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To cite this article: Abdul Hafidz Yusoff *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **596** 012053

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240th ECS Meeting ORLANDO, FL

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Abstract submission due: April 9

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Heavy Metals Accumulation in River Water and Sediment Core at Kelantan River Tributaries of Gua Musang, Kelantan

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Abstract. Several rivers around Gua Musang had been suspected as polluted area due to waste discharge from ore mining and palm oil factories located near the rivers. However, more evidence is needed to support the statement. Therefore, this study had been carried out to determine the water quality of Aring, Lebir and Relai Rivers at Gua Musang, Kelantan via its physiochemical parameters. Elemental concentrations of Fe, Al, Mn, Zn and Pb were determined in both water samples and sediment cores collected from Aring, Lebir and Relai Rivers to evaluate the accumulation trend of the heavy metal. The pollution level of heavy metals in Aring, Lebir and Relai Rivers were then investigated by using geo-accumulation index. The heavy metals of sediment were analysed by Atomic Absorption Spectrometer (AAS) after being digested by an acid mixture of HNO₃/HCL (1:3; v/v). This study shows that Aring, Lebir and Relai Rivers need to treated before direct consumption. The horizontal spatial distribution of heavy metals in water and sediment suggests that the rivers were contaminated with Mn, Fe, Al and Zn. Although Aring Rivers shows the highest concentration of Mn in both water and surface sediment, the inconsistent trend of vertical profiling of heavy metals through sediment cores shows Lebir River has the highest Fe, Pb, Zn and Al geoaccumulation while Relai River has the highest Mn geoaccumulation.

1. Introduction

Although it has been confirmed by the Malaysian Health Ministry that the death of 16 indigenous people or Orang Asli of Batek tribe in Kampung Kuala Koh, Kelantan in May and June of 2019 related to the highly contagious infectious measles disease and heavy metal poisoning was not the cause of death [1], it has become an alarming sign for the whole society to aware the detrimental effect of river pollution due to anthropogenic activities along the rapid trend of industrialization. The substantial amount of heavy metals discharges from different types of human activities can enter water systems either directly through wastewater discharge or indirectly through rainfall and atmospheric deposition [2]. Heavy metals are dangerous due to its indestructibility; tendency to accumulate in water column, sediment, and aquatic organisms which leads to the most persistent pollution in the aquatic system [3]. River sediments are the matrices of minerals settled on the river bed after being disintegrated from rock through weathering and erosion and sometimes can contain organic debris. Other than the natural metal constituent of the mineral chemical compound, metals can adsorb on the sediment matrices through physical and chemical mechanisms.

The second longest river of the Peninsular Malaysia, Kelantan River is confluence of two tributaries Lebir and Galas Rivers, serves a catchment area of around 12,000 km² and supports the state domestics,



agricultural, fishing and mining industries yet it was and is still being polluted by logging, mining and other industrial activities [4, 5]. This study was thus carried out to study the water quality of Aring, Lebir and Relai Rivers at Gua Musang, Kelantan by assessing physical parameter (dissolved oxygen) and concentration of heavy metals such as iron (Fe), aluminium (Al), manganese (Mn), zinc (Zn) and lead (Pb); to determine the vertical profile of heavy metals in sediment core from Aring, Lebir and Relai Rivers at Gua Musang, Kelantan; and to investigate the pollution level of heavy metals from Aring, Lebir and Relai Rivers by using geo-accumulation index (Igeo).

2. Methodology

2.1 Sampling

Three set of water and sediment core samples were collected in July 2019 at one locality in each main tributaries of Kelantan River in Gua Musang, namely Aring, Lebir and Relai Rivers as shown in Table 1 and Figure 1. Water samples were collected by immersing the rinsed polyethylene bottles in the river and added 0.5 M of nitric acid to avoid adhesion of heavy metals in the bottle. Whereas, sediment cores were collected using gravity type sediment corer and each of them were sliced at 3 centimeter- interval, stored in zipper bag before lab analysis.

Table 1. Coordinates of Sampling Localities

	Latitude	Longitude
Aring River	5° 0' 43.2576" N	102° 23' 1.8708" E
Lebir River	5° 2' 26.556" N	102° 23' 8.0376" E
Relai River	5° 0' 4.248" N	102° 19' 52.5504" E

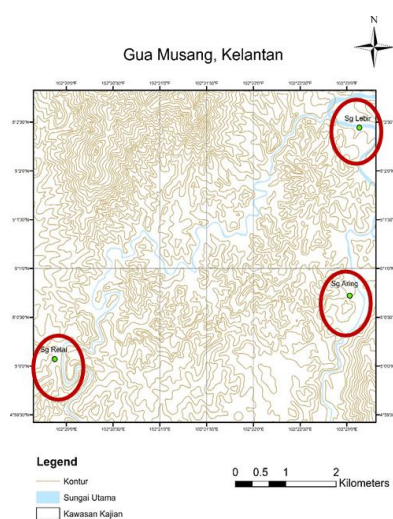


Figure 1. Map of Sampling Localities in Gua Musang, Kelantan. Note that the green dots in red circles are the sampling localities.

2.2 Physiochemical Analysis of Water

Physiochemical properties of water were tested in situ by YSI multiparameter, turbidity parameter and pH meter. In this paper, only dissolved oxygen result is shown. For water quality, the result was compared with National Water Quality Standards (NWQS) for Malaysia.

2.3 Sediment Digestion

Sediment samples were dried at 100° C for 24 hours. 1.0 g of each dried sediment sample was placed in the beaker and digested by acid mixture of 20 mL of 8 M aqua regia (nitric acid: hydrochloric acid; 1:3; v/v), while being heated on the hot plate for 45 minutes with watch glass cover to avoid the mixture evaporation and continue heating for another 45 minutes without being covered [6]. The cooled to room temperature digested samples were filtered through filter paper and 0.45 µm syringe filter. The filtrates

were then heated to near dryness and allowed to cool before 50 mL of 0.5 M nitric acid was added [7]. Then, it was transferred to 50 mL of polyethylene bottle (stock sample) 15 mL from the stock sample was transferred into 15 mL falcon tube. 1.5 mL of sample was transferred into 13.5 mL of deionized water and shook to mix well. The dilution of sample was done until $\times 10^{-4}$.

2.4 Heavy Metal Analysis

Atomic Absorption Spectrophotometer (AAS) was used to determine the concentration of heavy metals in both digested sediment sample and water sample. Water sample with addition of 0.5 M nitric acid was also tri-diluted prior to the heavy metal testing. Concentration of heavy metals in both water and vertical profile of sediment cores at the depth between 0- 33 cm were compared with World Health Organization (WHO).

2.5 Geo-Accumulation Index

Geo-accumulation index or I_{geo} was used to measure the presence and intensity of anthropogenic pollutants deposition in sediment [8]. $I_{geo} = \log_2[C_n/1.5B_n]$ where C_n is the elemental concentration; B_n is the world surface rock average geochemical background value; 1.5 is the possible background data relationship due to lithogenic effect.

3. Results

3.1 Dissolved Oxygen

Dissolved oxygen is oxygen that is dissolved in water and expressed as milligrams per litre (mg/L). It has significant effects on the biological activities in water.

Figure 2 shows the result of physical parameter that being analysed in this study compared with National Water Quality Standard for Malaysia. Lebir River shows the lowest of dissolved oxygen with 5.1 mg/L and Aring River shows the highest of dissolved oxygen with 5.8 mg/L. According to NWQS for Malaysia, all the three rivers were categorized under class II which conventional treatment required for water supply. This is probably due to its location at the upstream and the nearest with ore and palm oil factory. Moreover, Kelantan River is polluted since 1990s due to suspended solids from the logging activities upstream and sand mining activities along the river [9]. All of these activities can cause soil erosion and weathering of sedimentary rocks that contain high heavy metals and flow into the nearby rivers [4]. All of the three has lower dissolved oxygen probably due to over fertilization by run-off from rubber and palm oil plantation nearby that might contain phosphates and nitrates.

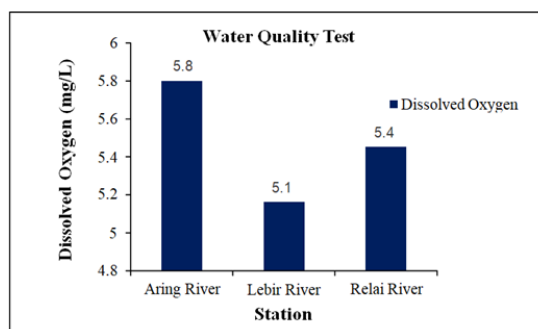


Figure 2. Dissolved Oxygen at Aring, Lebir and Relai Rivers

3.2 Heavy Metals in River Water

Heavy metals are naturally occurring in the environment but they increase due to natural and anthropogenic activities. The presence of heavy metal in the aquatic environment is a major concern due to its toxicity as they tend to accumulate for a long time in water, aquatic organisms and sediments. The heavy metals that been analysed in this study are Fe, Al, Mn, Pb and Zn at Aring, Lebir and Relai Rivers from Gua Musang, Kelantan as shown in Figure 3.

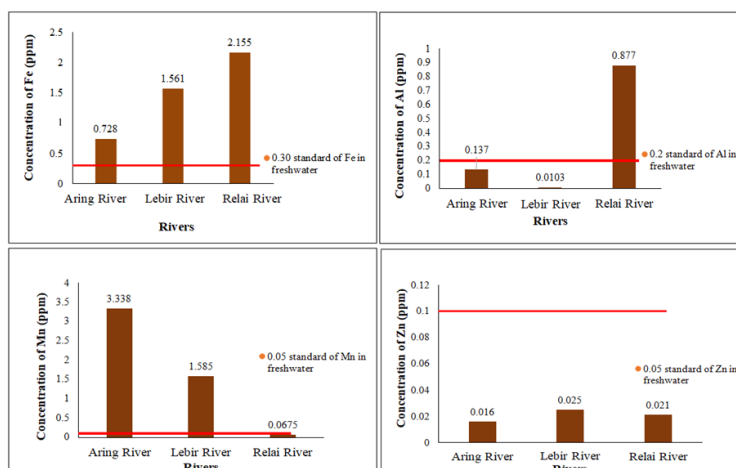


Figure 3. Concentration of Fe, Al, Mn and Zn in river water with the permissible limits of WHO standards.

Iron (Fe) is relatively rich in the earth's crust and Fe is commonly in igneous and sedimentary rocks. Igneous rocks are formed through the cooling and solidification of magma or lava meanwhile sedimentary rocks formed by the deposition of material at the Earth's surface and within bodies of water. Concentration of Fe in ascending order: Aring River (0.728 ppm) < Lebir River (1.561 ppm) < Relai River (2.155 ppm). According to WHO standard, all the three rivers exceed the permissible limit of 0.30 ppm Fe in freshwater which shows that all the three rivers were contaminated with Fe. Aluminium is the second abundant metals in sedimentary rocks. Bauxite is one of the sedimentary rocks that contain major source of aluminium. Concentration of Al in ascending order: Lebir River (0.0103 ppm) < Aring River (0.137 ppm) < Relai River (0.877 ppm). According to WHO standard, Relai River is the only that exceed the permissible limit of 0.2 ppm Al in freshwater.

Manganese is one of the most abundant metals in soils. It occurs as oxides and hydroxides and cycles through its various oxidation states. Concentration of Mn in ascending order: Relai River (0.0675 ppm) < Lebir River (1.585 ppm) < Aring River (3.338 ppm). All of the three rivers exceed WHO standard of 0.05 ppm Mn in freshwater which may relate to the nearby manganese mine sites. Zinc is naturally present in water. Aring, Lebir and Relai Rivers showed slightly different of concentration of Zn in freshwater and do not exceed the WHO standard of 0.05 ppm. Concentration of Zn in ascending order: Aring River (0.016 ppm) < Relai River (0.021 ppm) < Lebir River (0.025 ppm). Element lead, Pb in Aring, Lebir and Relai Rivers cannot be detected using AAS probably due to its low sensitivity.

3.3 Horizontal Spatial Distribution of Heavy Metals in Sediment Cores

Apart from accumulating in water, heavy metals such as Fe, Al, Mn, Zn and Pb also accumulate in sediments as shown in Figure 4. Concentration of Fe in ascending order: Lebir River (40.13%) < Aring River (40.42%) < Relai River (40.66%). All the three rivers exceed the permissible limit of WHO/EU standard of 5%. Concentration of Al in ascending order: Aring River (9.24%) < Lebir River (10.93%) < Relai River (12.23%). All the three rivers did not exceed the permissible limit of WHO/EU standard of 30%.

Concentration of Mn in ascending order: Relai River (0.42%) < Lebir River (16.98%) < Aring River (19.86%). All the three rivers exceed the permissible limit of WHO/EU standard of 0.2%. Concentration of Zn in ascending order: Relai River (259.49 ppm) < Lebir River (517.99 ppm) < Aring River (658.85 ppm). Aring River and Lebir River exceed the permissible limit of WHO/EU standard of 300ppm, meanwhile Relai River did not exceed the permissible limit of WHO/EU standard. Concentration of Pb in ascending order: Lebir River (25.78 ppm) < Relai River (27.39 ppm) < Aring River (36.27 ppm). All the three rivers did not exceed the permissible limit of WHO/EU standard of 100 ppm. Generally, all the elemental concentration in surface sediment conform with their concentrations in water except Zn which may due to its low dissolvability.

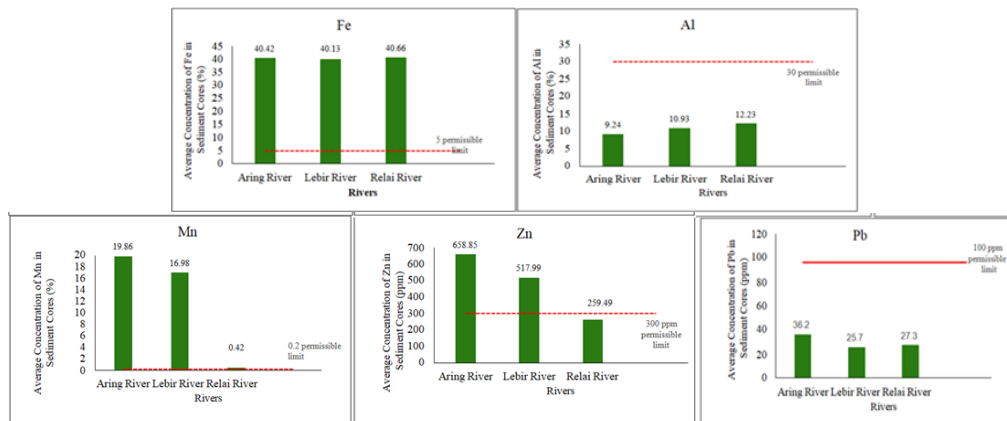


Figure 4. Concentration of Fe, Al, Mn, Zn and Pb in sediment with the permissible limits of WHO/EU standards.

3.4 Vertical Profile of Heavy Metals in Sediment Cores

As shown in Figure 5a, the lowest concentration of Fe acquired at Aring River was 30.87% and the highest concentration of Fe was 49.64% with average 40.42%; the lowest concentration of Fe acquired in Lebir River was 26.23% and the highest concentration was 54.69%, at the bottom of core, averaging concentration was 40.13%. The lowest concentration of Fe acquired in Relai River was 37.18% and the highest concentration was 49.82%, averaging concentration 40.66%. Based on the Figure 5b, the lowest concentration of Mn acquired at Aring River was 15.82% and the highest concentration of Mn was 24.83% with average 19.87%. Meanwhile, the lowest concentration of Mn acquired in Lebir River was 11.75% and the highest concentration was 22.31%, at the bottom of core, averaging concentration was 16.99%. The lowest concentration of Mn acquired in Relai River was 0.29% and the highest concentration was 50.74%, averaging concentration 0.43%.

Based on the Figure 5c, the lowest concentration of Pb acquired at Aring River was 28.65 ppm and the highest concentration of Pb was 51.95 ppm with average 36.27 ppm. The lowest concentration of Pb acquired in Lebir River was 17.3 ppm and the highest concentration was 29.55 ppm, averaging concentration was 25.78 ppm. The lowest concentration of Pb acquired in Relai River was 21.9 ppm and the highest concentration was 52.05 ppm, averaging concentration 27.39 ppm. Based on the Figure 5d, the lowest concentration of Zn acquired at Aring River was 490.85 ppm and the highest concentration of Zn was 984.35 ppm with average 658.85 ppm. Meanwhile, the lowest concentration of Zn acquired in Lebir River was 312.85 ppm and the highest concentration was 693.85 ppm, averaging concentration was 517.99 ppm. The lowest concentration of Zn acquired in Relai River was 173.35 ppm and the highest concentration was 622.35 ppm, averaging concentration 259.49 ppm. Based on the Figure 5 e) below, the lowest concentration of Al acquired at Aring River was 6.98 ppm and the highest concentration of Al was 11.11 ppm with average 9.24 ppm. Meanwhile, the lowest concentration of Al acquired in Lebir River was 7.65 ppm and the highest concentration was 13.35 ppm, averaging concentration was 10.93 ppm. The lowest concentration of Al acquired in Relai River was 9.58 ppm and the highest concentration was 14.32 ppm, averaging concentration 12.23 ppm.

Most of the profile of heavy metals as shown in Figure 5 showed inconsistent trends from the upper to the lowest depth probably influences by some factors. Some of the heavy metals such as Zn have high concentration at the upper surface and decreased with the depth. This is probably due to influences of the increasing discharge from the ore mining factory nearby. The sudden increase of heavy metals such as Fe and Pb were most probably caused by other events such as absorptions of particulates during immobilization and resuspension from the surface sediment. The high concentration of heavy metals and irregular trends in sediment cores probably also influences by big flood occurred in December 2014 because of mixing or suspension process. Flood contains high suspended solids and it mixed with suspended solid that naturally occurred in the rivers and sedimentation. During flood, there were two underlying processes; first, the content of the well. Second, as the flood moved downstream it washed out dissolved and suspended materials along its flow path. Gradually, the flood water was enriched with dissolved solutes and suspended sediment until it approached the densely populated estuary.

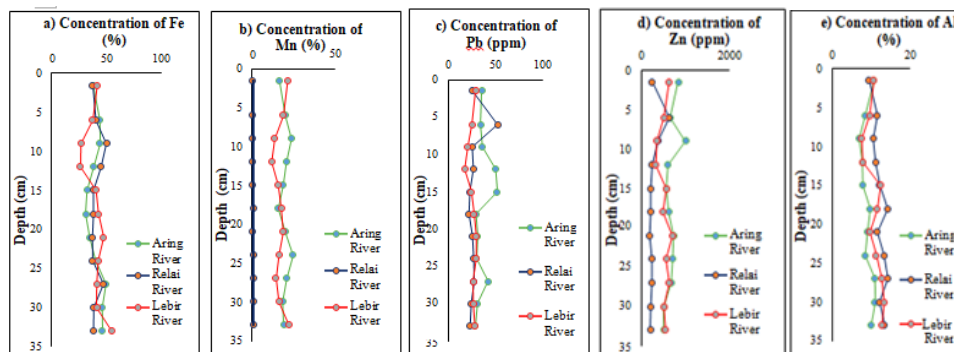


Figure 5. Vertical profile of Fe, Mn, Pb, Zn and Al of Aring, Relai and Lebir Rivers sediment.

3.5 Geoaccumulation Index (I_{geo})

Based on the Figure 6a), the highest geoaccumulation index of Fe was Lebir River with average -0.00154 and the lowest geoaccumulation index of Fe was Relai River with average -0.46322. The average geoaccumulation index of Fe at Aring River was -0.21239. Meanwhile, according to Figure 6b), the highest geoaccumulation index of Mn was Relai River with average -0.07749 and the lowest geoaccumulation index of Mn was Aring River with average -0.26858. The average geoaccumulation index of Mn at Lebir In Figure 6c), the highest geoaccumulation index of Pb was Lebir River with average -0.026194 and the lowest geoaccumulation index of Pb was Relai River with average -0.30483. The average geoaccumulation index of Pb at Aring River was -0.27546. And from the Figure 6d), the highest geoaccumulation index of Zn was Lebir River with average 0.10652 and the lowest geoaccumulation index of Zn was Relai River with average -0.212382. The average geoaccumulation index of Zn at Aring River was -0.18975. Based on the Figure 6e), the highest geoaccumulation index of Al was Lebir River with average -0.09405 and the lowest geoaccumulation index of Al was Relai River with average -0.24335. The average geoaccumulation index of Al at Aring River was -0.19527.

All values of geoaccumulation index showed uncontaminated degree due to the value is < 0 except for geoaccumulation of Zn at Lebir River. Its value > 0 showed that uncontaminated to moderately contaminated. Based on the previous study, I_{geo} results for Mn (-1.89), Pb (-0.57) and Zn (-1.98) at Kelantan River also showed that the sediments were still uncontaminated [7-8]. The changes values of I_{geo} at Kelantan River indicate that the river become more polluted as the day pass.

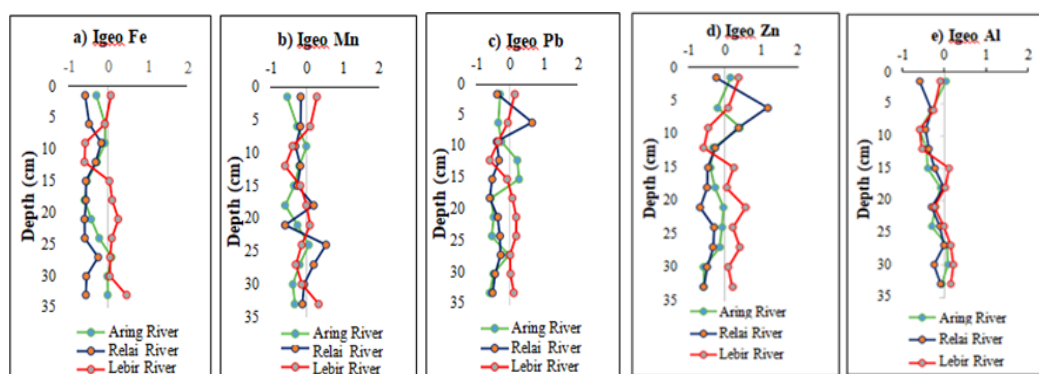


Figure 6. Geo-accumulation Index a) I_{geo} Fe, b) I_{geo} Mn, c) I_{geo} Pb, d) I_{geo} Zn and e) I_{geo} Al at Aring, Lebir and Relai River

4. Conclusions

In conclusion, the dissolved oxygen and concentration of Mn, Fe and Al of Aring, Lebir and Relai River water shows they need to be treated before direct consumption. The horizontal spatial distribution of

heavy metals in surface sediment suggested that the rivers were contaminated with Mn, Fe and Zn as the values were exceeding the WHO and National Water Quality Standard. Aring Rivers shows the highest concentration of Mn in both water and surface sediment. While, the vertical profile of heavy metals in sediment cores from Aring, Lebir and Relai Rivers showed inconsistent trends that suggested due to anthropogenic and natural sources. Vertically, the geoaccumulation indices of Fe, Pb, Zn and Al were highest at Lebir River while the highest geoaccumulation of Mn were at Relai River.

Acknowledgement

Thanks to Universiti Malaysia Kelantan for supporting this project by providing two grants with code number R/SGJP/A13.00/01684A/003/2019/00610 and R/SGJP/A1300/01684A/004/2019/00682.

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