

Vertical Variation of Lead, Copper and Manganese in Core Sediments Collected From Tanjung Lumpur Mangrove Forest, Pahang, Malaysia

(Kepelbagaian Menegak Plumbum, Kuprum dan Manganese di Dalam Teras Sedimen Hutan Paya Bakau Tanjung Lumpur, Pahang, Malaysia)

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ABSTRACT

Two core sediment samples collected from Tanjung Lumpur mangrove forest were analysed for lead, copper and manganese using the sensitive Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The average concentrations of Pb, Cu, and Mn in core samples were 36.28 ± 7.04 $\mu\text{g/g}$ dry weights, 50.17 ± 5.84 $\mu\text{g/g}$ dry weights, and 110.41 ± 14.48 $\mu\text{g/g}$ dry weights, respectively. From the calculated enrichment factors (EF), only Mn was considered to be predominantly terrigenous in origin, while Pb and Cu have slightly higher EF values which were related to anthropogenic input.

Keywords: Cu; enrichment factor; Mn; Pb; Tanjung Lumpur mangrove forest

ABSTRAK

Dua sampel teras yang diperoleh dari hutan paya bakau Tanjung Lumpur dianalisis untuk plumbum, kuprum dan mangan dengan menggunakan peralatan sensitif Spektrometri Jisim - Plasma Gandingan Induktif (ICP-MS). Purata kepekatan Pb, Cu dan Mn adalah masing-masing 36.28 ± 7.04 $\mu\text{g/g}$ berat kering, 50.17 ± 5.84 $\mu\text{g/g}$ berat kering, and 110.41 ± 14.48 $\mu\text{g/g}$ berat kering. Daripada pengiraan faktor pengkayaan (EF), Mn didapati dominan kepada sumber semula jadi, manakala Pb dan Cu yang mempunyai nilai EF yang lebih tinggi berkemungkinan mempunyai sumber hubungan dengan sumber antropogenik.

Kata kunci: Cu; faktor pengayaan; hutan paya bakau Tanjung Lumpur; Mn; Pb

INTRODUCTION

Recently, reclamation of mangrove ecosystems for industrial, urban and other forms of development has been increasing and it causes irreversible damage in coastal regions throughout the tropics. Mangrove sediments are anaerobic and reducing, rich in sulphide and organic matter content, thus favoring the retention of the water-borne heavy metals (Silva et al. 1990). Elevated metal concentration related with long-term pollution caused by human activities has been recorded in mangrove sediment. Similarly, several studies have shown that mangrove sediments have a high capacity to retain heavy metals from tidal water and water runoff, and therefore they often act as sinks for heavy metal (Kamaruzzaman et al. 2004; Tam & Yao 1998). Besides, mangrove ecosystems contain high organic matter and sulfide; anaerobic and reduced state favoring the heavy metals retention in the water-borne (Lacerda & Abrao 1984).

The sediments from mangrove areas contain a historical record of information on the temporal changes that have been brought about as a result of these actions. This record is altered or smeared by the effects of sediment mixing, which influences the preservation of the physical sedimentary structures (Nittrouer et al. 1979). However, the alteration of the record depends on the intensity,

depth and nature of the sediment mixing as well as the sediment accumulation rates. Sediment mixing also alters the biogenic components and pore water concentrations of dissolved chemical species within the sediment mixed layer (Aller 1982; Berner 1980). In Malaysia, studies relating to mangroves are not well documented and only little information is known concerning the sedimentation and some geochemical background of the mangrove forest (Kamaruzzaman 1994). In view of the importance of the mangrove to various aspects of the environment, the main objective of this study is to obtain the vertical concentration of heavy metals as well as their distribution pattern in sediment.

MATERIALS AND METHODS

SAMPLING SITES

Tanjung Lumpur mangrove is one of compartments of Kuantan mangrove forest. It is located in the Kuantan town, the capital city of Pahang state. The system water discharge is high and influenced by a high inundation and strong bi-directional current. The mangrove community in this area is extensive and well distributed over several kilometers inland (State Forestry Department of Pahang

2006). In this study, two transects line were set-up, one close to river mouth (TL1) and the other one located more upstream (TL2) with 20 fixed points in each transect. The core sediments were collected using 50 cm PVC tube and were cut into segments of approximately 5 cm interval, labelled and stored in acid cleaned bottles for analysis.

ANALYTICAL METHOD FOR METALS

The core sample was digested according to established methods (Kamaruzzaman et al. 2001; Nozaki et al. 1999) with some modifications. An inductively-coupled plasma mass spectrometer (ICP-MS) was used for quick and precise determinations of Pb, Cu and Mn in the digested marine sediment. Briefly, 50 mg of <63 μm size sample was digested with mixed acid (HCl: HNO₃: HF) in the ratios 3.5: 3.5: 3 for 5 h and temperature at 150°C. After that, EDTA and boric acid was added and digested back in 150°C for at least 5 h. Teflon bomb method was applied for this analysis. After cooling to room temperature, the content of the vessel was thoroughly transferred into a 10 mL polypropylene test tube and was diluted to 10 mL with deionized water. A clear solution with no residue should be obtained at this stage. Blank and estuarine Sediment Reference Materials (SRM 1646) were also subjected to the same procedure (Table.1). The recovery test for sediments

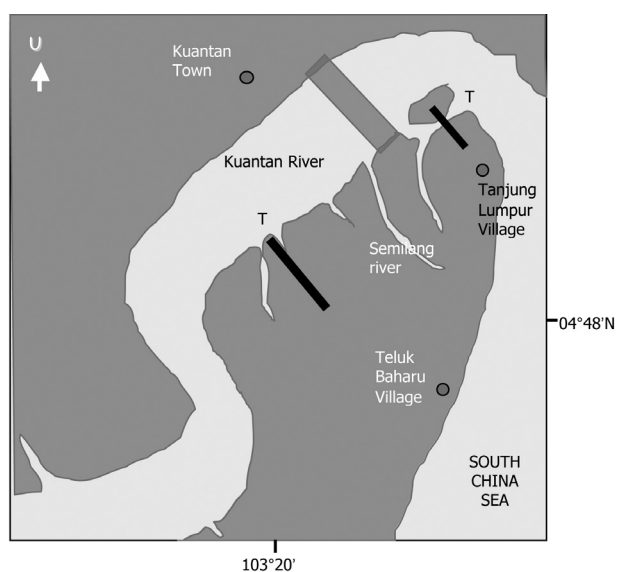


FIGURE 1. Map of the Tanjung Lumpur Mangrove Forest, Kuantan, Pahang, Malaysia

TABLE 1. The recovery test for sediment analysis using SRM 1646 (Estuarine Sediment) with percentage of recovery ranged from 95% to 100%

Element	Certified Value	Analyzed Value	Recovery %
Pb	11.7 \pm 1.2	11.16 \pm 1.8	95.44
Cu	10.01 \pm 0.34	9.74 \pm 0.41	97.3
Mn	234.5 \pm 2.8	234.08 \pm 7.36	99.82

was done using standard analysis and the percentage of recovery ranged from 95% to 105%.

In order to understand the level of contamination factor with respect to heavy metals, the values were utilised to find the value of enrichment factor (EF). Enrichment factor was calculated for each metal by dividing its ratio to the normalizing element by the same ratio found in the chosen baseline. Table 1 shows the calculated EFs of the analysed elements with respect to those determined in the crustal abundance (Kamaruzzaman et al. 2002), employing the equation:

$$EF = (E/Al)_{\text{sed}} / (E/Al)_{\text{crust}}$$

where $(E/Al)_{\text{sed}}$ and $(E/Al)_{\text{crust}}$ are the relative concentrations of the respective element E and Al in the sediment and in the crustal material, respectively (Kremling & Streu 1993; Molinari et al. 1993).

RESULTS AND DISCUSSION

Depth profiles of Pb, Cu, and Mn are shown in Figure 2. Generally, the mean concentrations comparable to those reported by Kamaruzzaman et al. (2005) and no specific patterns were observed. Based on the previous studies (Kamaruzzaman et al. 2000), sediments from the mangrove forests of Tanjung Lumpur, seemed to be well mixed, and the sediment supply was homogeneous. Although some of these profiles showed an increase in metal concentrations towards the surface layer, this is not necessarily an indication for anthropogenic input. It is more likely due to early diagenetic processes (Macdonald et al. 1991; Ridgway & Price 1987).

The concentrations of Pb for both TL1 and TL2 ranged from 9.98 to 82.67 $\mu\text{g/g}$ dry weights, with an average of $36.28 \pm 18.18 \mu\text{g/g}$ dry weights (Figure 2). Their average concentration was 1.5 times higher than average shales value of 20 $\mu\text{g/g}$ dry weights (Manson & Moore 1982). The concentration of Pb in TL1 was less varied compared to the concentration in TL2. The vertical variations in the depth profile might be due probably to temporal changes in biological productivity (Leong 2001). However, postdepositional oxidation of organic rich layers may lead to redistribution of Pb in the sediment (Francois et al. 1993; Thomson et al. 1990).

Some higher concentrations of Pb observed in the upper boundary could be primarily derived from the increased productivity as inferred from the distribution of organic matter content as reported by Leong (2001). The concentrations of Mn for both cores ranged from 21.99 to 180.87 $\mu\text{g/g}$ dry weights and averaged to $110.32 \pm 40.25 \mu\text{g/g}$ dry weights. Their average concentration was much lower than average shales value (Manson & Moore 1982). Vertical profiles of Mn showed the decrease in their concentrations from the surface denote the diagenetic enrichment during Fe-Mn oxyhydroxides dissolved in reduced layer and migrate upward in the sediment column (Froelich et al. 1979; Skey & Paus 1979). A subsurface maximum in the Mn content within

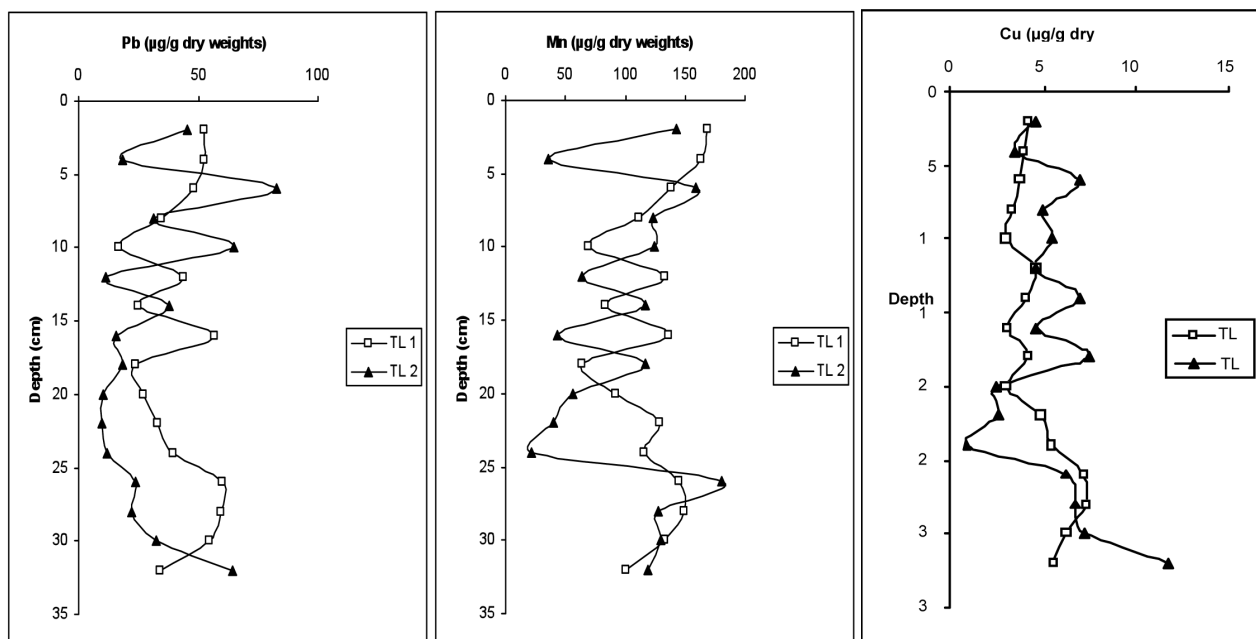


FIGURE 2. Concentration of Pb, Cu, and Mn in the core samples of TL1 and TL2

the enriched layer has also been observed in continental shelf sediments (Hartman et al. 1979) and is common in pelagic sediments (Wangersky 1962). Since the source of Mn^{2+} is not limited at a certain depth, both the dissolution (reduction) of Mn oxide and precipitation as carbonate may occur simultaneously as observed at some depths (Figure 2). As the sedimentation proceeds, the redox condition of the buried sediment changes to a reducing state and the alkalinity in the interstitial water begins to increase (Hartman et al. 1979).

The interstitial Mn in the lower part migrates downward through interstitial and forms manganese carbonate precipitate when the carbonate level in the water is sufficiently high. Although it is known that Mn migrates into the reducing environment, depositional migrations for other components including Pb and Cu have not been established. Therefore one should be cautious when interpreting the concentration profiles of metals in a sediment core.

The concentrations of Cu ranged from 8.69 to 117.40 $\mu\text{g/g}$ dry weights (Figure 2) and averaged to 50.17 ± 19.65 dry weights. Their average concentration was slightly higher than average shales value (Manson & Moore 1982). Overall, the concentrations were almost constant with the

depth and were observed to be increased at the depth of 20 cm. This might be due to process of the Cu absorption and scavenging by Fe and Mn oxides and hydroxides (Prohic & Kniewald 1987).

The enrichment factors for all metals are presented in Table 2. The enrichment factors less than 10 indicate the sources were terrigenous origin and if factor greater than 10, it probably enrich from anthropogenic origin (Kremling & Streu 1993; Molinari et al. 1993). From Table 2, only Mn can be categorized as crustal or natural in origin. However, Pb and Cu which has higher value are probably influenced by the anthropogenic input.

CONCLUSION

The present study indicates that heavy metal content has not been a serious problem in the Tanjung Lumpur mangrove areas. Although there are very few data on sediment heavy metals concentrations in mangrove ecosystems available, the concentrations of Pb, Cu, and Mn in the sediments were generally comparable to and/or below the values reported by previous researchers on other mangrove sediments. However, some relative high concentrations of some metals might have come from the same source of pollution, probably human input.

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TABLE 2. Calculated average values of enrichment factor (EF) for Pb, Cu, and Mn in the study area for both transects

Element	EF Value	Contamination Categories
Pb	11.7 ± 1.2	Significant Contamination
Cu	10.01 ± 0.34	Moderate Contamination
Mn	234.5 ± 2.8	Deficiency to minimal Contamination

REFERENCES

- Aller, R.C. 1982. The effects of microbenthos on chemical properties of marine sediment and overlying water. In *Animal-Sediment Relations*. McCall, P. L. and Tevesz, M. S. J. (eds.) 53-102. Plenum Press, New York.
- Berner, R.A. 1980. *Early Diagenesis: A Theoretical Approach*. Princeton: Princeton University Press,
- Francois, R., Emerson, S. & Huested, S.S. 1993. Glacial/interglacial changes in sediment rain rate in the SW Indian sector of sunAntarctic waters as recorded by ^{231}Th , ^{231}Pa , U and $\delta^{15}\text{N}$. *Paleoceanography* 8: 611-629.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B. & Maynard, V. 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *Geochim. Cosmochim. Acta* 43: 1075-1090.
- Hartman, M., Muller, P.J., Suess, E. & Van Der Weijden, C.H. 1979. Chemistry of late quaternary sediments and their interstitial waters from the NW African continental margin. *Meteor* 24: 1-67.
- Kamaruzzaman, K.Y. 1994. A study of some physico-chemical parameters in the estuarine system of Chukai-Kemaman rivers, Terengganu. M. Sc. Thesis. Universiti Putra Malaysia, 222 pp. (Unpublished)
- Kamaruzzaman, B.Y., Jamil, T. & Hasrizal, S. 2004. Organic Carbon in Sediments and Particulate Organic Carbon in water of the Chukai-Kemaman Estuarine System. *Journal of BioScience* 15(1): 89-97.
- Kamaruzzaman, B.Y., Ong, M.C. & Willison, K.Y.S. 2005. Taburan Kepekatan Unsur Kimia Di Dalam Teras Sediment Di Hutan Paya Bakau, Terengganu. *Malaysian Journal of Analytical Sciences* 9(1): 111-115.
- Kamaruzzaman, B.Y., Shazili, N.A.M., Mohd Lokman, H. & Sulong, I. 2002. Geochemistry of some heavy metals as recorded in the sediment of the Kuala Kemaman Mangrove Forests, Terengganu, Malaysia. *Oriental Journal of Chemistry* 18(1): 7-14.
- Kamaruzzaman, B.Y., Suhaimi, H., Teh, E.K., Leong, H.F., Soon, K.H. & Chong, K.Y. 2001. The determination of ^{230}Th in the sediments: Sedimentation in the mangrove Forests of Pulau Sekeping, Kemaman, Terengganu. *Journal of Ultra Scientist of Physical Sciences* 13(2): 239-245.
- Kremling, K. & Streu, P. 1993. Saharan dust influence trace element fluxes in deep North Atlantic subtropical waters. *Deep Sea Research* 40: 1155-1168.
- Lacerda, L.D. & Abrao, J.J. 1984. Heavy metals accumulation by mangrove and salt marsh intertidal sediments. *Rev. Bras. Bot.* 7: 49-52.
- Leong, H.F. 2001. Geochemical proxy for mangrove forest of Pulau Sekeping, Kemaman. Final Year report, Bachelor Science (Marine Science), Faculty of Applied Science and Technology, Universiti Putra Malaysia Terengganu. 71p. (Unpublished)
- Macdonald, R.W., Macdonald, D.M., O'Brien, M.C. & Gobeil, C. 1991. Accumulation of heavy metals (Pb, Zn, Cu Cd), carbon and nitrogen in sediments from strait of Georgia, B.C., Canada. *Marine Chemistry* 34: 109-135.
- Manson, B. & Moore, C.B. 1982. *Principles of Chemistry*, 4th Edition. New York: J. Wiley and Sons.
- Molinari, E., Guerzoni, S. & Rampazzo, G. 1993. Contribution of Saharan dust to the central Mediterranean Basin. *Geological Society of America, special paper* 284: 303-312.
- Nittrouer, C.A., Sternberg, R.W., Carpenter, R. & Bennett, J.T. 1979. The use of ^{210}Pb geochronology as a sedimentological tool: application to the Washington continental shelf. *Marine Geology* 3: 297-316.
- Noriki, S.K., Nakanishi, T., Fukawa, M., Uematsu, T., Uchida & S. Tsunogai 1980. Use of a teflon vessel for the decomposition followed by the determination of chemical constituents of various marine samples. *Bull. Fac. Fish, Hokkaido Univ.* 31: 354-465.
- Prohic, E. & Kniewald, G. 1987. Heavy metal distribution in recent sediments of the Krka River estuary – an example of sequential extraction analysis. *Marine Chemistry* 22: 279-297.
- Ridgway, I.M. & Price, N.B. 1987. Geochemical associations and post depositional mobility of heavy metals in coastal sediments: Loch Etive, Scotland. *Marine Chemistry* 21: 229-248.
- Silva, C.A.R., Lacerda, L.D. & Rezende, C.E. 1990. Heavy metal reservoirs in a red mangrove forest. *Biotropica* 22: 339-345.
- Skei, J. & Paus, P.E. 1979. Surface metal enrichment and partitioning of metals in a dated sediment core from a Norwegian fjord, *Geochim. Cosmochim. Acta.* 43: 239-246.
- Tam, N.F.Y. & Yao, M.W.Y. 1998. Normalization and heavy metal contamination in mangrove sediments. *Science of the Total Environment* 216: 33-39.
- Thomson, J., Wallace, H.E., Colley, S. & Toole, J. 1990. Authigenic uranium in Atlantic sediments of last glacial stage – a diagenetic phenomenon. *Earth Planet. Sci. Lett.* 98: 222-229.
- Wangersky, P.J. 1962. Sedimentation in three carbonate cores. *Journal Geol.* 70: 364-375.
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