SERPENTINE SOILS, ADVERSE HABITAT FOR PLANTS CASE STUDY AT PENINSULAR

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ABSTRACT

The unpleasant effect of serpentine soil on plant life has been a topic of many studies for several decades. Infertility and flora selectivity nature of serpentine soils are the features, which made them of interest throughout the world. This research includes a geochemical study on two Malaysian serpentine massifs to introduce their harmful factors concerning vegetation. X-ray fluorescence results on 11 soil samples showed that serpentine soils comprise large values of iron and magnesium (up to 55 wt and 65 wt% respectively) and high amounts of some heavy metals like chromium (1248-18990 $\mu g\ g^{-1}$), nickel (189-1692 $\mu g\ g^{-1}$) and cobalt (95-478 $\mu g\ g^{-1}$). However, soil extraction by ammonium acetate solution revealed that only magnesium is plant available. Besides, serpentine soils are poor in some major plant nutrients such as nitrogen, potassium and phosphorus. This substantial paucity is the main cause of bareness in these lands. Soils in the studied areas are moderately acidic and have the adequate cation holding capacity. Their Ca/Mg quotient is very low (less than 1). The latter with the low availability of the calcium (0.34 m-equiv 100 g^{-1} in average) is another challenging parameter in serpentine soils, which exerts negative influence on plant growing.

Keywords: Serpentine Soils, Geochemistry, Harmful Effects, Plant Life

1. INTRODUCTION

Ultramafic rocks cover about 1% of the world continental surfaces (Garnier *et al*., 2009). They are located along convergent plate boundaries often associated with obducted oceanic crust (ophiolites). Ultramafic rocks are the source of the well-known "Serpentine soils". Serpentinized ultramafic soils have been of interest to soil scientists and plant biologists since the last century because they create an unpleasant environment for plant life.

The 'serpentine syndrome" term was coined first time by Jenny (1981) to illustrate restricted growth, physiognomic alterations and element accumulations of plant species grown on serpentine soils. Flora depauperation is an important feature of serpentine soils throughout the world, which comes from the interplay of their distinctive physical, chemical and biotic factors.

Typical serpentine areas are more barren than their surroundings and in agricultural areas they are recognized as infertile (Kim and Shim, 2008). Moreover, the selective nature of serpentine-drive soils controls the species of flora communities in these lands. Ultramafic soils support a number of plants that are endemic and restricted to these substrata. Soils derived from serpentines are commonly hosts of unusual and highly specialized flora. In the other word, serpentine soils are of interest because of their biodiversity factor. Since the fertility is limited, the plants are usually endemic.

Mostly, serpentine-tolerant species are unable to survive in non-serpentine environments and the growth of plants on non-serpentine origin is usually inhibited on serpentine soils. The morphology of serpentine adapted plants distinct slightly from closely related species not adapted to serpentine sites. Furthermore, the climate is a

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factor which controls the number of endemic plant species on serpentine lands; in tropical and subtropical regions like New Caledonia and Cuba, they are high (Dissanayake and Chandrajith, 2009), while in other regions such as some parts of Europe and New Zealand, they are lower.

Extensive worldwide studies have been conducted on different aspects of plant life growing on ultramafic lands, but in this research the focus is on those edaphic characters which inherited from parent rocks and can create an abnormal environment.

Serpentines are metal-loaded soils. Weathering of serpentine bodies under tropical climate produces thick profiles of reddish to black-brown lateritic soils rich of iron and manganese oxides. Serpentine soils have excessive amounts of siderophile elements such as chromium, cobalt and nickel which are partly responsible for infertility and the paucity of vegetation.

Although certain metals like Cu, Fe, Mn and Ni are essential macronutrients for plant growth, in some concentrations they become entirely toxic for plants and microorganism (Siebecker and Sparks, 2010). Nagy and Proctor (2008) has described that the high soil porosity of an ultrabasic soils and its propensity for high concentrations of elements such as nickel, cobalt, copper might cause toxicity problems for agricultural products. However, there are certain plants which are geobotanical-biochemical indicators and they can tolerate heavy metals or even accumulate them. According to Morrison *et al.* (2009) the poor vegetation on serpentine soil is mostly related to Ni toxicity rather than high contents of Cr and Co. The plant uptake of Cr is usually very low while Ni can be taken up by some native herb and crops to elevated amounts. *Alyssum* is an example of these plants that is able to exceptionally enrich Ni. Plants are intermediate containers of heavy metals which through them metallic contaminants move from soil to human and animals. Thus, studying the effect of heavy metal hyperaccumulation on plant health and growth is of great importance.

In contrast with elevated heavy metal contents, serpentine soils are characterized by deficiency of essential plant nutrients such as nitrogen, phosphorus and potassium. Calcium and Magnesium imbalance is another challenge that serpentine poses. It can affect the vegetation providing three circumstances; (a) toxicity of magnesium, (b) Lacking of calcium and (c) Diminishing Ca/Mg quotient (Cheng *et al.*, 2011). Many researchers have described that how a low Ca/Mg ratio, lack of mineral nutrients and a high content of metals like Ni and Cr creates a strong infertility in soils.

Serpentine bodies are scattered in many places in the world include New Caledonia, Zimbabwe, Western North America, Central Brazil, Middle east and South East Asia. Regions of Asia are generally the least explored and poorly described of such regions in the world. The tropical Southeast Asian lands have a large number of serpentine bodies including outcrops of Peninsular and Sabah Malaysia. This study investigates the above mentioned properties of serpentine soils in two Malaysian massifs. Serpentine outcrops in Malaysia occur as several isolated lenses along Bentong-Raub suture zone in the Peninsular (Hutchison, 2005). This research has been accomplished on Bukit Rokan and Petasih outcrops in Peninsular Malaysia and attempts to show the undesirability of these serpentine lands for plant life from soil geochemistry point of view.

2. MATERIALS AND METHODS

2.1. Study Area

Soil sampling was conducted at Bukit Rokan and Petasih locations representing serpentine sites along the Bentong-Raub suture zone of Peninsular Malaysia. The most accessible outcrop is located at Bukit Rokan Barat housing estate. This body occurs within the chert-argillite and is in fault contact with the Kepis Formation. The serpentinites of this area are commonly sheared and show yellow and green colors. They are strongly weathered and thus the village is surrounded by dark brownish-red Laterites arise from them.

At Petasih in Negri Sembilan, the serpentines have a fault contact with the schists. They are highly foliated, sheared and faulted. Only a small part of this massif was accessible and sampling was performed on the road cut outcrop.

The choice of the most suitable sampling sites is subject to accessibility. A total of 11 samples collected from top soil (less than 10cm thick) after cleaning superficial debris and vegetations. Sampling locations are depicted in **Fig. 1**.

2.2. Sample Preparation and Analysis

The chemical composition of soil samples, comprising 10 major elements and 20 trace elements were determined by employing the X-Ray Fluorescence spectrometer (XRF, Bruker S8 Tiger), house at Faculty of Science and Technology UKM. The soil samples were air-dried, crushed and disaggregated in an agate mortar. The homogenized and pulverized soil samples increase the precision of the analysis. Soils were powdered to 30 μm grain size and were made into 32 mm diameter fused-beads for measuring major elements and 32 mm diameter press-powder pallets for measuring trace elements.
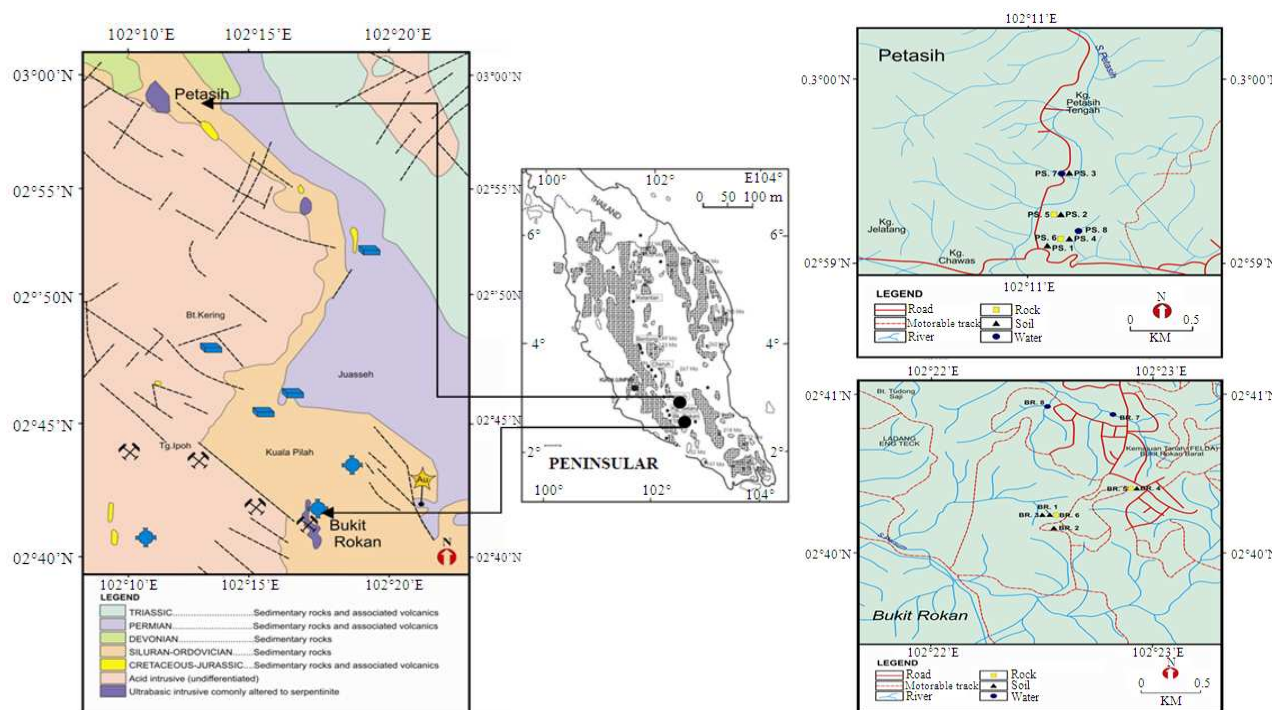
Fig. 1. The locations of the studied serpentine massifs in Peninsular Malaysia

The fused beads have been prepared by igniting 0.5 g of sample with 5.0 g of Johnson-Matthey 110 spectroflux, giving a dilution ratio of 1:10. As for the pressed-powder palettes, the preparation involves applying a pressure of 20 tonnes for one minute to 1 g of sample against 6 g of pure boric acid powder. The Loss on Ignition test was performed to estimate the amount of moisture, organic matter and impurities of soil samples. 1 g of oven dried soil weighed accurately in a platinum crucible and transferred into an electric furnace for one hour. After ignition at 1100°C samples were cooled in desiccators and weighted again accurately.

In order to find the plant-available concentrations of elements in soils, extraction of soil was conducted using saturation test with 0.5 M ammonium acetate exchange as described by ASTM D4319 (ASTM, 1993) 4 g of air-dried and pulverized soil was accurately weighed into a plastic centrifuge tube. 33 mL of ammonium acetate solution was added and was shaken in a mechanical shaker for 1 h. Then, the tube was centrifuged and clear supernatant was decanted into 100 mL volumetric flask. The procedures above were repeated twice on the same soil and all supernatants were placed into the same flask and top-up to the mark with distilled water. Specimens were then analyzed using Inductively Coupled Plasma (ICP) machine, housed in the faculty of Engineering University Kebangsaan Malaysia (UKM). Exchangeable cations and CEC amounts were calculated thereafter.

3. RESULTS

The elemental composition of 11 serpentine soils from Bukit Rokan and Petasih massifs are outlined in **Table 1**. The results of X-ray fluorescence analysis approved the strongly enhancement of some heavy metals in serpentine soils relative to other soil types. As it was expected, among 20 analyzed trace elements, Chromium (Cr), Cobalt (Co) and Nickel (Ni) showed anomalously elevated concentrations by the following observed range; Cr 1248-18990 $\mu g\ g^{-1}$, Co 95-478 $\mu g\ g$ and Ni 189-1692 $\mu g\ g^{-1}$. The comparison between heavy metal concentration in studied serpentine soils with average soil compositions of the earth and phytotoxic level of elements in soils are presented in **Table 1**.

Major and macronutrient oxides have also been the subject of XRF analysis. As it is quite apparent from **Table 1**, Fe_2O_3 in 64% of samples changes in the range of 27.34-55.65 (in weights percentage), while these samples have only less than 1wt% MgO. In contrast, 36% of soil samples are rich of MgO varying from 49.16 to 65.88 weights percentage, whereas they are depilated from Fe_2O_3.

Table 1. The average concentration of Cr, Co and Ni (in μg g^{-1}), the means of some major and macronutrient oxides (in weight %) and the percentage losses-on-ignition in 11 soil samples from Bukit Rokan and Petasih serpentine outcrops in Malaysia

	Cr$_{(t)}$ (μg g^{-1})	Co$_{(t)}$	Ni$_{(t)}$	Fe$_2$O$_3$ (%)	MgO (%)	CaO (wt%)	Na$_2$O (%)	K$_2$O (%)	P$_2$O$_5$ (%)	L.O.I (%)
BR1	9487	464	1687	0.02	65.88	0.18	0.72	0.12	0.45	10.89
BR2	2133	154	435	53.64	0.37	0.23	0.05	0.22	0.08	16.48
BR3	1248	98	189	23.08	0.30	0.18	0.03	0.18	0.05	17.53
BR4	11276	236	483	0.09	53.35	0.19	0.29	0.21	0.31	13.49
BR5	18990	478	1692	0.02	65.88	0.18	0.72	0.12	0.45	15.84
PS1	4164	104	371	0.06	49.16	0.18	0.56	0.21	0.74	20.75
PS2	9297	149	587	44.03	0.50	0.18	0.03	0.14	0.07	17.30
PS3	8128	126	526	37.65	0.33	0.19	0.03	0.14	0.06	9.39
PS4	4523	95	342	27.34	0.21	0.18	0.06	0.13	0.06	16.21
PS5	2512	298	1105	45.58	0.54	0.19	0.05	0.16	0.07	12.91
PS6	4089	98	376	55.65	0.60	0.18	0.03	0.21	0.07	14.96
Range	1248-18990	95-478	189-1692							
Average	6895±5236	209±144	708±537							
Average soil composition	100	10	40							
Phytotoxic level	75-100		100							

Table 2. The pH values, cation exchange capacity, exchangeable Na+1, K+1, Ca+2, Mg+2 and Ca/Mg ratio of 11 soil samples from Bukit Rokan and Petasih serpentine outcrops in Peninsular Malaysia.

	pH H$_2$O	CEC (m-equiv 100 g^{-1})	Exchangeable cations (m-equiv 100 g^{-1})			Exchangeable trace metals (m-equiv100 g^{-1})			Ca/Mg Ni
			Na^{+1}	K^{+1}	Ca^{+2}	Mg^{+2}	Co	Cr	
BR1	5.84	22.96	0.18	0.04	0.27	22.46	0.001	0.199	0.169	0.01
BR2	5.15	3.23	0.42	0.02	0.35	2.44	0.000	0.019	0.006	0.14
BR3	5.33	3.05	0.83	0.03	0.32	1.87	0.006	0.018	0.035	0.18
BR4	5.56	8.31	0.27	0.09	0.84	7.10	0.001	0.050	0.106	0.12
BR5	5.89	5.47	0.21	0.04	0.35	4.86	0.003	0.022	0.033	0.08
PS1	5.91	4.67	0.44	0.03	0.33	3.87	0.002	0.089	0.032	0.09
PS2	6.38	1.19	0.15	0.03	0.13	0.90	0.006	0.009	0.017	0.15
PS3	5.02	3.67	0.14	0.05	0.44	2.95	0.001	0.013	0.010	0.15
PS4	5.27	2.77	0.19	0.13	0.23	2.29	0.006	0.013	0.021	0.11
PS5	5.64	8.14	0.14	0.01	0.17	7.81	0.000	0.093	0.021	0.02
PS6	6.17	23.72	1.70	0.17	0.43	21.41	0.003	0.013	0.079	0.02

The average amounts of CaO and plant nutrients such as Na$_2$O, K$_2$O and P$_2$O$_5$ in 11 studied soil samples were detected in the range of 0.18-0.23, 0.03-0.72, 0.12-0.22 and 0.05-0.74 (in weights percentage) respectively (**Table 1**).

Table 2 provides the revealing data on soil pH of Bukit Rokan and Petasih areas which was moderately to slightly acidic with the range of 5-6 unit.

The maximum amount of Cation Exchange Capacity (CEC) in analyzed soils was observed in sample PS6 of Petasih (22.96 m-equiv 100 g^{-1}) follow by sample BR1 of Bukit Rokan (23.72 m-equiv 100 g^{-1}). Sample PS2 of Petasih showed the lowest CEC value of 1.19 m-equiv 100 g^{-1}. As it is seen in **Table 2**, the values of CEC were dominated by exchangeable Mg^{+2}. Soils are very poor in exchangeable cations of Na^{+1}, K^{+1}, Ca^{+2}. The rate of

Ca/Mg as it is summarized in **Table 2** is less than 1 m-equiv 100 g^{-1} for all studied soils. Moreover, the obtained values of exchangeable Cr, Co and Ni are negligible.

4. DISCUSSION

Comparing the chemical composition of serpentine soils with the average soil composition of the earth showed the overwhelmingly excess of serpentine soils for Chrome, Cobalt and Nickel by the following factors: Cr 68, Co 20 and Ni 17. The main reason of high cobalt and nickel content in serpentine is Ionic substitution of these elements into a magnesium-rich mineral such as olivine and pyroxene. Chromium is enriched because its substitution in iron rich minerals readily occurs.

Base on the nature of the parent rocks the produced soils would be rich in Fe or Mg. Weathering process also

has a key role in the elemental abundance model. Caillaud *et al*. (2009) believes that the main weathering process in well drained serpentine soil profile is associated the removal of Si and Mg and concentration of Fe. This phase occurs in wet condition and produce ferralitic soil (oxisols). After measuring major elements of 11 soil samples, two types of lateritic soils are distinguished in Bukit Rokan and Petasih serpentine soils. The type soils rich in Fe and soils rich in Mg (**Table 1**) which in both cases the unusual richness makes hardships to plant life.

Toxic effect of Mg is exacerbated along with low levels of calcium. Since Mg and Ca ions have same uptake sites in plant roots, high Mg saturates antagonistically obtaining sites and depresses Ca availability for plants. This condition is happening in Bukit Rokan with about 66 wt% of Mg (as MgO). The average amount of CaO in both areas is less than 1 wt%. Beside Ca, other nutrient deficiencies are observed (**Table 1**). The mean levels of potassium and phosphorous in all measured serpentine soils are less than 1 wt% which reveals the nature of their ultramafic parent rocks. Lack of nutrient elements shows also their rapid lost through weathering and leaching process. The scarcity of calcium, potassium and phosphorous makes a hard stress for vegetated plants on serpentine lands.

The solubility of siderophile elements is a function of pH and the order of increasing solubility is Fe, Cr, Ni and Co. As can be seen from **Table 2**, the pH of soils in the studied areas changes in slightly acidic ranges (5-6 unit). This measured pH value is less than the typical mean pH of serpentine soils which is 6.8 according to Lessovaia *et al*. (2010). At the mean pH of serpentine soils, the solubility of the metals is 10^{-7}, 10^{-4} and 10^5 µg mL^{-1} for Cr, Ni and Co respectively. The optimum availability of phosphorous obtains at a pH of 6.5-7. Potassium easily leached from soil at all pH.

The rate of exchangeable magnesium is markedly more than other determinant cations and this clarifies incomplete hydrolysis of weatherable minerals and high magnesium mobility in serpentine soil profile. This observation intensifies the possibility of magnesium toxicity in the studied serpentine soils. Poor exchangeable calcium, potassium and sodium which are less than 1 m-equiv 100 g^{-1} at all studied station is a result of the ultramafic parent rock composition. This plant nutrient deficiency is another suggested reason for infertility of serpentine soils. The average exchangeability of Cr and Ni is almost the same (0.048 m-equiv 100 g^{-1}) which is 24 times more than Co exchangeability (0.002 m-equiv 100 g^{-1}). However Cr and

Ni exchangeability is almost negligible. Thus, it is concluded that even though serpentine soils contain very elevated amounts of these harmful metals, the proportion of plant available Cr, Co and Ni is largely low.

5. CONCLUSION

Serpentine soils are unfavorable environment for plants. Multiple ranges of factors are responsible in serpentine soil infertility. The deficiency of macronutrient elements such as calcium, potassium and phosphorus and very low quotient of Ca versus Mg can be considered as the main harmful factors. However, Mg toxicity due to the excessively high exchangeable magnesium level remains a probable dangerous cause. Despite the first thought, chromium and cobalt are not controlling factor on serpentine vegetation because of their low exchangeability in soil. Even with the extremely high total concentration of Cr, Co and Ni in serpentine soils, their negative effect on plant life is tiny.

Author suggests some elemental analyses on roots and leaves of plants growing on studied serpentine soils.

6. ACKNOWLEDGMENT

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