Assessment of selected sequential extraction and the toxicity characteristic leaching test as indices of metal mobility in serpentinite soils

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Assessment of selected sequential extraction and the toxicity characteristic leaching test as indices of metal mobility in serpentinite soils

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ABSTRACT

Serpentinite soils are characterised by high concentrations of chromium, nickel, and cobalt. The accumulation of heavy metals as non-degradable inorganic contaminants is of great concern. Under normal circumstances the form in which a metal exists governs its transport in the environment and thus, its hazards. In this study, a specific developed speciation analysis for tropical soils was applied to determine the mobility of Cr, Ni and Co in two serpentinitic soil outcrops in Malaysia. The combination of selective sequential extraction analysis (SEE) and X-ray diffraction of soil powders showed that Cr and Ni are primarily associated with the residual fraction of soil which is inherited from resistant silicates. The crystalline Fe-oxide fraction of soil is the second substantial scavenger of Cr and Ni, whilst the dynamics of Co are mostly controlled by Mn-oxide and the poor crystalline Fe-oxide. The more easily mobilised forms of the studied metals carried on soluble-exchangeable, surface adsorbed and organic matter fractions are of minimal compartments. Therefore these metals are basically not available in the environment. On the other hand, corroborating information on the mobility of the metals was gained by applying the toxicity characteristic leaching procedure test (TCLP). The consistent results of the TCLP with the SSE revealed the non-toxic effects of Cr, Ni and Co in the environment despite their overload accumulation in the analysed serpentinite soils.

Keywords: sequential extraction, serpentinite soil, toxicity leaching test, chromium, nickel and cobalt

INTRODUCTION

Soils are dependent on the geochemistry and mineralogy of the underlying parent materials that influence their range of heavy metal concentrations. Serpentinite soils are known as a major source of geogenic metal hyperaccumulation, because these soils are exceptionally rich in chromium, nickel and cobalt (Kierczak et al., 2007; Quantin et al., 2008; Siebecker, 2010; Tashakor et al., 2012). Heavy metals are persistent contaminants which may be released into the ecosystem through weathering, erosion, leaching and other geo-environmental processes, and cause serious hazards. However, evidence indicates that the total metal concentration in the soil is an insufficient criterion to assess environmental impact because concentration alone provides no information regarding the availability and potential toxicity of the metals (Vijver et al., 2004; Jin et al., 2005; Powell et al., 2005; Echevarria et al., 2006; Iizuka et al., 2011). Therefore, knowledge of the geochemical form and speciation of metals in soil fractions is important for predicting the mobility and bioavailability of heavy metals under natural circumstance (Cancès et al., 2003; Kierczak et al., 2008; Garnier et al., 2009).

Speciation of metals is the identification and quantification of various forms, species, or phases of the elements. It reveals the affinity of heavy metals to bind between different soil fractions which include the following recognisable groups; (i) adsorbed and exchangeable, (ii) contained in carbonate
phases, (iii) bound to reducible phases (Fe and Mn oxides), (iv) occluded with organic matter and sulfides, and (v) residual or lattice metals (McCarty et al., 1998; Ryan et al., 2002). It is assumed that metals in water soluble (adsorbed) and exchangeable fractions are readily mobilised in the environment, whereas the metals in residual fractions are tightly bound and are not expected to be mobile in the soil nor available to the biota under normal conditions. A common operational method of speciation to determine the metal distribution within soil solid fractions is the selective sequential extraction (SSE). SSE includes progressively using appropriate reagents to destroy the binding agents between the target metal and the specific soil fraction to release the heavy metals selectively from their structural context. Reagents for each step of the extraction are chosen depending on their specificity towards particular forms. Successive extraction may be considered an index of the potential reactivity of the metals under different physical-chemical conditions and permits the relative binding strength of the metals to be detected.

Although a large number of sequential extraction analyses has been applied to fractionate metals in contaminated soils and sediments to assess the metal bioavailability (Haq and Miller, 1972; Cottenie et al., 1980; Garcia-Miragaya et al., 1981; Cleverger and Mullins, 1982; Soon and Bates, 1982; Lake et al., 1984; Xian, 1987, 1989; Kaasalainen and Yli-Halla, 2003; Qiao et al., 2003), the proposed sequential fractionation schemes specific for tropical soils are very limited (Ma and Uren, 1998). Tropical oxisols are distinctive by their mineralogy which is dominated by Fe and Mn oxides. Extraction of these soils requires a method which is able to dissolve the Fe and Mn oxides efficiently.

Along with SSE, this study assessed the toxicity characteristic leaching procedure (TCLP) as a test to evaluate the mobility and hazard potential of Cr, Ni and Co in serpentinitic soils. The TCLP is an international standard test for assessing the migration of contaminants in liquid, solid and multiphase wastes (Sun et al., 2006). This test was established by the US Environmental Protection Agency (USEPA) as the basis for the promulgation of the best demonstrated available technologies for treatment standards under the land disposal restriction program. The current study focuses on two serpentinite outcrops in Peninsular Malaysia where the availability of heavy metals has previously received little attention.

**MATERIALS AND METHODS**

**Field and samples**

The study was carried out in the Negri Sembilan state of Peninsular Malaysia, on soils developed on the serpentinised ultramafic rocks of Bukit Rokan (N 02° 4’ E 102° 22’) and Petasih (N 02° 59’ E 102° 11’). Serpentinised ultramafic bodies of west of Malaysia appear as several small secluded lenses along the central Malaya Bentong–Raub suture zone (Hutchison et al., 2009). They have the direction towards N 340°–350° E and contain structures explaining the deformation history along the boundary of central belt of Peninsular Malaysia (Jatmika Setiawan, 2009). These outcrops are assigned to the ophiolitic complex representing the Paleo-Tethys oceanic closure and exhibit the composition of mantle peridotite. From soil and morphological interest, weathering products of these outcrops are characteristically dark red in colour and the alignment of hill is towards north northwest–south southeast (NNW–SSE).

Serpentinities of the Bukit Rokan occurs within the chert-argillite and is in fault contact with the Kepis Formation (Yeap, 1986). The exposure is commonly sheared and shows various colours from pale yellowish green to dark green and grey with rather greenish waxy appearance. As a result of the tropical nature of Malaysia and elevated degree of weathering, the serpentinite bodies are strongly weathered and thick layers of lateritic serpentinitic soils surround the villages and the housing estate regions. The serpentinite massif of Petasih has a fault contact with schist which is highly foliated, sheared, and faulted. The serpentinitic soils in this area are covered by dense tropical forests which limits the accessibility of outcrops. Hence, the sampling was obtained from along the roads and hill cuts.

Soils derived from serpentinite massifs in the investigated areas, were characterised by their distinctive reddish-brown colour. A total of eight soil samples were collected from four locations in Bukit Rokan and Petasih. Soil samples in the surveyed sites were taken from the superficial parts (less than 10 cm thick) after cleaning up the debris and vegetation.

Prior to the mineralogical and chemical analysis, samples were air dried at room temperature and were crushed with Rocklabs grinder. Thereafter, samples were disaggregated using an agate mortar and pestle. The purpose of producing fine fraction soils is to create the bigger surface area of the particles and increase the feasibility of chemical reactions. Also, homogenised and pulverised soil samples augment the precision of the analysis. The soils obtained were sieved through a 2 mm plastic sieve to provide the optimal soil fraction size. To prevent any changes in chemical status of the soil, specimens underwent further analytical steps within a short period of time after sampling.

**Mineralogical study**

The mineralogical study was carried out on air-dried, pulverised and sieved soils, regardless of the constituent particle size. The identification of minerals in the soil samples was achieved using X-ray diffraction (XRD). The applied instrument was a D8 advance Bruker AXS diffractometer. The analysing radiation was CuK-alpha with wavelength of 1.5406 Å (0.15406 NM). X-ray diffractograms were collected on powder samples within the 20 range [5°–60°], with 0.02/0.1s step. The X-ray diffraction was then attached to the advanced diffract plus evaluation software through the computer. The reliability of the X-ray diffractometry experiment was checked by comparing with the International Standard for Corundum mineral.
Chemical methods

The total concentrations of chromium, nickel, and cobalt were determined using the X-ray fluorescence analysis (XRF) instrument Bruker S8 Tiger X-ray Digital with the exciting energy source of the rhodium K-α line. Soil samples were powdered to 30 μm grain size after air-drying and pulverisation. Thereafter, soils were made into 32 mm diameter press-powder pallets by applying a pressure of 20 tonnes for 1 minute to 1 g of sample against 6 g of pure boric acid powder. The accuracy of the XRF analysis was checked by using several certified reference materials (CRMs) with varying SiO₂ content (Tashakor et al., 2011).

The applied SSE method followed the extraction scheme proposed by Silveira et al. (2006), which is an adapted method for tropical soils. The SSE was conducted on 1 g of air-dried and crushed soil in 50 mL centrifuge tubes. The extraction was accomplished in seven successive steps. Between each step the supernatant was separated from the solid phases by centrifuging at the speed of 12,880g. The resulting centrifuge cake was washed with 5 mL of 0.1 M NaCl, and centrifuged again. The supernatant solutions were added to the former extracted solution. The purpose was to displace the extractant from the previous step, minimise the sample dispersion and reduce the re-adsorption of the metal (Silveira et al., 2006). At the final stage, the supernatant was filtered through 45μm Cellulose nitrate membrane filters and analysed by ICP to measure the heavy metals from each step of extraction.

The extraction was carried out in duplicate to ensure precision. The accuracy of the extraction was verified by calculating the difference between the total and the extracted amounts of each heavy metal. Total values were obtained by X-ray fractionation (XRF) analysis on soil press-powder pallets. According to Tessier et al. (1979), the experiment is reasonable when the total concentration measured by a single analysis and the sum of element amounts extracted by SEE show a difference of less than 20%.

The potential toxicity of heavy metals was assessed by the TCLP test employing the USEPA SW-846 Method 1311 (USEPA, 1992). The TCLP requires a buffering of acidic leaching extractions based on the alkalinity of the soil. When the pH of a soil is <5, the extraction fluid 1 is used. This fluid is a combination of 5.7 mL glacial acetic acid (CH₃CH₂OOH) and 64.3 mL 1 M NaOH diluted in 1 L water. It adjusts the pH to 4.93. Otherwise, the extraction fluid 2 is applied which is made up of 5.7 mL glacial acetic acid (CH₃CH₂OOH) diluted in 1 L water. The pH of this fluid was adjusted to 2.88. The pH was controlled by 1 mol L⁻¹ HNO₃ or 1 mol L⁻¹ NaOH. Prior to extraction, 5.0g of each soil specimen was weighed out and transferred to a 500 mL beaker. 96.5 mL distilled water was added to the beakers and the pH was recorded after 24 hours. Since all tested samples showed a pH > 5, 3.5 mL of 1 M HCl was added to each sample and then heated to 50 °C. The pH reading was taken again after cooling the beakers. At this point, all the pH values recorded were <5. Therefore, fluid 1 was chosen to be applied in the analysis. 2.0 g of soil and 40 mL of extract fluid 1 were transferred into a 50 mL centrifuge tube and shaken by a mechanical shaker for 18–24 hours at a speed of 12,880g. At the end of extraction period, solutions from each tube was separated from the solid phase by vacuum-filtration through 45 μm cellulose nitrate membrane filters. The extracted solutions were finally sent for ICP to determine the heavy metal contents.

RESULTS

Physicochemical properties of the studied soils

The average pH of 8 serpenticin soil samples was 5.5 which is in agreement with the pH range for mafic and ultramafic soils in tropical regions (5.1–6.3), as reported by Garnier et al. (2009). The sorption of metal ions on the mineral surface is influenced by the pH factor whereby the binding forces of metals to the solid phase increases with the increasing the soil pH. The average of the CEC figures (about 12 cmol(+) kg⁻¹) is in the CEC range of silty loamy soils (8–20 cmol(+) kg⁻¹).

The particle size distribution of the Bukit Rokan soils showed the predominance of silt loam soil textures by having 48–59% of the soil in the silt size fractions. However, in Petash the clay-sized particles seem to be slightly more abundant and the soils have silty clay loam textures, which are expected to be more sticky and plastic with a higher capacity of metal retention.

Mineralogical composition of soils

The mineralogical composition of the analysed serpentine soils is presented as X-ray diffractograms in Figure 1. The mineralogical of the soils were predominantly composed of secondary phyllosilicates, iron oxide, and hydroxides. The diffracted peaks of haematite are shown at d= 2.69, 1.69, 2.51 and 3.66 Å. The very strong peaks of goethite occur at 4.14-4.19 Å, however, the weaker peaks are at 2.42 and 2.16 Å. Various forms of spinels were found in the serpentine derived soils. The occurrence of Fe-rich spinels in the Bukit Rokan soils was suggested by the presence of diffracted peaks at d=2.44, 2.02, 1.43 and 4.66 Å. Chromite was an abundant mineral identified in all the analysed samples. The strongest line for chromite was observed at 2.52 Å and it usually overlapped with the magnetite peak at 2.53 Å. Nevertheless, the presence of chromite was confirmed by the existing representative peaks at d=1.6, 1.46 and 4.82 Å. According to the XRD diffractograms, some of the important elements of serpentinite soils such as magnesium, manganese, cobalt, and nickel do not seem to form independent and discrete minerals. They appear mostly inside the spinel structures or show less obvious XRD peaks of manganese chromium cobalt oxide, nickel iron manganese oxide magnesium oxide, or aluminium hydroxide. The common clay mineral in the studied soils was Kaolinite. Quartz, a non-ultramafic allochthonous mineral, presented very strong diffracted peaks at the crystal surfaces of (100) and (011) in all the analysed soils.
Indices of metal mobility in serpentinite soils

Sequential extraction

The sequential extraction results showed that chromium was found mainly in the residual fraction of soils in all of the analysed samples. The average amount of extracted Cr from the residual part was 6.583 mg L⁻¹, which is equal to about 96% of the total extracted Cr (Figure 2a). Second to the residual fraction, crystalline iron oxide was the most abundant pool for Cr. On average, 134 mg L⁻¹ (2%) of Cr was extracted from the crystalline iron oxide fraction. Sample BR.1 had the largest proportion of Cr trapped in the crystalline Fe-oxide fraction, assuming that the XRF results represent the total concentration of heavy metals, this value is 17% of the total extracted Cr (174 mg L⁻¹). The average concentration of Cr in the Mn-oxide fraction (53 mg L⁻¹) is greater than that in the poorly crystalline Fe-oxide fraction (38 mg L⁻¹). These values are equal to 0.8% of total extracted Cr in the former and 0.5% of that in the latter. The non-resistant parts include the first three fractions of soluble-exchangeable, surface adsorbed and organic matter (EFLE), which contributed very small amounts (less than 1%) of Cr from the total soil extracted in all the samples.

Nickel partitioning revealed a preferential association with the residual fraction in all the soils (Figure 2b). The mean value of the extracted Ni from the residual fraction of the analysed soils is 779 mg L⁻¹. In the other words, 90% of the total extracted Ni remained in the residual fraction. However, only 2% of Ni which is an average of about 20 mg L⁻¹ is fixed in the crystalline Fe-oxide. The contribution of Ni in the poor crystalline Fe-oxide is even larger (25 mg L⁻¹ on average, and 3% of the total extracted Ni).

The amounts of Ni found in the Mn-oxide fraction are variable and range from 1 to 143 mg L⁻¹. On average, the Mn-oxide fraction contains 37 mg L⁻¹ Ni which is about 4% of the total extracted nickel. Ni content in the adsorbed surface and organic matter fractions shows roughly the same variation in all the investigated soils (between 0.1 to 0.6 mg L⁻¹), whereas the soluble-exchangeable fraction contains a slightly higher amount of nickel (between 0.5 to 1.4 mg L⁻¹).

In addition to its abundance in the residual fraction, Co is also tightly bound to Mn-oxide fraction (Figure 2c). The range of cobalt extracted (in mg L⁻¹) from Mn-oxide fraction is as follows; 40 (PS.1), 11 (PS.2), 32 (BR.1) and 223 (BR.2). On average, 77 mg L⁻¹ Co is incorporated in the Mn-oxide fraction which is equal to 39% of the total extracted Co. Aside from Mn-oxide fraction, about 38% of the total extracted cobalt remains in the residual fraction (75 mg L⁻¹ on averages). The value of cobalt in the poor crystalline iron oxide is almost double that in the crystalline iron oxide fraction, representing average concentrations of 27 and 14 mg L⁻¹, and the average percentages of 14% and 7%, respectively. The first three soil fractions (EFLE) contain a very small amount of Co in all the analysed soils, which is between 0.1 and 9.6 mg L⁻¹ for soluble exchangeable and 0.2 to 0.7 mg L⁻¹ for surface adsorbed organic matter fractions. The average concentration of Co in the exchangeable phase (3 mg L⁻¹) is 7.5 times higher than that in the surface adsorbed and organic matter phases (0.4 mg L⁻¹).

In order to evaluate the efficiency of the experimented extraction, the concentrations of the various forms of Cr, Ni and Co calculated after sequential extraction from each serpentinitic soil sample were normalised to their total concentrations obtained by a single determination (XRF) of the

Figure 1 X-ray diffractograms from serpentinite soils of Bukit Rokan (a) and Petasih (b). The X-ray source is CuKα, λ = 1.5418.
bulk samples. The relative difference between the total metal concentrations and the sum of the amount of metal extracted from each step of the SSE analysis indicates the efficiency of the extraction. In a reliable extraction analysis, the relative percent difference (RPD) is lower than 20% (Tessier et al., 1979). Table 1 compares the total and the sum of Cr, Ni and Co amounts extracted from four soil samples. As seen, the efficiency of the performed selective sequential extraction test is reasonably high.

Toxicity test
The TCLP is commonly used to evaluate the toxicity of pollutants in the environment. In this method, an extreme condition with a pH lower than normal water is made by using a buffered organic acid (acetic acid). The extraction fluid for the TCLP is an aggressive solution which can release elements from all kinds of soils by affecting the binding energy between the elements and the soil particles, especially oxides and residual parts. Thus, the TCLP provides an idea of the strength or weakness of the chemical binds and the required energies for disassembling the elements from the soil fractions. In the present study, eight serpentinitic soil samples from the Bukit Rokan and Petasih areas were the subject of the toxicity characteristic leaching test. The average of a three-time analysis of the samples for Cr, Ni and Co is listed in Table 2. The following ranges were observed for the extracted heavy metals: Cr, 0.03–0.15, Ni; 0.09–1.07; and Co, 0.02–0.27 (mg L⁻¹).

The results were compared with the TCLP regulatory limits including those of Cr and Ni that are adopted for waste contaminants. As can be seen, the average amounts of extracted Cr (0.06 mg L⁻¹) and Ni (0.42 mg L⁻¹) are appreciably lower the toxic levels (5 and 70 mg L⁻¹ for Cr and Ni, respectively). Nevertheless, the mean value of extracted Ni is relatively higher than that for Cr and Co (0.09 mg L⁻¹).

<table>
<thead>
<tr>
<th>Extracted metals</th>
<th>BR.1</th>
<th>BR.2</th>
<th>PS.1</th>
<th>PS.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr Total concentration</td>
<td>1248</td>
<td>18990</td>
<td>2512</td>
<td>9297</td>
</tr>
<tr>
<td>Sum of extracted metals (F1–F7)</td>
<td>1017</td>
<td>16270</td>
<td>2355</td>
<td>7757</td>
</tr>
<tr>
<td>(Σ(F1–F7)/Total) 100 [%]</td>
<td>81</td>
<td>86</td>
<td>94</td>
<td>83</td>
</tr>
<tr>
<td>Ni Total concentration</td>
<td>189</td>
<td>1692</td>
<td>1105</td>
<td>587</td>
</tr>
<tr>
<td>Sum of extracted metals (F1–F7)</td>
<td>149</td>
<td>1648</td>
<td>1097</td>
<td>553</td>
</tr>
<tr>
<td>(Σ(F1–F7)/Total) 100 [%]</td>
<td>79</td>
<td>97</td>
<td>99</td>
<td>94</td>
</tr>
<tr>
<td>Co Total concentration</td>
<td>98</td>
<td>478</td>
<td>298</td>
<td>149</td>
</tr>
<tr>
<td>Sum of extracted metals (F1–F7)</td>
<td>79</td>
<td>343</td>
<td>241</td>
<td>121</td>
</tr>
<tr>
<td>(Σ(F1–F7)/Total) 100 [%]</td>
<td>80</td>
<td>72</td>
<td>81</td>
<td>81</td>
</tr>
</tbody>
</table>

* SEE fractions.
Indices of metal mobility in serpentinite soils

DISCUSSION

The major amounts of Cr and Ni in residual fraction of the soils are attributed to the host minerals resistance to weathering, such as silicates (serpentine and chlorite), spinels (magnetite), and chromite. These recalcitrant minerals hold tightly to Cr and Ni until the final step of the extraction, making them almost immobile. However, Co showed a preferable affinity with Mn-oxide than with residual fraction. In lateritic soils, the mobility of Cr, Ni and Co is significantly controlled by their distribution in oxy-hydroxide (Fe-Mn oxide) fractions. In the other word, among the non-residual fractions, Fe and Mn oxides are the most important metal holders in tropical soils. Mn-oxide is a moderately reducible fraction and can be a major resource for bioavailable Co. Fe-oxides have a high ability to adsorb poorly leachable elements from migrating solutions and fix them in their lattice because of their large surface area. Previous research findings have shown similar stabilities between the studied heavy metals and Fe in soil profiles (Schwertmann and Latham, 1986; Garnier et al., 2009). In fact, when a solution moves latterly, especially in well drained soils, Fe oxidises and precipitates as ferric hydroxide and then it loses water and creates goethite and haematite. XRD patterns affirm the abundance of goethite and haematite in the studied soils. Silicon rich goethite immobilises Cr, Ni and Co while poor crystalline iron oxides are more responsible for Co availability (Kierczak et al., 2008). In all the analysed soils, the lowest concentrations of Cr, Ni and Co were observed in the mobile phases of the soluble-exchangeable, surface adsorbed and organic matter fractions. Low EFLE supports the idea that these elements do not easily leach out in water and are not able to transfer into the environment readily. Nevertheless, the amount of Co in these fractions was higher than Cr and Ni. This is consistent with previous observations in New Caledonia (Becquer et al., 2003), Brazil (Garnier et al., 2009), Poland (Kierczak et al., 2008), Taiwan (Iizuka et al., 2011) and Sabah, Malaysia (Tashakor et al., 2011).

The comparison between the average distributions of Cr, Ni and Co in the various soil fractions (exchangeable in clay interlayers, adsorbed on clay edge/oxy-hydroxide surfaces, fixed on amorphous or on crystallised oxy-hydroxides and structural in residual silicate) are given in Figure 3. As may be seen, the three heavy metals have similar positive trends toward the seventh fraction which implies their close association with the residual part. Previous research shows that even though the heavy metals attached to this part are not expected to be immediately reactive in the environment, changing the chemical conditions of the soils might affect their availability, thereby releasing them into the soil system (Caillaud et al., 2009). Among non-residual fractions, significant proportions of the elements were held in the crystalline Fe-oxide and Mn-oxide and smaller ones were present in the poor crystalline Fe-oxide. The lowest concentrations of Cr, Ni and Co were observed in the soluble exchangeable fraction. This finding supports the idea that as a result of complete hydrolysis in tropical climates, clay minerals have a weak chance to form and heavy metals are directly immobilised in oxides.

Table 2 Values of pH (H₂O and HCl) and the amounts of Cr, Ni and Co extracted by toxic leaching experiment

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>pH (H₂O)</th>
<th>pH (HCl)</th>
<th>Cr</th>
<th>Ni</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR. 1</td>
<td>5.84</td>
<td>2.38</td>
<td>0.15</td>
<td>1.07</td>
<td>0.02</td>
</tr>
<tr>
<td>BR. 2</td>
<td>5.15</td>
<td>2.43</td>
<td>0.04</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>BR. 3</td>
<td>5.33</td>
<td>2.4</td>
<td>0.06</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>BR. 4</td>
<td>5.56</td>
<td>2.36</td>
<td>0.09</td>
<td>0.49</td>
<td>0.05</td>
</tr>
<tr>
<td>PS. 1</td>
<td>5.91</td>
<td>2.39</td>
<td>0.06</td>
<td>0.83</td>
<td>0.07</td>
</tr>
<tr>
<td>PS. 2</td>
<td>6.38</td>
<td>2.48</td>
<td>0.04</td>
<td>0.36</td>
<td>0.24</td>
</tr>
<tr>
<td>PS. 3</td>
<td>5.02</td>
<td>2.36</td>
<td>0.04</td>
<td>0.2</td>
<td>0.27</td>
</tr>
<tr>
<td>PS. 4</td>
<td>5.27</td>
<td>2.47</td>
<td>0.03</td>
<td>0.13</td>
<td>0.03</td>
</tr>
<tr>
<td>Average</td>
<td>5.6</td>
<td>2.4</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
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<tr>
<td>SD</td>
<td></td>
<td></td>
<td>0.04</td>
<td>0.34</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* Source: CFR Title 40 part 261.24.

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<td>2.43</td>
<td>0.04</td>
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</tr>
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<td>BR. 3</td>
<td>5.33</td>
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<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>BR. 4</td>
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<td>2.36</td>
<td>0.09</td>
<td>0.49</td>
<td>0.05</td>
</tr>
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<td>0.06</td>
<td>0.83</td>
<td>0.07</td>
</tr>
<tr>
<td>PS. 2</td>
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<td>2.48</td>
<td>0.04</td>
<td>0.36</td>
<td>0.24</td>
</tr>
<tr>
<td>PS. 3</td>
<td>5.02</td>
<td>2.36</td>
<td>0.04</td>
<td>0.2</td>
<td>0.27</td>
</tr>
<tr>
<td>PS. 4</td>
<td>5.27</td>
<td>2.47</td>
<td>0.03</td>
<td>0.13</td>
<td>0.03</td>
</tr>
<tr>
<td>Average</td>
<td>5.6</td>
<td>2.4</td>
<td>0.1</td>
<td>0.4</td>
<td>0.1</td>
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<tr>
<td>SD</td>
<td></td>
<td></td>
<td>0.04</td>
<td>0.34</td>
<td>0.10</td>
</tr>
</tbody>
</table>

* TCLP Regulatory Limit (mg L⁻¹)

BR, Bukit Rokan; PS, Petaseh.

Figure 3 Comparison between the average distributions of Cr, Ni and Co among the soil fractions.
In the set of soil samples we studied, oxides are the main contributor to the available heavy metals rather than clay minerals. The only identified clay mineral in the analysed soils was kaolinite. According to Massoura et al. (2006), the possible source of kaolinite in serpentinic soils could be the complex geological history of the parent minerals. Kostic et al. (1998) have reported disordered kaolinite in the serpentinite soils of Serbia as a result of feldspar conversion. However, it is more likely that the mineralogy of tropical oxisols, which is dominated by kaolinite (Dissanayake and Chandrajith, 2009; Shamshuddin and Anda, 2008), affects the composition of serpentinic soils developed in these regions.

Another important result emerging from Figure 3 is that in all the fractions the extracted contents of Co exceed those of Ni and Cr. Thus, the relative availability of the elements shows the following sequence: Co>Ni>Cr. Nevertheless, the geochemical background of the soil should be considered in the interpretation of the frequency of these elements in the environment.

One of the issues of this study is how consistent relations can be recognised between the selective sequential extraction and the toxicity leaching test applied in order to evaluate the mobility of Cr, Ni and Co and environmental concerns. Selective sequential extraction is one of the most useful techniques to assess environmental risk because it provides information about the amount of metals and their mobility under different field conditions.

The three first fractions of soluble-exchangeable, surface adsorbed and organic matter indicate that easily and freely leachable and exchangeable elements (EFLE) are more available for liberation into the ecosystem and for uptake by plants. On the other hand, the toxicity leaching procedure is able to evaluate the potential hazards associated with heavy metal concentrations using a weak natural organic acid or water. Hence, each of the mentioned tests addresses a specific aspect of heavy metal behaviour. However, for comparative purposes the data of extraction and leaching tests for mobilisable fractions are depicted in Figure 4. As can be seen, the TCLP results are in agreement with those obtained with the first three steps of the SSE scheme for all the studied heavy metals (Cr, Ni and Co) in serpentinite soils. However, because of the smaller ratio of solid–acetic acid solution used during the TCLP analysis, the leaching heavy metal content from all the samples show lower values than those from the SSE analysis.

**CONCLUSIONS**

The fractionation of chromium, nickel, Cr, Ni and Co was studied by applying the seven-step selective sequential extraction method that was adapted for tropical soils. From the result of partitioning analysis it can be concluded that behaviour, transport and the ultimate fate of heavy metals in the soil environment depend largely on their association with different fractions of the soil which is related to the mineralogical origin of the metals. Cr, Ni, and Co are concentrated in the residual fraction of soils in considerable amounts, which is inherited from their resistant mineral-bearing phases (chromite, spinel, and serpentine). Cr and Ni are also associated significantly with the secondary oxides.
of Fe. This evidence shows the important roles of haematite and goethite as the main scavengers for heavy metals in tropical soils. The availability of Co, however, is controlled by the Mn-oxide and poor crystalline iron oxide fractions. Since Mn oxide is moderately reducible, the liberation of Co into the environment seems likely. Interestingly, none of the investigated heavy metals are remarkable in the three available fractions of soluble-exchangeable, surface adsorbed and organic matter. Taken together, we can conclude that even though Cr, Ni and Co are highly concentrated in serpentinitic soils, they do not appear to be a serious threat to the environment because of their low availability in the soil system. Nevertheless, Co is slightly more mobile than Cr and Ni, probably because of its mineralogical host (Quentin et al., 2002).

It must be added that besides the nature of the parent minerals, some other factors crucially affect the availability of heavy metals in the soil. Such factors include climatic conditions, weathering history and certain characteristics of the soil such as pH, Eh, organic matter, and clay minerals.

The leaching test of toxicity of metal-loaded serpentinitic soils lead to the conclusion that despite the elevated concentration of heavy metals, the analysed soils can be classified as non-toxic according to the USEPA regulations regarding TCLP. A comparison between the amounts of the more mobile heavy metal fractions obtained by selective sequential extraction and toxicity leaching test showed that the TCLP results are lower, but are in agreement with the three first steps of the SSE.

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