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An Assessment of Metals (Pb and Cu) Contamination in Bottom Sediment from South China Sea Coastal Waters, Malaysia

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Abstract: Problem statement: The accumulation of metal contaminants in sediments can pose serious environmental problems to the surrounding areas. Trace metal contamination in sediment could affect the water quality and the bio-assimilation and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implications on human health and ecosystem. **Approach:** About 154 bottom sediment samples were collected using Smith McIntyre in a transect pattern from South China Sea East Coast coastal water (Terengganu, Pahang and Johor coastal area). The study focused on the levels of Pb and Cu in order to assess the extent of environment pollution and to discuss the origin of these contaminants in the sediment. **Results:** Results showed that the average concentration of Pb and Cu was $33.70 \mu\text{g g}^{-1}$ dry weights and $22.40 \mu\text{g g}^{-1}$ dry weights, respectively. Pb and Cu have relatively lower Enrichment Factors (EF) value and geo-accumulation (I_{geo}) indices in study area and these analysis validated that elevated heavy metals concentration in most sample are not due to artificial contamination. **Conclusion:** Overall, geochemistry of the samples showed the effect of both natural and anthropogenic inputs to the catchment, however, natural processes were more dominant than anthropogenic inputs in concentrating metals. Results obtained would help to develop strategies for pollution control and sediment remediation of coastal waters in the South China Sea.

Key words: South China Sea, Pb, Cu, Enrichment Factor (EF), I_{geo}

INTRODUCTION

Pollution of the natural environment by heavy metals is a worldwide problem because these metals are indestructible and most of them have toxic effects on living organisms, when they exceed a certain concentration^[1-3]. Heavy metals are of high ecological significance since they are not removed from water as a result of self purification, but accumulate in reservoirs and enter the food chain^[4]. The elevation of metal levels in a reservoir is shown mainly by an increase in their concentrations in the bottom sediment^[5]. Their occurrence in the environment results primarily from anthropogenic activities. The natural process, such as weathering of rocks and volcanic activities plays a noticeable role in enriching the water of reservoirs with heavy metals^[6,7].

Trace metal contamination in a marine coastal environment is related to sources of pollution in the adjacent estuaries and rivers. Metals are mainly

transported to the marine environment by rivers through estuaries. In most circumstances, the major contribution of anthropogenic metals in a marine coastal area is of terrestrial origin, i.e., from mining, industrial and urban development and other human practices near rivers and estuaries^[8,9]. Grain size of sediment is one of the major controlling factors for the distribution of trace metals in coastal area^[10].

As a combined result of these factors, metal concentrations in the sediment change in space and time. In fact, during the last few decades, industrial and urban activities have contributed to the increase of metals contamination into marine environment and have directly influenced the coastal ecosystems. The aim of this study is to describe the distribution of heavy metals, to provide preliminary data on the environmental conditions and to evaluate the risks from metal contamination, the impact of the industrial and the agriculture areas, in this area compared with other marine environment^[11].

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MATERIALS AND METHODS

Study area: The coastal waters in South China Sea are dissected by many meandering and slow flowing rivers and streams. The largest river is the Pahang river which slightly over 434 km length and has a catchments area of about 29,137 km². The main economic yield of this coastal water includes fishery resources with an utilizable mangrove forest resources and swamp peat areas along the back-shore of the coast. This waters is shared to three developing countries namely Thailand, Indonesia and Malaysia were important as an international shipping route especially for the northern countries such as Thailand, Vietnam, China, Taiwan, Japan and Korea which particular on logistic purpose.

Sampling: The samples were collected from 20 transects (154 sampling stations) in South China Sea East Coast coastal water (Fig. 1) with a Smith McIntyre to obtain surface sediment. This oceanographic fieldwork was accomplished with the research vessel from University Malaysia Terengganu, UNIPERTAMA VII and Malaysian Fishery Department (KL CERMIN). During sampling, precautions will be taken to minimize any disturbance in the grain-size distribution of the original sediment. The sample will be taken only when the grab was firmly closed on the arrival to the boat, so as to avoid any leaks of fine material withdrawn by water. In addition, to avoid metal contamination from grab's wall, the outer part of the sediment sample was removed and only the inner part was further processed.

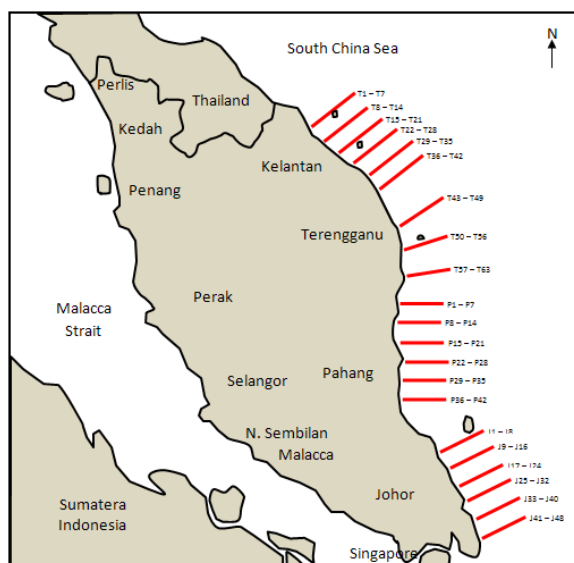


Fig. 1: Study area at South China Sea East Coast coastal water

So, even if removal of fine material had occurred, this would affect only the outer part of the sediment sample and not the sub-sample used for the analysis. After collection the samples were placed in plastic containers and kept in 4°C until analysis^[12].

Analytical method: The sediment sample were digested and the analyses for total Pb and Cu following the published methodologies with some modifications^[13-15]. An inductively coupled plasma mass spectrometer (ICP-MS) was used, for the quick and precise determination of Co, Cu, Pb and Zn in the digested sediment. The digestion method involved heating of 50 mg of a finely powdered sample in a sealed Teflon vessel in a mixture with a mixed acid solution (1.5 mL) of concentrated HF, HNO₃ and HCl. The Teflon vessel was kept at 150°C for 5 h. After cooling, a mixed solution of boric acid and EDTA (3 mL) was added and the vessel was again heated at 150°C for 5 h. After cooling at room temperature, the content of the vessel was transferred into a 10 mL polypropylene test tube and was dilute to 10 mL with deionized water. A clear solution with no residue should be obtained at the last stage. The precision assessed by the replicate analyses was less than 3%. The accuracy was also examined by analyzing duplicate a Canadian Certified Reference Materials Project standard and the result coincided with the certified values within a different of ±3%.

RESULTS

Figure 2a shows the concentration of Pb and Cu in surface sediment of South China Sea East Coast coastal water (Terengganu, Pahang and Johor coastal area). Two general zone of Pb was identified in the study area with the northern coastal water (Terengganu waters) are characterized by higher Pb concentration followed by Pahang coastal waters and Johor coastal waters. For Pb, the maximum concentration was observed at southern part of Terengganu coastal waters, T54 (98.6 μg g⁻¹ dry weights) and the minimum concentration was at northern part of Johor waters, J4 (0.14 μg g⁻¹ dry weights). The average concentration of Pb at Terengganu, Pahang and Johor coastal waters was 53.87 μg g⁻¹ dry weights, 24.49 μg g⁻¹ dry weights and 13.77 μg g⁻¹ dry weights, respectively. As overall, the average concentration of Pb was 33.70±25.25 μg g⁻¹ dry weights, higher compared to average shales, 20 μg g⁻¹ dry weights^[16].

Similarly with Pb, Cu average concentration also higher at the northern part, Terengganu waters followed by southern part, Johor coastal water and Pahang coastal waters (Fig. 2b). The average concentration of Cu was 24.21 μg g⁻¹ dry weights, 19.17 μg g⁻¹ dry weights and 22.91 μg g⁻¹ dry weights for Terengganu,

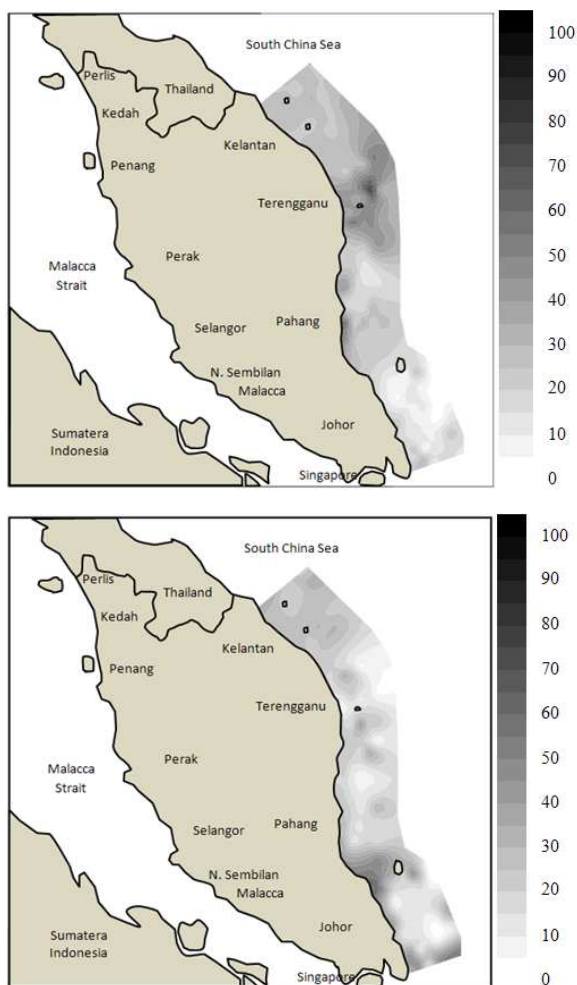


Fig. 2: Pb and Cu ($\mu\text{g g}^{-1}$ dry weights) distribution at Terengganu, Pahang and Johor Coastal waters

Pahang and Johor coastal waters, respectively. The highest and lowest concentration of Cu was observed in Johor coastal waters, J43 $91.87 \mu\text{g g}^{-1}$ dry weights and J8, $0.85 \mu\text{g g}^{-1}$ dry weights. The overall average concentration of Cu, $22.40 \pm 14.36 \mu\text{g g}^{-1}$ dry weights was lower than the average shales, $45 \mu\text{g g}^{-1}$ dry weights^[16].

DISCUSSION

Anthropogenic activities had caused important transformation in coastal environments during the last 150 years. Heavy metals were among the most widespread of the various pollutants originating from anthropogenic activities, particularly from mining and smelting waste sites^[17,18]. The approach most often used to determine the sources of the pollutant is through the normalization of geochemical data to reference metal.

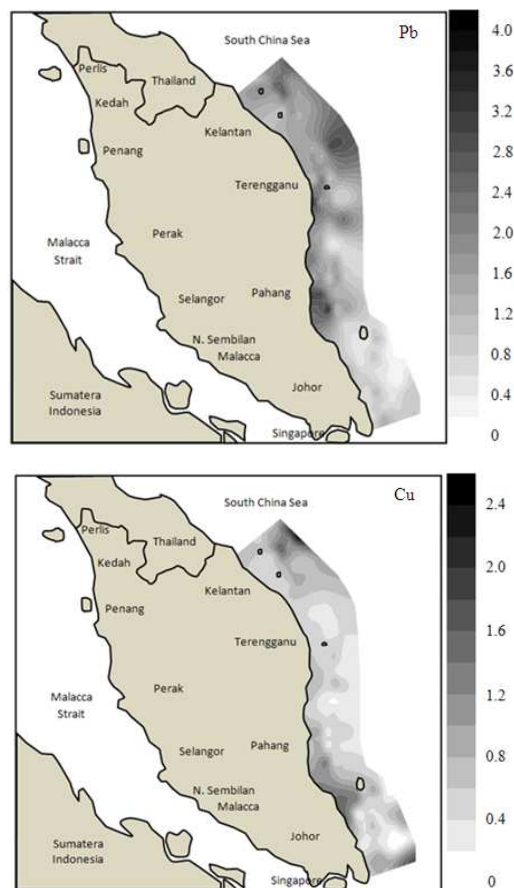


Fig. 3: EF value for Pb and Cu at Terengganu, Pahang and Johor Coastal waters

The reference metal must therefore be an important constituent of one or more of the major fine-grained trace metal carriers reflect their granular variability in the sediment. The most often used reference metal is Al, which represents a chemical tracer of Al-silicates, particularly the clay minerals^[19-21]. For a better estimation of anthropogenic input, an enrichment factor was calculated for each metal by dividing its ratio to the normalizing element by the same ratio found in the chosen baseline. EF values are applied to evaluate the dominant source of the sediments and as indicators for pollution^[22,23] and describe as $EF = (E/Al)_{\text{sed}} / (E/Al)_{\text{crust}}$ where $(E/Al)_{\text{sed}} / (E/Al)_{\text{crust}}$ are the relative concentrations of the respective element E and Al in the sediment and in the crustal material, respectively^[24,25]. EF close to 1 point to a crustal origin, while those with a factor more than 10 are considered to have a non-crustal source. In this study, the elements studied were proven to be deficiency to minimal enrichment, with EF values were ranged from 0.05-3.82 for Pb and 0.06-2.75 for Cu (Table 1 and Fig. 3).

Table 1: EF value for Pb and Cu at Terengganu, Pahang and Johor coastal area

Metals	EF values				Source
	Terengganu	Pahang	Johor	Average	
Pb	1.86	1.75	0.79	1.47	Deficiency to minimal contamination
Cu	0.71	0.63	0.67	0.67	Natural

Table 2: I_{geo} value for Pb and Cu at Terengganu, Pahang and Johor coastal area

Metals	I_{geo}				Source
	Terengganu	Pahang	Johor	Average	
Pb	0.99	0.90	0.60	0.85	Uncontaminated
Cu	0.71	0.68	0.63	0.68	to moderately contaminated

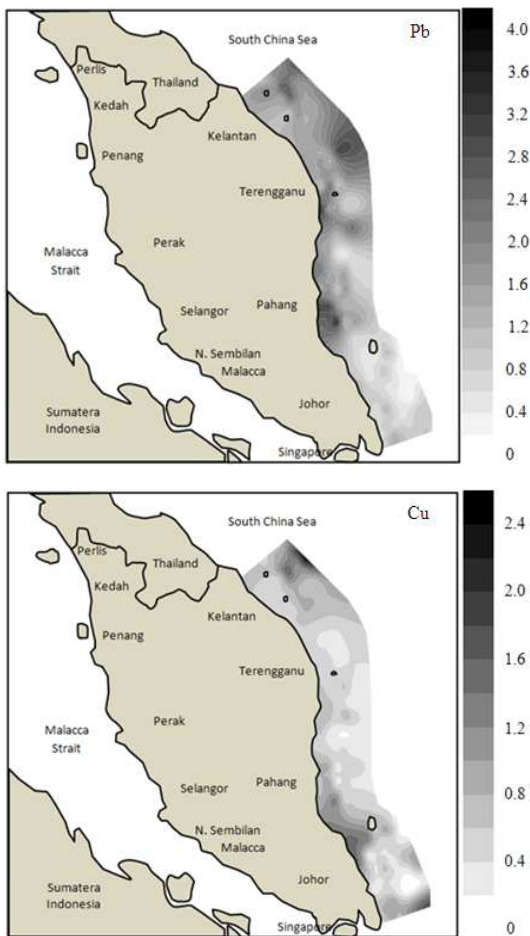


Fig. 4: I_{geo} value for Pb and Cu at Terengganu, Pahang and Johor Coastal waters

In order to compare the status of heavy metal concentration with the background values, index of geoaccumulation (I_{geo}) was computed. I_{geo} describe the relationship between the measured element concentration in the sediment fraction (C_n) and the geochemical value in fossil argillaceous sediment (average shales), B_n (Fig. 4). The constant value, 1.5 allows natural fluctuations in the content of a given substance in the environment and has very small anthropogenic influences^[26,27]:

$$I_{geo} = \log_2 (C_n / 1.5B_n)$$

In this study, Pb and Cu have calculated I_{geo} values were less than 1.0 and therefore can classified as practically uncontaminated to moderately contaminated (Table 2). Based on the EF and I_{geo} values, it can be suggested that the sources of heavy metal is solely natural, coming from the earth's surface that supplies particulate component to the atmosphere via the low temperature mechanical mobilization of surface deposit by wind erosion and thus incorporated into the coastal sediment.

CONCLUSION

Generally metals concentration in the sediment was much influenced by natural processes. The EF and I_{geo} values indicates all metal studied occurrence in both lithogenous and non-lithogenous fractions. The relatively high concentration of studied metals at some sampling point in the study are clearly indicates that the main sources of pollution were probably come from urban sewage, industrial effluents and shipping transportation.

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