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The Pollution Characteristics of Harmful Heavy Metal in Surface Sediment of Sepang River, Malaysia

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Abstract The presence of heavy metal in environment is commonly associated with environmental pollution, which requires monitoring. Human activities have caused a tremendous increase in heavy metal pollution in aquatic environment that includes mangroves, rivers, estuaries, and coastal wetlands. With that, it is critical to assess environmental and health impacts of pollution in Sepang River. In this study, the presence of heavy metal in the mangrove sediment from Sepang River was detected. The concentrations of As, Mn, Zn, Cr, Fe and Co in the sediment were measured using instrumental neutron activation analysis (INAA). It is found that the concentration of As was determined to be higher than the geochemical background value of shale, across all sampling sites, while Co concentrations were observed to be the lowest. The enrichment factor (EF) and geo-accumulation index (I_{geo}) of the heavy metals were calculated. The study indicated that, both EF and I_{geo} of As, 8.09 and 1.84 respectively show severe to excessive enrichment and moderate pollution. Overall, the study suggests that heavy metal pollution in the Sepang River, particularly with respect to As, needs to be closely monitored to prevent it from becoming a major environmental and health hazard. The study also highlights the importance of using advanced analytical techniques, such as INAA, to accurately measure the concentrations of heavy metals in environmental samples.

Keywords Heavy Metal, Mangrove, Pollution, Enrichment, Geo-accumulation

1. Introduction

One of the most challenging global environmental issues is heavy metal contamination [1]. Due to the toxicity, long environmental persistence, and bioaccumulative nature, heavy metals are normally considered as pollutants. Moreover, due to the economic growth and the expansion of anthropogenic activities such as agriculture and industry, the environment is growing more polluted [2]. The influx of heavy metals into environment has led to major pollutants in the aquatic environment [3]. Aquatic environments are more likely to be polluted due to the open environmental spaces, such as rivers, estuaries, mangroves and coastal areas [4]. Heavy metal pollution in mangrove sediment is a growing concern due to the negative impacts it can have on both the mangrove ecosystem and the species that depend on it. The increase of heavy metal concentration in this environment not only affects the local organisms, but also other living things through food chain, which finally will affect the health of human population [5,6]. Furthermore, the accumulation of heavy metals in the sediment can also lead to decreased productivity and biodiversity in the mangrove ecosystem. The most common heavy metals found in mangrove sediment include lead, zinc, copper, and cadmium. These metals can have toxic effects on a variety of organisms, including fish, crustaceans, and plants.

Malaysia is a fast-developing country. Numerous multi-element studies have been carried out along Peninsular Malaysia's west coast as a result of the region's rapid economic growth and activity, as well as the population of people and agricultural land there. The trends of development in Malaysia now are obviously inducing the pollution, regardless of the air, soil or even water [7]. Chemical industries, coal conversion, and garbage burning are a few examples of environmental activities that might have dangerous effects on non-living things and living things as well. Contaminants or toxicants, such as heavy metals, typically pose a major danger to the health and structure of the entire ecosystem [8]. Furthermore, anthropogenic point and area sources connected to industrial and agricultural activity are the most prevalent sources of heavy metals.

In 2019, research on pollution in Sepang River revealed serious problems with contamination in the river that is due to human activity. This activity is also known as anthropogenic causes in leading to a variety of environmental problems. This particulate matter will end up settling and gather in the aquatic environment's surface sediment [9]. Surface sediments serve as the last resting place for all types of pollution produced by human activity [10]. Since sediment samples are able to provide valuable information about aquatic pollution, it is necessary to assess the degree of pollution of various elements using these samples. Hence, evaluation of sediment is significant because it can affect the fate, effect and movement of heavy metal. This is due to the changes in physico-chemical parameters which are known to operate as both, the source of water pollution and the sink for heavy metal [11]. The purpose of this paper is to assess the level of heavy metal contamination in Sepang River. From a globalization perspective, the assessment of pollution and sediment health in the Sepang river's sediment is important because it can impact not only the local ecosystem but also the global community. The Sepang River is in Malaysia, which is an important player in the global economy. As such, any contamination of its waterways and sediment could potentially have negative impacts on industries such as tourism and fisheries, which in turn could affect the country's economy and trade relationships with other countries.

The geo-accumulation index (Igeo) and enrichment factor (EF) are commonly used measurement tools in the assessment of pollution and sediment health. The Igeo measures the accumulation of trace metals in sediment, while the EF compares the concentration of a particular element in sediment to its concentration in the earth's crust. By using these measurement tools, scientists and policymakers can better understand the extent of pollution and contamination in the Sepang River's sediment and take appropriate actions to mitigate its impacts on both the local and global communities. In conclusion, the assessment of pollution and sediment health in the Sepang River's sediment is important from a globalization perspective as it can have far-reaching impacts beyond the local environment. The use of measurement tools such as the Igeo and EF can provide valuable insights into the extent of contamination and inform policy decisions to mitigate its impacts.

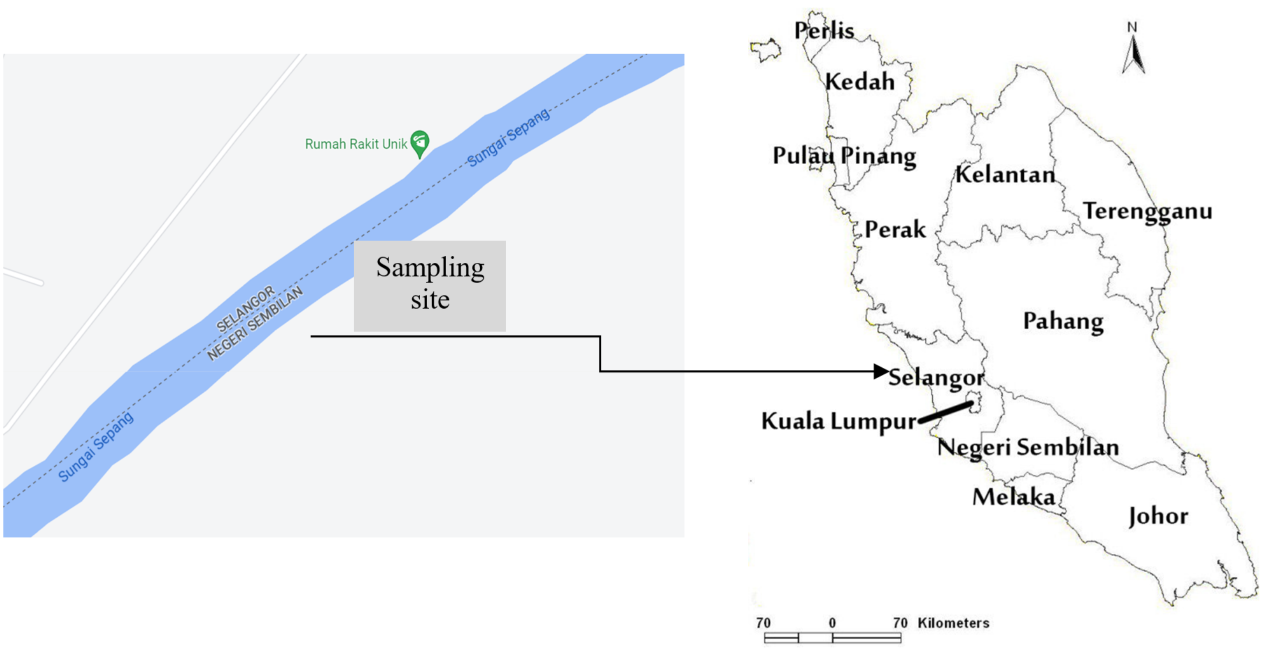

Figure 1. Map of the mangrove sampling site along the Sepang River in Selangor, Malaysia

2. Materials and Methods

Study Area and Sampling Method

Sungai Sepang or known as Sepang River, is in Sepang District of Selangor, Malaysia. It is a small river that originates in the Titiwangsa Mountains and flows through the Sepang district before emptying into the Straits of Malacca. Historically, the river played an important role in the local economy as it provided water for irrigation and was used for transportation. The river is known for its rich biodiversity, including various species of fish, birds, and plants. Figure 1 shows the map of the sampling site along the Sepang River. The river is exposed to a variety of pollution causes, mostly as a result of agriculture, aquaculture, tourism, and other factors. Table 1 states the nearby activities that can be found along the sampling station [10].

Table 1. The description of sampling sites

Nearby activities	GPS Coordinate
Pig Farm, Bukit Pelanduk	2 °39'18.6" N 101 °44'7.85" E
Sepang Fish Farm	2 °36'7.41" N 101 °42'39.4" E
Shrimp pond, Bukit Pelanduk	2 °39'35.8" N 101 °44'8.62" E

Samples of surface sediment were collected along the Sepang River on Malaysia's west coast at a depth of 3.0-5.0 cm. Four samples of surface sediment were taken from each site, scraping the top layer using a clean implement (a plastic spoon) to prevent elemental contamination. All the samples were gathered and blended for homogeneity. They were then gathered in acid-washed polyethylene bags, and all samples were sent to the lab in an icebox. To maintain dry weight and completely remove moisture, the samples from each location were baked at 80℃ for a minimum of 72 hours.

Analytical Method

The powdered samples were divided into four subsamples for both short and long radiation. All of them were irradiated at the same time in the pneumatic transport facility at the 750 kW (MINT TRIGA) research reactor with a thermal neutron flux of 4.0 x 1012 $cm^{-2}s^{-1}$. Then each sample was preserved in a sealed polyethylene vial and weighed approximately 150 mg and 200 mg. The gamma energies and half-lives of the radionuclides were used to identify them. The element concentrations were also determined using a comparable approach [12,13]. The standard reference materials SRM (SJS, SL-1 (Lake Sediment)) were used for a multi-element comparison. In order to ensure quality, these SRM and blank samples were all radioactively irradiated simultaneously at the research reactor.

After cooling for twenty and twenty-four hours, the samples were exposed to short radiation for one minute, counting for five and twenty minutes, respectively. Following that, the samples were subjected to intense radiation for six hours. The samples were counted for an hour following cooling periods of 3-4 and 21-28 days. Counting of the irradiated samples was carried out using a high-resolution HPGe detector that had been calibrated. During the process, the sample and the detector were positioned at a distance of 12 cm and 2 cm, respectively, for short and long radiation. The presence of the elements in the sample and their concentration were determined using the precise energy of delayed gamma rays. Using 133Ba, 60Co, 57Co, 137Cs, 54Mn, and 24lAm reference point sources, the performance of the gamma spectroscopy system was calibrated with an energy range of 60-2 MeV under the same geochemical conditions. Every count was done in a situation where the dead time was less than 10% [3,12].

Heavy Metal Enrichment

Different indicators, such as the enrichment factor (EF) and geo-accumulation index (Igeo) were used to evaluate the metal status of the collected sediments.

Enrichment Factor (EF)

The heavy metal enrichment factor (EF) is a measure of the degree to which the concentration of a specific heavy metal in each environment or sample has been increased relative to a reference concentration. The usual method of determining it involves comparing the amount of a particular heavy metal present in a sample with the amount of the same heavy metal found in a reference material, such as uncontaminated soil or a nearby area that is unaffected by human influence. This calculation, known as the EF, is employed to assess the significance of human-induced metal inputs. The following formula can be used to perform this evaluation [14];

$$EF_{metal} = (M_{exp}/Fe_{exp})_{sample} / (M_{ref}/Fe_{ref})_{shale}$$

The symbols used in the equation are as follows: M_{exp} represents the concentration of the element in the experimental sample, Fe_{exp} represents the concentration of iron in the sample, M_{ref} represents the concentration of the element in the average shale, and Fe_{ref} represents the concentration of iron in the average shale. Sutherland (2000) proposed that EF values can be interpreted as follows: an EF of 1 indicates no enrichment, EF values ranging from 3-5 indicate minor enrichment, EF values ranging from 5-10 indicate moderately severe enrichment, EF values ranging from 10-25 indicate severe enrichment, EF values ranging from 25-50 indicate extremely severe enrichment, and EF values greater than 50 indicate extremely severe enrichment of the sediment.

Geo-accumulation Index (Igeo)

The geo-accumulation index (Igeo), developed by Muller (1969), is a measurement of the level of heavy metal contamination in a certain area or sample. It is similar to the enrichment factor (EF), but it takes into account not only the concentration of the heavy metal in the sample, but also the background concentration of the same heavy metal in the environment. Ever since, many studies throughout the world have utilized this index to assess the status of sediment because it is simple to calculate and the results can be easily understood [15-17]. To determine the index, a calculation is performed which involves dividing the concentration of the heavy metal in the sample by the background concentration, and then multiplying the result by a factor that is dependent on the level of pollution. The equation used for this calculation is as follows:

$$Igeo = \log_2 (C_n/1.5 \text{ x } Bn)$$

By using a background matrix correction factor of 1.5, the variation impact of lithogenic effects is lessened. Muller (1969) classified the Igeo values can range from -1 to > 5. Negative values of Igeo imply that the concentration of heavy metal in the sample is lower than the background concentration, indicating no pollution, whereas values 0 ≤ Igeo ≤ 1 indicate uncontaminated to moderately contaminated, values 1 ≤ Igeo ≤ 2 show moderately contaminated, values 2 ≤ Igeo ≤ 3 indicate moderately to heavily contaminated, values 3 ≤ Igeo ≤ 4 indicate heavily contaminated, values 4 ≤ Igeo ≤ 5 show heavily to extremely contaminated and values ≥ 5 indicate extremely high levels contamination.

3. Results and Discussion

The quality and analytical procedures for the sediment were checked with standard Certified Reference Material (CRM) SJS and SL-1. As shown in Table 2, the analytical results of the standard reference material (SRM) and measured values of each element are calculated. Through applying the standard reference material (SRM) SJS and SL-1, it validates the efficacy of the results. To summarize, table 2 shows the acceptable recoveries percentage between the standard reference material and measured value which varies from 68% to 135%. According to Rouessac [18], the acceptable range of recoveries between the measured and certified value is within 70% to 120%.

Sediment collected from the Sepang River has its own level of heavy metal concentration, which is summarized in Table 3. The concentrations of As, Mn, Zn, Cr, and Co (in mg/kg) from the river were ranging 9.75 - 11.5, 109 - 1401, 48.0 - 57.0, 36.9 - 45.9, and 4.12 - 4.83 respectively. On the whole, the accumulation of heavy metal in the river sediment is in the order of Mn>Zn>Cr>As>Co. According to Ashraf [19], heavy metals including As, Cd, Cr, Cu, Ni, Pb and Zn are some of the common pollutants that bring negative effects to the mangrove area. The enrichment of these elements in the sediment can be attributed to the direct uptake of heavy metals by clay particles in the soil, which is believed to be caused by anthropogenic activities in the vicinity of the sampling site [20].

Table 2. The analysis of the standard reference material and comparison with certified values of SL-1 and SJS (mg/kg)

Element	Standard value (mg/kg)	Measured value (mg/kg)	Recovery (%)
As	10.5	9.66	92.0
Mn	529	497	94.0
Zn	103	70.1	68.1
Cr	130	94.2	72.45
Fe	33600	44700	133
Co	12.8	11.9	92.89

According to Table 3, the element with the highest mean concentration is Mn at 126 mg/kg, while the lowest mean concentration is for Co at 4.57 mg/kg. A high mean concentration of Mn can indicate that there is a high level of manganese present in that area. This can be due to natural processes or human activities such as mining, industrial processes, or agricultural practices. Nonetheless, high levels of manganese can have negative impacts on the environment and human health, particularly if the exposure is prolonged. Besides that, a low mean concentration of Co shows that there is a relatively small amount of cobalt present in that area or sample. Co is an essential mineral that is required in small amounts by humans and animals for proper growth and development [21]. To sustain healthy aquatic ecosystems, modest levels of cobalt in sediment can have major ecological effects. For this reason, they should be closely monitored and maintained.

Table 3. Level of heavy metal concentration in mangrove sediment of Sepang River (mg/kg)

Element	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)	Std dev
As	9.75	11.5	10.5	0.67
Mn	109	141	126	9.68
Zn	48.0	57.0	53.7	2.93
Cr	36.9	45.9	42.6	4.32
Co	4.12	4.83	4.57	0.21

Table 4 displays the enrichment factor (EF) values for the heavy metals present in the samples collected. Calculating the EF of each element provides an indirect means of evaluating the degree of toxicity and pollution present in the sediment. The EF study also proved that human activity causes the metal deposition in the mangrove area [10]. From the results, the EF of As (8.09) shows severe to excessive enrichment. This implies a significant pollution problem and a potential health risk to humans and animals. High levels of As can be toxic if ingested or inhaled and can cause a range of health problems, including cancer and skin lesions. As a result, it is critical to act to establish the source of the contamination and to take efforts to mitigate or eradicate the pollution.

Accumulation of heavy metal in the sediment goes through chemical and physical binding. Moreover, due to anthropogenic activities near the river, heavy metal can be gathered by the process of adsorption onto organic and inorganic particles [22]. Agriculture uses many arsenic-containing fertilizers, insecticides, including animal feed. This may penetrate the lake during precipitation through river discharge [23]. However, the EF of Mn, Zn, Cr and Co ranged from 1.50 to below, which reveals that they are low enriched and explains that the concentration of these metals in the sediment is relatively low compared to what is normal or healthy. Furthermore, low enrichment levels of heavy metals are generally considered to be less of a concern for human health and the environment than high enrichment levels.

Consequently, it's crucial to note that even low levels of heavy metal pollution can have negative impacts on the environment and human health over time, particularly if the exposure is prolonged. Some heavy metals, such as lead and mercury, are toxic even at very low concentrations and can have serious health effects [24].

Table 4. Enrichment Factor (EF) of heavy metal in mangrove sediment from Sepang Besar River

Element	Enrichment Factor (EF)
As	8.09
Mn	0.79
Zn	1.50
Cr	1.39
Co	0.71

Nevertheless, simply depending on the enrichment factor (EF) to determine the toxicity of a sediment is inadequate. According to the data presented in Table 5, Sepang River is moderately polluted with As. The positive data of the As geo-accumulation index (Igeo) shows the range between 1 and 2, specifying that it is moderately polluted. Anyhow, the readings of other elements are recorded to be below 0. This explains that the sediment collected from the Sepang River is not polluted with Mn, Zn, Cr and Co. When the Igeo of As is moderately polluted, it shows that the concentration in that area is higher than what is normal.

Anthropogenic activities are assumed to cause the contamination of As at the study area. Table 5 indicates that the use of fertilizers or insecticides containing arsenic in agricultural practices can affect the bioavailability of As in the sediment [25, 26]. As concentration in a mangrove can be high due to natural occurrences, such as the erosion of arsenic-containing minerals, or human activities, such as mining, agriculture, and industrial processes. Furthermore, poor disposal of arsenic-containing material can contribute to excessive quantities in waterways. It's indeed important to point out that large quantities of As can be harmful to people and animals, causing health concerns if consumed or breathed.

Besides that, the presence of many jetties at the river causes residues from boats and oil spills which are attributed to the greater enrichment of As and eventually the accumulation in the mangrove sediment [27]. A substantial change in mangrove forest was observed in Sepang River. The changes on the mangrove indicate a process of transformation to become mixed and second-rate mangroves. Degradation of mangrove results from the changes that occur at the river mouth of study area [3]. According to Mokhtar [28], a noticeable shift at the mangrove area influenced the features of the river causing it to be reduced and degraded.

Table 5. Geo-accumulation index (I_{geo}) of heavy metal in the sediment

Element	I_{geo}
As	1.84
Mn	-1.52
Zn	-0.580
Cr	-0.699
Co	-1.66

4. Conclusions

The study found that the Sepang River has low enrichment of heavy metals such as Mn, Zn, Cr, and Co, but is moderately polluted with As. Continuous monitoring of heavy metal levels in sediment is crucial to ensure the long-term health of mangrove ecosystems. Strategies should be implemented to reduce heavy metal emissions, restore degraded mangrove ecosystems, and monitor and manage the restoration site. The study's data can inform policymaking and management strategies to protect natural resources. The concentration and enrichment of heavy metals can be used by environmental regulatory agencies to establish guidelines and regulations for limiting the discharge of pollutants into the river. The finding that As is moderately polluted in the surface sediment of Sepang River highlights the need for targeted remediation efforts to reduce its concentration in the sediment. The EF and Igeo values can provide a basis for monitoring and managing the restoration site, and the data collected can serve as a baseline for future studies to assess changes in heavy metal concentrations in the sediment over time.

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