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Correlation of Heavy Metal Concentration in Selected Hyperaccumulator Plants to The Lithologies in Sokor, Kelantan

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Abstract. Sokor, Kelantan is quite well known with gold deposition and few gold mines have been operated there. Located within the central gold belt, it is highly potential to be found with more valuable metals deposit. Thus, this study was conducted using hyperaccumulator plants as a medium to check the absorption of metal compound in the plant body as well as to measure the concentration of heavy metal elements in the soil around the potential area. The plants such as *Melastoma Malabathricum, Mimosa Pudica, Dactylis Glomerate, Rhamnus Frangula* and *Syzygium Zeylanicum* have been sampled together with the soil samples at nine different locations within the study area. The samples were prepared appropriately before analysed using Atomic Absorption Spectrometry (AAS) and X-Ray Fluorescence (XRF). The results for sample 18AFDS1 and 18AFD8(5) have shown promising concentration of manganese and iron respectively. Bioaccumulation Factor (BF) that represents the ratio of element concentration between plants and soil also was used as an indicator for metal adsorption within the collected samples. It is assumed that the samples with BF value more than 1, are located close to the potential deposit with the lithology of tuff and schist. *Melastoma Malabathricum, Rhamnus Frangula* and *Dactylis Glomerate* are amongst the plant species that have BF values more than 1. In conclusion, the concentration of heavy metal elements in the hyperaccumulator plants aside from the soil samples can act as a medium or indicator to locate the potential gold deposition with the reference of BF value.

INTRODUCTION

Hyperaccumulator plants can grow in soil with high concentration of metal and capable to absorb or extract metal as their nutrient. These plants are called metallocoles or metallophytes or in another term as hyperaccumulators and normally undergoes phythoextraction process in order to extract the heavy metals to their cells as well as stored it in the plant tissues [1-2]. Additionally, a plant which can gather a higher assimilation of metal from the substrate can be a marker for the biogeochemical prospect, especially in distinguishing the secured mineralization targets. The elongated and extension of the plant's root led to the high rate of absorption of nutrient needed by the plants for growth and reproduction. The uptake of minerals gives the insight of the sediment and groundwater as well as representation of the geochemical environments. Hyperaccumulator plant tends to exhibit a certain type of mineralization, rock types or specific content of substrate [3-7].

The study of heavy metal contamination analysis conducted by [8] at mining area in Bukit Besi, Selangor. The findings have shown *Melastoma Malabathricum* and *Pityrogramma Calomelanos* can act as iron (Fe) and aluminium (Al) hyperaccumulators, while *Scirpus Triqueter,* and *Pityrogramma Calomelanos* were undoubtedly hyperaccumulator for Cd. *Melastoma Malabathricum* is classified as good bioindicators plants species for iron (Fe) and aluminium (Al) as well as cadmium (Cd). Meanwhile, in Sabah, the biogeochemical study has been done for *Marsypopetalum pallidum sp*., *Ptyssiglottis cf.fusca,* and *hydnocarpus calophylla sp.* to study the present of nickel using XRF method [9].

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This research is mainly focused on the hyperaccumulator plant in Ulu Sokor, Tanah Merah. The heavy metal that associates with the ore mineral such as cadmium (Cd), arsenic (As), chromium (Cr), cobalt (Co), zinc (Zn), manganese (Mn), silver (Ag) and lead (Pb) have been analysed in the soil and the plant sample. A plant which can gather a higher assimilation of metal from the substrate can be a marker for the mineralised prospect, especially in distinguishing the secured mineralisation targets.

MATERIALS AND METHODS

Study Area and Sampling Procedure

Fig. 1 represents the selected study area of 25km^2 in Sokor, Kelantan. Sokor is located about 35 km southwest of Tanah Merah, within the Central Gold Belt in Peninsular Malaysia and in the middle state of Kelantan. The Central Gold Belt of Malaysia consist of a series of alkali range from gabbro-diorite at approximately 157 Ma, monzonite at approximately 163 Ma to quartz syenite at approximately 127 Ma until granodiorites and granite (calcium alkali series) [10]. According to [11], Ulu Sokor was affected by the volcanic event during the Permian to Triassic age and the area was then composed of volcanic massive sulfide deposit. Gold in the Ulu Sokor was the result from the decomposition or deposit of the volcanic event [10,12].

Sampling has been conducted on 9 locations, randomly based on the rock types and geological condition within the selected study area as shown in Fig. 1. Soil samples have been collected in the same area according to the plant samples. The soil was taken from the depth of 20 cm around 500 gm. The elements of heavy metal concentrations such as copper (Cu), iron (Fe), manganese (Mn), silver (Ag) and lead (Pb) in soil and plants were determined using Atomic Absorption Spectrometer (AAS).

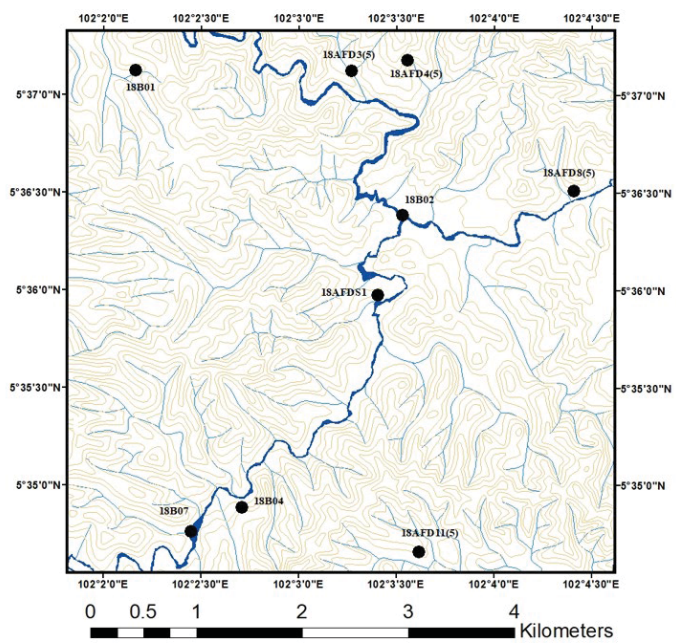

FIGURE 1. Sampling location within the study area in Sokor, Kelantan

Sample Preparation for Geochemical Analysis

Plant and soil samples need to be prepared accordingly before proceed to the geochemical analysis. For the plant samples, it needs to be cut into several parts and washed thoroughly using deionised water. About 2 grams of sample was placed in the crucible and turned into ash for 24 hours at 550°C using muffle furnace. After cooled down to the room temperature, 5ml of 20% hydrochloric acid (HCl) were added to the sample for digestion. The sample was then filtered for two times and for the second filtering, 0.45µ syringe filter was used to prevent contamination. Then, the samples were transferred into 50 ml volumetric flask and diluted until it reached the calibration mark before analysed it using Atomic Absorption Spectrometer (AAS) [13]. Meanwhile, the soil samples are required to be dried at 40°C, pulverized in a porcelain mortar to reduce agglomeration, and passed through 2 mm sieve for further analyses using AAS.

RESULTS AND DISCUSSION

Plant and Soil Samples Description

The descriptions for plant and soil samples are listed accordingly based on the coordinates as shown in Table 1. The plants such as *Melastoma Malabathricum, Syzygium Zeylanicum, Rhamnus Frangula, Dacytylis Glomerate* and *Mimosa Pudica* have been selected for sampling in this study and the plants figures are shown in Figure 2. *Melastoma Malabathricum* is usually found growing as a little bush and the heights can achieved up to 5 meters. The stems are rosy in coloured, secured with little scales. The flowers can be up to 8cm wide with petals of light to dull fuschia pink or occasionally white in coloured. This plant can tolerate poor soils and considered as weedy or invasive in a few nations. Besides that, *Syzygium Zeylanicum* that located near the river also have been sampled for elemental analysis. Mostly the soil samples contain high amount of weathered schist and had shiny characteristics. *Mimosa Pudica sp.* is found grow abundantly nearby the gold mining area and three of soil samples have been collected at this point which represent different types of colours, that varied from brown, grey-brown and greyish black.

TABLE 1. Description of samples from selected sampling locations within the study area

Sample names and coordinates	Sample Description
18B01 N 5°37'7.631" E 102°2'9.724"	*Melastoma Malabathricum* species has been sampled for this location. Most of the rock are schist. The colour of soil is greyish and contain high amount of weathered schist.
18B04 N 5°34'53.105" E 102°2'42.522"	*Melastoma Malabathricum* sp. was quite abundant and been sampled here. The colour of the soil is yellowish brown and thick like mud.
18AFDS1 N 5°35'58.502" E 102°3'24.174"	*Mimosa Pudica* was sampled for elemental analysis as it quite dominant within this area. The colour of the soil was from dark- brown, grey-brown and greyish black in colour.
18B02 N 5°36'23.216" E 102°3'31.651"	*Syzygium Zeylanicum* has been sampled for further analysis. Mostly the soil sample contain high amount of weathered schist and showed shiny characteristics.
18B07 N 5°34'45.584" E 102°2'27.042"	*Melastoma Malabathricum* has been sampled here. The soil sample was yellowish-brown in colour and dominated by phyllite.
18AFD11(5) N 5°34'39.526" E 102°3'37.037"	*Rhamnus Frangula* was taken as a plant sample with the greyish brown and medium coarse-sized of soil.
18AFD8(5) N 5°36'30.683" E 102°4'24.283"	*Dactylis Glomerate* is quite abundant and have been sampled for analysis. The soil represents of fine grain sized and light-brown coloured.
18AFD3(5) N 5°37'7.594" E 102°3'16.081"	*Melastoma Malabathicum* has been sampled together with the soil from the fine grain sediment.
18AFD4(5) N 5°37'10.859" E 102°3'33.221"	*Melastoma Malabathricum* has been sampled together with the fine-grained and yellowish-brown coloured soil.

FIGURE 2. Type of plants that have been sampled (a) *Melastoma Malabathricum*, (b) *Syzygium Zeylanicum*, (c) *Rhamnus Frangula* (d) *Dacytylis Glomerate*

Elemental Concentration of Plant and Soil Samples from AAS Analysis

Both plant and soil samples have been analysed for elemental concentration using Atomic Adsorption Spectrometer (AAS) for the elements such as Fe, Cu, Mn, Ag and Pb throughout the study area (Table 2). The value of Ag however is very low among the elements. The highest Ag content in soil can be found in 18AFDS1 with 0.027 ppm and followed by sample 18B02 with 0.014 ppm. The concentration of Ag in plant have shown the highest concentration for sample 18B01 (*Melastoma Malabathricum*) and 18AFDS1 (*Mimosa Pudica*), with the concentration of 0.022 ppm and 0.020 ppm respectively. 18AFDS1 also has the highest concentration of manganese in soil, which is 86.760 ppm. For manganese concentration in plant, the highest concentration is found at sample 18AFD3(5) (*Melastoma malabathricum*) with concentration of 156 ppm while the medium concentration is located at 18AFD8(5) (*Dactylis glomerate*) with 13.740 ppm. Sample 18AFDS1 is located within the active gold mining area whereas for 18AFD8(5) is located toward east of the abandoned gold mining site. The highest concentration for Fe in plant is recorded in sample 18AFD3(5) with 1.181 ppm. Meanwhile, the highest of Fe in soil is found in sample 18AFD8 (5) with the value of 173.1 ppm.

TABLE 2. AAS results of soil and plant samples respectively

Locations	Silver (Ag)		Manganese (Mn)		Copper (Cu)		Iron (Fe)		Lead (Pb)	
	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant
18B01	0.006	0.022	1.554	12.840	0.158	0.051	5.064	0.430	0.467	0.350
18B04	0.002	0.004	35.590	2.169	0.422	0.018	18.730	1.078	0.947	0.391
18AFDS1	0.027	0.020	86.760	45.130	1.094	0.024	49.990	0.194	3.716	BDL
18B02	0.014	0.001	53.370	0.208	0.350	0.018	27.140	0.200	0.396	0.280
18B07	0.004	0.009	26.940	2.789	0.459	0.006	25.600	0.063	1.164	0.047
18AFD11(5)	0.003	0.010	10.130	12.180	0.198	0.024	9.942	0.782	0.375	0.241
18AFD8(5)	0.007	0.012	42.360	13.740	1.606	0.011	173.100	0.063	1.861	BDL
18AFD3(5)	0.002	0.005	33.170	156.000	0.613	0.038	23.260	1.181	0.452	0.223
18AFD4(5)	BDL	BDL	0.344	1.747	0.447	0.024	18.140	0.446	2.790	0.270

BDL = below detection limit.

Bioaccumulation Factor

Plants normally uptake the nutrients that presence in the soils. Some plants have a high tendency to absorb heavy metals and accumulate them inside the tissue. This biogeochemical cycle gives an overview that every element that contains in the soil can be absorbed by the plant. Bioaccumulation factor (BF) was used to determine the degree of metal accumulation inside the plant. According to [14], the plant is categorized as a hyperaccumulator plant if the value of BF is greater than 1. The calculation formula of BF is shown in equation 1 as follow.

$$\text{Bioaccumulation Factor (BF)} = \frac{\text{Metal concentration in plant sample}}{\text{Metal concentration in soil sample}} \qquad (1)$$

Table 3 represents the Bioaccumulation Factor (BF) for nine samples for Ag, Mn, Cu, Fe and Pb elements. *Melastoma Malabathricum* has capability to adsorb heavy metals elements as it showed BF value more than 1 especially for Ag, Mn and Cu. However, the BF value for Fe and Pb elements are still too low and the ratio is less than 1. The BF value greater than 1 for Cu element can be identified in sample 18AFD4(5) only which also the species from *Melastoma Malabathricum.* Meanwhile, the higher ratio of BF value can be spotted in sample 18B01 and 18AFD4(5) for Mn element whereas the BF ratio is over than 5. Both samples represent *Melastoma Malabathricum sp.* as well. Thus, *Melastoma Malabathricum* is the main species in Sokor that can accumulate more elements such as Ag, Mn and Cu compared to the other species. *Rhamnus frangula* from sample 18AFD11(5) also showed BF value more than 1 for Ag and Mn elements.

TABLE 3. Result of Bioaccumulation Factor (BF)

Elements / Sample name	Silver (Ag)	Manganese (Mn)	Copper (Cu)	Iron (Fe)	Lead (Pb)
18B01 (*Melastoma malabathricum*)	0.300	**8.263**	0.323	0.085	0.750
18B04 (*Melastoma malabathricum*)	**2.000**	0.061	0.043	0.058	0.413
18AFDS1 (*Mimosa pudica*)	0.741	0.520	0.022	0.004	-
18B02 (*Syzygium zeylanicum*)	0.071	0.004	0.051	0.007	0.707
18B07 (*Melastoma malabathricum*)	**2.250**	0.104	0.013	0.002	0.040
18AFD11(5) (*Rhamnus frangula*)	**3.333**	**1.202**	0.121	0.079	0.463
18AFD8(5) (*Dactylis glomerate*)	0.714	0.324	0.007	-	-
18AFD3(5) (*Melastoma malabathricum*)	**2.500**	**4.703**	0.062	0.051	0.493
18AFD4(5) (*Melastoma malabathricum*)	-	**5.088**	**1.000**	0.025	0.097

Correlation of Heavy Metal Elements Distribution Within the Study Area

Manganese (Mn) and lead (Pb) have shown parallel patterns of element distribution within the study area with the highest concentration of elements are found to be located at the centre of the area (see blue area in Figure 3). The distribution pattern for silver (Ag) element is also similar but not shown here. These distributions were plotted based on the elements concentrations from AAS results in Table 2. Based on the results, sample 18AFDS1 which located in the centre of the map have the highest concentration for most of the elements especially Mn and Ag. This sample is found located within tuff and schist lithology which also adjacent to the active mining site. Most of the BF value especially for Ag and Mn elements (refer Table 3), have shown ratio more than 1 compared to the other elements. The plant of *Melastoma Malabathricum* is found to have the characters of hyperaccumulator for this location. Generally, the colour of soil tends to be darker if there is abundance of Mn within the soils. In both locations, the soil's colour was light reddish to greyish. The soil also tends to have greyish to lighter grey coloured when associated with Pb element. Since the soil in the mining area was greyish, this gave a hint that the presence of Pb is quite high. However, according to [15], the greyish colour in soil represents a very poor drainage soils where the anaerobic condition has favoured the reaction between manganese and iron minerals. When there is the presence of Ag in soil, the soil tends to have lighter colour, however, in both locations the soil has darker reddish-brown colour. Thus, indicate that the residual silver content in both location is very small and can be neglected. The soil wetness also an important sign for the presence of indicator elements. The element of Ag that contained in the soil also depends on the waterlog properties. The higher the wetness of the soil, the higher the content of the silver.

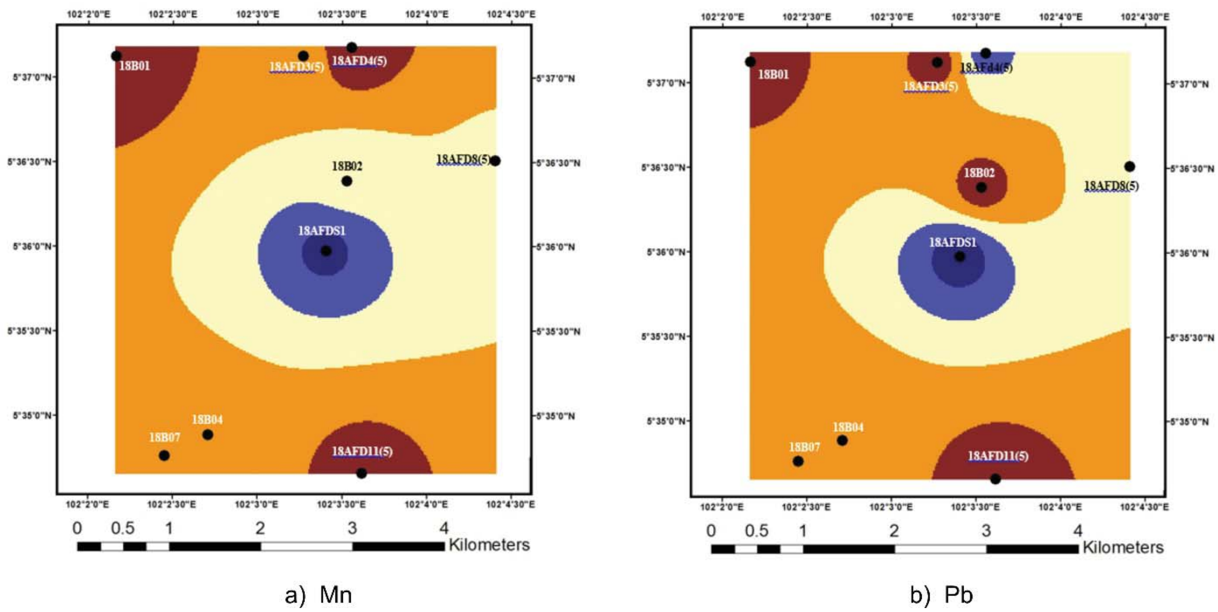

FIGURE 3. Element distribution of manganese (Mn) and lead (Pb) within the study area (note: blue represents the highest value of element concentration)

CONCLUSION

The heavy metal elements such as Ag and Mn are important elements in determining the potential location of the valuable gold deposit with the application of BF ratio. *Melastoma Malabathricum* and *Rhamnus Frangula* can act as hyperaccumulator plants because have shown the Bioaccumulation Factor (BF) higher than 1. *Melastoma Malabathricum* can absorb silver, manganese and copper at high rate while *Rhamnus Frangula* can absorb silver and manganese elements.

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