Asian Journal of
Earth Sciences

ISSN 1819-1886

Academic
Journals Inc.

www.academicjournals.com

Asian Journal of Earth Sciences 8 (2): 45-53, 2015
ISSN 1819-1886 / DOI: 10.3923/ajes.2015.45.53

Control of Grain-Size Distribution of Serpentinite Soils on Mineralogy and Heavy Metal Concentration

[1]Mahsa Tashakor, [2]Bernhard Hochwimmer and [3]Saman Imanifard
[1]Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia
[2]B. Ho Chwimmer and Associate Pty Ltd., Consultants in Mineral Exploration, Mine Geology, Environmental-Medical Geology, Albury, NSW, Australia
[3]Faculty of Social Sciences and Humanities (FSSK), Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia

Corresponding Author: Mahsa Tashakor, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia

ABSTRACT

The proportion of various grain size particles in soils is controlled largely by climate condition and moisture regimes. In general, tropical regions produce thick layers of fine grain soils due to high degree of weathering. Depends on the texture of soils, the capacity for storage of heavy metals changes. Serpentinized-ultramafic soils of Malaysia are of concern in this study containing high natural content of chromium, nickel and cobalt. These soils are comprised of a mixture of variable minerals ranging from inherited serpentines to magnetite, chlorite, ilmenite and minor to trace amounts of allochthonous quartz, clay minerals and phyllosilicates, such as kaolinite oxides and hydrous oxides of iron and manganese. The particle size distribution of serpentinite soils in Malaysia has received very limited study previously. This study attempts to find a relationship between the partitioning of Cr, Ni and Co among different soil size fractions with the mineralogical composition of serpentinite soils.

Key words: Particle size distribution, serpentinite soil, mineralogy, heavy metals

INTRODUCTION

Ultramafic-serpentinized rocks are abundant in ophiolitic belts along convergent continental margins. The world wide distribution of these rocks has caused a variety of weathering and pedogenic processes. Under tropical climate, serpentine derived soils undergo an elevated degree of weathering, which influences the soil particle size. In the recent decades great attention has been paid to serpentine soils as major sources of heavy metal pollution (Kierczak *et al*., 2007; Lee *et al*., 2004; Lottermoser, 1997; Tashakor *et al*., 2013). While, decomposition of serpentine rocks occurs a mixture of variable proportions of minerals form which according to weathering intensity range from primary minerals to secondary phyllosilicates and lastly to Mn and Fe oxides. The chemical make-up of the minerals from which soil were formed determines the properties of soils (Saad, 2001). As a general rule, the sidrophile elements such as cobalt, chromium and nickel are strongly elevated in serpentinized ultramafic soils due to substitution of cations (Fe, Mn, Mg) by Ni and Cr in octahedral sheets of the primary serpentinite minerals (Brooks, 1987). Soil storage capacity for heavy metal concentration changes according to the soil particle size. In another words, the accommodation and the release of heavy metals varies with soil texture, which reflexes the particle size distribution of the soil. The sorption of heavy metals is inversely correlated by particle size (Dube *et al*., 2001). According to Schluten and Leinweber (2000), the heavy metal contents decreases from clay to clay loam, loam, silt and sand. Sabra *et al*. (2011) demonstrated that heavy metals are mainly accompanied with the fine particles less than 53 µm. However, it is possible to hypothesis that mineralogy of soil affects the heavy metal contents of the inherited particles.

The evidence of the relation between soil particle size, mineralogy and metal concentration in Malaysian serpentine soils is still lacking. This study focuses on physico-chemical characterization of tropical serpentine soils developed on large numbers of Eastern and Western Malaysian serpentine out crops. The objectives are to determine the soil size distributions and the control of particle size on concentration of chromium, nickel and cobalt in these soils. The acid digestion was conducted to verify the quantitative metal contents in each soil fraction of sand, silt and clay. This study also constitutes a diagnosis of heavy metal bearing mineral phases by applying X-ray diffraction analysis on soil particles.

MATERIALS AND METHODS

Field and samples: The study was carried out on two soils developed from serpentinized-ultramafic formations that are located in Peninsular Malaysia and Sabah. The reason of choosing 2 distant geographical areas were to provide a greater bigger diversity of serpentine samples for study. Different modes of serpentine soil occurrence were observed but they were principally road cut and stream banks, especially in Sabah, where accessibility is limited.

Serpentinite derived soils in the investigated areas were characterized by their specific reddish-brown color derived from iron oxide and hydroxide contents. Being in tropical climate, high rainfall effectively leaches soluble components and accumulates iron oxide. In the current research a total of 20 serpentine soil samples were collected from the upper layers (less than 10 cm thick) of land cleared of debris and vegetation.

Particle size distribution analysis: Suitable method for evaluating particle size distribution in coarse-grained soils, such as sandy and gravely soils is the dry sieving method. For determining the grain-size distribution of cohesive soils with significant amounts of silt and clay, wet sieving and hydrometer analysis are applied. The combination of both methods is required to ascertain the particle size distribution of mixed soils. In the present study, combination of the dry and wet methods followed the British Standard Institution, BSI 1377: Part 2: 9.4 (BSI., 1990).

Mineralogical study: X-Ray Diffraction (XRD) analysis was undertaken on sand, silt and clay fractions of each soil sample to identify their constituent minerals. Analyses were performed on powdered samples using a D8 advance Bruker AXS diffractometer, with CuK-alpha analyzing radiation wavelength of 1.5406 Å (0.15406 NM). X-ray diffractograms were collected within the 2 θ range (5-60°) with 0.02/0.1 sec step. The XRD instrument connected to advance diffract plus evaluation software through computer provided. Experimental reliability was checking with the international standard for corundum mineral.

Microwave soil digestion: Acid digestion is a strong technique to dissolve almost all environmentally available elements in soil. Dissolution of 45 soil specimen of sand, silt and clay sizes was performed by acid digestion using microwave oven VAC-1000. The applied method was 3050 b after modification (Alshaebi *et al*., 2009).

The amount of 5±0.1 g of each sample was weighed out in a 250 mL polycarbonate bottle. Then, 2.0 mL of concentrated nitric acid (HNO_3) was added to the bottle, followed by 5.0 mL of 7:3 mixture of hydrochloric-hydrofluoric acid (HCL-HF). Samples were transferred into the microwave oven and heated at 400-500 watt with 120°C for 15 min. Thereafter, when samples were cooled down to room temperature, they were mixed with 40 mL of 1.5% boric acid (H_3BO_3). The bottles were recapped and returned into the microwave oven and heated again at 400-500 w, at 130°C for 15 min. At the last stage, the digested solution was voluminized by water made up to 100 mL and mixed thoroughly. The solution was then sent to the ICP laboratory for analysis of heavy metal contents.

The accuracy of microwave soil digestion was proved by 2 measurements of the Standard Reference Material (SRM) of NIST2711a.

RESULTS

According to the U.S. Department of Agriculture (USDA), soils are categorized in the size class of gravel (2-4 mm), sands (0.05-2 mm), silts (0.002-0.05 mm) and clay (<0.002 mm). The percentage of each class of size for the analyzed soils is provided in Table 1.

It is apparent from Table 1 that only less than 1% of the soil particles are gravel or stone size and more than 99% of them are distributed in <2 mm range sizes. The result revealed that silt is the most predominant fraction in all the studied soils. Over half of the total measured soils are silt size. The lowest amount of silt (25%) is observed in soil PS. 1 from Petasih and the largest amount (61%) belongs to soil BM. 2 collected from Batu Malim. The sand size grains seem to be slightly

Table 1: Particle size distribution of 20 serpentine soil samples from the Malaysian Peninsular (Bukit Rokan, Petasih, Batu Malim, Cheroh) and Sabah (Ranau) areas

		Particle size distribution			
		<2 mm (%)			
Sample station	Location	Clay	Silt	Sand	>2 mm (%)
BR. 1	Bukit rokan	15	55	30	0
BR. 2		18	59	22	1
BR. 3		32	48	18	2
BR. 4		21	58	21	0
PS. 1	Petaseh	55	25	20	0
PS. 2		29	51	19	1
PS. 3		28	53	19	0
PS. 4		34	48	18	0
BM. 1	Batu malim	13	54	34	0
BM. 2		12	61	27	1
BM. 3		0	32	67	1
BM. 4		23	58	20	0
CH. 1	Ceruh	9	60	32	0
CH. 2		11	59	30	0
CH. 3		10	50	39	3
S4	Sabah	13	54	33	0
S6		28	52	20	0
S7		16	58	25	1
S10		31	50	19	0
S15		25	45	30	0
Mean		21	52	27	1
Min		0	25	18	0
Max		55	61	67	3
STD		12	9	11	1

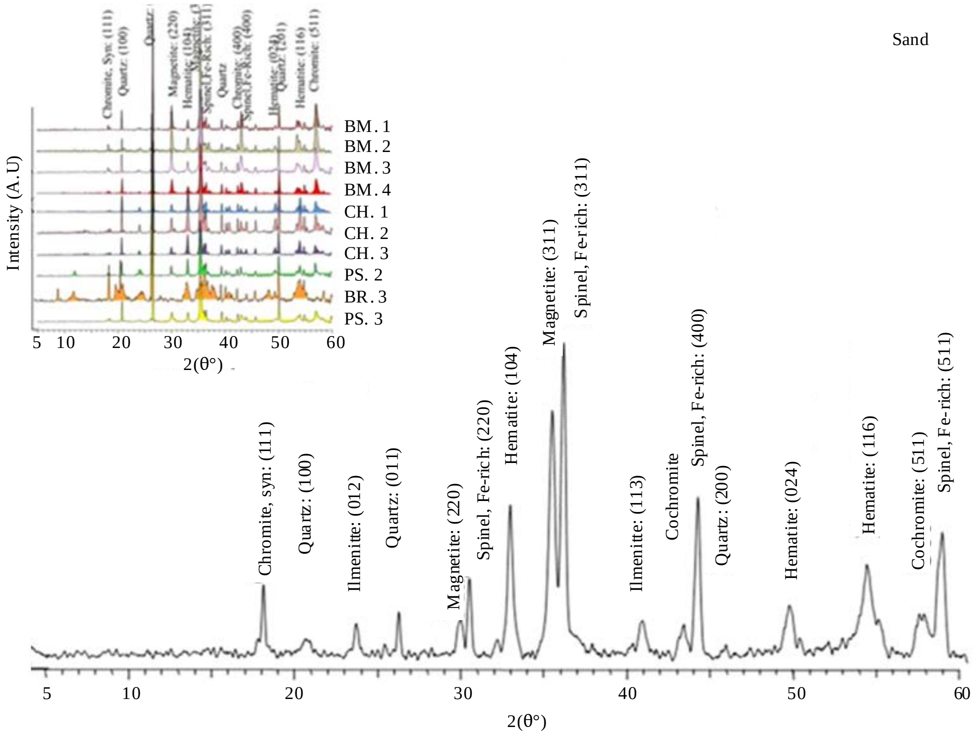

Fig. 1: X-ray diffractograms of sand size soils (X-ray source is CuKα, λ = 1.5418)

more than clay size particles by showing the average of 27% sand versus 21% clay. Interestingly, sample BM. 3 contains 67% sand and without any clay. However, sample PS. 1 have 55% of particles distributed in clay class size and only 20% in sand size.

Each portion of sand, silt and clay from 15 soil samples had been the subject of X-ray diffraction analysis to determine the control of particle size on mineralogical distribution of serpentinite soils.

The XRD patterns obtained for each size fraction group were similar in all of the studied soils. However, every individual division of sand, silt and clay carried a specific mineralogical contents.

In general, X-ray diffractograms of sand, silt and clay showed the following mineral assemblages (Fig. 1-3); ferrite and chrome spinels, chromite, oxides and hydrous oxides of manganese, nickel and iron, especially hematite and goethite, kaolinite clay mineral and allochthonous quartz.

The occurrence of Fe-rich spinel is proven by the existing of characteristic (311) peak with d = 2.44 Å, supported by other peaks with d = 2.02, 1.43 and 4.66 Å. According to the XRD patterns, Fe-rich spinel is abundant in sand portion of the soils (Fig. 1) while, it does not exist in the silt and clay fractions (Fig. 2 and 3). Magnetite concentration in soils featured the same pattern, occurring commonly in sand size, yet is not revealed in silt and clay size soil fractions. The strongest line of magnetite is observed in 2.53 Å and its presence is proven by the occurrence of the characteristic peak with d = 2.97 Å. Chromite is another common component of sand size soils. Its concentration in the silt fraction is rare. Chromite was not found in clay size soils (Fig. 3). Chromite minerals were characterized in the studied soils by the diffracted peaks of 2.52, 1.6, 1.46 and 4.82 Å. Hematite and goethite are dominant iron oxides in lateritic soils. The XRD patterns from the Malaysian Peninnsular soils tested showed that hematite is an abundant mineral in sand size soil fractions and also commonly presents, in silt and clay portions. The diffracted peaks of hematite

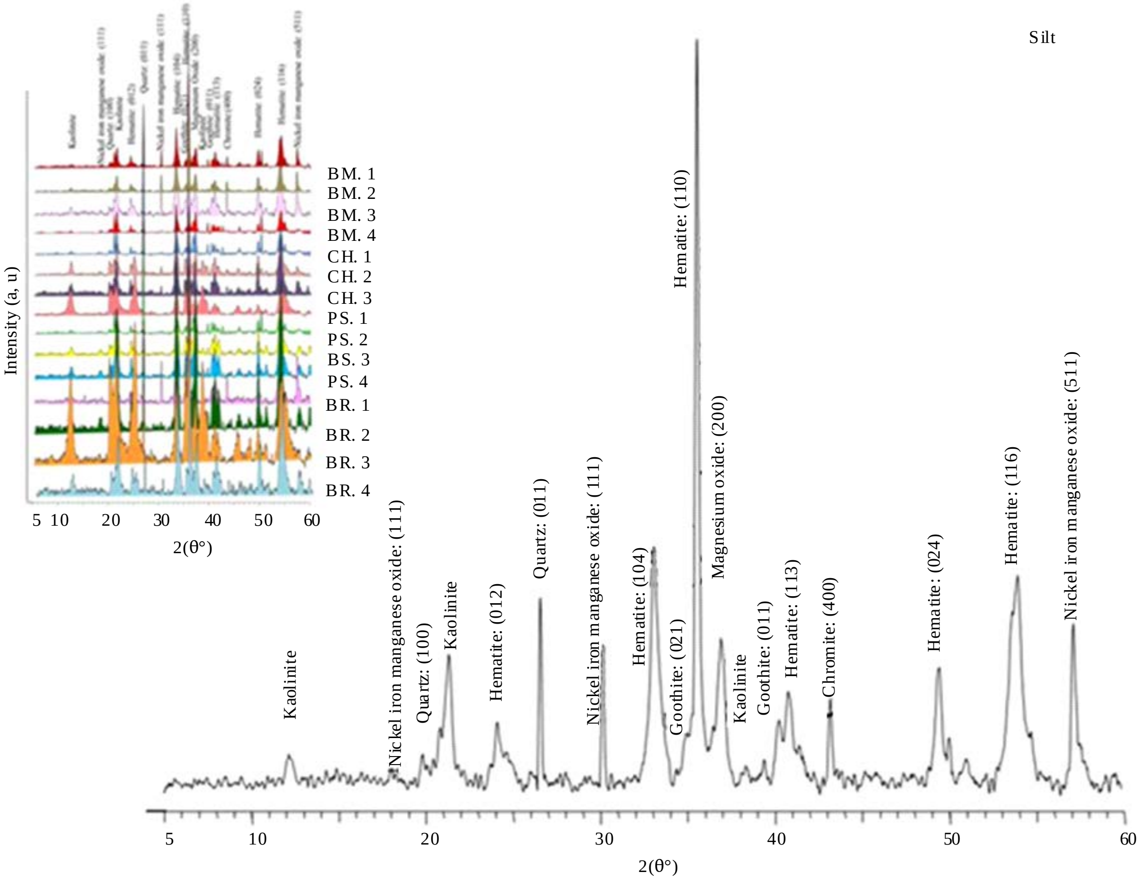

Fig. 2: X-ray diffractograms of silt size soils (X-ray source is CuKα, λ = 1.5418)

are 2.69, 1.96, 2.51 and 3.66 Å. Despite presence of hematite, goethite was not found in the sand fraction of soils (Fig. 1). However, its occurrence in silt and clay portions was proven by displaying the characteristic peak with d = 4.19 Å and confirmed with the peaks around 2.42 and 2.16 Å. Silt size soils contain minor amounts of goethite (Fig. 2) while, goethite is a common mineral in the most of the clay fraction soils (Fig. 3).

The XRD diffractograms of allochthonous quartz show distinctive peaks at the crystal surface of (100) and (011), with minor concentration in sand and silt fractions and does not appear in clay fractions. Certain compositions of iron, manganese, nickel and cobalt present in various amounts in the soil fractions but not as identifiably unique mineral species. For instance, nickel iron manganese oxide is found in minor values in the silt size soils and interestingly, nickel titanium oxide is a common composite in clay portions. Among the sand fractions, 5 samples showed ilmenite in their mineralogical compositions. The silt and clay fractions posse kaolinite commonly indicated by characteristic peaks with d = 7.18, 1.49 and 3.58 Å.

DISCUSSION

Based on the relative proportion of each specific fraction of sand, silt and clay in soils, the texture class of soil was determined. Soil texture has a significant role in controlling the physical and chemical properties of soils and it affects the holding capacity, moisture content, fertility and availability of components in soils. In order to characterize the texture of the Malaysian Peninsular soils studied, the textural triangle of 12 major soils defined by USDA was utilized (Fig. 4).

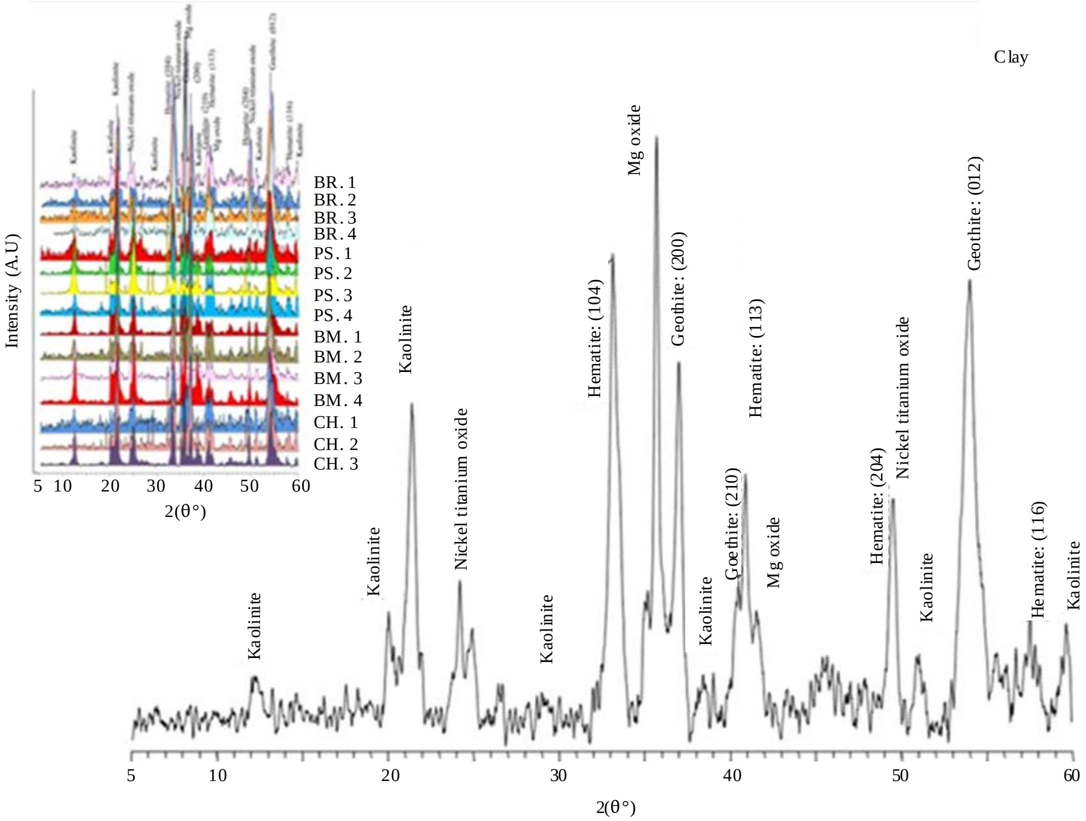

Fig. 3: X-ray diffractograms of clay size soils (X-ray source is CuKα, λ = 1.5418)

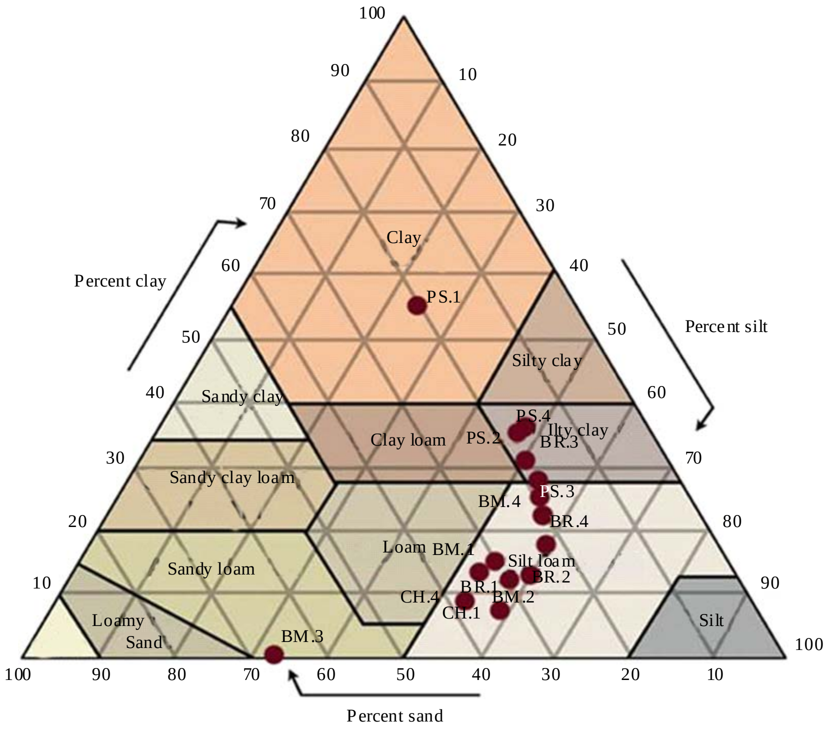

Fig. 4: Position of soil samples on the soil textural triangle (Proposed by USDA)

Table 2: Mineralogical composition of different granulometric fractions

Minerals	Formula	Sand	Silt	Clay
Quartz	SiO_2	**	**	-
Hematite	Fe_2O_3	****	***	***
Goethite	$Fe^{3+}O (OH)$	-	**	***
Fe-rich Spinel	$Mg (Al, Fe)_2O_4$	****	-	-
Magnetite	Fe_3O_4	***	-	-
Chromite	$(CO, Ni, Fe^{2+}) (Cr,Al)_2O_4$	***	*	-
Ni Fe Mn Oxide	$NiFeMn.5O_4$	-	**	-
Ni Ti Oxide	$Ni (TiO_3)$	-	-	***
Kaolinite	$Al_2Si_2O_5 (OH)_4$	-	***	***
Ilmenite	$FeTiO_3$	**	-	-

****Abundant, ***Common, **Minor, *Rare, -: No existence

This classification is named for the primary particle size component and combination of the most frequent particle sizes, thereby referred to as, “sandy clay” or “silty clay”. The term of loam refers to a roughly equal proportion of sand, silt and clay and prefixed with the more common components, there by classified as “Clay loam” or “silt loam” etc. As can be seen in Fig. 4, 65% of the soil samples are in the silty loam class. They contain moderate amounts of sand, lower than 27% clay and over 50% silt size grains. Some 25% of the total analyzed samples are silty clay loam textured that are more sticky and plastic with high metal retention capacity. Sample BM. 3 with 65% sand and sample PS. 1 with 55% clay, are classified as sandy loam and clay textures, respectively.

The relative concentrations of minerals in sand, silt and clay size fractions of the studied serpentinite soils are summarized in the Table 2. As it can be seen, sand portion is dominated by hematite and Fe-rich spinel. It contains magnetite and chromite commonly and quartz and ilmenite rarely. The sand portion is devoid of goethite, nickel iron manganese oxide, nickel titanium oxide and Kaolinite. Regarding the silt fraction, hematite and kaolinite are common minerals. Quartz, goethite and nickel iron manganese oxide are found in minor amounts. Chromite is rare and Fe-rich spinel, magnetite, nickel titanium oxide and ilmenite do not exist in the silt fraction. Moving to the finest fraction of soils, clay is commonly composed of kaolinite, hematite, goethite and nickel-titanium oxide. However, it is deprived of quartz, Fe-rich Spinel, magnetite, chromite, nickel iron, manganese oxide and ilmenite.

Since soil particles control the accommodation and the release of heavy metals in the environment, the association of chromium, nickel and cobalt within each soil size fraction of sand, silt and clay was verified. Figure 5 displays the correlation between the bulk concentration of Cr, Ni and Co in soils obtained by XRF analysis and the extracted amounts of these metals obtained by digestion of each soil size portion. As it is evident Cr is more associated with the sand fractions and shows $r = 0.41$ which is a medium correlation according to Cohen (1988). However the result of this study showed that Co and Ni are mainly found in silt fraction with a large correlation of $r = 0.88$ and $r = 0.94$, respectively.

Combined with the mineralogical data; we can deduce that Cr is found in coarse grains, where chromite and magnetite dominate while, Co and Ni are frequent in medium to fine fractions where secondary minerals such as, serpentine, smectite, goethite and poorly crystallized Fe-Mn hydroxides comprise most of these fractions. This finding accords with the mineralogical study and XRD patterns of sand, silt and clay fractions of the studied soils.

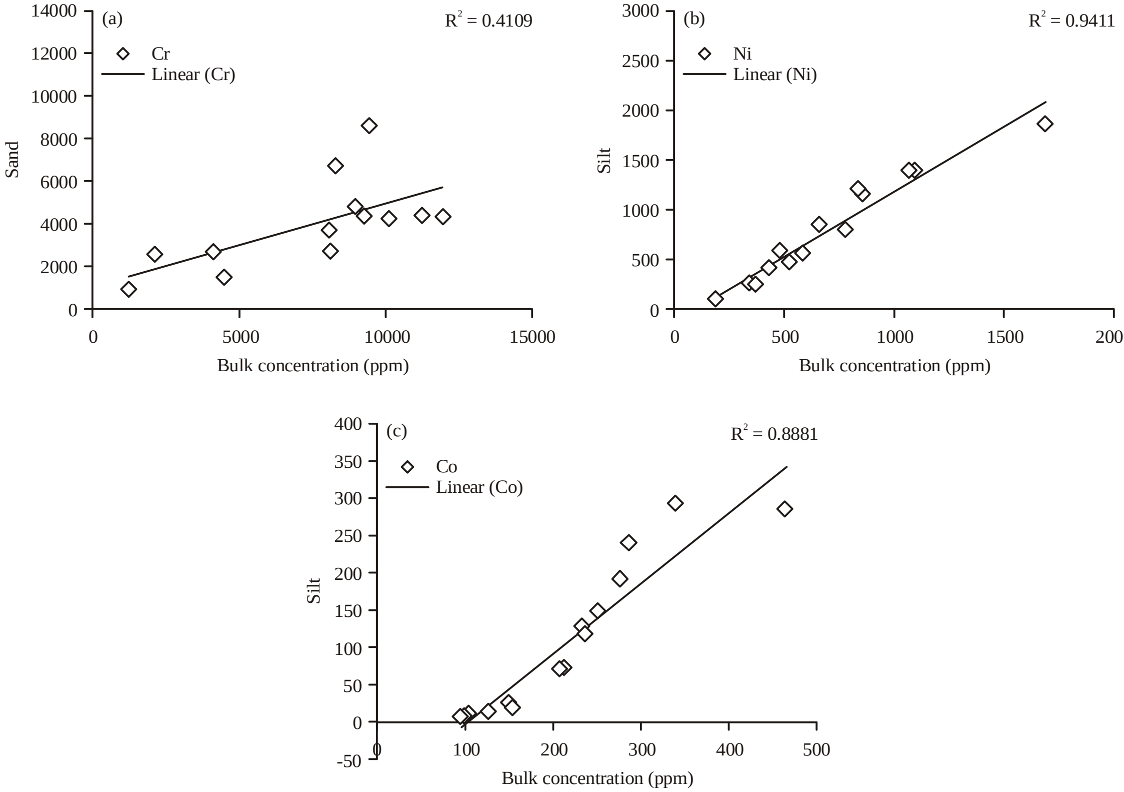

Fig. 5(a-c): Control of soil size on Cr, Ni and Co concentration in serpentine soils, (a) Chromium, (b) Nickel and (c) Cobalt

CONCLUSION

In this study, the particle size distribution and textures of tropical soils developed on serpentinite lands of the Petasih Negri Sembilan and Ranau Sabah East and West Malaysian districts were determined and characterized, then reconciled with XRD and XRF findings in size fractions. The control of soil fraction size and overall textures on mineralogy and heavy metal concentration were verified. Soils exhibited a fine granular structure and a silty loam to silty clay loam texture due to the prevalence of silt size grains. Since fine grains have larger specific surface areas and able to exchange and retain more substrates and products from soil solutions. It was expected that under study serpentine soils attributed larger contents of metals, than other soils. However, this study suggested an important controlling relationship between the mineralogical features and the consequent heavy metal distribution among the soil grain size fraction. According to the mineralogical analysis, sand was the only fraction containing chromite, Fe-rich spinel, magnetite and in lesser amounts ilmenite. Quartz was incorporated in coarser fractions of sand and silt. All 3 fractions of sand silt and clay contained hematite, however, only the iron oxide form of goethite occurred in the clay fraction of kaolinite which makes a mere appearance in silt portions. Hence, the host mineralogical phase could be a major factor, if not the only one, causing Cr contribution with coarse grains and Ni and Co association with fine particles of soils. This may have important implications for metal contents in hydrology and the biosphere.

ACKNOWLEDGMENTS

The researchers wish to thank the technical staffs from school of Science and Technology, UKM. The helps given by the staffs of Geology program and Physic program for the geochemistry laboratory and XRD works, respectively are also acknowledged.

REFERENCES

Alshaebi, F.Y., W.Z. Wan Yaacob, A.R. Samsudin and E. Alsabahi, 2009. Risk assessment at abandoned tin mine In Sungai Lembing, Pahang, Malaysia. Electronic J. Geotechnical Eng., Vol. 14.

BSI., 1990. BS 1377-3:1990 Methods of test for soils for civil engineering purposes chemical and electro-chemical tests. British Standards Instituition, London.

Brooks, R.R., 1987. Serpentine and its Vegetation: A Multidisciplinary Approach. Vol. 1, Dioscorides Press, Portland, ISBN-13: 978-0931146046, Pages: 462.

Cohen, J., 1988. Statistical Power Analysis for the Behavioral Sciences. 2nd Edn., Lawrence Erlbaum, Hillsdale, New Jersey, USA., ISBN: 0-8058-6283-5, Pages: 128.

Dube, A., R. Zbytniewski, T. Kowalkowski, E. Cukrowska and B. Buszewski, 2001. Adsorption and migration of heavy metals in soil. Pol. J. Environ. Stud., 10: 1-10.

Kierczak, J., C. Neel, H. Bril and J. Puziewicz, 2007. Effect of mineralogy and pedoclimatic variations on Ni and Cr distribution in serpentine soils under temperate climate. Geoderma, 142: 165-177.

Lee, B.D., R.C. Graham, T.E. Laurent and C. Amrhein, 2004. Pedogenesis in a wetland meadow and surrounding serpentinitic landslide terrain, Northern California, USA. Geoderma, 118: 303-320.

Lottermoser, B.G., 1997. Natural enrichment of topsoils with chromium and other heavy metals, Port Macquarie, New South Wales, Australia. Aust. J. Soil Res., 35: 1165-1176.

Saad, I.A.A., 2001. Investigations on the environmental significance and the bioavailability of heavy metals in soils. Ph.D. Thesis, Universiti Malaya.

Sabra, N., H.C. Dubourguier and T. Hamieh, 2011. Sequential extraction and particle size analysis of heavy metals in sediments dredged from the Deule Canal, France. Open Environ. Eng. J., 4: 11-17.

Schluten, H.R. and P. Leinweber, 2000. New insights into organic-mineral particles: Composition, properties and models of molecular structure. Biol. Fert. Soils, 30: 399-432.

Tashakor, M., W.Z.W. Yaacob and H. Mohamad, 2013. Speciation and availability of Cr, Ni and Co in serpentine soils of ranau, Sabah. Am. J. Geosci., 2: 4-9.