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EVALUATION OF SEDIMENT QUALITY ALONG THE RIVER OF BALOK MANGROVE FOREST, KUANTAN, PAHANG, MALAYSIA

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ABSTRACT
In the modern world, water has been a serious threat including heavy metals contamination. Certain heavy metals can be hazardous when accumulated and can travel through several routes to reach different parts of the body. A field study has been conducted to determine the heavy metals and selected nutrients content in sediment collected along the river of mangrove area located in Balok River, Kuantan, Pahang. A total of 10 sediment samples were collected and analysed for pH, total organic carbon (TOC), heavy metals mainly Zn and Cu) and selected available nutrients particularly Ca, Mg, and K using atomic absorption spectroscopy (AAS). Sediment samples were digested with aqua regia acids prior to the analysis. To assess the level of contamination, heavy metals results were compared to the average continental shale level and assessment through Geoaccumulation Index ($I_{geo)}$ value. The soil pH ranges from neutral to slightly acidic and the TOC showed a comparable value with other studies. The average concentration of Zn and Cu were 152.985 ± 36.93 ppm and 31.125 ± 15 ppm, respectively. The average concentration of nutrients element, Ca, Mg, and K were 239.1 ± 147.04, 587.9 ± 326.87 and 176.891 ± 178.76 ppm. The Cu was categorized as uncontaminated and Zn were in the category 1, range from uncontaminated to moderately contaminated. Hence, findings of this study may suggest that Balok mangrove river is contaminated by Zn element.
Keywords: Soil, Heavy Metals, River, Contamination

ABSTRAK
Pada zaman kini, medium air dan tanah telah menjadi ancaman serius termasuk pencemaran logam berat. Logam berat boleh mendatangkan bahaya apabila terkumpul banyak dan boleh tersebar ke medium lain dan mencemarkan kawasan. Kajian lapangan telah dijalankan untuk menentukan kandungan logam berat dan nutrien terpilih dalam sedimen yang disampel sekitar kawasan bakau yang terletak di Sungai Balok, Kuantan, Pahang. Sebanyak 10 sampel sedimen telah dikumpul dan dianalisis untuk pH, jumlah karbon organik (TOC), logam berat Zn dan Cu dan nutrien, Ca, Mg, dan K menggunakan AAS. Sampel sedimen dicerna dengan menggunakan asid aqua regia sebelum dianalisis. Untuk penilaian tahap pencemaran, keputusan logam berat yang diperolehi dibandingkan dengan purata syal benua dan dinilai melalui nilai Index Geoaccumulation (Igeo). pH tanah didapati berada pada kadar neutral hingga sedikit berasid dan TOC menunjukkan nilai yang setara dengan kajian lain. Purata kepekatan Zn dan Cu ialah 152.985 ± 36.93 ppm dan 31.125 ± 15 ppm. Purata kepekatan unsur nutrien, Ca, Mg, dan K ialah 239.1 ± 147.04, 587.9 ± 326.87 dan 176.891 ± 178.76 ppm. Cu telah dikategorikan sebagai tidak tercemar dan Zn berada dalam kategori 1, iaitu berada pada julat tidak tercemar sehingga tercemar sederhana. Kesimpulannya, pemantauan logam berat di kawasan bakau adalah penting untuk mengekalkan keseimbangan ekologi, menjaga kesihatan manusia, dan menggalakkan amalan pengurusan mampan.

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1. INTRODUCTION

1.1 Background

Heavy metals contamination is one of the environmental concerns that threatens the safety of the ecosystem worldwide. It is due to their toxicity, persistence in the environment, and bio accumulative. They are one of the main factors of soil water pollution, genotoxic, teratogenic, and mutagenic effects in living beings (Dixit et al., 2015). Metals with relatively large densities, atomic weights, or atomic numbers are classified as heavy metals.

Mangroves ecosystem are important in supporting sustainable coastal as it protects nearby areas from tsunamis and extreme weather events. They are resilient to changes like extreme weather and sea level rise. Mangrove forests are also effective for carbon sequestration and storage (Friess et al., 2019). Mangroves are thought to be a major sink of suspended sediment since one of their significant functions to the environment is to provide a mechanism for trapping sediment (Punarbasu et al., 2019). They also help prevent erosion by stabilizing sediments with their tangled root system as well as preserving and regenerating soil.

There are 641,886 ha of mangrove forests in Malaysia, of which 57% are found in Sabah and 26% in Sarawak and the remaining 17% in Peninsular Malaysia (Hamid, 2004). Mangrove roots, once grown, provide oyster habitat and slow water flow, thus, promoting sediment deposition in the sites. In nature, the fine, anoxic sediments beneath mangroves operate as sinks for a variety of heavy metals that have been concentrated from the water by colloidal particles in the sediments. However, it has been reported there is an increasing number of the release of heavy metals from the pollutant's industrial activities into the coastal environment that has the significant impacts on humans and others living diversity (Chowdhury & Maiti, 2016). Despite efforts for constant monitoring by the authority, contamination made in mangroves around Malaysia is less to be controlled and not completely reported.

In this study, the content of heavy metals, Zn and Cu and available nutrients, K, Ca and Mg in the sediment collected along the river of Balok mangrove forest, Kuantan were determined. The relationship between the heavy metals and nutrients availability with pH and total organic carbon (TOC) were observed in order to explain the occurrence. The study is vital as a preliminary study to observe the status of contamination as currently, the area has been used as a main jetty for the fishermen at Balok. According to John and Waznah (2011), due to urban runoff, sewage treatment plants, industrial effluents, mining operations, boating activities, domestic garbage dumps, and agricultural fungicides, mangrove sediment has the tendency to absorb more trace metals dramatically, which may contribute to pollutants and exceed acceptable levels. Hence, the present study was conducted with an objective to assess the quality of the river sediments of Balok Mangrove Forest, Pahang.

2. MATERIALS AND METHOD

2.1 Study Area

The study was conducted at the area between 3°56.31'N to3°56.23'N in latitudes and 103°22.20'E to 103°22.26'E in longitudes. The area were surrounded by a fishing village and jetties where the local community makes a living from the sea. Apart from fishing activities, this forest is also an immense value for the aquatic organism and other varieties of plant and bird species. Nearly located in the urbanized Kuantan city, Balok river encounters enormous pressure on the ecology system due to development for residential and industry purposes, followed by anthropogenic activities. As the river of Balok mangrove forest, Kuantan, Pahang are related and connected with the Balok river, the activities encountered in Balok river has the potential to cause pollution into the mangrove sediment. Figure 1 shows the location of the mangrove forest in Kuantan and the sampling points where samples had been obtained.

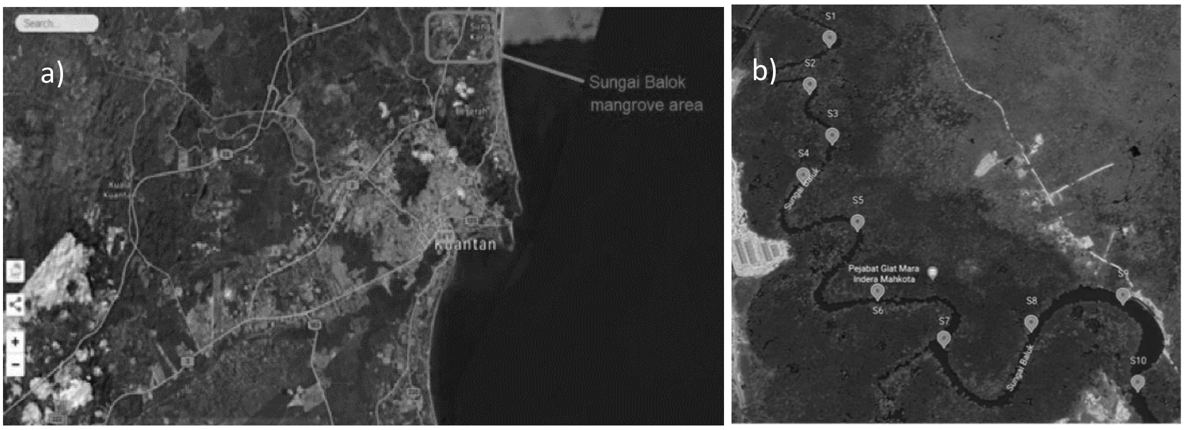

Figure 1: a) Location of the river of Balok Mangrove Forest, Kuantan, Pahang, and b) sampling points S1 to S10

2.2 Sampling and Sample Preparations

A total of 10 samples labelled as S1 to S10 were collected along the river of Balok mangrove forest, Kuantan. The point of S1 were located upstream, while as it move towards the river mouth, the sample were labelled as S2 to S10. The S10 were at the river mouth located near to the open ocean. Global Positioning System device (GPS) was used for the sampling location. Soil auger was used to collect the samples from the top surface sediment with the depth of 1–15 cm was taken at each sampling site and kept prior to analyses.

Soil pH was determined using potassium chloride (KCl) with 1:2.5 ratio. Total organic carbon (TOC) was determined using Walkley-Black dichromate methods (Walkley Black, 1934). Soil exchangeable K, Ca and Mg were extracted using Mehlich 3 procedures (Mehlich, 1984), which is suitable for acidic soil type. Total content of Cu, Zn, Mn, Pb and Fe were digested using mixed acid with ratio of 3: 3.5: 3.5; HF: HNO3: HCl and analysed by using inductively coupled plasma mass spectrometry (ICP-MS) (Elan 9000, Perkin Elmer, U.S.A).

3. RESULTS AND DISCUSSION

3.1 Soil pH and Total Organic Matter content

Commonly, the ideal soil pH in mangroves area ranged between 6.7 to 7.13 (Alsumaiti et al., (2014) and usually the pH in mangrove sediments is slightly acidic due to high presence of organic matter, which undergo decomposition process, and the mangrove itself that act as sink for marine litter and traps for land originated litter. Previous study recorded the average pH in mangrove area was pH around 6.2 ± 1.09 (Turk et al., 2018). Based on the pH obtained, the sediment of Balok mangrove were considered as acidic with an average of 3.73 (Figure 2a). The pH values may not suitable for rehabilitation and re-plantation of mangroves that is crucial to assures the growth of mangrove seedlings at the highest rate. If the pH in mangrove sediment acidic, it can cause adverse effects on the plants and animals that live in the mangrove ecosystem. Acidic conditions can disrupt the balance of nutrients in the soil, making it difficult for mangrove roots to absorb the minerals they need to grow.

Figure 2b shows the result of soil TOC in sample collected in the river of Balok Mangrove Forest, Kuantan, Pahang. Total organic carbon in mangrove sample range between 0.36% to 3.72%. The highest of soil TOC percent was obtained in S1 (3.72%) whereas the lowest soil TOC percent was occupied in S4 (0.36%) with an average of 2.1% ± 1.22 for soil TOC. Other studies recorded around 2.74% ± 1.42 for soil TOC reading (Hasrizal et al., 2020).

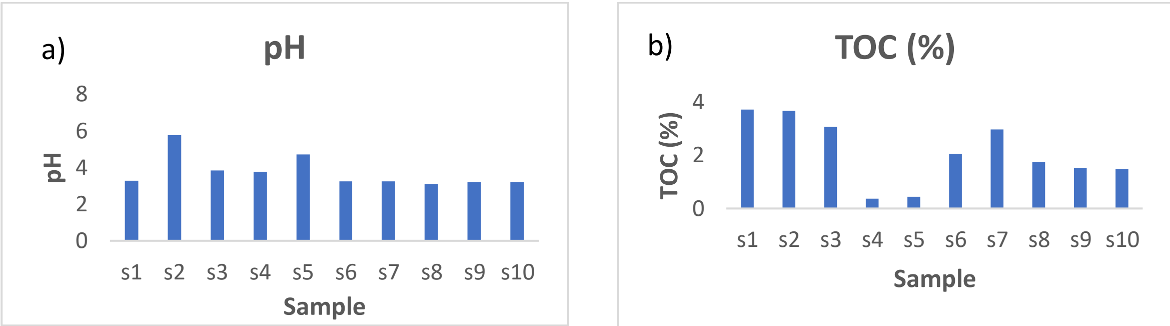

Figure 2: a) Soil pH of sediment samples, and b) TOC of sediment samples.

Total organic carbon (TOC) in the river sediment of Balok mangrove forest can be an important indicator for health and productivity assessments of these ecosystems. Mangrove sediments are typically rich in organic matter as it can store large amounts of organic carbon and are rich in organic carbon in sediments which mainly originated from litter that is derived from the accumulation of leaves, roots, and other plant debris (Yong et al., 2011). This organic matter can be a significant source of carbon storage, and the TOC content can range from several percent to over 30%. The mean TOC value in the river sediment of Balok mangrove forest are considered having a good amount of TOC (2.1%). It can be used as an indicator of the amount of organic matter in the mangrove sediment, and mangrove ecosystems that are exposed to higher levels of nutrients will tend to have higher TOC content. Low TOC value in S4 and S5 could be due to the soil texture and land conditions as some of the areas were identified having erosion.

3.2 Sediments Content of Zn and Cu

Heavy metal pollution in mangrove sediment is a concern because heavy metals can be toxic to organisms and can accumulate in the environment over time. Heavy metal pollution in mangrove sediment can have a wide range of negative effects on the environment and the organisms that live there. Heavy metals can be toxic to aquatic life, including fish and crustaceans, and can cause a variety of negative effects such as reduced growth, reproduction, and survival of biodiversity including mangrove plant.

The content of Cu and Zn found in soil may come from natural sources, such as weathering of rocks, but are increasing from anthropogenic sources, such as effluents, boating activities, domestic garbage dumps, agricultural runoff, mining activities and sewage treatment plant (Kamaruzzaman et al., 2011). Overall, the order of heavy metal concentration in these studies were as follows: Zn > Cu. The S2 sample had the highest content of Zn and Cd Figure 3a and 3b. The S2 sample was taken nearest the industrial factory at the area at 3°57.02'N in latitudes and 103°21.47'E in longitudes. By hypothesis, this industrial factory can be the main reason of pollution in the mangrove sediment.

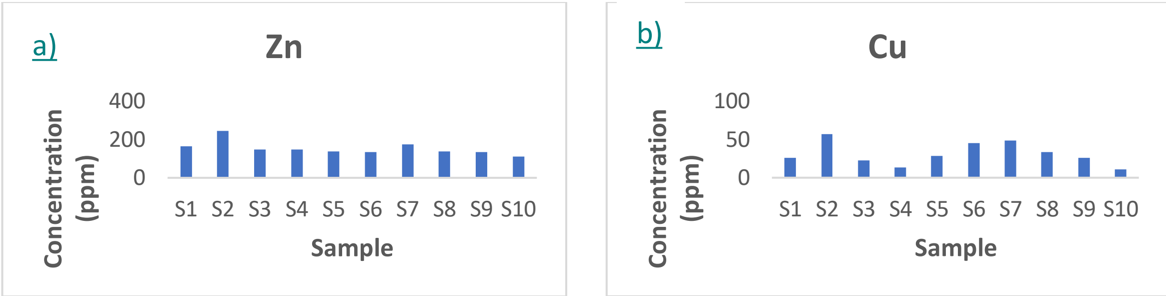

Figure 3: Distribution of a) Zn and b) Cu in the river sediment of Balok mangrove forest, Kuantan.

The content of Cu and Zn were compared to the concentration of other studies (Table 1) (Udechukwu et al., 2015; EL Turk et al 2018; Kamaruzzaman et al., 2011) and with average continental shale (Turekian and Wedepohl., 1961). The highest Zn value was also observed in S2 (245.4 ppm), whilst the lowest value was identified in S8 at 137.25 ppm. The average concentration of Zn obtained in this study was 152.985 ± 36.93 ppm. Basically, the concentration of Zn in present study were found lower compared to Sg. Puloh mangrove estuary, Selangor (Udechukwu et al., 2015) but higher than in Mangrove Forest of Kuala Selangor estuary (ELTurk et al., 2018). The result from recent study was also higher than standard quality guidelines, average continental shale (Turekian and Wedepohl., 1961), which is 95 ppm. The concentration of Cu in present study were found lower compared to Tanjung Lumpur Mangrove, Kuantan. (Kamaruzzaman et al., 2011) and Sg. Puloh mangrove estuary, Selangor (Udechukwu et al., 2015). The recent study was lower than standard quality guidelines, average continental shale, which is 45 ppm (Turekian and Wedepohl., 1961).

In this study, Cu content in the Sungai Balok mangrove, Kuantan, Pahang are still not excessive safe and not in the scale of polluted the water in Sungai Balok mangrove. In high amount, Cu may affect and pollute the environment, but Cu is one of eight essential plant micronutrients. Copper is required for physiological activities in plants and especially for chlorophylls and seeds production (Rehman et al., 2019).

Table 1: Comparison of Zn and Cu concentration with other mangrove areas.

Research study	**Zn mean concentration (ppm)**	**Cu mean concentration (ppm)**	**Research area**
Present study	152.985 ± 36.93	31.125 ± 15	Sungai Balok mangrove, Kuantan
Udechukwu et al., 2015	1023.68 ± 762.93	50.17 ± 5.84	Sg. Puloh mangrove estuary, Selangor.
EL Turk et al., 2018	28.84 ± 6.96	46.89 ± 43.79	Mangrove Forest of Kuala Selangor estuary
Turekian & Wedepohl., 1961	95	45	Average continental shale

3.3 Sediments content of K, Ca and Mg

Figure 2 illustrates the concentration of K, Ca and Mg in Sungai Balok Mangrove sediment. The highest value of Ca was observed in S2 at 608.85 ppm, whilst the lowest value was identified in S10 at 50.325 ppm. The mean concentration of Ca obtained was 239.1 ± 147.04 ppm. Whilst, the highest value of K and Mg were also observed in S2 at 521.95 ppm and 1388.75 ppm, respectively whilstand the lowest value was foundidentified in S6 at 19.25 ppm and S10 at 84.7 ppm. The mean concentration were 176.891 ± 178.76 ppm for K and was 587.9 ppm ± 326.87 for Mg.

Comparison of mean concentration of K, Ca and Mg found in this study with other documented mangrove sediments were shown in Table 2. the concentration of K in present study was found to be higher than that of Tumpat Mangrove Swamp Forest, Kelantan (Salam et al., 2018) and lower compared to Sundarban mangrove, West Bengal. India (Bakshi et al., 2017) and mangrove estuary of the Sao Mateus River, Brazil (Bernini et al., 2010).

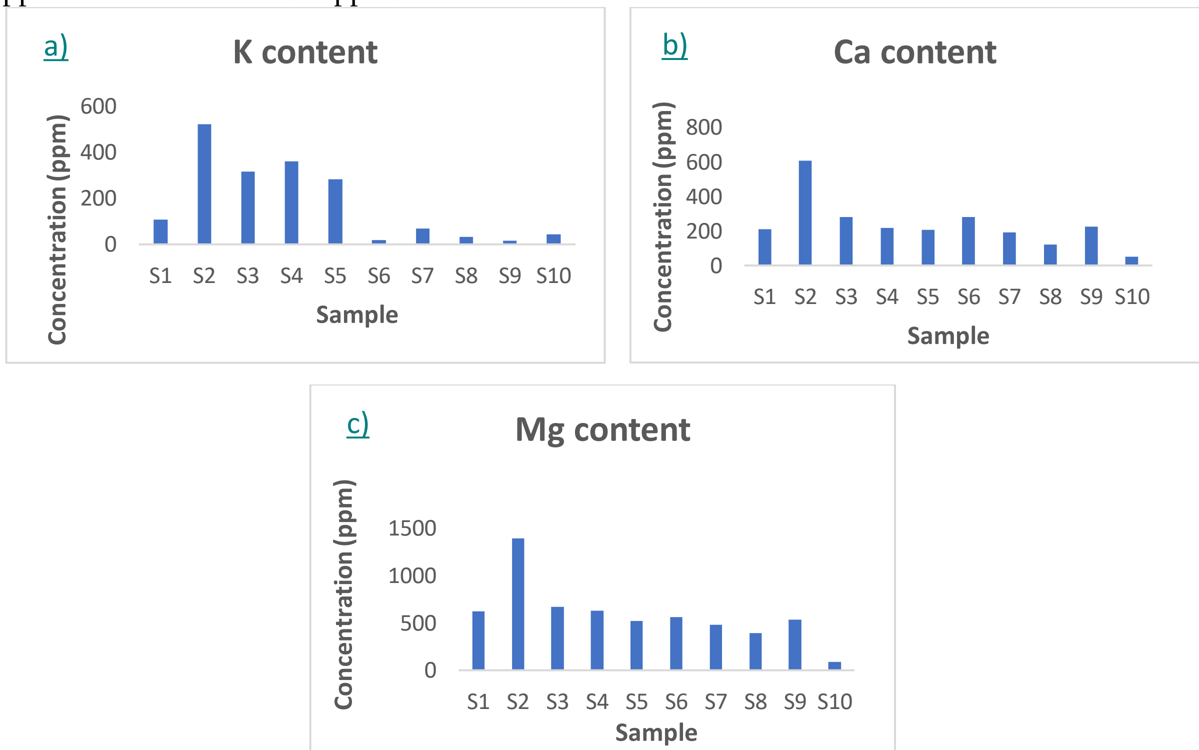

Figure 4: Distribution of a) K, b) Ca and c) Mg in the river sediment of Balok mangrove forest, Kuantan.

Table 2: Comparison of Ca, Mg, and K concentration with other mangrove areas.				
Research study	**Ca mean concentration (ppm)**	**Mg mean concentration (ppm)**	**K mean concentration (ppm)**	**Research area**
Present study	**239.1 ± 147.04**	**587.9 ± 326.87**	**176.891 ± 178.76**	**Sungai Balok mangrove, Kuantan**
Salam et al., 2018	83.15 ± 11.78	57.92 ± 11.2	50.61 ± 10.58	Tumpat mangrove swamp forest, Kelantan
Bakshi et al., 2017	15,611.2 ± 442.78	203.42 ± 44.2	25,705 ± 1142.78	Sundarban mangrove, West Bengal. India
Bernini et al., 2010	2016.67 ± 322.42	2933.4 ± 432.42	643.4 ± 32.42	Mangrove estuary of the Sao Mateus River, Brazil

The concentration of Ca in present study were found higher value than in Tumpat mangrove swamp forest, Kelantan (Salam et al., 2018). However, the result from this study was and lower compared to few other places such as in Sundarban mangrove, West Bengal, India (Bakshi et al., 2017) and Mangrove estuary of the Sao Mateus River, Brazil (Bernini et al., 2010). Calcium is a nutrient element that is important for the growth and development of many organisms, including those found in mangrove ecosystems. In this study, Ca content in the Sungai Balok Mangrove, Kuantan, Pahang are considered quite high. This might be due to high number of gastropod species which commonly known as particularly snails and slugs (Salam et al., 2018), and from the animals or other crustaceans such as crabs and prawns. Those animals have shells which made up by calcium carbonate, thus, increased the Ca content might deposit in the sediment during the decomposition of the shell.

Comparison of mean concentration of Mg found in this study was found to be higher compared to other documented mangrove sediments such as Sungai Kerteh Mangrove area, Terengganu (Hasrizal et al., 2020) and Tumpat Mangrove Swamp Forest, Kelantan (Salam et al., 2018). However, the value was lower than in Mangrove estuary of the Sao Mateus River, Brazil (Bernini et al., 2010).

The Mg content river sediment of Balok mangrove forest, Kuantan can be considered higher than other studies . Magnesium is a natural element normally found in mangrove sediment and important in ensuring optimal primary and secondary productivity of the marine and brackish ecosystems (Essien et al., 2009). However, excessive amounts of Mg can change the chemistry of the sediment, making it less favourable for the growth of certain microorganisms and plants, and can also affect the pH of the water which can in turn affect the survival and growth of other organisms. In figure 4C, S2 have highest Mg content. The S2 was located nearer to the industrial factory at 3°57.02'N latitudes and 103°21.47'E longitudes. Industrial factory could be the main reason of the significant difference of Mg content in S2 compared to other samples in the Sungai Balok mangrove sediment.

The concentration of K in present study were higher than in Tumpat Mangrove Swamp Forest, Kelantan (Salam et al., 2018) and lower compared to Sundarban mangrove, West Bengal. India (Bakshi et al., 2017) and mangrove estuary of the Sao Mateus River, Brazil (Bernini et al., 2010). In this study, K content in the Sungai Balok Mangrove, Kuantan, Pahang are considered normal in mangrove area as the mangrove provide a mechanism for trapping sediment, thus it is believed to be an important sink of suspended sediment including K content (Kathiresan, 2003).

3.4 Correlation analysis between pH, TOC, Zn, Cu, Ca, Mg, and K

The selected heavy metals, Zn and Cu, have a positive correlation with soil pH of the river sediment of Balok mangrove forest, Kuantan as in Figure 5. The correlation indicates that the increasing of Cu and Zn in soil sediments are affected by the increasing soil pH. The soil pH can directly or indirectly affect the concentration on heavy metals in soil sediments (Mustafa et al., 2020). Heavy metals are easily mobile in an acidic condition compared to alkaline as increasing in soil pH diminish the heavy metals solubility (Kazlauskaitė et al., 2014). Zn have moderate correlation (R^2=0.53) while Cu have weak correlation (R^2 = 0.16) with the increased pH levels. The selected nutrient element, Ca, Mg and K, have a positive correlation between soil pH in of Sungai Balok mangrove sediments.

The correlation indicates that the increasing of Ca, Mg and K in soil sediments are affected by increasing soil pH because at higher pH levels, the nutrient elements in the soil can attract and hold nutrients in the ionic forms at CEC site, which can be more readily available for plant uptake. Selected nutrient, Ca, Mg and K also are in the form of base or alkaline, thus, increase the pH of soil sediment. The strong correlation of element and pH are only in K element (R^2 = 0.7827), while other elements have moderate correlation with the pH levels (Ca; R^2 = 0.6502, Mg; R^2 = 0.6432).

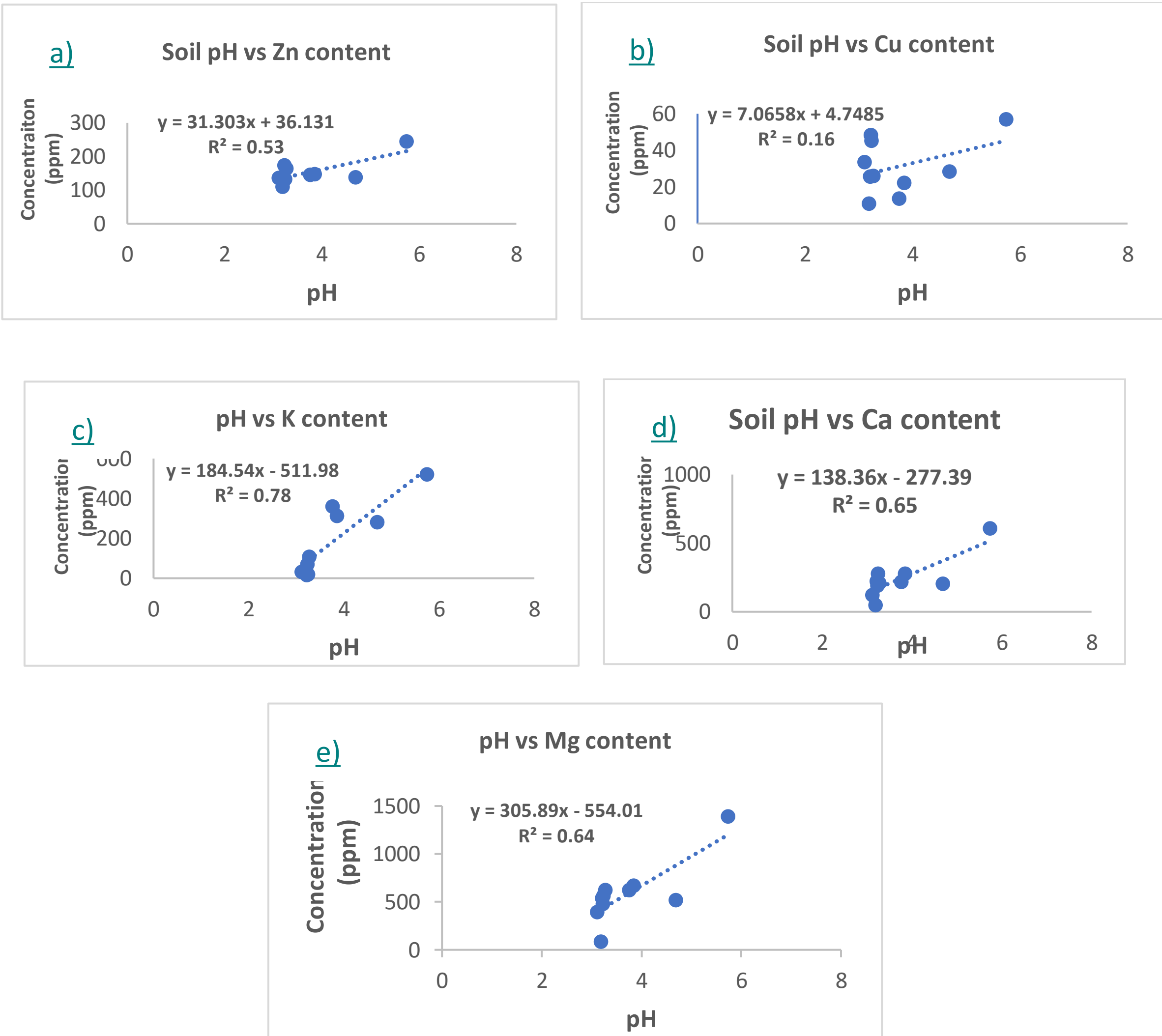

Figure 5: Correlation of soil pH with the content of K, Ca,Mg, Cu and Zn in the river sediment of Balok mangrove forest, Kuantan.

The selected heavy metals, Zn and Cu, showed a positive correlation between soil TOC in the river of Balok mangrove forest, Kuantan as shown in Figure 6d and 6e. The correlation indicates that the increasing of Cu and Zn in soil sediments were affected by the increase of soil TOC. The soil TOC can directly or indirectly affect the concentration on heavy metals in term of ion exchange, adsorption, precipitation, and complexation, which occur when TOC binds to heavy metals in the sediment (Yuan et al., 2004). The Zn (R^2= 0.40) and Cu (R^2 = 0.28) have moderate correlation with the soil TOC.

The selected nutrient element, Ca, Mg and K, also showed a positive correlation with soil TOC in mangrove sediments of Sungai Balok as shown in Figure 4a to 4c. The correlation indicates that the increasing of Ca, Mg and K in soil sediments are affected by the presence of increasing soil TOC. However, nutrients element (Ca; R^2 = 0.24, Mg; R^2 = 0.24 and K; R^2 = 0.01) showed a weak correlation to soil TOC.

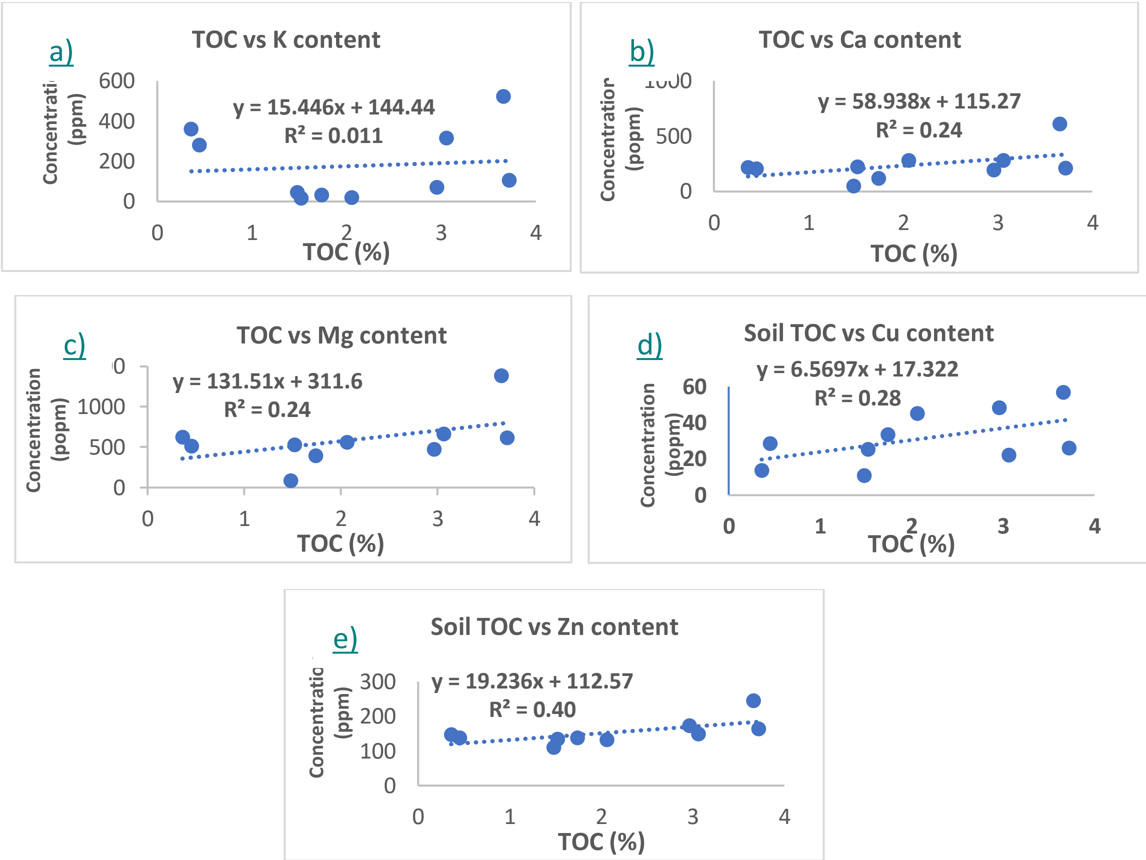

Figure 6: Correlation of soil TOC and the content of K, Ca,Mg, Cu and Zn in the river sediment of Balok mangrove forest, Kuantan.

3.5 Pollution Assessment of Selected Heavy Metals Using the Geoaccumulation Index (I_{geo})

Geochemical index (I_{geo}) was originally stated by Muller (1969) in order to determine and define metal contamination in sediments by comparing current concentrations with preindustrial levels (Nowrouzi et al., 2014). In this study, the pollution assessment of Cu and Zn was determined using the geoaccumulation index (I_{geo} to assess metal contamination in soils by comparing with the average continental shale (Turekian and Wedepohl., 1961).

The I_{geo} can range from negative values (indicating that the element is less concentrated in the sediment of interest than in the reference sediment) to positive values (indicating that the element is more concentrated in the sediment of interest than in the reference sediment (Figure 7). Hypothetically, the higher the I_{geo} value, the higher the level of pollution. The average I_{geo} of Zn (0.07 ± 0.31) showed a positive value while Cu (-1.29 ± 0.76) showed a negative value. This indicate that Cu in the study area were categorized as uncontaminated, while Zn were in category 1, range from uncontaminated to moderately contaminated.

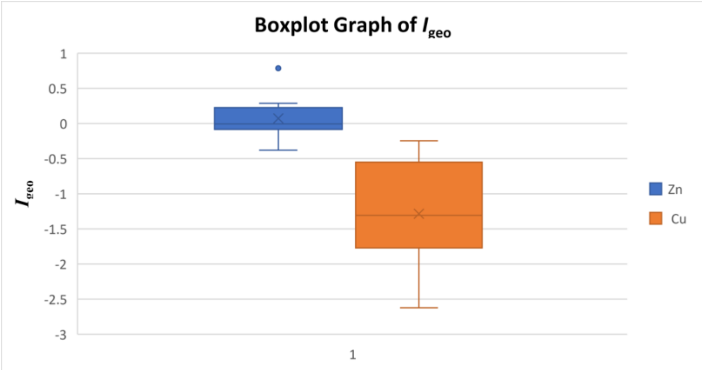

Figure 7: Boxplot of I_{geo} of Zn and Cu in the river sediment of Balok mangrove forest, Kuantan.

4. CONCLUSION

The status of selected heavy metals and nutrients element distribution in mangrove Sungai Balok, Kuantan, Pahang was evaluated by investigating the total metal and nutrient concentration in soil sediments. Generally, for heavy metals element, the concentration of Pb was not detected while the other elements that were recorded to have highest content was Zn followed by Cu in soil sediments. For nutrient element, the highest element content in sediment was Mg > Ca > K. The soil pH of Sungai Balok, Kuantan, Pahang mangrove were classified as acidic, that may affect the balance of available nutrients in the soil and could bring adverse effects on the biodiversity in the mangrove ecosystem. In addition, heavy metals, (Zn and Cu) and nutrient elements (K, Ca, Mg) have shown positive correlations with soil pH, with K element having the strongestcorrelation against pH levels. Heavy metals element, (Zn, Cu) and nutrient element (K, Ca, Mg) also have a positive correlation with soil TOC. Overall, there are also weak correlation of element with pH (Cu; $R^2 = 0.16$) and with TOC (Ca; $R^2 = 0.24$, Mg; $R^2 = 0.24$ and K; $R2^2 = 0.011$). This implies that those elements were not mainly influenced by soil pH and TOC but may also relates with a higher anthropogenic activities and natural process as had been discussed. For the pollution assessment, the sediments in Sungai Balok mangrove were uncontaminated by the Cu elements while for the Zn, the sediment is slightly contaminated.

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