a microwave digestion method 3050b

Between each step of the successive extraction, the supernatant was separated from the solid phases by centrifuging in the speed of 25 ± 2 rpm. The centrifuge cake then washed with 5 mL of 0.1 M NaCl and centrifuge again. The resulted supernatant was added to the former extracted solution. This step intends to displace the extractant from the previous step, minimize the sample dispersion and reduce the readsorption of the metal (Silveira *et al*., 2006).

The supernatants then were filtered through 45µm Cellulose Nitrate Membrane filters and sent to the ICP laboratory at the Faculty of Science and Technology UKM, to measure the decanted heavy metals from each stage of extraction.

RESULTS

Soil mineralogy: The mineralogical composition of the soils was determined by X-Ray Diffraction (XRD) and semi-quantification has been evaluated from XRD spectra.
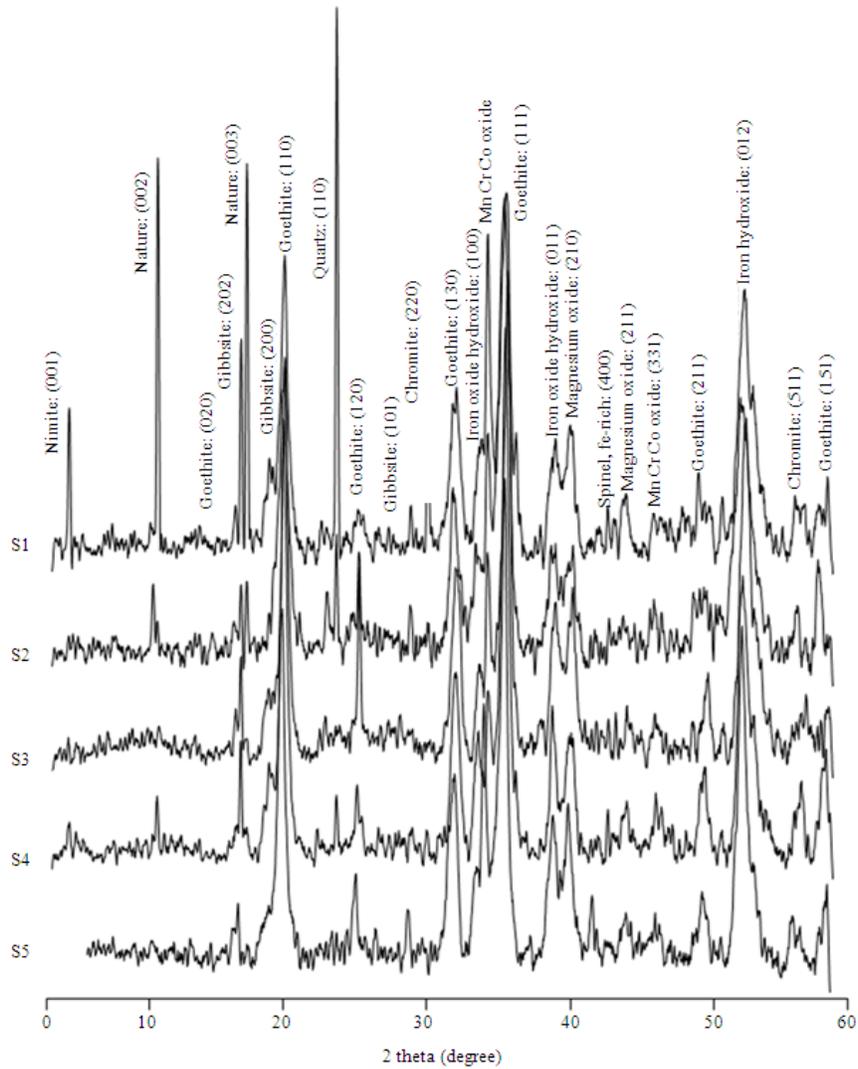
Fig. 2: X-ray diffractogramms from serpentine soils of Ranau area

Table 1: Chromium, nickel and cobalt concentrations ($\mu g\ g^{-1}$) extracted from different steps of selective sequential extraction analysis on serpentine soils of Ranau, Sabah.

Analytes	Sample ID	F1	F2	F3	F4	F5	F6	F7
Cr	S1	4.1	49.0	47.0	414	215	611	11912
	S4	1.0	12.0	48.0	327	54	252	12599
Ni	S1	1.0	0.2	0.2	82	39	104	1345
	S4	1.5	0.7	0.7	16	9	41	1120
Co	S1	0.3	0.3	0.9	80	14	9	12
	S4	0.5	0.2	0.2	51	9	7	37

F1: Soluble-Exchangeable fraction; F2: Surface adsorbed fraction; F3: Organic matter fraction; F4: Mn-oxide fraction; F5: Poor crystalline Fe-oxide fraction; F6: Crystalline Fe-oxide fraction; F7: Residual fraction

The XRD patterns revealed that serpentine soils of Ranau area are mainly made up of oxides and oxyhydroxides of iron notably goethite and maghemite. Furthermore, all soils were dominated by magnetite and chromite with main reflections around 4.85, 4.82 Å. Other mixed spinels are well characterized by reflections around 2.44, 2.02, 1.43 and 4.66 Å. Soils S1 and S4 contain magnesium oxide which its strong line is on crystal surface of (210). Manganese doesn't seem to form an independent mineral and appears mostly as manganese chromium cobalt oxide and in certain spinel compositions. Magnesium chromium iron oxide and iron cobalt chromium oxide show less obvious XRD peaks in the investigated serpentine soils. Nimite reflection peaks were identified inside S1. Trace of aluminum hydroxide (gibbsite) is also seen in certain soils. Non-ultramafic minerals like quartz in topsoil are allochthonous and probably are related to their eolian origin. The XRD patterns of Ranau serpentine soil are shown in Fig. 2.

Soil extraction: Table 1 shows the experimental data on the extraction of chromium, nickel and cobalt from soil samples of S1 and S4. The most striking result to emerge from the data is that the largest amounts of Cr and Ni is associated with the residual fraction which is as follows for S1 and S4 respectively: Cr 11912, 12599 µg g^{-1} and Ni 1345, 1120 µg g^{-1}. These amounts are equal with 85 to 95% of total extracted elements. However, over half of the extracted Co is present in Mn-oxide fraction (80 and 51 µg g^{-1} for S1 and S4). Residual fractions of S1 and S4 by having 12 and 37 µg g^{-1} Co are the second preferential phase in which Co is distributed. Aside from Mn-oxide, Fe-oxide which consist of poor crystalline and crystalline subdivisions has trapped more amounts of elements among non-residual fractions. 611 µg g^{-1} and 252 µg g^{-1} Cr, 104 µg g^{-1} and 41 µg g^{-1} Ni, 9 µg g^{-1} and 7 µg g^{-1} Co of samples S1 and S4, are fixed in crystalline iron-oxide fraction. These values are equal to 2-5%, 3-7% and 7-8% of total extracted amounts of Cr, Ni and Co respectively. Whereas the poor crystalline iron-oxide fraction carries mainly Co than other cations. As shown in Table 1, the proportion of Co in the poor crystalline iron-oxide fraction is 14 µg g^{-1} and 9 µg g^{-1} for S1 and S4. This is equal to 8 and 12 % of total extracted Co.

The lowest concentrations of Cr, Ni and Co were noted in soluble-exchangeable, surface adsorbed and organic matter fractions so that only less than 1% of cations are occluded to these fractions. Nevertheless, the sum of Coin soluble-exchangeable, surface adsorbed and organic matter fractions (1.1 µg g^{-1} on average) is bigger than those for Cr and Ni with an overall mean of 0.6 and 0.2 µg g^{-1} respectively.

DISCUSSION

Figure 3 depicts the percentage of chromium, nickel and cobalt which are extracted from the studied soils in each stage of analysis. The positive trend is repeated for all three line charts. The residual fraction is the most abundant pool for Cr and Ni. Combining this result with mineralogical data, one can conclude that Cr and Ni are tightly fixed in recalcitrant minerals of the serpentine soils like silicates (serpentine and chlorite) and spinels (Cr-magnetite). These primary minerals are very resistant to weathering in the soil environment and they get dissolve merely during the last step of extraction. Thus, chromium and nickel are almost non extractable and consequently their availability is very low.
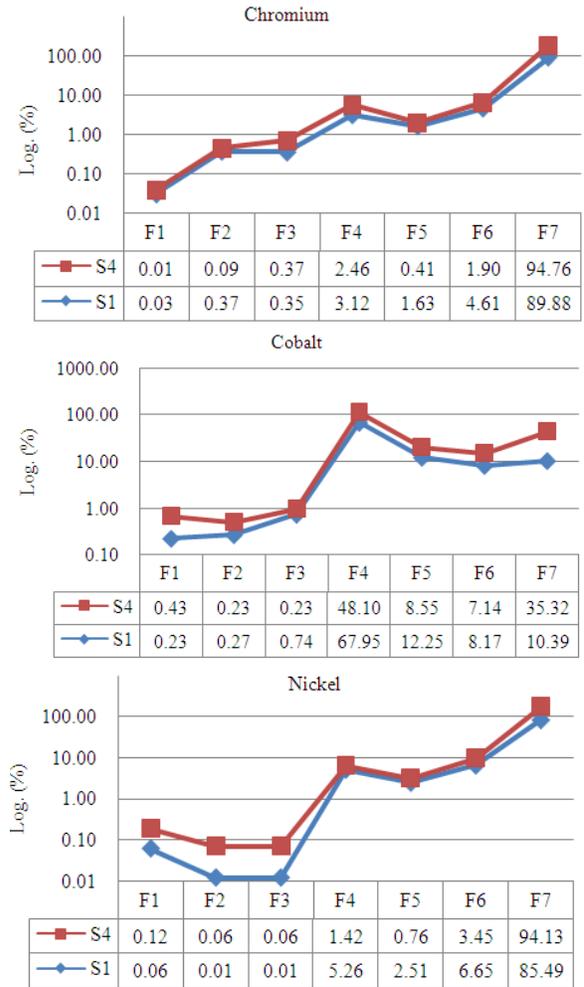
	F1	F2	F3	F4	F5	F6	F7
Chromium							
S4	0.01	0.09	0.37	2.46	0.41	1.90	94.76
S1	0.03	0.37	0.35	3.12	1.63	4.61	89.88
Cobalt							
S4	0.43	0.23	0.23	48.10	8.55	7.14	35.32
S1	0.23	0.27	0.74	67.95	12.25	8.17	10.39
Nickel							
S4	0.12	0.06	0.06	1.42	0.76	3.45	94.13
S1	0.06	0.01	0.01	5.26	2.51	6.65	85.49

F1: Soluble-Exchangeable fraction; F2: Surface adsorbed fraction; F3: Organic matter fraction; F4: Mn-oxide fraction; F5: Poor crystalline Fe-oxide fraction; F6: Crystalline Fe-oxide fraction Residual fraction

Fig. 3: The line charts of extracted chromium, nickel and cobalt (in percentage) from 7 fractions of two serpentine soil samples

As well described in the literature review, weathering of serpentine rocks specially under tropical climates begets lateritic soils rich of Oxy-hydroxide of iron, magnesium and manganese. Magnesium leaches readily from topsoils during the first stages of weathering process. Mn-oxide shows a strong affinity with Co (Fig. 3). This may be confirmed by the mineralogical observations indicating spinels as the main Co-carrier minerals. Mn-oxide is a moderately reducible fraction and can liberate Co easy.

Fe-oxides in serpentine soils of tropical areas are the substantial scavenger of metal cations specially Cr and Ni. They show high ability to absorb poorly

leachable elements from migrating solutions and fix them in their lattice because of their large surface area. Figure 3 shows that large proportions of Cr and Ni and lesser proportions Co are associated with crystalline Fe-oxide. They are attributed in goethite, hematite and magnetite minerals. This in accordance with XRD observation affirming the frequency of goethite in the studied serpentine soils (Fig. 2). Silicon rich goethite immobilizes Cr, Ni and Co while poor crystalline iron oxides are more responsible for Co availability. In fact, higher availability of elements occurs when the amounts of amorphous Fe-oxide is more than goethite. Such a situation exists in moderately weathered serpentine soils. In contrast, under intense weathering conditions like what exist in Ranau area, goethite controls the elemental distribution. Thus, metal cations like Co which attach to amorphous components are more available.

Figure 3 illustrates that the values of Cr, Ni and Co in most mobile phases of soluble-exchangeable, surface adsorbed and organic matter is very low. This supports the idea that these elements are not able to transfer into the environment readily. However, Co shows higher concentrations in these fractions rather than Cr and Ni.

CONCLUSION

In the present study, the speciation of Cr, Ni and Co in some serpentine soils of Ranau area was verified in order to determine the availability of these heavy metals in the environment base on their carring minerals. The finding results indicate that Cr and Ni are predominantly associated with the residual fraction of soil which is inherited from resistant silicates. Cr and Ni also fixed in the crystalline Fe-oxide fraction of soil in considerable amounts. This evidence shows the important role of goethite in immobilization of elements in tropical serpentine soils. Whereas the availability of Co mostly controls by Mn-Oxide and poor crystalline Fe-oxide. None of the investigated heavy metals is significant in soluble-exchangeable, surface adsorbed and organic matter fractions of the soils. Taken together, these results suggest that even though Cr, Ni and Co are very concentrated in serpentine soils, they are not a serious threat to the environment because of their low availability in the soil system. However, Co is slightly more mobile than Cr and Ni probably because of its mineralogical host.

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