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# Geology and distribution of heavy metals in topsoil, Kuala Krai, Kelantan.

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**Abstract.** The study for geology of Guchil, Kuala Krai, Kelantan was carried out approximately 25 km<sup>2</sup> in and around Guchil. Preliminary research and field studies conducted to produce geological map of Guchil, Kuala kra, Kelantan. Based on the field study carried, carbonaceous mudstone interbedded with greywacke sandstone, shale and ignimbrite distribution of rock found in this study. Meanwhile, investigation on distribution and potential heavy metals (Cu, Fe, Mn, Pb and Zn) in topsoil Guchil, Kuala Krai, Kelantan was conducted. Total of nine soil sample in and around Guchil undergo soil digestion and analyzed by Inductively Coupled Plasma Spectroscopy (ICP-OES). The heavy metals concentration in the topsoil was varied between 21176-138962; 649-8411; 11-505; 43-455; and 11-115 mg/kg for Fe, Pb, Mn, Zn and Cu respectively. The average concentration of heavy metals in this study followed the order of Fe > Pb > Mn > Zn > Cu. The spatial distribution pattern shows similar distribution pattern of heavy metals in residential area. The concentration of Cu, Fe, Mn, Pb and Zn from the soil samples compared with naturally occurring value of contaminated land management and control guidelines of Department of Environment Malaysia (DOE), 2009 and Barceloux (1999) as well as with permissible limit values in soil of Polish Ministry of the Environment, 2002. From this assessment method, highly potential element was Pb followed by Zn and Cu. Besides that soil characteristic of this study shows that soil pH which is acidic condition with low total organic matter. The soil fractions tend to dominated by clay fraction in topsoil.

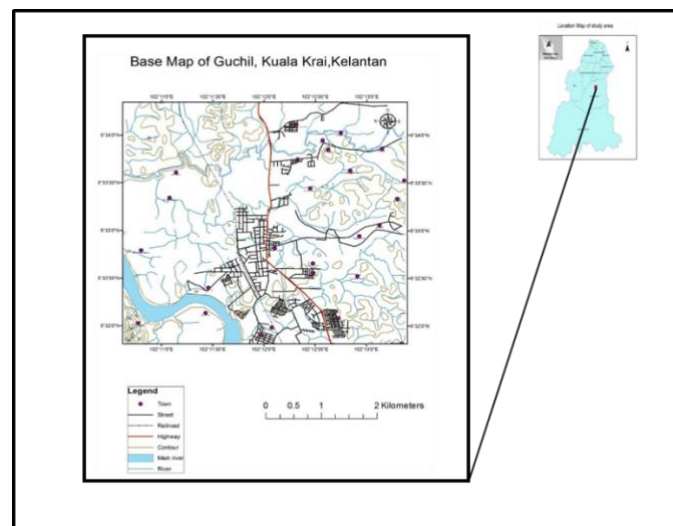
## 1. Introduction

Heavy metals is the large series of elements with the specific density over 5 gcm<sup>-3</sup> and the relative atomic mass is above 40 [1]. Heavy metal usually occurs naturally in soil due to soil forming factors that is weathering of parent materials at a level of trace [2]. However rapid development of economy causes production and toxic chemical to increase in Malaysia [3]. This is because different type of anthropogenic source such as agriculture and mining causes soil to be the major sink of heavy metals. The most abundance and common heavy metals found at contaminated soil is Pb, Cr, As, Zn, Cd, Mn, Cu and Hg. Soil contamination is the main type of pollution that affects the biotic community. Dangerous possibility of may occur to human and ecosystem through contact with contaminated soil, by usage of groundwater that close to the surface which is more prone to polluted and food chain [2] Based on previous research on distribution of heavy metals contamination in Perlis, Malaysia result shows that Pb, Cu, Zn and Cr the source is from industrial and traffic emission. Meanwhile Ni, Co and Mn from the naturally occurring material in that region [4]. In similar research at Perlis, Malaysia the contamination of heavy metals is due to industrial activity, urbanization and agricultural activities. Based on Pollution index as mentioned, 11% of Cu, and 6% of Cd shows above the standard limit of contamination [5].



In this study, a special emphasis had been laid on geology and geochemistry of soil. The studies involve geological features of study area, sampling of rock for petrology studies, sampling of soil for geochemical studies and determination of contamination level of heavy metal in the study area. Updating geological features gives make easier for interpretation and for research purposes by determining the distribution of chemical elements especially heavy metals, gives awareness among people at the area of consuming in future purpose and environmental management. Thus enhancing the geochemical database of an area contributes to various development of the particular area [6].

The study area is located at Kuala Krai, northern Kelantan. Kuala Krai is bordering with Machang in the northern part and Gua Musang in the southern part. The study area is covered approximately 25 km<sup>2</sup> and lies between latitude of 5° 31.49' 49.317'' to 5° 34'24.041'' and longitude between 101° 10' 44.958'' and 102° 11'58.692''. The topography of Kuala Krai is typically lowland and it consists of two major rivers, Sungai Lebir and Sungai Galas that forms the Kelantan River. Kelantan River system flows northward passing Kuala Krai which is one of the town in Kelantan, then finally discharge into South China Sea. Due to the flat surface, majority land are used for rubber and oil palm plantation as it provides the main economic contribution of the community. Figure 1 shows the location of study area at Guchil, Kuala Krai, Kelantan.



**Figure 1.** Location map of Guchil, Kuala Krai, Kelantan

## 2. Methodology

### 2.1. Thin section preparation

Thin section is for the petrography study of rock. The steps included sectioning, vacuum impregnation, grinding, cementing, re-sectioning, grinding and polishing. Initially, glass slide prepared by polishing the chosen surface using diamond grinder. The fresh rock sample was prepared by cutting using rock saw with a dimension of 5 cm x 2 cm. Canada balsam was added onto the polished rock sample and glass slide place on the surface of rock. The sample is then cooled overnight. The sample is then polished by using Carborandum grit 180 until a smooth surface was produced. Next, resin and hardener were mixed together in ratio of 1:1 and stirred evenly. The mixture is the spread at one side of the smooth surface sample, then the rough surface glass slide was place in 45 degree against the smooth surface of sample and placed the glass slide without any bubbles. The mounted sample was placed aside and cooled for 24 hours. Once thin section prepared, it was examined under a petrographic microscope to determine the mineral composition of the rock and textures.

## 2.2. Soil pH

Soil pH was determined by pH meter in a distilled water; 1 part soil to 2 parts of distilled water. To get accurate reading the pH meter calibrated with standard buffer solution.

## 2.3. Organic matter

1 g of dry soil with the size of 60 mesh was weighed and labelled in a 500 ml conical flask. 10 ml of  $K_2Cr_2O_7$  and 20 ml of concentrated sulphuric acid added. The solutions shake for one minutes and left for 30 minutes. Then, 200 ml of distilled water, 5 ml of ortho-phosphoric acid and 1 ml of diphenylamine indicator added. The indicator is to determine the colour change to dark blue. The sample was titrated with 1N of  $FeSO_4(NH_4)2SO_4.6H_2O$  until the mixture changes to purplish blue and continued until the last drop (green color). 0.5 ml of  $K_2Cr_2O_7$  added and titration process continued until the blue colour disappeared.

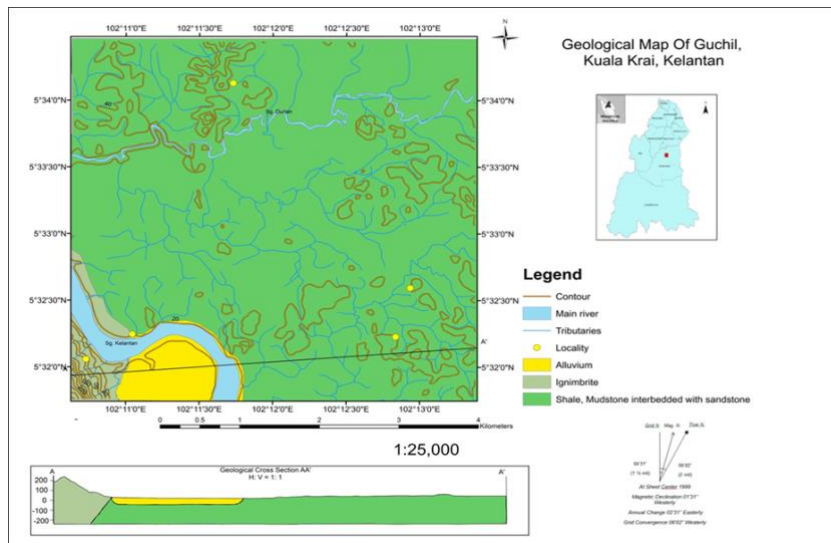
## 2.4. Analysis of soil sample using acid digestion method

Acid digestion method is required for dissolving the metal in solution, which then analyse by analytical method to determine the concentration of element present in sample by using Inductively Coupled Plasma Spectroscopy (ICP-OES). 1 gram of soil sample prepared added into beaker. 50 ml of 70% concentrated nitric acid solution was added into soil sample. The mixture was boiled on a hot plate until the solution level becomes half from the original level. 50 ml of 70% Nitric acid solution added again in the mixture and half the solution by heating. The sample was allowed to cool before centrifuge for 15 minutes. The mixture was filtered by filter paper. The filtrate poured into 100ml conical flask. Distilled water added until the solution volume was 100 ml. The digested solution is then used to determine the concentration of selected elements using ICP-OES. Steps repeated using 9 soil samples.

# 3. Results and discussion

## 3.1. General geology

Field observation was conducted by traversing along the study area. Several outcrops have been determined by observation of the lithology and geological structures in the form of lithostratigraphy. Two types of rock were observed which are igneous rock and sedimentary rock as shown in Figure 2. Igneous rock is identified as pyroclastic deposit known as ignimbrite. Sedimentary rock that observed is shale and sandstone interbedded with mudstone. The lithostratigraphy of the study area consists of ignimbrite, shale, greywacke sandstone interbedded with carbonaceous mudstone. The oldest formation in this study area is Telong formation which composed of arenaceous and argillaceous units during Triassic period consists of shale and mudstone interbedded with sandstone. Temangan Ignimbrite which is an extrusive igneous rock occurred as dyke during Triassic period also. The youngest formation in the study area was Beruas formation which composed of loose unconsolidated Quaternary sediment deposits with the presence of clay, sand clay, silty clay, sand, granules and pebbles [7] come in contact with river.



**Figure 2.** Geological Map of Guchil, Kuala Krai

**3.1.1. Shale.** Shale is a fine grained sedimentary rock that composed of silt and clay- sized grains through compaction. Based on the hand specimen (Figure 3), the colour of shale is dark grey and readily spilt into thin pieces along the lamination. From the colour of shale almost specify the presence of organic material.



**Figure 3.** Hand specimen of weathered shale

**3.1.2. Interbedded mudstone and sandstone.** This interbedded mudstone and medium sandstone consists of thick mudstone beds that range from 40-60 cm in thickness and sandstone bed that thickness of 8 cm. The mudstone is composed of carbonaceous material and fine grained sedimentary rock that can be typified by it is ability to easily leave black streaks of carbon on paper. This indicates that carbonaceous mudstone containing high carbon contain (Figure 4). Sandstone bed consists of fine grained with fewer grain made of clay clast that is poorly sorted. Referring to Figure 5, the clast roundness is more likely to be rounded with high sphericity.



**Figure 4.** Hand specimen of weathered mudstone



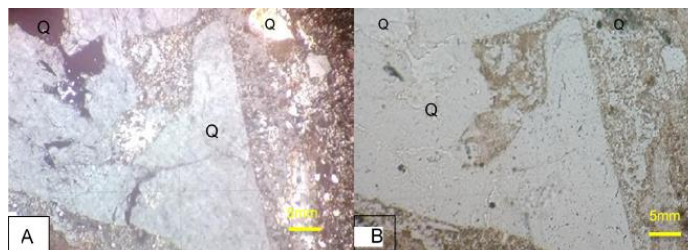
**Figure 5.** Hand specimen of weathered greywacke sandstone, contain clay clasts.

**3.1.3. Ignimbrite.** Ignimbrite dyke in the study area presents a distinguished ridge about 5 km long with 1.2 km width trending approximately N-S. The colour of ignimbrite is pink with homogeneous texture (Figure 6). The quartz mineral visible through naked eye.



**Figure 6.** Hand specimen of ignimbrite

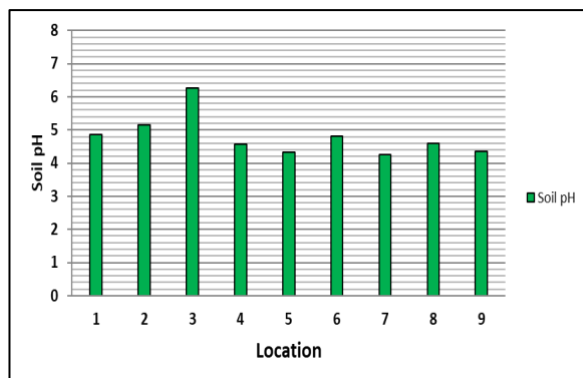
The mineral composition and also the texture of the rock were being studied involving the description of rock composition and textures. A light transmitting microscope was used to study the optical properties of rocks, minerals and other earth materials. Figure 7 shows the thin section of ignimbrite in PPL and XPL, with phenocrysts of quartz and K-feldspar and glass fragments. The mineral shapes are euhedral.



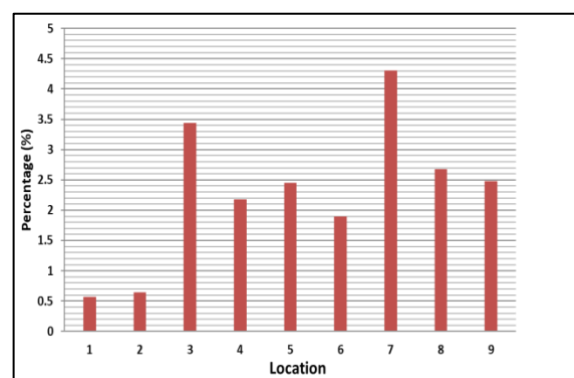
**Figure 7.** Thin section of Ignimbrite in (A) XPL and (B) PPL microscope , Q– Quartz and F-Alkali Feldspar.

### 3.2. Soil characteristic

The pH values of studied soils ranged from extremely acidic to slightly acidic by referring to U.S Department of Agriculture (USDA), soil quality indicator between pH 4.26 to 6.26. The soil pH is represented in the form of bar chart, Figure 8. The lowest soil pH was at location 7 and the highest pH recorded at location 3. In Figure 9 shows the total organic matter content was between 0.57% to 4.31%. The highest value of organic matter recorded at location 7 and the lowest at location 1. These values are within the normal characteristic of Malaysian Topsoil where the average pH values between 3.04 to 7.01 and total organic matter between 0.06 to 34.4%. [8].

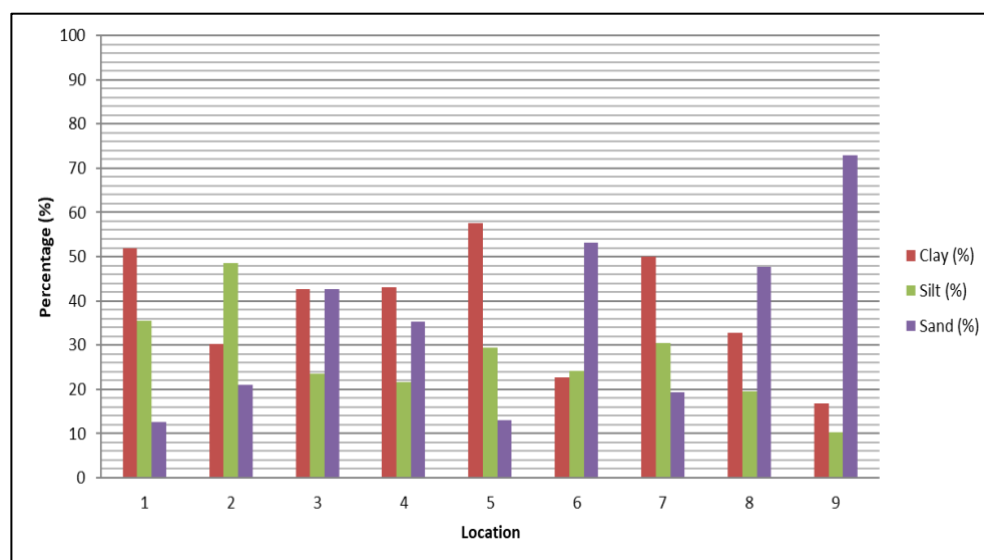


**Figure 8.** Soil pH of Guchil, Kuala Krai, Kelantan



**Figure 9.** Total Organic Matter of Guchil, Kuala Krai, Kelantan

The soil fraction is shown in Figure 10, there are two major types of soils in the study area. The first being clay soils. This was the major soil type for location 1, 5 and 7. The second type of soil is sand. This was the major soil type for location 6 and 9. The overall soil characteristics include soil pH, total organic matter; Soil fraction and texture are shown in Table 1. From the percentage of soil fraction, the soil texture can be determined by USDA textural classification chart. From the soil texture we can deduce that the soil texture found to be more clay compare to sandy texture.



**Figure 10.** Soil Fraction of Guchil, Kuala Krai, Kelantan

**Table 1.** Soil Characteristics of Study Area

Soil Parameters	Sample location									Statistical Parameters		
	#1	#2	#3	#4	#5	#6	#7	#8	#9	Min	Max	Mean
TOC (%)	0.57	0.64	3.44	2.18	2.45	1.9	4.31	2.68	2.48	0.57	4.31	2.29
Soil pH	4.86	5.15	6.26	4.57	4.33	4.82	4.26	4.6	4.36	4.26	6.26	4.80
Clay (%)	51.94	30.31	42.67	43.07	57.66	22.63	50.1	32.79	16.89	16.89	57.66	38.67
Silt (%)	35.45	48.61	23.53	21.67	29.31	24.22	30.49	19.44	10.26	10.26	48.61	26.99
Sand (%)	12.61	21.08	42.67	35.25	13.03	53.15	19.41	47.76	72.85	12.61	72.85	35.31
Soil Texture	Clay	Clay loam	Clay	Clay	Clay	Sandy clay loam	Clay	Sandy clay loam	Sandy loam			

### 3.3. Concentration of heavy metals in topsoil

Table 2 shows the concentration of heavy metals in the topsoil that is differentiated between agriculture and residential area with shaded column. The most abundant element found in the topsoil was Fe ranged from 21176 to 138962 mg/kg. The concentration of Fe was high in residential area compare to agricultural area. The location that shows highest concentration at location 4, 1 and 3. Pb was the second highest metal concentration found in the topsoil ranged from 649 to 8411 mg/kg. Pb mostly found in residential area which is maximum at location 3 and 6. However, Pb also shows higher concentration in agriculture area which is location 5. The highest Zn and Cu detected in residential area which is location 6 and location 3 respectively. The average concentration of heavy metals in this study followed the order of Fe > Pb > Mn > Zn > Cu.

The comparison of heavy metals in this study to the standard typical range of naturally occurring metals concentration in soil which is adopted from Department of Environment of Malaysia, DOE, 2009 indicate Cu, Fe, Pb and Zn exceeded the background value of soil. Based on the permissible limit value adopted from Polish Ministry of the Environment, 2002, which is average value for each element shows Pb is above permissible limit. Cu and Zn are below permissible limit.

**Table 2.** Heavy Metals Concentration in (mg/kg)

Heavy Metals	Sample Location									Statistical Parameter		
	#1	#2	#3	#4	#5	#6	#7	#8	#9	Min	Max	Mean
Cu	41	17	115	24	32	80	18	11	11	11	115	39
Fe	111504	21176	78805	138962	58940	36099	43481	32322	26373	21176	138962	60851
Mn	11	27	290	389	446	505	395	136	31	11	505	248
Pb	2039	664	8411	2618	5938	7417	5060	3260	649	649	8411	4006
Zn	45	43	254	97	196	455	145	66	55	43	455	151

Note: #1-#4 Residential Area #5-#9 Agricultural Area

Fe in this study was high for both residential and agriculture area. This was possibly related to the clay soil type in these areas. Fe is the main component in the clayey soil. In higher weathering environments such as in tropical region, Fe is abundant in clay minerals [9]. The concentration of Fe exceeded the background value however the abundant of Fe can be influenced by the iron mineralisation or iron deposited in the form of residual that found in Kuala Krai, Kelantan. Thus, Fe could not be categorized as contaminant or potential heavy metal in this study.

Pb was high in residential area compared to agricultural area. This concentration is higher than the average permissible limit, these can be affected by other sources rather than natural occurring value. High value of Pb in the topsoil in this study may due to anthropogenic activities such as fertilizers especially phosphatic fertilizers unintentionally adds Pb in soil, atmospheric deposition from waste dumping activities and roadways [10]. Therefore, Pb is the potential heavy metal that can be found in Kuala Krai, Kelantan. Mn found to be within the background value which is not being harmful metal for environment. The average concentration of Zn in this study exceeds the background value it shows possible anthropogenic sources can be from agrochemical which is phosphate fertilizer and pesticides [11]. While in residential area, the possible sources are from motor oil, grease, sewage and concrete [12]. It was slightly lower than the average concentration in Malaysia topsoil (2.9 to 137 mg/kg) [9] and lower than average permissible limit in soil. Cu in the residential and agricultural soil shows lower concentration based on the permissible limit.

The soil characteristics of this study shows; clayey soil is dominant with acidic condition and has low total organic matter. The clayey soil with acidic condition influences the mobility of heavy metals that tend to increase the concentration of metals. The distribution pattern of Cu, Fe, Mn, Pb and Zn significantly similar spatially in Kuala Krai, Kelantan, most of them were consistent high concentration at residential area compare to agricultural area. It seems that anthropogenic activities and flood that overflow during high level of rain precipitation discussed earlier may associate with Cu, Pb and Zn that can increase the concentration.



#### 4. Conclusion

In total of nine samples collected and analysed for five heavy metals. The distribution patterns of heavy metals were highlighted at residential area compare to agricultural area. To determine the potential heavy metals, naturally occurring values and permissible limit were used in order to differentiate the level of contaminant. It was established that distribution of Mn associations result of background value. Pb, Cu and Zn is associated with anthropogenic influence that shows potential elements whereby, Pb is highly potential and Cu and Zn have possibility to be potential heavy metals. The heavy metals assessment indicate that agrochemicals, waste dumping, natural disasters and roadways could be the sources of Pb, Cu and Zn whereas Fe and Mn mainly from natural resources. Increase anthropogenic sources affects the environment and human health, therefore monitoring the permissible limit of land used for residential, agricultural, industrial and protected area might control the concentration of heavy metals present in soil for sustainable environment.

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