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ORIGINAL ARTICLE

Geochemical assessment of metal transfer from rock and soil to water in serpentine areas of Sabah (Malaysia)

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Abstract The mobility of metals in ultramafic rock–soil systems and metal contamination in serpentine soils were investigated from the Ranau area in Sabah, East Malaysia. Metal concentrations were analysed after division into seven operationally defined fractions by selective sequential extraction (SSE). Geochemical studies showed that the soils are exceptionally high in Cr ($<$19,000 mg kg^{-1}), Ni ($<$4800 mg kg^{-1}) and Co ($<$170 mg kg^{-1}), about 140, 16 and 10 times higher than global soil averages, respectively. Thus, the soil can be categorized as unusually contaminated in comparison with relevant guidelines. Nevertheless, despite expectations, low concentrations of Cr, Ni and Co were found in surface waters flowing over the serpentine massifs ($<$14, 94 and 7 µg L^{-1}, respectively), indicating mobile ingress into river waters is low or, alternatively, diluted in the tropical environment resulting in minimal decline in their quality ascribed to the regional ultramafic geology of the area. The main reason is revealed by the SSE finding of very low ($<$1%) mobile metal abundances in available fractions of Ranau soils. While this study is one of the first to use a comprehensive SSE in tropical serpentine soils, the major SSE finding highlights the majority of metals ($>$95%) residing in refractory residual fractions. Metal speciation studies will shed further light on toxicities in the Malaysian ultramafic tropical environment, reconciled against elemental metal tenure, adopted by common standards.

Introduction

Serpentinites are hydrothermally altered ultramafic rocks with heavy metal enrichment compared to many other rock types, which cover about 1% of the earth's surface (Turekian and Wedepohl 1961; Brooks 1987; Proctor 2003). It is well documented that a substantial quantity of siderophile elements including chromium (Cr), nickel (Ni) and cobalt (Co) in these rocks are exceptionally high compared to the Earth's crust. The concentrations, fractionation and availability of metals in soils over ultramafic rocks throughout the world have been extensively studied (Turekian and Wedepohl 1961; Schwertmann and Latham 1986; Graham et al. 1990; Bonifacio et al. 1997; Dinelli et al. 1997; Shallari et al. 1998; Godard et al. 2000; Quantin et al. 2002b; Proctor 2003; Lee et al. 2004; Brearley 2005; Skordas and Kelepertsis 2005; Becquer et al. 2006; Kierczak et al. 2007; Rashmi et al. 2009; Alves et al. 2011; Tashakor et al. 2014a). The concentrations up to 125,000 mg kg^{-1} Cr (Adriano 2001) and more than 10,000 mg kg^{-1} Ni (Hseu 2006) were observed in serpentinite soils, while the concentration of these metals in other soils commonly ranges up to 100 mg kg^{-1} (Kabata-Pendias 2000). Heavy metals in the environment are receiving increasing attention among soil scientists and biologists (Ashraf et al. 2015) due to growing scientific and public awareness of their polluting and potential

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carcinogenic role, with heavy metal contamination representing a significant challenge due to their persistence in the environment. While metals from anthropogenic origins are often considered to be more of an environmental problem, lithogenic metal release should be considered in certain areas, such as those over ultramafic rocks. Soils over ultramafic rocks represent sources of natural geogenic contamination (Oze et al. 2004; Hseu et al. 2007; Kierczak et al. 2008), particularly in areas where there are significant human populations. It is not surprising that parent rock metal content is transferred to soils, though their geochemical and mineralogical characteristics have the potential to alter metal tenure and mobility, and therefore influence the environment with possible knock-on effects on human health. These soil quality issues are particularly important in South-East Asia given the presence of large area of ultramafic rocks (Repin 1998; Proctor 2003; Tashakor et al. 2014b; van der Ent et al. 2016). The natural metal sources can be traced back to geological and pedogenic processes through which metals are liberated from parent materials and may enter the wider environment. However, it is more important to understand the stocks and fluxes within and between different fractions in which such metals are held in rocks and soils if we are to gain a full understanding of the importance of ultramafic lithologies in potential geogenic contamination. Though emphasis is often placed on the role of pH in mobility and solubility of metals, the presence of soil organic matter, oxides and hydroxides plays an inhibiting role in release of metallic elements. In fact, our findings and others (Kaasalainen and Yli-Halla 2003) show the affinity of heavy metals to bind with different soil fractions, which may vary significantly, determines how strongly metals are retained in soils and how easily they might be released into soil solution and subsequently to adjacent surface waters (Vardaki and Kelepertsis 1999; Cancès et al. 2003). As soil is composed of a heterogeneous mixture of organic and inorganic constituents with varying ability to interact physically and chemically with heavy metals, metals present in soils can be associated with several reactive components. Soil metal mobility is limited largely by initial mineralogical speciation and subsequent metal binding forms associated with soil constituents and/or speciation that may partition into various soil fractions. Based on the affinity of metals to bind with different soil constituents, they are defined representing a decreasing degree of metal availability, ranging from ions in soil solution to ions in rock crystal lattices that can be assessed using sequential extraction procedures (Tessier et al. 1979; Silveira et al. 2006). Few studies have addressed potential pollutants in water resources and agricultural or natural soils resulting from the large regional extent of ultramafic rocks in the Malaysian tropical setting, particularly with methods revealing species contributions such as the selective sequential extraction (SSE) method. This is one of the first studies using a combination of mineralogical analysis (XRD), elemental content (XRF) and soil physical and chemical characteristics, in which we aim to determine the availability of metals in rocks, soils and waters in such environments. It therefore contributes to our understanding of potential health effects on populations living on or near ultramafic lithologies.

Materials and methods

Study area and sampling

Sabah is one of the two Malaysian states located in north-west Borneo. Ultramafic peridotite outcrops extend widely over about 3500 km^2 (Repin 1998). The current study focuses on the Ranau area in north-west Sabah between the latitudes of 5°57′–6°02′N and longitudes of 116°40′–116°45′E (Fig. 1) where the ultramafic series forms a broad expanse of land covering about 41 km^2 (Hing 1969). The common rock types in the area are tremolite peridotites and spinel lherzolites (Hutchison 2005). However, peridotites of Ranau are partially to totally altered through intense serpentinization and weathering and are difficult to recognize in the field. Serpentinites are characterized by their blue colour with small ill-defined greenish lenses. Their appearance is waxy, although some specimens appear to be crystalline. Associated metamorphic rocks are greenschists and amphibolites. The serpentinites are in fault contacts associated with hornblende gabbro. Diabase dikes intrude the ultramafic formations in some areas. The sedimentary rocks of the Ranau area are mainly associated with the north-west Borneo eugeosyncline of late Cretaceous to Tertiary age. These sedimentary rocks (Trusmadi or Crocker formations) consist of thick successions of sandstones and shale.

Four rock and ten soil samples (<20 cm depth including A and upper B horizons) were taken from the environs of the villages of Kinaratuan, Lohan Skim 1 and 2, Lohan Ulu and Tuhan (Fig. 1). Soils were taken from upper horizons after removal of debris and vegetation. Water sampling (from c. 10 cm depth) included samples taken from rivers flowing over serpentinites, namely Bongkud, Liwagu, Lohan, Napatau and Takorek. The focus of this study is on the surface water composition, though additional seepage water from Lohan Ulu, collected by hand pumping through a plastic pipe, was also analysed for comparison. Samples of 150 mL were kept in pre-washed polyethylene containers, and 2 mL of concentrated high-purity HNO_3 was added to each of them to
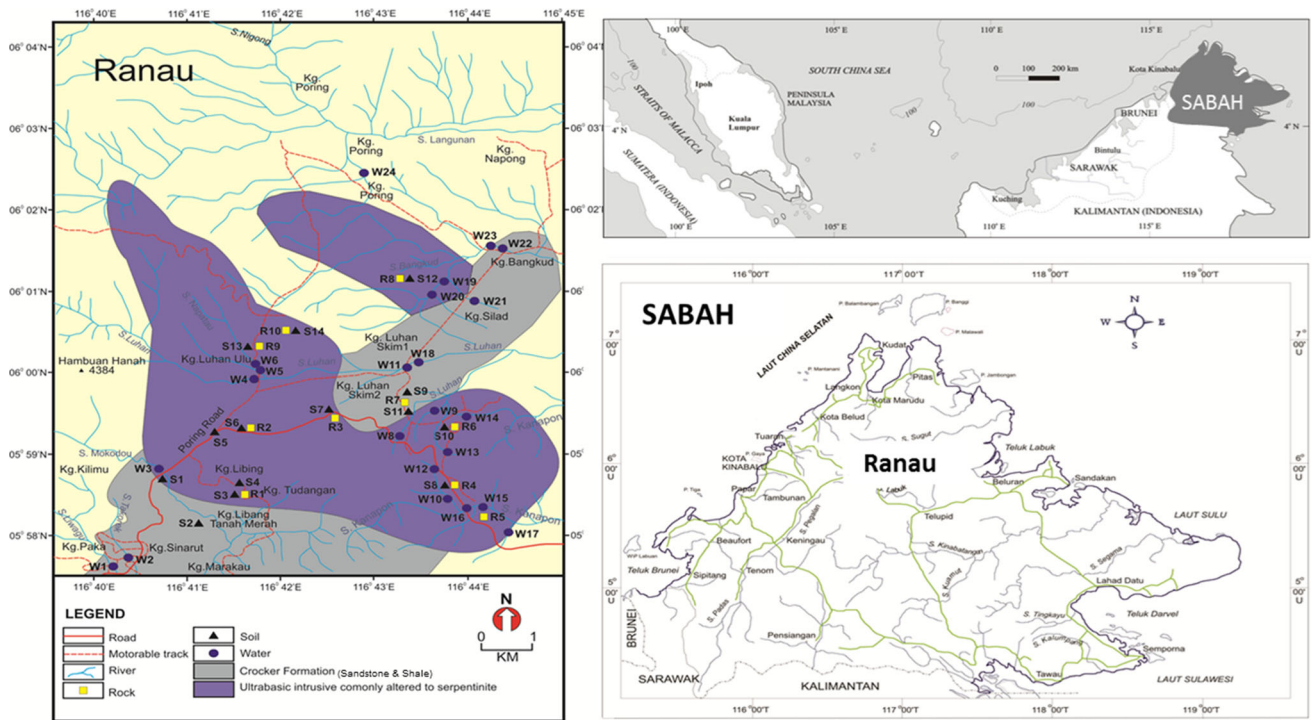
Fig. 1 Map of Ranau area (Sabah, Malaysian Borneo) studying the geochemistry of metal transfer between rocks, soils and water. Sampling locations are noted as rock (R), soil (S) and water (W)

preserve the samples and avoid precipitation of oxyanions. They were analysed elementally by ICP-MS (Perkin-Elmer ELAN 9000).

Soil physical and chemical characterization

Particle size distribution of soil samples was determined using the hydrometer method (British Standard Institution 1990). The pH was measured in a 1:2.5 (w:v) soil:distilled water suspension. The cation exchange capacity (CEC) was calculated by summation of Ca, Mg, K, Na and titratable acidity, all extracted with 1 M ammonium acetate (CH_3COONH_4). The solutions were filtered through cellulose nitrate membrane filters (45 μm) and were analysed elementally by ICP-MS (as above).

Mineralogical analyses

X-ray diffraction (XRD) analysis of rock and air-dried, pulverized and sieved (<2 mm) soil samples was performed on a Bruker D8 Advance diffractometer. The analysing radiation was CuKα with a wavelength of 1.5406 Å (0.15406 nm). X-ray diffractograms were collected on powder samples within the 2θ range [5°–60°], with 0.02° 0.1 s step.

Bulk elemental analyses

The bulk chemical composition of rock and soil samples was determined by X-ray fluorescence spectrometry (XRF) using a Bruker S8 Tiger X-ray with the exciting energy source of Rhodium K-α line. In order to measure ten major oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5), the powdered soils (<30 μm) were made into 32-mm-diameter fused beads, by igniting 0.5 g of sample with 5.0 g of Johnson–Matthey Spectroflux 110. To measure trace elements (Appendix), pressed powder pellets were prepared by applying a pressure of 20 tonnes for one minute to 1 g of sample with 6 g of pure boric acid powder.

Elemental speciation

Chromium, Ni and Co were fractionated with the seven-step extraction procedure scheme proposed by Tessier et al. (1979) and modified by Silveira et al. (2006) (Table 1). This method is adapted for tropical Oxisols in which the mineralogy is dominated by Fe and Mn oxides and provides data on operationally defined soil fractions. Unlike many extraction procedures, the extraction scheme of Silveira et al. (2006) is capable of differentiating metals trapped in amorphous or poorly crystalline oxides from crystalline forms. Selective sequential extraction was

Table 1 Sequential extraction procedure for metals in tropical soils as proposed by Silveira et al. (2006) *Source:* Silveira et al. (2006)

Fraction	Solution	Equilibrium conditions
Soluble–exchangeable	15 mL 0.1 M $CaCl_2 \cdot 2H_2O$	2 h, room temperature
Surface adsorbed	30 mL 1 M NaOAC (at pH 5 with CH_3CO_2H)	5 h, room temperature
Organic matter	5 mL NaOCl (at pH 8.5 with HCl)	30 min, 90–95 °C
Mn oxides	30 mL 0.05 M $NH_2OH \cdot HCl$ (at pH 2 with HCl)	30 min, room temperature
Poorly crystalline Fe oxides	30 mL 0.2 M $H_2C_2O_2$ + 0.2 M $(NH_4)_2C_2O_4$ (at pH 3 with NH_4OH)	2 h, dark
Crystalline Fe oxides	40 mL 6 M HCl	24 h, room temperature
Residual	HNO_3–HCl–HF + 1.5% H_3BO_3 digestion	3050 bar

performed using 1 g of air-dried and sieved soil samples (<2 mm) in 50-mL polycarbonate centrifuge tubes. Reagents were added in a stepwise fashion to digest the soils, and the suspensions were equilibrated as described in Table 1. The supernatants were separated from the solid phases by centrifugation for 18–24 h at 12,880 RCF. They were then filtered through 45-µm cellulose nitrate membrane filters and analysed by ICP-MS (as above) following each stage of extraction.

Data quality

All samples were analysed in duplicate to verify the precision of analysis; the relative percentage difference between duplicate measurements was always less than 10%. Precision of the ICP-MS was shown by analysing the international reference standard STD 125 ppb-1 five times giving a relative standard deviation of less than 1.6% in all cases. Detection limits for Cr, Ni and Co were 0.05 µg g^{-1} and 0.1 µg L^{-1} for soil and water samples, respectively. The international standard for corundum was used as a reference material for the XRD analysis, whereas several certified reference materials with varying SiO_2 content (USGS-BCR-2, SO-2, W-2a, CANMET SY-2 and CRPG-GSN) were analysed by XRF. There are no reference materials certified for all steps of the SSE, so, in order to evaluate the extraction efficiency, the concentrations of the various forms of Cr, Ni and Co were summed after extraction from each sample and compared to their total concentration obtained by XRF determination of the bulk sample.

Results and discussion

Mineralogical composition of rocks and soils

The rock mineral assemblage is characteristic for ultramafics containing antigorite, chrysotile and lizardite (Fig. 2). Different types of spinel, especially chromite and

magnetite, also occur in the rocks. The studied serpentinite-derived soils typically showed representative features of tropical soils with major contents of oxides and hydrous oxides dominated by hematite and including goethite (that are weathering products of magnetite) (Fig. 2). The serpentine soils typically contain chromite and minor amounts of chlorite and ilmenite and trace amounts of inherited serpentine minerals are also recognized. The dominant clay mineral is kaolinite. Allochthonous quartz is present in almost all the soil samples, probably related to their aeolian origin.

Bulk composition of serpentinite rocks and soils

The mean SiO_2 content in the rocks was 43.2% (by weight) (Table 2). The mean content of MgO was 35.5% and Fe_2O_3 showed a mean content of 8.8% (Table 2). The mean CaO content was very low (2.5%) as were Na_2O (0.18%), K_2O (0.09%) and P_2O_5 (0.01%). Analyses of major oxides of rocks from Ranau accord with the chemical compositions of numerous ultramafic massifs throughout the world listed by Brooks (1987). Among the 20 trace metals analysed, Cr, Ni and Co are considered further (Table 2). The total concentrations of Cr and Ni ranged from 2622 to 2781 mg kg^{-1} and 1602 to 1840 mg kg^{-1}, respectively, and the observed range of Co was between 61 and 64 mg kg^{-1}. The former two elements are notably higher compared to the average Earth's crust (Cr 100 mg kg^{-1} and Ni 25 mg kg^{-1}) (Mason and Moore 1982). The most striking result with regard to the soils was, again, notably high concentrations of Cr, Ni and Co (Table 2). Chromium in Ranau soils had a high mean value of 14,208 mg kg^{-1} (range 2427–27,863 mg kg^{-1}). The global content of Cr in soils range up to 200 mg kg^{-1} (Bourrelier and Berthelin 1998); however, in the presence of ultramafic bedrocks, such as serpentinites, the Cr concentration is up to 10,000 mg kg^{-1} (Stueber and Goles 1967; Schwertmann and Latham 1986). This study showed a mean Ni concentration of 1647 mg kg^{-1} (range 850–4753 mg kg^{-1}). The common background average for Ni is less than
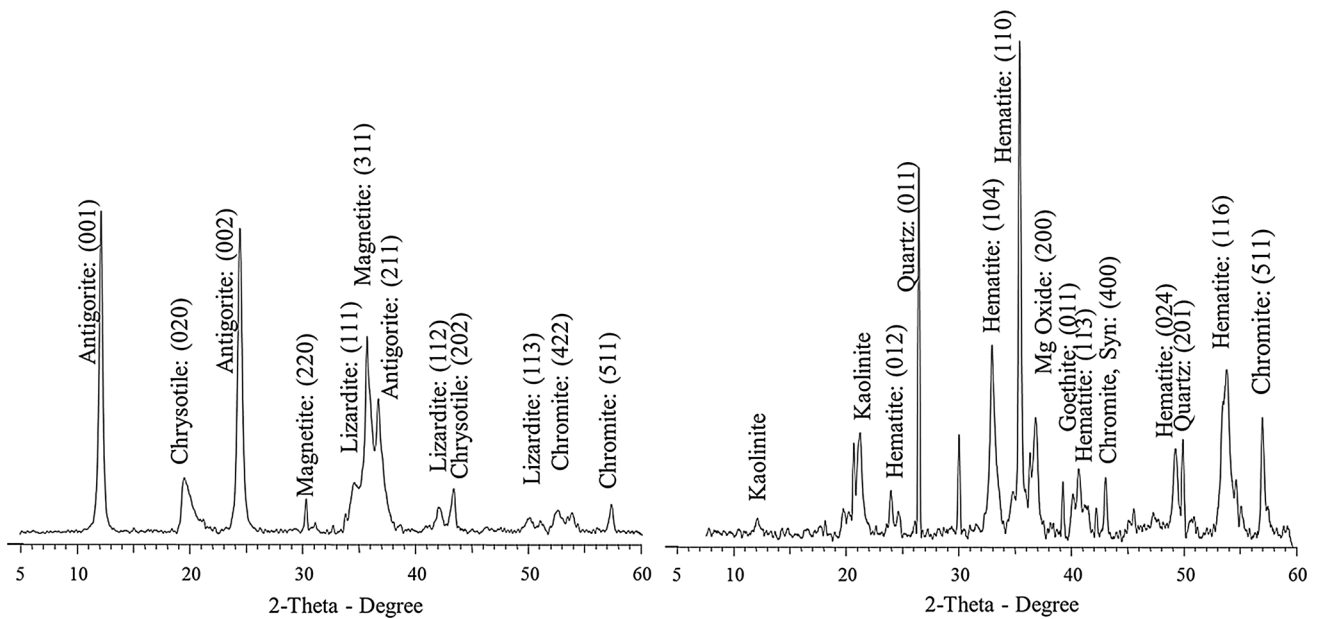
Fig. 2 X-ray diffractograms of representative serpentinite rock (*left*) and soil (*right*) samples in the vicinity of Ranau, Sabah (Malaysian Borneo)

100 mg kg^{-1} (Kabata-Pendias 2000), while numerous studies have reported Ni concentrations of more than 10,000 mg kg^{-1} in ultramafic soils (Brooks 1987; Hseu 2006). Cobalt had a mean concentration of 112 mg kg^{-1} and ranged from 35 to 167 mg kg^{-1}. According to Kabata-Pendias and Mukherjee (2007), surface soil Co ranges from 4.5 to 12 mg kg^{-1}. Chromium, Ni and Co concentrations in serpentinite rocks and soils of Sabah were also in agreement with the reported values from serpentinites of India (Rashmi et al. 2009), Oman (Godard et al. 2000), Greece (Skordas and Kelepertsis 2005) and Iran (Ghaderian and Baker 2007). Nevertheless, serpentinite soils of New Caledonia contained much higher concentrations of Cr (31,000 mg kg^{-1}) and Ni (12,000 mg kg^{-1}) (Massoura et al. 2006). SiO$_2$ shows strong positive correlation with CaO (0.81), Na$_2$O (0.82) and K$_2$O (0.87) (Appendix) and these alkali and alkali earth elements also indicate the same correlation with each other, whereas Fe$_2$O$_3$ forms another very strongly correlated pair with MnO having a correlation coefficient of 0.80. Cobalt and Cr correlate with this group showing strong coefficients: Fe$_2$O$_3$–Co (0.66), Fe$_2$O$_3$–Cr (0.80), MnO–Co (0.61) and MnO–Cr (0.67). There is a strong positive correlation between Cr and Co (0.96). However, Ni presents a different behaviour and shows moderate association with MgO with a correlation coefficient of 0.60 due to its calchophile nature.

Physico-chemical characteristics of soils

The soils are slightly acidic, showing a mean pH value of 5.8 ± 0.6 (Table 3). The pH ranges from 5.2 to 7.2 in line with soils derived from mafic and ultramafic rocks in lowland tropical regions (Brearley 2005; Massoura et al. 2006; Garnier et al. 2009). Silt is the predominant fraction in all of the soils except for sample S12, which is mainly composed of clay particles (Table 3). The soils are thus classified as silty loam to silty clay loam and clay (Soil Survey Division Staff 1993). Cation exchange capacity (CEC) shows a broad range with a mean of 12.0 ± 10.4 cmol(+) kg^{-1} (Table 3); the CEC was dominated by exchangeable Mg^{2+} with the mean value of 11.3 ± 10.2 cmol(+) kg^{-1}, over 90% of the mean CEC. The highest CEC was shown by sample S3 (33.9 cmol(+) kg^{-1}), followed by clay sample S12 (23.7 cmol(+) kg^{-1}). Sample S4 showed the lowest CEC (1.2 cmol(+) kg^{-1}), near a regional contact inflexion, and possible faulting, approximately midway between the highest S3 and S12 CEC samples.

Enrichment and depletion of elements from rocks to soils

During chemical weathering and pedogeological processes, the concentrations of certain elements from the parent rocks may significantly increase or decrease in the resultant soils (Osama 2007). Al$_2$O$_3$ and MnO were minor components of bulk rock composition, while the amounts of these elements showed a threefold to fivefold increase in derived soils along with Fe$_2$O$_3$ (Table 2). The concentrations of Cr and Co were also enriched five and two times, respectively, in the soils compared to parent materials. The concentration of Ni in the soils was equal to that in the parent rocks

Table 2 The concentration of major oxides and trace elements in serpentinite rocks and soils in the vicinity of Ranau, Sabah (Malaysian Borneo)
Source: Tashakor et al. (2014b) for soil data

	Major oxides (wt %)						
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO
Rock							
R1	43.20	0.14	3.23	8.74	0.12	35.45	2.75
R3	42.60	0.08	2.29	8.53	0.12	37.32	1.80
R4	43.70	0.17	3.71	9.17	0.13	35.32	3.20
R7	42.50	0.14	3.41	8.92	0.11	34.07	2.40
Mean ± SD	43.20 ± 0.50	0.13 ± 0.03	3.20 ± 0.60	8.84 ± 0.30	0.12 ± 0.01	35.54 ± 1.34	2.54 ± 0.59
Soil							
S1	60.50	0.63	16.84	11.35	0.08	0.76	0.36
S3	26.40	0.25	9.77	41.04	0.73	8.47	0.10
S4	14.50	0.47	17.75	38.82	0.59	2.83	0.03
S5	5.10	0.94	22.89	42.69	0.29	0.31	0.04
S6	17.60	0.24	12.85	42.90	0.75	7.97	0.17
S7	13.60	0.61	19.34	45.47	0.81	0.86	0.02
S8	58.00	0.61	10.18	11.47	0.17	3.70	0.13
S10	19.10	0.99	22.63	42.05	0.40	1.31	0.09
S12	25.30	0.29	5.87	25.62	0.12	0.29	0.10
S13	54.60	0.57	11.88	12.78	0.18	8.71	0.33
Mean ± SD	29.47 ± 20.42	0.56 ± 0.26	15.00 ± 5.76	31.42 ± 14.52	0.41 ± 0.28	3.52 ± 3.52	0.10 ± 0.11
Enrichment and depletion factors	0.68	4.30*	4.69*	3.55*	3.42*	0.10*	0.04*

	Major oxides (wt %)			Trace metals (mg kg^{-1})		
	Na_2O	K_2O	P_2O_5	Co	Cr	Ni
Rock						
R.1	0.23	0.09	0.01	63	2743	1609
R.3	0.10	0.09	0.00	64	2622	1840
R.4	0.23	0.09	0.01	62	2641	1602
R.7	0.14	0.10	0.00	61	2781	1658
Mean ± SD	0.18 ± 0.07	0.09 ± 0.01	0.01 ± 0.01	62 ± 1	2697 ± 77	1677 ± 111
Soil						
S1	0.09	1.95	0.12	136	13,929	1675
S3	0.05	0.00	0.05	122	14,720	2237
S4	0.01	0.00	0.03	146	16,381	1573
S5	0.03	0.00	0.05	112	14,029	850
S6	0.07	0.00	0.04	167	19,025	4753
S7	0.02	0.00	0.04	127	17,233	1219
S8	0.16	0.63	0.02	35	2427	865
S10	0.04	0.01	0.06	114	15,807	1311
S12	0.00	0.01	0.04	93	11,277	972
S13	0.11	1.26	0.02	46	2828	1418
Mean ± SD	0.06 ± 0.05	0.40 ± 0.70	0.04 ± 0.02	109 ± 41	12,766 ± 5736	1687 ± 1156
Enrichment and depletion factors	0.33*	4.32	8.00*	1.76*	4.73*	1.01

Enrichment or depletion factors are the ratio between the concentration of the element of interest in the rock compared to the soil; significant differences ($p < 0.05$) are marked by an asterisk

whereas MgO showed a tenfold depletion. The observed enrichment and depletion pattern in this study is similar to that proposed by Kostić et al. (1998) for wet environments.

In general, tropical climates, by inducing intense and complete hydrolysis, lead to the immobilization of poorly leachable metals in the secondary minerals and oxides and

Table 3 Physical and chemical characteristics of serpentine soils in the vicinity of Ranau, Sabah (Malaysian Borneo)

	S1	S3	S4	S5	S6	S7	S8	S10	S12	S13	Mean ± SD
pH	5.6	7.2	5.8	5.7	5.4	5.8	5.2	5.3	5.9	6.4	5.8 ± 0.6
>2 mm (%)	1	0	0	0	0	0	1	2	0	1	0.5 ± 0.7
<2 mm (%)											
Sand	25	20	33	19	30	30	22	18	20	19	23.6 ± 5.5
Silt	58	52	54	50	52	55	59	48	25	51	50.4 ± 9.6
Clay	16	28	13	31	18	15	18	32	55	29	25.5 ± 12.6
Texture	Silt loam	Silt clay loam	Silt loam	Silt clay loam	Silt loam	Silt loam	Silt loam	Silt clay loam	Clay	Silt clay loam	
Exchangeable cations (cmol(+) kg^{-1})											
CEC	5.3	33.9	1.2	11.8	7.3	3.7	3.2	12.0	23.7	17.8	12.0 ± 10.4
Mg^{2+}	4.9	33.5	0.9	11.2	7.0	3.5	2.4	11.0	21.4	17.4	11.3 ± 10.2
Ca^{2+}	0.3	0.3	0.1	0.6	0.2	0.1	0.4	0.3	0.4	0.2	0.3 ± 0.1
K$^+$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.2	0.0	0.0 ± 0.1
Na$^+$	0.2	0.1	0.1	0.1	0.1	0.1	0.4	0.5	1.7	0.2	0.4 ± 0.5

accumulation in soil profiles, especially towards the surface. During the pedogenesis of serpentinite, highly mobile elements such as Mg and Si leach from the soil profile at the early stages of weathering, while newly formed clay minerals become enriched in less mobile elements such as Fe and Al.

Distribution of Cr, Ni and Co in various soil fractions

The difference between the total metal concentrations (by XRF) and the sum of the concentration of metals extracted from each step of the SSE analysis was less than 20% in all cases indicating a reliable extraction (Tessier et al. 1979). The SSE indicated the main incorporation of Cr and Ni was within the residual fractions of soils (Fig. 3); this was 12,256 mg kg^{-1} for Cr and 1233 mg kg^{-1} representing 92.3 and 89.8% of the total extracted metals (assuming the XRF analyses represent the total concentration of the metals). Combining this result with mineralogical observation, we conclude that Cr and Ni are bound in serpentine minerals and chromite spinels that are highly resistant to weathering, extracted only at the last stage using strong acidic reagents. This is in agreement with other research in New Caledonia (Quantin et al. 2002a), Brazil (Garnier et al. 2009), Poland (Kierczak et al. 2008) and Taiwan (Cheng et al. 2011). The use of microscopic (e.g. synchrotron, EDX, electron microprobe) techniques would aid further research to determine the co-location of these metals with certain primary or secondary minerals. Amorphous (poorly crystalline) and crystalline Fe-oxide and Mn-oxide fractions were the most abundant metal
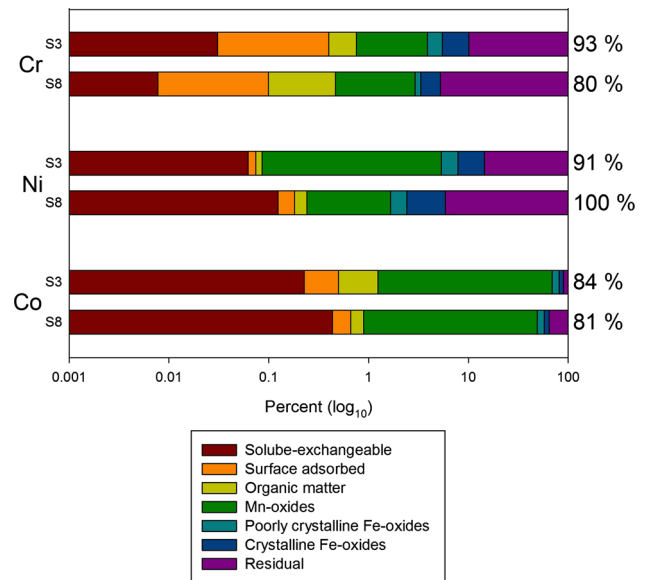

Fig. 3 Percentage of chromium, nickel and cobalt found in seven soil fractions following selective sequential extraction (see Table 1) for serpentinite soils in the vicinity of Ranau, Sabah (Malaysian Borneo). Percentage recovery (in relation to total determination by XRF) is noted on the *right-hand side* of the figure

pools among the non-residual fractions, as predicted for 'lateritic' tropical soils. About 3.3% of the total extracted Cr (432 mg kg^{-1}) was 'trapped' in the crystalline Fe-oxide fraction, and the concentration of Cr in the Mn-oxide fraction (371 mg kg^{-1}; 2.8%) was higher than that in the poorly crystalline Fe-oxide fraction (135 mg kg^{-1}; 1.0%). With respect to Ni, a preferential association with crystalline Fe oxide (73 mg kg^{-1}; 5.0%) rather than with poorly crystalline Fe oxide (25 mg kg^{-1}; 1.6%) or Mn

oxide (50 mg kg^{-1}; 3.3%) was observed. This result is in agreement with the work of Garnier et al. (2009) who found Ni to be preferentially associated with crystalline Fe oxide over poorly crystalline Fe oxide and Alves et al. (2011) who found comparable amounts of Ni in crystalline Fe oxides compared with poorly crystalline Fe oxide plus Mn oxides. However, it contrasts with the work of Massoura et al. (2006) who suggested that in highly weathered tropical soils, a higher proportion of the Ni should be found in the poorly crystalline Fe-oxide fraction. van der Ent et al. (2016) found higher proportions of Ni in the amorphous Fe oxides (<30%) and crystalline Fe oxides (<10%). However, these soils were covered by Ni hyperaccumulator plants with >0.01% Ni in plant parts that may return Ni to the surface soil and increase the soil Ni content. In comparison with Cr and Ni, Co showed a much higher affinity for the Mn-oxide fraction of soils (65.6 mg g^{-1}; 58%) in addition to its abundance in the residual fraction (24.8 mg g^{-1}; 23%). The non-resistant components including the first three fractions of soluble–exchangeable, surface adsorbed and organic matter contained very small quantities (less than 1.5% in total) of Cr, Ni and Co extracted from all the samples (Fig. 3). This suggests that the metals of concern are not easily leachable and thus not readily transferable within the environment under ambient conditions. This is also influenced by the nature of these soils being low in organic matter as soils with higher organic matter content are likely to have more Ni in organic fractions (Hseu et al. 2016).

The 'quality' of serpentinite soils

The mean concentrations of Cr, Ni and Co in the serpentine soils are about 130, 40 and 10 times higher than average global soil composition (Table 4). Using the geoaccumulation index (I*geo*) of Müller (1969) and the background values for relevant soil Fe concentrations from Hamon et al. (2004), we determined that the soils were moderately to strongly contaminated (I*geo* class 3 on a six-point scale) by Ni and strongly contaminated (I*geo* class 4) by Cr. Based on the concentration of Cr and Ni, all the soils were attributed to group C in the Dutchlist (2009) standard (indicating significant pollution and a serious toxic threat to the environment), while the Co concentration corresponds to group B (referring to polluted soils that may lead to possible harmful effects) (Table 4). Comparing with soil quality guidelines developed by Australian and New Zealand Environment and Conservation Council (ANZECC/NHMRC 1992), the concentration of Cr in the studied soils is about two orders of magnitude higher than the maximum background value for Cr (110 mg kg^{-1}). Similarly, Ni in the investigated soils exceeds the highest background concentration level (400 mg kg^{-1}) given by ANZECC/NHMRC (1992). Thus, the metals in the surveyed serpentinite soils are also considered polluted by this standard. Using the Greater London Council (2001) guidelines, with regard to Ni and Cr, the soils are categorized as 'unusually heavily contaminated', which is point 5 on a five-point scale; these guidelines do not furnish any classification for Co contamination. It should, of course, be noted that these standards do not necessarily relate to the specifics of tropical soil characteristics as they were largely and obscurely adopted from European standards (McLaughlin et al. 2000). In a comprehensive study, Zarcinas et al. (2004) suggested the 95th percentile values of the 241 randomly selected soils sampled from Peninsular Malaysia as 'Investigation Level' (Table 4); this would apply to all soils sampled from Ranau in this study. Nevertheless, the 95th percentile via random sampling does not reconcile differing parent geology, mineralogy and climate or the interactions between them to either mitigate or accelerate potential bio-toxicity.

Metal concentrations in waters

Surprisingly, few studies have examined metal concentrations in water samples over ultramafic areas; those found here were comparable to those observed by Vardaki and Kelepertsis (1999) in Greece and Migon et al. (2011) in New Caledonia although Cr was, in general, lower. The maximum concentrations of Cr (14 µg L^{-1}), Ni (94 µg L^{-1}) and Co (7 µg L^{-1}) in river samples (Table 5) were lower than the maximum permissible values (Cr 50 µg L^{-1}, Ni 200 µg L^{-1}, Co 50 µg L^{-1}) proposed by Interim National Water Quality Standards of Malaysia (INWQS 2006). The metal concentrations in Ranau rivers also compared reasonably, with the exception of a single value for Ni, with the World Health Organization (WHO 2006) standard of 50 µg L^{-1} Cr and 70 µg L^{-1} Ni and the US drinking water quality guideline (EPA 2009) of 100 µg L^{-1} Cr. It was found that Cr, Ni and Co in all of the rivers flowing over serpentine soils fell within these 'permitted' INWQS thresholds and the majority were within the WHO threshold. Hence, according to these published standards, these rivers, limited by sampling constraints presented, appear safe both for drinking water and crop production. It must be noted, however, this does not address ionic complexion, speciation factors, for Cr in particular, and the potential bio-toxicity thereof. The seepage water sample analysed, however, had a Ni concentration considerably higher than in surface waters (Table 5) and clearly in excess of standards for Ni. It is conceivable that more extensive seep water sampling and more local fluvial waters will reveal analyses in excess of threshold standards. Possible reasons include low volume of seepage water relative to larger rivers subject to high

Table 4 The mean concentration of chromium, nickel and cobalt in serpentine soils in the vicinity of Ranau, Sabah (Malaysian Borneo), and their geoaccumulation index enrichment (Igeo) in comparison with the average global composition, the 95% 'Investigation Levels' determined for Malaysia, ANZECC/NHMRC and Greater London Council guideline (all values are mg kg^{-1})

	Ranau soil	Igeo[a]	Average global soil composition[b]	Malaysian investigation levels[c]	ANZECC/NHMRC[d]		Greater London Council guidelines[e]				
					Background level	Environmental investigation	I	II	III	IV	V
Cr	12,766	3.29	100	60	0.5–110	50	100	200	500	2500	>2500
Ni	1687	2.39	40	45	2–400	60	20	50	200	1000	>1000
Co	109	–	10	10	2–170	–	–	–	–	–	–

[a] Igeo = log2 ($M/1.5 \times B_n$) where M is the concentration of metal in soil and B_n is the background concentration of metal (Müller 1969)

[b] Average soil composition from Siegel (1975)

[c] The 95% 'Investigation Levels' determined for Peninsular Malaysia ($n = 241$ soils) (Zarcinas et al. 2004)

[d] Soil quality guideline developed by Australian and New Zealand Environment and Conservation Council (ANZECC/NHMRC 1992)

[e] Greater London Council guidelines (G.L.C (2001) definitions of contaminated soils (I = typical values for uncontaminated soils, II = slight contamination, III = contaminated, IV = heavy contamination, V = unusually heavy contamination)

Table 5 Concentrations of chromium, nickel and cobalt in river and seeping water traversing serpentinites in the vicinity of Ranau, Sabah (Malaysian Borneo)

	Sample ID	Cr (µg L^{-1})	Ni (µg L^{-1})	Co (µg L^{-1})
Surface water	W3	14	42	2
	W5	7	23	1
	W8	5	67	1
	W9	8	18	2
	W12	6	11	2
	W13	9	42	5
	W14	7	20	4
	W20	11	94	7
	Mean ± SD	8.3 ± 2.7	39.7 ± 26.6	3.0 ± 2.0
Seeping water	W4	23	936	22
Threshold standards	WHO[a]	50	70	–
	INWQS[b]	50	200	50
	EPA[c]	100	–	–

[a] World Health Organization (WHO 2006)

[b] Interim National Water Quality Standards for Malaysia (INWQS 2006)

[c] US drinking water quality guideline (EPA 2009)

flow surface run-off, regional outlier geological provenance dilution and local to regional metal precipitation through oxyanion species. While sampling was limited, evidently local seepage waters that ingress and flow through serpentine soil profiles do become enriched in these elements. Lottermoser (1997) believed almost all seepage and groundwater associated with ultramafic formations have elements beyond environmental quality guidelines in accordance with findings of this study showing, concentration of Ni up to nine times higher than INWQS standards, though Cr and Co in the seepage water are still within the 'safe' limits, albeit with the potential caveats aforementioned.

The relationship between Cr, Ni and Co in soil and surface water

This study showed that the geochemistry of the ultramafic parent materials has a minor effect on the chemical composition of regional flowing surface waters. This may be due to various factors, as noted above, though this study reveals the low contribution of the metals in the easily leachable and exchangeable fractions of soils is the main factor responsible. The metals concerned are held mainly in the residual fraction of soils as refractory latticed minerals and secondly sorbed in the oxide and hydroxides of Fe and Mn with relatively high affinity as liganded species.

Therefore, in accordance with previous studies (Becquer et al. 2003; Massoura et al. 2006), Cr, Ni and Co in the studied soils have low mobility with little tendency to readily migrate into the environment. On the other hand, the solubility of Cr and Ni in surface water is pH dependent to some degree. Chromium is soluble at pH values of less than 4 and the solubility of Ni occurs only at pH value of less than 5.5 (Rahim et al. 1996). The pH values of the investigated soils ranged from slightly acidic to circum-neutral preventing significant metal solubility. In addition, the soils displayed a fine granular structure and a silty loam to silty clay loam texture. Since silt and clay grain size fractions are capable of adsorbing more metals because of their larger specific surface area, it is assumed that these soils bound higher concentrations of metals and have low tendency to release them into the environment. In addition, the aerobic status of soils may affect metal release as waterlogged conditions may lead to the release of metals by reductive dissolution of Fe and Mn oxides (Rinklebe et al. 2016).

Conclusions and prospects

Malaysian serpentinites studied here showed a ferromagnesian mineralogy with high concentrations of Cr, Ni and Co, suggesting they are capable of inducing serious natural pollution. However, surface waters flowing over serpentinite soils revealed minimal notable concentration of Cr, Ni and Co and are considered 'safe' as defined by relevant threshold standards. Consequently, for the most part, chemical composition of surface water is concluded to ineffectively reflect bedrock and soil geochemistry of regional expanses of serpentinites. The main reason for this is concluded to be the very low proportion of metals associated with the easily leachable and ion exchangeable fractions of the soils. Being largely immobile, ingress of these metals into surface waters via leaching is minimized and subsequent dilution may be expected to further minimize wider fluvial metal transport and contamination. Therefore, despite their anomalously high natural concentrations of certain metals, these serpentine soils are not considered to pose a health or environmental risk. However, further work should examine metal speciation and soil Cr is of particular interest, given Cr^{3+} is considered an essential nutrient and Cr^{6+} carcinogenic.

Appendix

See Tables 6 and 7.

Table 6 The concentration of trace elements (mg kg^{-1}) in serpentinite rocks and soils from Ranau, Sabah, Malaysia

	As	Ba	Ce	Co	Cr	Cu	Ga	Hf	La	Nb
R1	bdl	493	636	63	2743	20	bdl	6	38	32
R3	bdl	466	616	64	2622	14	bdl	6	38	28
R4	bdl	491	699	62	2641	25	bdl	6	38	37
R7	bdl	552	600	61	2781	25	bdl	6	39	36
Mean ± SD	–	501 ± 36	638 ± 43	63 ± 1	2697 ± 77	21 ± 5	–	6 ± 0	38 ± 1	33 ± 4
S1	3	bdl	176	136	13,929	54	3	4	25	10
S3	2	bdl	159	122	14,720	45	3	5	21	9
S4	bdl	80	244	146	16,381	67	5	5	22	12
S5	2	bdl	144	112	14,029	52	8	4	21	12
S6	bdl	29	237	167	19,025	49	3	5	21	11
S7	bdl	136	295	127	17,233	49	5	4	23	15
S8	4	597	523	35	2427	55	8	6	28	29
S10	1	158	319	114	15,807	59	8	5	23	17
S12	3	201	332	93	11,277	26	6	5	23	18
S13	4	557	506	46	2828	33	10	6	26	28
Mean ± SD	3 ± 1	251 ± 230	294 ± 133	110 ± 42	12,766 ± 5736	49 ± 12	6 ± 3	5 ± 1	23 ± 2	16 ± 7

	Ni	Pb	Rb	Sr	Th	U	V	Y	Zn	Zr
R1	1609	22	8	18	bdl	9	78	bdl	53	21
R3	1840	23	7	9	bdl	9	62	bdl	59	16

Table 6 continued

	Ni	Pb	Rb	Sr	Th	U	V	Y	Zn	Zr
R4	1602	26	9	17	bdl	9	85	bdl	59	22
R7	1658	24	9	19	bdl	9	84	bdl	51	22
Mean ± SD	1677 ± 111	24 ± 2	8 ± 1	16 ± 5	–	9 ± 0	77 ± 11	–	56 ± 4	20 ± 3
S1	1675	bdl	3	bdl	bdl	9	134	bdl	89	54
S3	2237	bdl	2	bdl	bdl	9	189	bdl	88	14
S4	1573	bdl	2	bdl	bdl	9	240	bdl	75	21
S5	850	bdl	2	bdl	bdl	9	357	bdl	68	30
S6	4753	bdl	3	bdl	bdl	9	205	bdl	139	16
S7	1219	bdl	3	bdl	bdl	9	277	bdl	79	20
S8	865	16	32	6	bdl	9	132	bdl	86	62
S10	1311	bdl	3	bdl	bdl	9	279	bdl	85	30
S12	972	bdl	4	bdl	bdl	9	238	bdl	71	30
S13	1418	18	40	22	bdl	9	120	bdl	80	96
Mean ± SD	1687 ± 1156	17 ± 1	9 ± 14	14 ± 11	–	9 ± 0	217 ± 76	–	86 ± 20	37 ± 26

bdl below detection limits

Table 7 Correlation coefficients between elements in serpentine soils in the vicinity of Ranau, Sabah (Malaysian Borneo)

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Co	Cr
TiO_2	−0.07											
Al_2O_3	−0.44	**0.80**										
Fe_2O_3	−0.94	0.04	0.46									
MnO	−0.63	−0.32	0.18	**0.80**								
MgO	0.23	−0.54	−0.46	−0.06	0.32							
CaO	**0.81**	−0.09	−0.26	−0.75	−0.53	0.34						
Na_2O	**0.82**	0.05	−0.27	−0.71	−0.38	0.42	**0.60**					
K_2O	**0.87**	0.11	−0.09	−0.83	−0.62	0.06	**0.91**	**0.61**				
P_2O_5	0.20	0.22	0.31	−0.13	−0.23	−0.38	0.42	−0.06	0.51			
Co	−0.58	−0.20	0.37	**0.66**	**0.61**	−0.10	−0.23	−0.59	−0.29	0.44		
Cr	−0.73	−0.08	0.46	**0.80**	**0.67**	−0.22	−0.42	−0.70	−0.47	0.37	**0.96**	
Ni	−0.15	−0.55	−0.17	0.30	0.54	**0.60**	0.18	0.06	−0.12	0.04	0.59	0.47

Significant correlations ($p < 0.01$) are marked in bold

References

Adriano DC (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals, 2nd edn. Springer, New York

Alves S, Trancoso MA, Gonçalves MdLS, Correia dos Santos MM (2011) A nickel availability study in serpentinized areas of Portugal. Geoderma 164:155–163. doi:10.1016/j.geoderma.2011.05.019

ANZECC/NHMRC (1992) Australian and New Zealand guidelines for the assessment and management of contaminated sites. https://www.nhmrc.gov.au/_files_nhmrc/publications/attachments/eh17.pdf. Accessed 9 June 2016

Ashraf MA, Sarfraz M, Naureen R, Gharibreza M (2015) Environmental impacts of metallic elements: speciation, bioavailability and remediation. Springer, Singapore

Becquer T, Quantin C, Sicot M, Boudot J (2003) Chromium availability in ultramafic soils from New Caledonia. Sci Tot Environ 301:251–261. doi:10.1016/S0048-9697(02)00298-X

Becquer T, Quantin C, Rotte-Capet S, Ghanbaja J, Mustin C, Herbillon AJ (2006) Sources of trace metals in Ferralsols in New Caledonia. Eur J Soil Sci 57:200–213. doi:10.1111/j.1365-2389.2005.00730.x

Bonifacio E, Zanini E, Boero V, Franchini-Angela M (1997) Pedogenesis in a soil catena on serpentinite in north-western Italy. Geoderma 75:33–51. doi:10.1016/S0016-7061(96)00076-6

Bourrelier PH, Berthelin J (1998) Contamination des sols par les éléments en traces: les risques et leur gestion, Rapport no. 42. Académie des Sciences, Paris

Brearley FQ (2005) Nutrient limitation in a Malaysian ultramafic soil. J Trop For Sci 17:596–609

British Standard Institution (1990) Methods of test for soils for civil engineering purposes BS 1377-Part 2:9.4. Particle size analysis. British Standard Institution, London

Brooks RR (1987) Serpentine and its vegetation: a multidisciplinary approach. Dioscorides Press, Portland

Cancès B, Ponthieu M, Castrec-Rouelle M, Aubry E, Benedetti MF (2003) Metal ions speciation in a soil and its solution:

experimental data and model results. Geoderma 113:341–355. doi:10.1016/S0016-7061(02)00369-5

Cheng C-H, Jien S-H, Iizuka Y, Tsai H, Chang Y-H, Hseu Z-Y (2011) Pedogenic chromium and nickel partitioning in serpentine soils along a toposequence. Soil Sci Soc Am J 75:659–668. doi:10.2136/sssaj2010.0007

Dinelli E, Lombini A, Simoni A, Ferrari C (1997) Heavy metals in serpentine soils of selected outcrops of Piacenza and Parma provinces (Northern Apennines, Italy). Miner Petrogr Acta 40:241–255

Dutchlist (2009) Intervention values and target values: soil quality standards. http://www.contaminatedland.co.uk/std-guid/dutch-l.htm. Accessed 7 May 2009

EPA (2009) Drinking water quality standards. http://water.epa.gov/drink/contaminants/index.cfm. Accessed 7 May 2009

Garnier J, Quantin C, Guimarães E, Garg VK, Martins ES, Becquer T (2009) Understanding the genesis of ultramafic soils and catena dynamics in Niquelândia, Brazil. Geoderma 151:204–214. doi:10.1016/j.geoderma.2009.04.020

Ghaderian SM, Baker AJM (2007) Geobotanical and biogeochemical reconnaissance of the ultramafics of Central Iran. J Geochem Explor 92:34–42. doi:10.1016/j.gexplo.2006.06.002

Godard M, Jousselin D, Bodinier J-L (2000) Relationships between geochemistry and structure beneath a palaeo-spreading centre: a study of the mantle section in the Oman ophiolite. Earth Planet Sci Lett 180:133–148. doi:10.1016/S0012-821X(00)00149-7

Graham RC, Diallo MM, Lund LJ (1990) Soils and mineral weathering on phyllite colluvium and serpentinite in northwestern California. Soil Sci Soc Am J 54:1682–1690. doi:10.2136/sssaj1990.03615995005400060030x

Greater London Council (2001) Guidelines for contaminated soils. http://www.contaminatedland.co.uk/std-guid/kelly-l.htm. Accessed 11 May 2009

Hamon RE, McLaughlin MJ, Gilkes RJ, Rate AW, Zarcinas B, Robertson A, Cozens G, Radford N, Bettenay L (2004) Geochemical indices allow estimation of heavy metal background concentrations in soils. Global Biogeochem Cycles 18:GB1014. doi:10.1029/2003GB002063

Hing TT (1969). Geology and soils of the Ranau-Luhan area, Sabah, East Malaysia. Unpublished Ph.D. thesis, University of Malaya

Hseu Z-Y (2006) Concentration and distribution of chromium and nickel fractions along a serpentinitic toposequence. Soil Sci 171:341–353. doi:10.1097/01.ss.0000209354.68783.f3

Hseu Z-Y, Tsai H, Hsi HC, Chen YC (2007) Weathering sequences of clay minerals in soils along a serpentinitic toposequence. Clay Clay Miner 55:389–401. doi:10.1346/CCMN.2007.0550407

Hseu Z-Y, Su Y-C, Zehetner F, Hìs H-C (2016) Leaching potential of geogenic nickel in serpentine soils from Taiwan and Austria. J Environ Manag 186:151–157. doi:10.1016/j.jenvman.2016.02.034

Hutchison CS (2005) Geology of north-west Borneo: Sarawak, Brunei and Sabah. Elsevier, Amsterdam

INWQS (2006) Interim national water quality standards of Malaysia. http://www.wepa-db.net/policies/law/malaysia/eq_surface.htm. Accessed 1st April 2010

Kaasalainen M, Yli-Halla M (2003) Use of sequential extraction to assess metal partitioning in soils. Environ Pollut 126:225–233. doi:10.1016/S0269-7491(03)00191-X

Kabata-Pendias A (2000) Trace elements in soils and plants, 3rd edn. CRC Press, Boca Raton

Kabata-Pendias A, Mukherjee AB (2007) Trace elements from soil to human. Springer, New York

Kierczak J, Neel C, Bril H, Puziewicz J (2007) Effect of mineralogy and pedoclimatic variations on Ni and Cr distribution in serpentine soils under temperate climate. Geoderma 142:165–177. doi:10.1016/j.geoderma.2007.08.009

Kierczak J, Neel C, Aleksander-Kwaterczak U, Helios-Rybicka E, Bril H, Puziewicz J (2008) Solid speciation and mobility of potentially toxic elements from natural and contaminated soils: a combined approach. Chemosphere 73:776–784. doi:10.1016/j.chemosphere.2008.06.015

Kostić N, Wilson, JM, Živković M, Bain D (1998) Mineralogy and geochemical speciation of heavy metals in some serpentine soils of Serbia. In: 16th World Congress of Soil Science, Montpellier, August 20–26 1998. Elsevier, Amsterdam, pp 444–455

Lee BD, Graham RC, Laurent TE, Amrhein C (2004) Pedogenesis in a wetland meadow and surrounding serpentinitic landslide terrain, northern California, USA. Geoderma 118:303–320. doi:10.1016/S0016-7061(03)00214-3

Lottermoser BG (1997) Natural enrichment of topsoils with chromium and other heavy metals, Port Macquarie, New South Wales, Australia. Aust J Soil Res 35:1165–1176. doi:10.1071/S96108

Mason B, Moore CB (1982) Principles of geochemistry, 4th edn. Wiley, New York

Massoura ST, Echevarria G, Becquer T, Ghanbaja J, Leclerc-Cessac E, Morel J-L (2006) Control of nickel availability by nickel bearing minerals in natural and anthropogenic soils. Geoderma 136:28–37. doi:10.1016/j.geoderma.2006.01.008

McLaughlin MJ, Hamon RE, McLaren RG, Speir TW, Rogers SL (2000) Review: a bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. Aust J Soil Res 38:1037–1086. doi:10.1071/SR99128

Migon C, Motegi C, Mari X, Dufour A, Weinbauer M (2011) A preliminary study on metal and nutrient concentrations in running water systems in southern New Caledonia. Bull Environ Contam Toxicol 87:361–365. doi:10.1007/s00128-011-0367-z

Müller G (1969) Index of geoaccumulation in sediments of the Rhine River. Geol J 2:108–118

Osama AAT (2007) A study on the alternative resources of chromium, cobalt and nickel from ultrabasic soils of Sabah, Malaysia. Dissertation, University Kebangsaan Malaysia

Oze C, Fendorf S, Bird DK, Coleman RG (2004) Chromium geochemistry of serpentine soils. Int Geol Rev 46:97–126. doi:10.2747/0020-6814.46.2.97

Proctor J (2003) Vegetation and soil and plant chemistry on ultramafic rocks in the tropical Far East. Perspect Plant Ecol Evol Syst 6:105–124. doi:10.1078/1433-8319-00045

Quantin C, Becquer T, Berthelin J (2002a) Mn-oxide: a major source of easily mobilisable Co and Ni under reducing conditions in New Caledonia Ferralsols. C R Geosci 334:273–278

Quantin C, Becquer T, Rouiller J, Berthelin J (2002b) Redistribution of metals in a New Caledonia Ferralsol after microbial weathering. Soil Sci Soc Am J 66:1797–1804. doi:10.2136/sssaj2002.1797

Rahim SA, Tan MM, Musta B (1996) Heavy metals composition of some soils developed from basic and ultrabasic rocks in Malaysia. Borneo Sci 2:33–46

Rashmi BN, Prabhakar BC, Gireesh RV, Nijagunaiah R, Ranganath RM (2009) Nickel anomalies in ultramafic profiles of Jayachamarajapura schist belt, Western Dharwar Craton. Curr Sci 96:1512–1517

Repin R (1998) Preliminary survey of serpentine vegetation areas in Sabah. Sabah Parks Nat J 1:19–28

Rinklebe J, Antić-Mladenović S, Frohne T, Stärk H-J, Tomić Z, Ličina V (2016) Nickel in a serpentine-enriched Fluvisol: redox affected dynamics and binding forms. Geoderma 263:203–214. doi:10.1016/j.geoderma.2015.09.004

Schwertmann U, Latham M (1986) Properties of iron oxides in some New Caledonian Oxisols. Geoderma 39:105–123. doi:10.1016/0016-7061(86)90070-4

Shallari S, Schwartz C, Hasko A, Morel JL (1998) Heavy metals in soils and plants of serpentine and industrial sites of Albania. Sci Total Environ 209:133–142. doi:10.1016/S0048-9697(98)80104-6

Siegel FR (1975) Applied geochemistry. Wiley, New York

Silveira ML, Alleoni LRF, O'Connor GA, Chang AC (2006) Heavy metal sequential extraction methods—a modification for tropical soils. Chemosphere 64:1929–1938. doi:10.1016/j.chemosphere.2006.01.018

Skordas K, Kelepertsis A (2005) Soil contamination by toxic metals in the cultivated region of Agia, Thessaly, Greece: identification of sources of contamination. Environ Geol 48:615–624. doi:10.1007/s00254-005-1319-x

Soil Survey Division Staff (1993) Soil survey manual, U.S. Department of Agriculture Handbook 18. Washington, USA

Stueber AM, Goles GG (1967) Abundances of Na, Mn, Cr, Sc and Co in ultramafic rocks. Geochim Cosmochim Acta 31:75–93. doi:10.1016/0016-7037(67)90099-3

Tashakor M, Yaacob WZW, Mohamad H, Ghani AA, Saadati N (2014a) Assessment of selected sequential extraction and the toxicity characteristic leaching test as indices of metal mobility in serpentinite soils. Chem Spec Bioavailab 26:139–147. doi:10.3184/095422914X14036277112433

Tashakor M, Yaacob WZW, Mohamad H, Ghani AA (2014b) Geochemical characteristics of serpentinite soils from Malaysia. Malays J Soil Sci 18:35–49

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844–851. doi:10.1021/ac50043a017

Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the earth's crust. Geol Soc Am Bull 72:175–192. doi:10.1130/0016-7606(1961)72[175:DOTEIS]2.0.CO;2

van der Ent A, Echevarria G, Tibbett M (2016) Delimiting soil chemistry thresholds for nickel hyperaccumulator plants in Sabah (Malaysia). Chemoecology 26:67–82. doi:10.1007/s00049-016-0209-x

Vardaki C, Kelepertsis A (1999) Environmental impact of heavy metals (Fe, Ni, Cr, Co) in soils waters and plants of Triada in Euboea from ultrabasic rocks and nickeliferous mineralisation. Environ Geochem Health 21:211–226. doi:10.1023/A:1006648428381

WHO (2006) Guidelines for drinking-water quality, 3rd edn. World Health Organization, Geneva

Zarcinas B, Ishak CF, McLaughlin MJ, Cozens G (2004) Heavy metals in soils and crops in Southeast Asia 1. Peninsular Malaysia. Environ Geochem Health 26:343–357. doi:10.1007/s10653-005-4669-0