Pertanika J. Sci. & Technol. 14(1 & 2): 53 - 61 (2006)

ISSN: 0128-7680
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# The Concentration of Manganese, Copper, Zinc, Lead and Thorium in Sediments of Paka Estuary, Terengganu, Malaysia

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Received: 30 July 2004

## ABSTRAK

Sampel teras sepanjang 14 cm dari Sungai Paka telah diukur dengan peralatan ICP-MS bagi mendapatkan kepekatan Mn, Cu, Zn, Pb dan Th. Secara keseluruhannya, kepekatan semua logam didapati menurun mengikut kedalaman dan secara signifikannya mempunyai kepekatan yang tinggi di permukaan. Purata kepekatan Mn dan Cu adalah masing-masing 151.1 ± 59.1 mg/g berat kering dan 29.2 ± 6.9 mg/g berat kering, manakala Zn dan Pb mempunyai purata 72.5 ± 15.5 mg/g berat kering dan 54.9 ± 2.5 mg/g berat kering. Th pula didapati agak tidak sekata dan berada di antara 0.6 mg/g berat kering hingga 1.4 mg/g berat kering. Dalam kajian ini, hanya Mn dan Th mempunyai nilai faktor pengkayaan (EF) yang stabil dan ini boleh dianggap sebagai mempunyai sumber dominan secara semula jadi. Sebaliknya Cu, Zn dan Pb yang didapati mempunyai nilai EF yang lebih tinggi dan berkemungkinan mempunyai sedikit pengaruh kemasukan sumber-sumber antropogenik.

## ABSTRACT

14 cm cores sediments from the Paka River were analyzed for Mn, Cu, Zn, Pb and Th using the inductively coupled plasma mass spectrometer (ICP-MS). Generally, the concentrations of all elements decreased with depth and have significantly higher concentration at the surface depth of the core. The concentration of Mn and Cu have average value of 151.1 ± 59.1 mg/g dry weights and 29.2 ± 6.9 mg/g dry weights, while Zn and Pb averaged at 72.5 ± 15.5 mg/g dry weights and 54.9 ± 2.5 mg/g dry weights, respectively. Th were slightly varied widely and ranged from 0.6 mg/g dry weights to 1.4 mg/g dry weights. In this study, only Mn and Th have enrichment factor (EF) values close to unity and may therefore be considered to be predominantly terrigenous in origin. On the contrary, the higher EF values found for Cu, Zn and Pb indicate that these metals might have some influenced from the anthropogenic input.

**Keywords: Enrichment factor, heavy metals, ICP-MS, Paka River**

## INTRODUCTION

Estuarine areas where freshwater encounters seawater are characterized by a lateral variation in salinity, and can represent as a transfer box for the sediment between land and the open ocean (Meade 1972). They are very active areas where a huge amount of organic matter and trace metals are introduced into the ocean system through river runoff, *in situ* primary production and anthropogenic impacts. Estuary appeared generally to be important sink for trace metal by the rivers of the world (Barry and Simon 1979). Heavy metal tend to be trapped in estuarine sediment are thus persist as a source of pollutants long after the cessation of discharges. The most comprehensive study was conducted by Davies *et al.* (1991) and reported the average concentration of heavy metal in sediment decreased in the order Zn > Pb > Cu > Cr > Ni > Cd between Newport Bridge and the river mouth. In estuarine systems, heavy metals in the water column have been observed to exhibit both conservative and non-conservative behavior along salinity gradients. In conservative systems, trace metals are simply diluted by increasing amounts of saltwater along the salinity gradient. In non-conservative systems, a host of different biogeochemical mechanisms have been shown to affect trace metal behavior in the water column. In non-conservative systems, surface complexation (and subsequent particle sedimentation) and desorption from particles can decrease the particulate fraction of metals along the salinity gradient (Flegal *et al.* 1991).

There are only limited information regarding to the geochemical profile of riverine system in Malaysia and only some initial research had been done by Kamaruzzaman *et al.* (2002) and Noor Azhar *et al.* (2003). In recent years, the study area especially for the first kilometer along the Paka River has been heavily impacted by discharges from municipal and industrial outflows. This was due to the rapid development of the area via expansion of the industrialization area as well as the increase in population. Steel and petro-chemicals are the main industry in this area and is the catalyst for other supportive industries to develop around the same area. The aim of this work was to study the geochemical behaviour of metals, their source and mode of incorporation in their sediments with regards to the sedimentological conditions of the area.

## MATERIALS AND METHODS

### *Sampling Sites*

The Paka River is located in the Dungun district, which situated near the Paka town, southern of Kuala Terengganu, the capital state of Terengganu (*Fig. 1*). The study area lies in the wet tropics where high rainfall is recorded in the monsoon season with a high rainfall were recorded in the month of November and January. The length of Paka River is approximately 87 km long and with total catchment area of approximately 830 km$^2$. It extends and enlarges westerly from the mouth before turning south, bordering the smaller Kertih River catchments on the east (*Fig. 1*). The inland and mountainous regions of the catchments are mainly covered with natural tropical rain forest. The vegetation of both coastal breaches appear to be a mixture of grass and low scrub-land truncated in a north-south direction by long and narrow swamps which provide drainage to the revised beaches.

### *Analytical Method for Metals*

In this study a 14 cm sediment core was collected by using the D-section corer in the Paka estuary (*Fig. 1*). The core was cut into segments of approximately 5 cm interval, labeled and stored until analysis in the laboratory. The sediment samples were digested according to the published methods by several researchers (Noriki *et al.* 1980; Sen Gupta and Bertrand 1995; Kamaruzzaman 1999) with some modifications. An inductively-coupled plasma mass spectrometer (ICP-MS) was used for the quick and precise determinations of Mn, Cu, Zn, Pb and Th in the digested marine sediment. Briefly, the digestion method involved the heating of 50 mg of a $< 63\ \mu m$ size sample in a sealed teflon vessel with mixed concentrated acids of HF, $HNO_3$ and HCl in the ratio of 2.5 : 3.5 : 3.5. The teflon vessels were kept at 150 $^0$C for 3 – 5 hours. After cooling, a mixed solution of boric acid and EDTA was added, and the vessel was again heated at 150 $^0$C for at least 5 hours. 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. The precision assessed by replicate analyses was within 3%. The accuracy was also examined by analyzing, in duplicate a Canadian Certified Reference Materials Project standard (DL-1a) and the results coincided with the certified values within a difference of ± 3%.

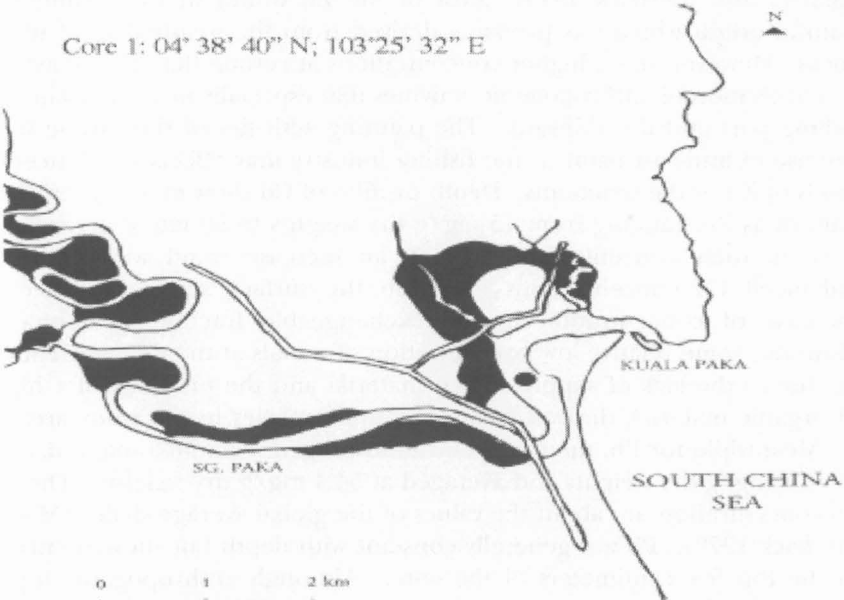

*Fig. 1: Location of the core (•) study area in the Paka Estuary, Terengganu, Malaysia*

## RESULTS AND DISCUSSION

Depth profiles of Mn, Cu, Zn, Pb and Th are given shown in *Fig. 2*. Generally, the concentrations of heavy metal recorded in this study were generally below the levels of most polluted estuaries, even though some high content of metals were discovered at several depths. Although no specific trend was identified, the concentrations of metals were relatively lower in the surface depth compared to the deeper depth. Since the study areas is located in an enclosed estuary with less industrial activities, the input of some high concentration of metals might have come from town residential areas, city sewage effluents and the fisheries activities. In this study, Mn ranged from 110 mg/g dry weights to 280 mg/g dry weights and averaged at 210 mg/g dry weights. The average Mn concentration was much lower than values of the global average shales (Martin and Meyback 1979), but is greater compared to the Mn content in Johor Straits (Khalik *et al.* 1997). The existence of the subsurface maxima of Mn are caused by the migration of $Mn^{2+}$ with interstitial water and subsequent precipitation as a kind of carbonate on the surface of volcanic pumice (Tsunogai *et al.* 1979). A subsurface maximum in the Mn content within the enriched layer has also been observed in continental shelf sediments (Hartman *et al.* 1979) and is common in pelagic sediments (Wangersky 1962). The depth profile of Zn was generally contants ranging from 50 mg/g dry weights to 100 mg/g dry weights. Their average concentrations are about the values of the global average shales (Martin and Meyback 1979). Most of the Zn found in the sediments is of natural origin which was probably derived from the weathering of ultramafic rocks. However, some higher concentrations at certain depth were assumed as a contribution of anthropogenic activities that especially near the vicinity of the fishing port and the shipyard. The painting activities of the fishing boat and the use of anti-rust paint in the fishing industry may effects the concentration levels of Zn in the sediments. Depth profiles of Cu show more or less the same pattern as Zn, ranging from 15 mg/g dry weights to 50 mg/g dry weights. In general, their concentration showing an increase trend with depth. The enhanced Cu concentrations found in the surface sediment reflected the increase of concentration in the exchangeable fraction (Johanna 2002). However, some relative low concentration of metals at the deeper depth might be due to the lack of supply of rich material and the presence of a high load of organic material, derived from planktonic species in the study areas.

Meanwhile for Pb, their concentration ranged from 50.6 mg/g dry weights to 60.6 mg/g dry weights and averaged at 54.4 mg/g dry weights. The average Pb concentration was about the values of the global average shales (Martin and Meyback 1979). Pb was generally constant with depth but showed enrichment in the top few centimeters of the core. Although anthropogenic inputs are supposed to be the major source for the increased Pb concentrations found in the study area, an increase due to diagenetic changes cannot be excluded, being a common phenomenon in the sediments. Furthermore, Pb is mostly supplied to the open marine environment by atmospheric inputs, and was used as an excellent tracer to study historical pollution records. Finally, the depth

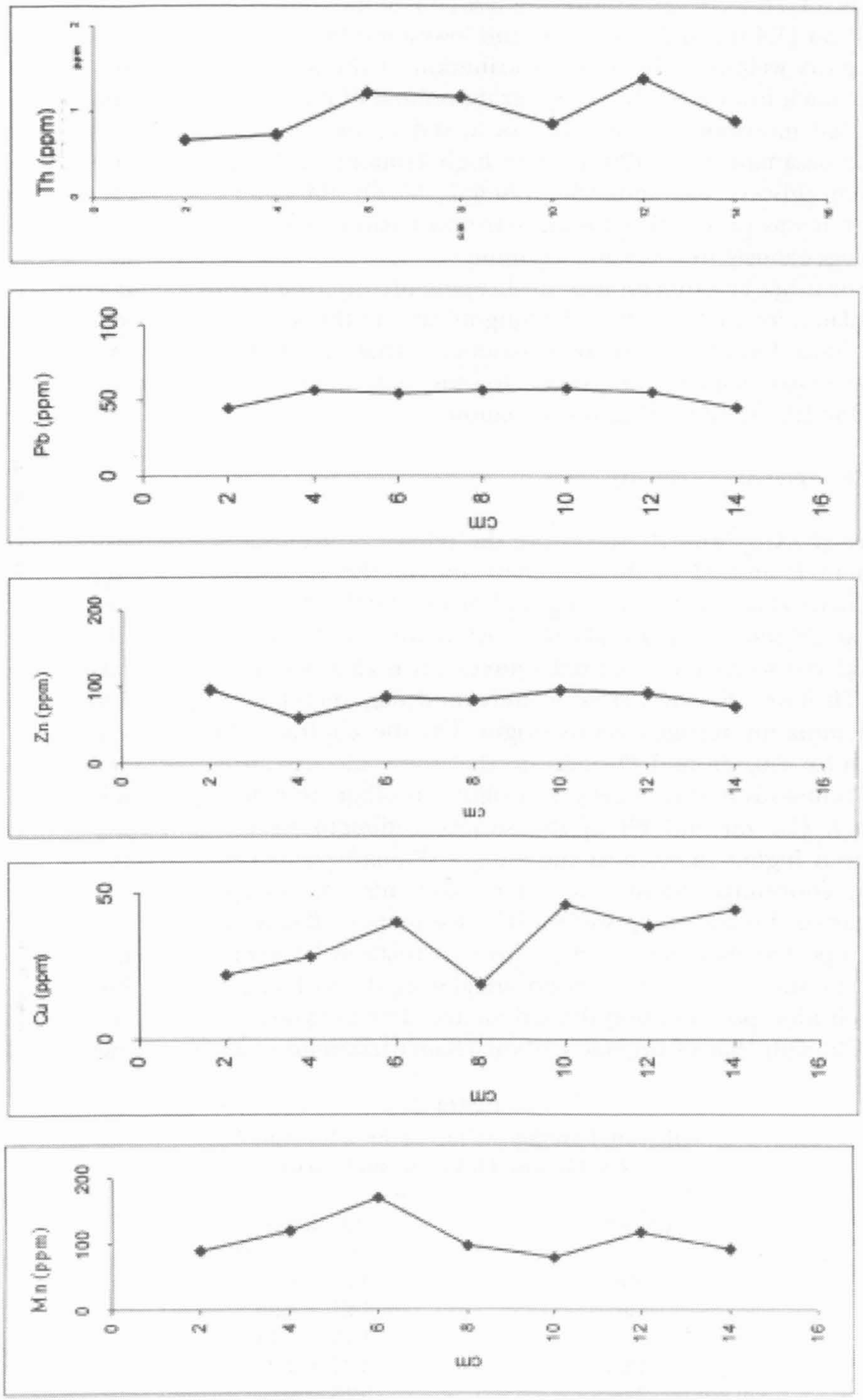

*Fig. 2: Vertical profiles of the concentration of Mn, Zn, Pb and Th against depth*

profile of Th were varied with highest concentration was observed at the depth of 12 cm (1.4 mg/g dry weights) and lowest was found at the surface depth (0.6 mg/g dry weights). In rivers, distribution or the inputs of Th is unstable and were much influenced by the water movement of fluvial and tidal, water velocity and the monsoon seasons that occurred in the study areas. According to Kamaruzzaman *et al.* (2001), the high content of Th probably cause from erosion process from monazite mineral. Mostly, the content of Th is constants where it was produced constantly from its parent $^{234}U$ solubility and disperses homogeneously in the water column.

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. Table 1 shows the calculated EFs of the analysed elements with respect to those determined in the crustal abundance (Taylor 1964), employing the equation:

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

where $(E/Al)_{sed}$ and $(E/Al)_{crust}$ are the relative concentrations of the respective element E and Al in the sediment and in the crustal material, respectively (Molinari *et al.* 1993; Kremling and Strue 1993). An enrichment factor close to 1 would indicate a crustal origin, while those with factors greater than 10 are considered to have non-crustal sources. It is clear from Table 1 that only Mn and Th have EF values close to unity and may therefore be considered to be predominantly terrigenous in origin. On the contrary, the higher EF values found for Cu, Zn and Pb indicate that these metals can be considered to be predominantly anthropogenic in origin. In other study near Chukai-Kemaman estuary, Cu, Zn and Pb in the surface sediment were also found to have relatively higher values near the estuary (Kamaruzzaman *et al.* 2002). In these areas, enormous amounts of finer sediments are transported by the river, increasing the adsorbing surface of trace metals. Kamaruzzaman *et al.* (2002) also reported that there is a positive correlation between grain size and the concentrations of Cu, Zn and Pb, suggesting the influence of the fine fraction in their incorporation into the sediments. The fairly well correlation of Cu, Zn and Pb, with that of organic carbon (Kamaruzzaman *et al.* 2004) suggests the

TABLE 1
Calculated average values of EF"s for Mn, Cu, Zn, Pb and Th in the study area

| Element | EF values |
|---|---|
| Mn | 0.5 ± 0.24 |
| Cu | 1.21 ± 2.50 |
| Zn | 1.72 ± 1.74 |
| Pb | 3.27 ± 4.94 |
| Th | 0.18 ± 0.08 |

association of these metals with organic material. The accumulation of organic material in the area not only providing the adsorbing surfaces but in addition, the reducing environment formed prevents their possible remobilization.

## ACKNOWLEDGEMENTS

This research was conducted with joint funding from the Malaysia Ministry of Science and Technology under the Intensified Research for Priority Areas (IRPA) project number 55007. The authors wish to express their gratitude to Oceanography Laboratory teams for their invaluable assistance and hospitality throughout the sampling period.

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