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Risk Assessment of Copper in Mangrove Sediments of Kuala Perlis

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ABSTRACT

Mangrove ecosystems are critical for coastal protection, carbon sequestration, and biodiversity, yet they face escalating threats from heavy metal contamination. This study assesses the ecological risk of copper (Cu) in the mangrove sediments of Kuala Perlis, Malaysia, a region that is increasingly affected by anthropogenic activities. Sediment samples from three intertidal zones, supralittoral, eulittoral, and infralittoral, were analysed for physicochemical properties and copper concentrations. The pH reading was taken using the HANNA instruments pH meter, while copper detection was conducted using the 8506 Powder Pillows Bicinchoninate method, and heavy metal analysis was performed using the HACH DR3900 Spectrophotometer. Sediments exhibited an alkaline pH (7.35), with silt and clay (50 % - 70 %) dominating the composition. Our findings demonstrated low copper levels across all zones: 0.23 ppm (Supralittoral), 0.26 ppm (Infralittoral), and 0.43 ppm (Eulittoral), and significantly below the threshold effect concentration (TEC) of 18.0 mg/kg. The Geo-accumulation Index (Igeo) and Contamination Factor (CF) both categorised the sediments as uncontaminated, indicating minimal ecological risk. However, the persistent threat of pollution demands ongoing monitoring to safeguard these vital ecosystems. This study not only highlights the current health of Kuala Perlis mangroves but also provides actionable insights for environmental management, emphasising the urgent need for proactive conservation and pollution control strategies to ensure the long-term resilience of mangrove habitats.

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1. Introduction

Mangroves, often dubbed as the "rainforests of the sea," are one of the most productive and ecologically important ecosystems on Earth. More than 50 unique species of woody plants are distributed along tropical and subtropical coastlines, and they grow freely under the pressures and are constrained by factors such as soil type, tidal fluctuations, salinity, and climate [1]. Mangroves are specially adapted to the intertidal zone, extending from the low tide mark to the high-water level during spring tides. Beyond their ecological adaptability, the ecosystem services that mangroves provide are indispensable. They serve as critical nurseries for marine life, and they support on and off-shore fisheries, including nitrogen input, while offering habitats and food sources for a diverse array of species [2]. Additionally, mangroves play a pivotal role in carbon sequestration because they store significant amounts of carbon in their biomass and sediments, making them vital in the global fight against climate change [3]. Most importantly, they act in the role of natural barriers. They thus defend coastlines from tsunamis, storm surges, and erosion, thereby, protect infrastructure along with human settlements [4].

Despite their ecological and socio-economic importance, mangrove ecosystems are threatened by anthropogenic activities, specifically heavy metal pollution. Copper (Cu), manganese (Mn), and lead (Pb), are persistently becoming environmental pollutants because they are of high toxicity, do not undergo biodegradation, and exhibit bioaccumulation [5]. These various pathways are what allow for these metals to enter mangrove ecosystems, including industrial discharge, agricultural runoff, and urban wastewater [6]. Once introduced, heavy metals accumulate in sediments, where they can persist for decades, posing long-term risks to both ecosystems and human health. As these metals infiltrate the food chain, they can disrupt plant growth, harm marine organisms, and ultimately endanger human populations that rely on these ecosystems for food and livelihoods [7]. Among these metals, copper is of particular concern. Copper exhibits poor water solubility but readily adheres to sediments, with their movement through river systems largely determined by sediment texture and organic content, leading to higher metal accumulation in intertidal zones subject to anthropogenic pressures [8,9]. Only a very low level of copper is needed to promote plant growth, but exposure to higher levels is toxic and damaging to mangroves as well as the delicate balance of coastal ecosystems [10]. In areas like Kuala Perlis, where rapid coastal development and industrialisation are taking place, the threat of copper contamination exists, especially in mangrove sediments, thus, it is important for risk assessment and mitigation on the threats [11]. Although heavy metal threats to mangrove ecosystems have been increasingly noticed, few studies have systematically examined the Cu distribution along the supralittoral, eulittoral, and infralittoral mangrove in this specific section. This lack of spatial knowledge is limiting the capacity to design conservation strategies for copper, as their movement and accumulation patterns remain poorly understood in this particular ecological setting.

The primary objective of this study is to evaluate the ecological risk of copper contamination in the mangrove sediments of Kuala Perlis, Malaysia. By analysing copper concentrations across different intertidal zones: supralittoral, eulittoral, and infralittoral, this research aims to determine the extent of contamination and its potential impact on the mangrove ecosystem. Understanding the current state of copper contamination is critical for developing effective environmental management strategies and safeguarding the health of mangrove ecosystems [12].

The precise objective of this research is to quantify copper concentrations in mangrove sediments using advanced analytical techniques, such as acid digestion and spectrophotometry, and to evaluate the ecological risk using established indices, including the Geo-accumulation Index (Igeo) and the Contamination Factor (CF) [13]. Additionally, the study aims to correlate copper levels with key sediment properties, such as pH, moisture content, and particle size distribution, to better understand the factors influencing metal retention and mobility in mangrove sediments [14]. By comparing the findings with global sediment quality guidelines, this research will provide a comprehensive assessment of the current contamination status and offer actionable recommendations for pollution control and conservation efforts in Kuala Perlis and similar mangrove ecosystems worldwide [15].

2. Methodology

2.1 Sampling Area

The study was conducted within the mangrove ecosystems of Kuala Perlis, Perlis, Malaysia, where sediment samples were systematically collected from three distinct zonation areas: the infralittoral zone, eulittoral zone, and supralittoral zone, as illustrated in Figure 1. Kuala Perlis has been identified as a critical hotspot for heavy metal contamination in mangrove sediments, primarily due to extensive anthropogenic influences. Key contributing factors include coastal urbanisation, discharge of industrial effluents, and intensified agricultural activities, all of which have led to the accumulation of copper within the sedimentary matrix of the mangrove ecosystem.

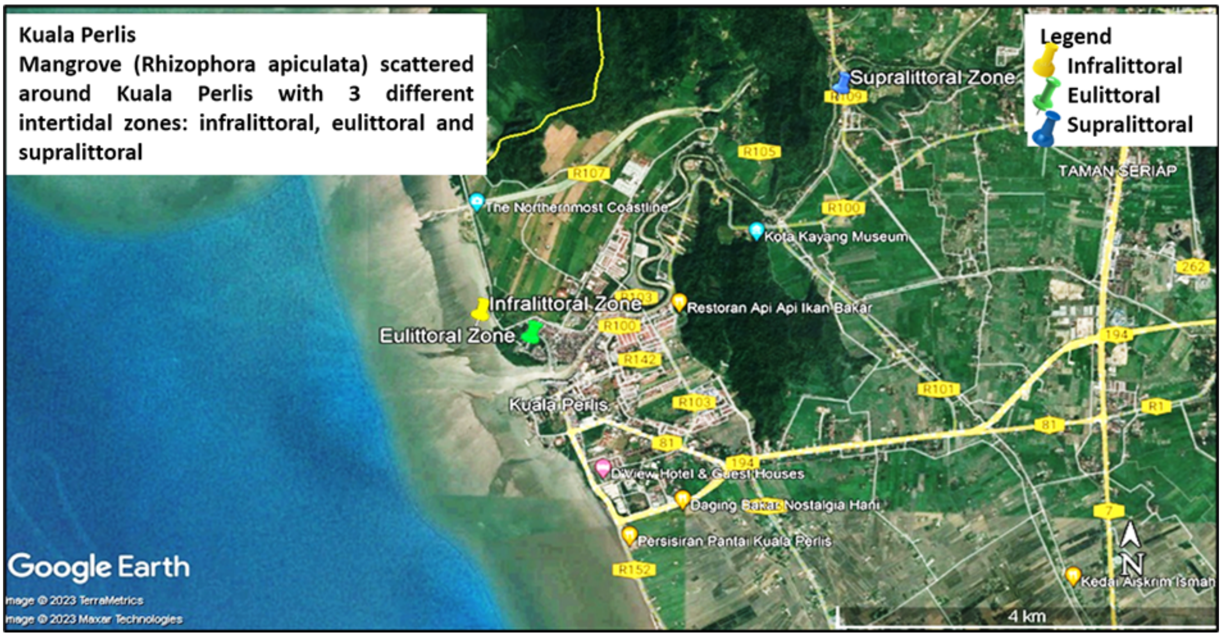

Fig. 1. Sampling locations in Kuala Perlis

2.2 Sediment Sampling

A total of nine sediment samples (0–15 cm depth, collected in triplicate for each station), with corresponding geographical coordinates provided in Table 1, were obtained from designated sampling sites within the remaining mangrove patches of Kuala Perlis using a stainless-steel auger. This sampling depth was selected to capture surface sediment layers, ensuring that recent depositional events such as fluvial inputs, tidal deposition, or anthropogenic disturbances could be effectively evaluated for their influence on sediment pollution dynamics.

Following collection, the samples were weighed immediately to determine their wet mass before undergoing a natural air-drying process for 72 hours in a controlled environment to prevent cross-contamination. Once the samples reached a constant weight, indicating the stabilization of moisture loss, they were further subjected to oven-drying at 105°C for 24 hours to eliminate residual moisture.

This step adhered to standard protocols of USEPA Method 160.3 for sediment moisture content determination.

Table 1
Coordinates of the sampling locations

Description	Sampling point	Latitude (N)	Longitude (E)
Supralittoral zone	S1	6° 25' 47.04''	100° 9' 25.26''
	S2	6° 25' 33.53''	100° 9' 24.82''
	S3	6° 24' 18.74''	100° 8' 06.10''
Eulittoral zone	E1	6° 13' 10.22''	100° 7' 39.31''
	E2	6° 24' 29.19''	100° 7' 26.91''
	E3	6° 24' 48.21''	100° 7' 23.84''
Infralittoral zone	L1	6° 24' 21.46''	100° 7' 27.87''
	L2	6° 24' 23.64''	100° 7' 27.99''
	L3	6° 24' 19.93''	100° 7' 30.57''

2.3 Physico-Chemical Properties of Mangrove Sediments

The dried samples were mechanically homogenised using an agate mortar and pestle to prevent cross-contamination from metal instruments. Initial sieving through a 2 mm mesh was performed to facilitate analysis of fundamental sediment properties, including moisture content, particle size distribution, bulk density, and pH, with measurements conducted separately for samples from each tidal zone (infralittoral, eulittoral, and supralittoral). For Copper analysis, a subsample of each homogenised sediment was further sieved through a 0.63-µm mesh to isolate the fine-grained fraction (<63 µm). This fraction was specifically targeted due to its high surface area and reactivity, which enhances its capacity for heavy metal adsorption. The <63 µm fraction was subsequently subjected to acid digestion following EPA Method 3050B to determine total metal concentrations.

2.4 Copper Extraction

The extraction of Copper from sediment samples involved acid digestion using 20 ml of nitric acid (HNO_3). During this process, samples were heated on a hot plate within a fume hood until the complete dissipation of brown fumes. Once the samples were digested and cooled to room temperature, they were diluted to 50 ml with distilled water and filtered through standard filter paper. The resulting solution underwent further dilution at a factor of 10 before copper concentration measurement. Copper concentrations were determined through the HACH DR3900 Spectrophotometer, employing the colourimetric determination of the Bicinchoninate Reagent Method to assess the copper levels in the sediment samples.

2.5 Copper Risk Assessment

The assessment of sediment pollution is primarily conducted using contamination indices, notably the geo-accumulation index (Igeo) and the contamination factor (CF). Both soil contamination indices are quantitative tools designed to evaluate the extent of soil contamination and are instrumental in determining the potential risks posed to human health and the environment. The concentrations of individual heavy metals, in conjunction with their respective background values, are utilised in the calculation of these indices, as well as the background concentration.

Metal sediment pollution was then assessed through the Geo-accumulation Index, which compares current levels to preindustrial levels [16]. Igeo value is classified into seven grades ranging from unpolluted to very strongly polluted. The calculation is referred to Eq. (1) below:

$$I_{geo} = log_2\left[\frac{Cn}{(1.5\times Bn)}\right] \tag{1}$$

C_n = concentration of the examined element in the bottom sediment
B_n = geochemical background of a given element in sediments

An Igeo value less than or equal to 0 indicates that the soil is practically unpolluted. Values ranging from 0 to 1 correspond to an unpolluted to moderately polluted classification. Soils with Igeo values between 1 and 2 are considered moderately polluted, whereas values between 2 and 3 suggest moderate to strong pollution. An Igeo range of 3 to 4 signifies strongly polluted conditions, while values between 4 and 5 indicate strong to very strong pollution. Values exceeding 5 are indicative of very strong pollution.

The contamination factor (CF) is a metric used to evaluate the degree of metal contamination in soil or sediment relative to either the average crustal abundance of the metal or the background concentrations found in geologically similar, uncontaminated areas. It is calculated using the following Eq. (2):

$$CF = \frac{M_x}{M_b} \tag{2}$$

M_x = the mean content of metals from at least five sampling sites
M_b = the pre-industrial concentration of the individual metal

A CF value less than 1 indicates low contamination, while values between 1 and 3 represent moderate contamination. Considerable contamination is indicated by CF values between 3 and 6, and CF values equal to or greater than 6 signify very high contamination levels. This classification system provides a clear understanding of the contamination severity in the area under assessment.

In addition, sediment quality is also evaluated using sediment quality guidelines (SQGs). The concentration of copper in the sediment was compared to sediment quality guidelines relatively, to assess its potential ecological impact. The comparison was made via two benchmark values: the Threshold Effect Concentration (TEC) and the Probable Effect Concentration (PEC). If the copper concentration in the sediment exceeds the PEC value of 108.0 mg/kg, the sediment is considered to be of poor quality and likely to pose adverse effects on benthic organisms. Conversely, if the concentration is below the TEC value of 18.0 mg/kg, the sediment is regarded as having good quality, with minimal risk of harmful biological effects. This guideline-based approach provides a scientifically grounded framework for interpreting sediment contamination levels and their potential ecological risks.

3. Results and Discussion

3.1 Physico-Chemical Properties

The physico-chemical characterisation of mangrove sediments revealed spatial variations between the three tidal zones, namely the infralittoral, eulittoral, and supralittoral zones. The pH values of the sediments ranged from 7.18 to 7.49, reflecting weakly alkaline conditions over all zones.

The pH showed maximum levels in the eulittoral zone (7.39), being closely followed by supralittoral zone (7.38), with the minimum pH recorded in the infralittoral zone (7.27). Under such alkaline conditions, these may affect the solubility of metals and overall biogeochemical processes in sediment [17].

Particle size distribution showed majority of fine fractions, with silt and clay being the major ones especially in the infralittoral zone, which accounted for approximately 68.76% of the total sediment composition. The relative degree of silt and clay content in the eulittoral (67.96%) and supralittoral zones (55.93%), was also somewhat reduced, whereas sand content increased accordingly, reaching up to 44.07% in the supralittoral zone. This gradation in particle size distribution suggests sediment sorting due to hydrodynamic conditions and tidal influence [18].

Moisture content was found to be highest in the infralittoral zone (68.72%), followed by the eulittoral (53.66%) and supralittoral zones (37.23%). This indicates that the infralittoral zone experiences prolonged water saturation, while the supralittoral zone remains relatively drier due to limited tidal inundation. High moisture content of sediments has the ability to increase the level of microbial activity and influence redox conditions, thus affecting nutrient cycling and contaminant mobility [19].

Bulk density revealed an increasing trend from the infralittoral to the supralittoral zone, ranging from 0.43 g/cm³ to 0.92 g/cm³. The highest bulk density observed in the supralittoral zone suggests more compacted sediments, likely due to reduced organic content and limited water retention. In contrast, the lower bulk density in the infralittoral zone reflects higher water and organic matter content [20].

Porosity values displayed a clear inverse relationship with bulk density, ranging from 92.28% in the infralittoral zone to 41.58% in the supralittoral zone. This inverse trend is consistent with sediment compaction, where highly porous sediments are typically less compact and contain more interstitial water, particularly in areas subjected to continuous submergence [21].

Table 2
The values of physico-chemical properties

	Infralittoral zone	Eulittoral zone	Supralittoral zone
pH	7.27	7.39	7.38
Porosity (%)	92.28	58.49	41.58
Bulk density (g/cm³)	0.43	0.67	0.92
Silt & clay (%)	68.76	67.96	55.93
Sand (%)	31.24	32.04	44.07
Moisture content (%)	68.72	53.66	37.23

3.2 Copper Concentration

Copper concentrations in mangrove sediments were analyzed across the infralittoral, eulittoral, and supralittoral zones and presented in Table 3 below, reveal spatial variation in copper levels, which may reflect differing degrees of exposure to contamination sources and hydrodynamic conditions among the zones.

Table 3
Mean copper concentration (mg/kg) in sediments across tidal zones

Sampling zone	Mean copper concentration (mg/kg)
Infralittoral zone	0.26
Eulittoral zone	0.42
Supralittoral zone	0.23

The eulittoral zone recorded the highest mean copper concentration at 0.42 mg/kg, followed by the infralittoral zone at 0.26 mg/kg, with the lowest concentration observed in the supralittoral zone at 0.23 mg/kg. The elevated copper levels in the eulittoral zone may be attributed to frequent tidal inundation, which enhances the deposition and retention of metal pollutants transported by surface runoff or tidal flows [22].

The presence of copper in these sediments is likely influenced by both point and non-point pollution sources. In the Kuala Perlis area, potential contributors include direct discharges of untreated or partially treated wastewater from small-scale enterprises and large industrial operations. These anthropogenic inputs may enter the aquatic system via drainage channels, runoff, or atmospheric deposition, leading to the accumulation of copper in the sediment over time.

Although the detected copper concentrations are relatively low, continued input and accumulation could pose long-term environmental concerns. Sediments act as both sinks and potential secondary sources of heavy metals, especially under changing redox or pH conditions that may remobilise bound metals into the water column [23].

3.3 Sediment Quality Guideline

Figure 2 shows the comparative value between copper concentration and the Sediment Quality Guideline (SQG). The concentration shows that the concentration of copper in the mangrove sediments of Kuala Perlis is less than 18.7 mg/kg which does not exceed the TEC value. As a result, the hazardous reaction of heavy metals in sediment has only recently begun to be seen in the environment.

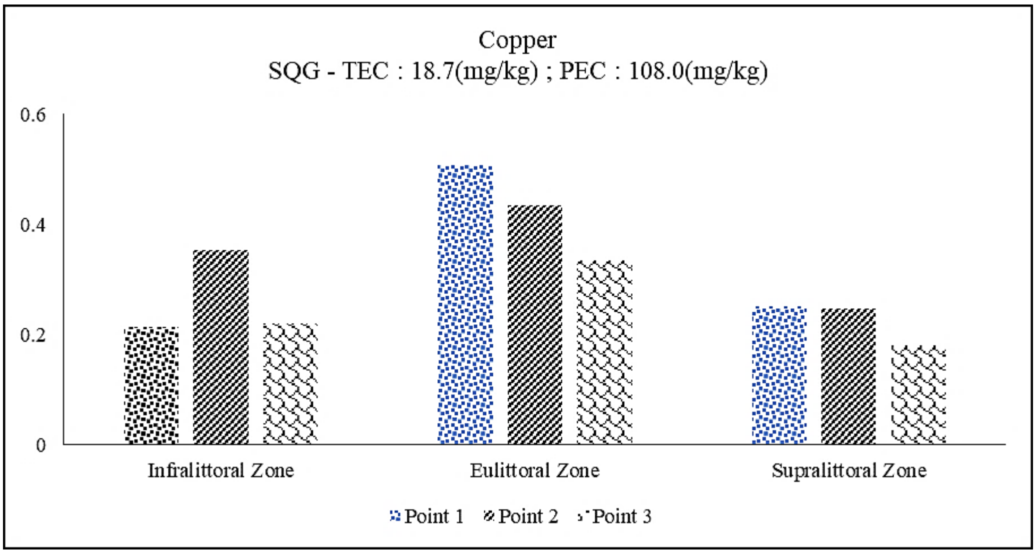

Fig. 2. Copper concentrations in mangrove sediments of Kuala Perlis compared to threshold effect concentrations (TEC)

3.4 Sediment Risk Assessments
3.4.1 Geo-accumulation index (Igeo)

The calculated geo-accumulation index (Igeo) for copper in the mangrove sediments of Kuala Perlis falls within Class 0, which corresponds to the unpolluted category according to the Igeo classification system. Such classification implies that the concentration of the copper in the sediments is either at or very close to the natural background levels, suggesting minimal or negligible anthropogenic effect. The Igeo value which was obtained by comparing current metal concentrations with pre-industrial reference values, provides a reliable indication of sediment quality concerning heavy metal contamination. The lack of substantial enrichment of copper indicates that the sediments have not been negatively affected by copper inputs and the sediments are about to maintained in a relatively pristine state [24]. Such findings are favourable from the standpoint of environmental management, as they reflect limited metal contamination, which in turn resulting in reduced ecological risk associated with copper accumulation in the benthic environment.

3.4.2 Contamination factor (CF)

The contamination factor (CF) analysis for copper also corroborates the findings obtained from the Igeo index. Copper contamination was categorized as low across different sampling areas of the intertidal zones, with CF values below the threshold of 1. This implies that the sediments in the Kuala Perlis mangrove area are only minimally affected by anthropogenic copper inputs.

The low CF values can be attributed to a set of interrelated environmental and ecological factors. Primarily, the region has limited industrialisation and there is relatively low levels of urbanisation, which minimizes the influx of copper and other heavy metals into the ecosystem. Second, the mangrove ecosystem itself plays a major role in reducing contamination through its natural filtering and sedimentation processes. Mangrove roots promotes particulates and associated metal trapping, while organic matter contributes to metal binding and immobilisation [25].

Moreover, active hydrodynamic processes such as tidal flushing minimize contaminant accumulation by presenting dispersion and dilution of pollutants. The physical and chemical properties of the sediments, including high porosity and fine particle content, also contribute to the retention and stabilisation of metals, thus limiting their mobility and bioavailability [26]. Finally, ongoing environmental management, with conservation initiatives and regulatory controls, could further help maintain the low contamination status of the area.

Overall, the risk assessment from the Igeo and CF indices shows that the mangrove sediments of Kuala Perlis are not significantly impacted by copper pollution. These results demonstrates the effectiveness of both natural and human controlled processes for improving the quality of sediment and minimizing ecological consequences of heavy metal contamination.

3.5 Correlation Analysis

In this study, the relationship between Cu concentrations and sediment physicochemical parameters such moisture content (MC), pH, bulk density, porosity, and particle size distribution (sand vs. silt/clay) were determined. The results of these associations are given in Table 4.

Table 4
Mean copper concentration (mg/kg) in sediments across tidal zones

	MC (%)	pH	Bulk density	Porosity	Sand (%)	Silt and Clay (%)	Cu
MC (%)	1						
pH	-0.412	1					
Bulk density	-0.863	0.439	1				
Porosity	0.945	-0.343	-0.652	1			
Sand (%)	-0.568	0.0569	0.816	-0.316	1		
Silt and clay (%)	0.568	-0.0569	-0.816	0.316	-1	1	
Cu	-0.246	-0.0619	-0.141	-0.466	-0.508	0.508	1

The results in Table 4 indicate a weak positive correlation (r = 0.508) between silt and clay content and copper (Cu) concentrations in the mangrove sediments of Kuala Perlis. This shows that sediments rich in silt and clay may hold slightly more copper. This finding is consistent with the previous study on estuarine sediments, where finer particles (silt and clay) are known to have higher affinities to heavy metals such as copper due to their larger surface areas and high cation exchange capacities (CEC) [27]. The negative association between sand content and Cu (r = -0.508) further supports this view, as coarser sand particles typically have lower metal adsorption capabilities than finer ones. However, the poor connection suggests that other factors, such as organic matter content, redox conditions, or anthropogenic inputs, may also play role in the Cu distribution in these sediments [28]. These findings are in accordance with previous research in estuarine systems, in which clay minerals and fine-grained sediments are important sinks for copper and other trace metals [29]. Future studies should consider more sediment parameters (such as organic carbon and Fe/Mn oxides) to further unravel more details on Cu retention processes in Kuala Perlis mangrove sediments.

4. Conclusions

In conclusion, copper was found to be quite low across all tidal zones. The sediment risk assessment using the Geo-accumulation Index (Igeo) and Contamination Factor (CF) indicated that the sediments are in the unpolluted and low contamination categories, indicating negligible anthropogenic influence. Furthermore, the study found a significant relationship between copper concentrations and key sediment physicochemical properties such as pH, moisture content, bulk density, porosity, and particle size distribution, all of which influence heavy metal retention and mobility. These findings highlight the ecological resilience of the Kuala Perlis mangrove ecosystem, as well as the importance of natural sediment features and environmental management in reducing heavy metal pollution.

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