Sains Malaysiana 39(4)(2010): 543–547

Spatial Distribution of Lead and Copper in the Bottom Sediments of Pahang River Estuary, Pahang, Malaysia

(Taburan Plumbum dan Kuprum di Sedimen Dasar Muara Sungai Pahang, Pahang, Malaysia)

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ABSTRACT

Bottom sediment samples from 30 stations of Pahang River estuary collected in April 2008 were analyzed for the concentration of Pb and Cu using the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The average concentrations of Pb and Cu were 74.31 ± 22.97 µg/g dry weights and 18.65 ± 7.65 µg/g dry weights, respectively. In this study, the concentrations were significantly higher near the mouth river and declined as the sampling points were further away from the estuary. Generally, the concentrations of heavy metals were relatively low when compare with other studies in Malaysia. However, the calculated enrichment factors (EF) obtained for Pb, has a slightly higher value, and was probably influenced by anthropogenic input. The concentration for both metals increased with the decrease of mean size, suggesting their association with the fine fraction of the sediments.

Keywords: Copper; enrichment factor; estuarine sediment; lead; Pahang River estuary

ABSTRAK

Sampel sedimen dasar dari 30 stesen di muara Sungai Pahang diambil pada bulan Ogos 2008 dan diukur kepekatan bagi Pb dan Cu dengan menggunakan peralatan Coupled Plasma-Mass Spectrometry (ICP-MS). Purata kepekatan Pb and Cu adalah masing-masing 74.31 ± 22.97 µg/g berat kering and 18.65 ± 7.65 µg/g berat kering. Dalam kajian ini, kepekatan bagi kedua-dua logam secara signifikan adalah tinggi di kawasan muara berbanding di kawasan yang lebih jauh daripada muara. Secara umumnya, kepekatan logam di kawasan kajian adalah secara relatifnya rendah berbanding dengan kawasan kajian lain di Malaysia. Walau bagaimanapun, nilai faktor pengkayaan (EF) yang dikira didapati mempunyai nilai yang sedikit tinggi bagi Pb, yang mana berkemungkinan dipengaruhi oleh input antropogenik. Kepekatan logam ini meningkat dengan pengecilan saiz sedimen, mencadangkan perhubungan logam dengan sedimen yang bersaiz kecil.

Kata kunci: Faktor pengkayaan; kuprum; muara Sungai Pahang; plumbum; sedimen muara

INTRODUCTION

Heavy metals are one of the more serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems (Balachandran et al. 2005; Caeiro et al. 2005; Tam & Wong 2000). Following the introduction of heavy metal contaminants into a river, whether via natural or anthropogenic sources, they partition between aqueous (pore water, overlying water) and solid phases (sediment, suspended particulate matter and biota) (Prudencioa et al. 2007; Zhang et al. 2007). Depending on hydrodynamics, biogeochemical processes and environmental conditions (redox, pH, salinity and temperature) of rivers, sediments are recognized as an important sink of heavy metals in aquatic systems as well as a potential non-point source which may directly affect overlying waters (Pekey 2006).

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 metals like Pb and Cu are introduced into the ocean system through river runoff, *in situ* primary production and anthropogenic impacts. Contamination caused by heavy metals affects both ocean waters, those of the continental shelf and the coastal zone where, besides having a longer residence time, metal concentrations are higher due to input and transport by river runoff and the proximity to industrial and urban zones (Alagarsamy 2005; Karageorgis et al. 1998).

In recent years, the study area especially for the first 5 km downstream, along the Kuala Pahang estuary 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. Sand mining and fishing activities 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 article was to discuss the distribution and levels of sediments contamination of Pb and Cu with regards to the sedimentological conditions of the area.

MATERIALS AND METHODS

SAMPLING SITE AND SAMPLES COLLECTION

The study was carried out at Pahang River estuary. The Pahang River estuary is located at Pekan which is situated 50 km south of Kuantan (Figure 1). This area has a humid tropical climate with two monsoon periods, characterized by bimodal pattern: southwest and northeast monsoons bringing an annual rainfall which varies between 1488 to 3071 mm. The Pekan area is mostly influenced by the semidiurnal tides with two high tides and two low tides, within a lunar day. The surface sediment samples of approximately 250 g were obtained from 30 stations in Pahang waters using a Smith McIntyre in April 2008 using a speed boat.

HEAVY METALS ANALYSIS METHODS

The sediment samples were digested for the analyses of total Pb and Cu following the published methods with some modifications (Defew et al. 2005; Noriki et al. 1980; Sen Gupta & Bertrand 1995). An inductively-coupled plasma mass spectrometer (ICP-MS) was used for the precise determination of Pb and Cu in the digested sediment. The digestion method involved heating of 50 mg of a fine powdered sample in a sealed Teflon vessel with a 1.5 mL of mixed acid solution (concentrated HF, HNO_3 and HCl). The Teflon vessel was kept at 150°C for 5 h. After cooling, a 3.0 mL of mixed solution of EDTA and boric acid was added and the vessel was heated again at 150°C for 5 h. The content of the vessel was transferred into a 15 mL polypropylene test tube and was dilute to 10 mL with deionized water. The precision assessed by the replicate analyses was less than 3%.

SEDIMENT CHARACTERISTICS ANALYSIS METHODS

A sample which consists of more than 90% sand were analyzed using the dry sieving and wet sieving techniques. Meanwhile samples having more than 90% fine sediments were analyzed using the laser diffraction method (PSA). For the PSA method, the organic components were first removed by adding 20% hydrogen peroxide (H_2O_2) solution to the samples. The floc of finer particles was destroyed by adding a dispersing agent (5% calgon solution). Sediments collected composed of mostly (80% by weight) fine sediments, which is still within the detection limit of the laser diffraction machine. Thus, sediment grain size was analyzed using the laser diffraction method only. The mean, standard deviation and skewness of each sample were calculated by the moment's method using equations defined by McBride (1971).

RESULTS AND DISCUSSION

Figures 2 and 3 show the concentration of Pb and Cu in the bottom sediments of Pahang river estuary. The Pb concentration averaging 29.98 ± 30.48 μg/g dry weight, and varied from 6.80 - 86.49 μg/g dry weight and the

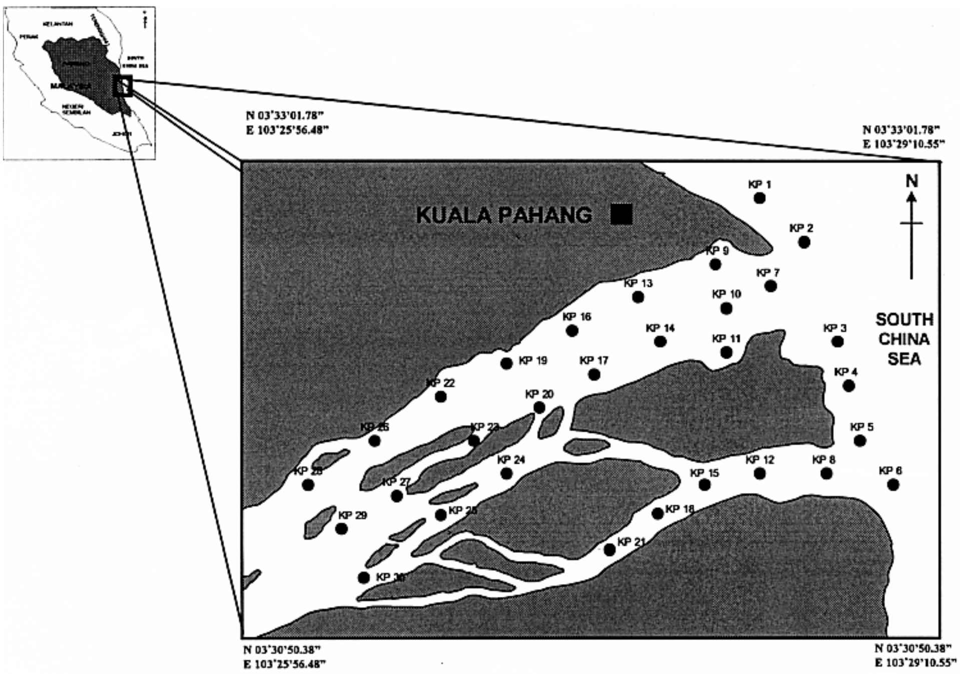

FIGURE 1. Location of the study area showing sampling site along Pahang River- Estuary, Pahang

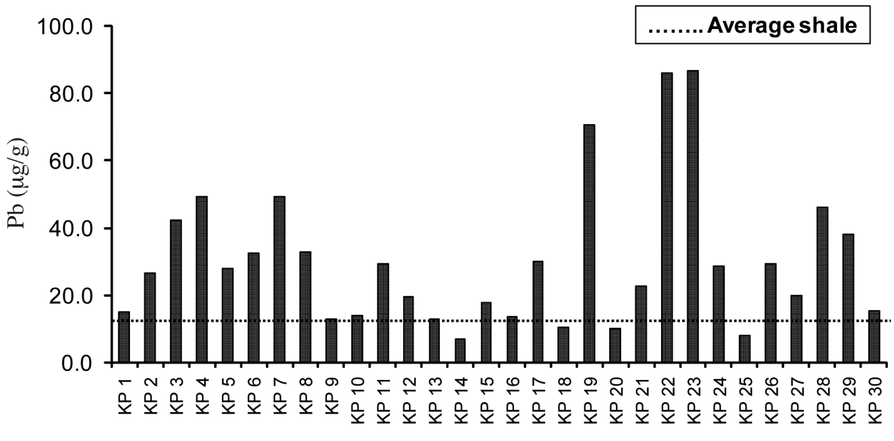

FIGURE 2. Pb concentrations versus Stations

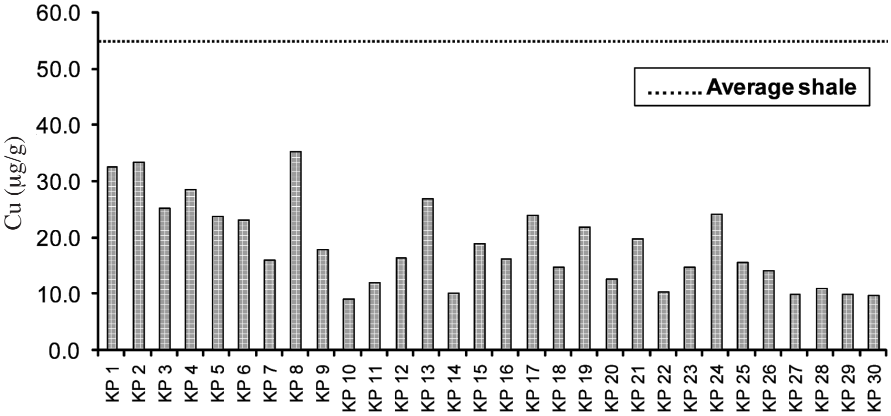

FIGURE 3. Cu concentrations versus Stations

average concentration was relatively higher than mean crustal materials values (Mason & Moore 1982). The highest concentration was found at station KP14, whilst the lowest was at station KP23. The average concentration of Cu is 18.65 ± 7.65 µg/g dry weights, and their average concentration was relatively lower than the mean crustal materials values (Mason & Moore 1982). The minimum concentration of Cu was observed at station KP10 (9.10 µg/g dry weights), whereas the maximum concentration was observed at station KP8 (35.36 µg/g dry weights). The higher Cu concentrations in station KP8 found were mostly caused by domestic waste and herbicide and pesticide surrounding agricultural areas.

Relatively higher Pb and Cu concentration were likely due to seabed topography which is capable of trapping metals containing sediments. The contribution of these metals in the study area would likely be due to the anthropogenic activities such as boating, sand mining (Kamaruzzaman et al. 2003), and sea dumping activities. Analysis of variance (ANOVA) for both Pb and Cu concentrations shows a significant difference between the stations ($P<0.05$). The fate and consequences of metals in the aquatic environment depend largely on the physical and chemical conditions of the water. For example, metals are generally more toxic at lower salinities, and a reduction in pH can increase the concentration of soluble heavy metals in water (Gambrell et al. 1991; Gambrell 1994). Furthermore, the significance difference might be the effects of different sources of heavy metal inputs into the estuary.

The sedimentological characteristics of Pahang river-estuary, like most other coastal environments, are much dependent upon the combination of physical forces such as freshwater runoff, tidal currents and waves (Kamaruzzaman et al. 2003). In this study area, particle mean size ranged from -0.24 Ø to 7.23 Ø with the average of 4.51 ± 3.13 Ø. The sediment mean size shows a significant difference between all stations with the $p<0.05$.

Pb and Cu show a significant relationship with the sediment mean size. This phenomenon was also found at Terengganu river- estuary (Kamaruzzaman et al. 2004b) and Paka river estuary (Kamaruzzaman et al. 2006). These correlations show that the fine-grained suspended and bottom sediment particles (silt and clay) accumulate greater concentrations of contaminants than coarser particles, especially those contaminants with low water solubility. Fine-grained particles have properties that allow different physiochemical sorption and ion exchange of contaminants than coarser particles (Kamaruzzaman et al. 2008; Lu et al. 2005).

A common approach to estimating the anthropogenic impact on sediments is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background (Adamo et al. 2005; Mendil & Uluozlu 2005). The EF method normalizes the measured heavy metal content with respect to a sample reference metal such as Fe or Al (Daessle et al. 2004; Liaghanti et al. 2003). In this study, Al was used as normalizing element for determining anthropogenic pollution sources in the Pahang river estuarine sediment according to the formula below:

$$\mathrm{EF} = (E/\,Al)\ \text{sediment} / (E/\,Al)\ \text{crust},$$

where, (E/ Al) sediment and (E/ Al) crust are the relative concentrations of the respective element E and Al in the sediment and in the crustal material, respectively (Prudencioa et al. 2007; Zhang et al. 2007).

The calculated EF value for Pb and Cu are 3.03 ± 3.11 and 0.39 ± 0.13, respectively. In this study, the levels of Cu proved to be deficiency to minimal enrichment and it can be concluded that the sources of Cu is solely natural and coming from the earth's surface and thus incorporated into the sediments. However, the relatively higher EF value found in Pb indicates that this metal can be considered to be predominantly anthropogenic in origin in the study area.

Conclusion

The EF value indicated that the sediments at Pahang River-estuary were moderately enriched by Pb, while the Cu occurs naturally and not greatly caused by anthropogenic and human activities. The relatively high concentration of the studied metal clearly indicates that the main sources of pollution were probably come from anthropogenic inputs such as fishing activities and dumping of sediment dredged which actively occurred along the Pahang River estuary.

References

Adamo P., Arienzo M., Impreto M., Naimo D., Nardi G. & Stanzione D. 2005. Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. *Chemosphere* 61: 800-809.

Alagarsamy R. 2006. Distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary, west coast of India. *Estuarine, Coastal and Shelf Science* 67: 333-339.

Balachandran K. K., Lalu Raj C. M., Nair M., Joseph T., Sheeba P. & Venugopal P. 2005. Heavy metal accumulation in a flow restricted, tropical estuary. *Estuarine, Coastal and Shelf Science* 65: 361-370.

Caeiro S., Costa M.H., Ramos T.B., Fernandes F., Silveria N., Coimbra A., Medeiros G. & Painho M. 2005. Assessing heavy metal contamination in Sado Estuary sediment: An index analysis approach. *Ecological Indicators* 5: 151-169.

Daeselle L.W., Camacho- Ibar V.F., Carriquiry J.D. & Ortiz-Hernandez M.C. 2004. The geochemistry and sources of metals and phosphorus in the recent sediments from the Northern Gulf of California. *Continental Shelf Research* 24: 2093-2106.

Defew L.H., Mair J.M. & Guzman H.M. 2005. An assessment of metal contamination in mangrove sediments and leaves from Punta mala Bay, Pacific Panama. *Marine Pollution Bulletin* 50: 547-552.

Gambrel, R.P., Wiesepape, J.B., Patrick, W.H. & Duff, M.C. 1991. The effects of pH, redox and salinity on metal release from a contaminated sediment. *Water Air Soil Pollut*. 57: 359-367.

Gambrell, R.P. 1994. Trace and toxic metals in wetland: A review. *J. Environ. Qual*. 23: 883-891.

Kamaruzzaman, B.Y., Sulong, I., Jamil, B.T. & Hasrizal, S. 2003. Sediment accretion and trace metal concentrations in the surface sediment of Kuantan mangrove forest, Malaysia. *Chemical Research Communication* 16: 2-13.

Kamaruzzaman B.Y., Ong M.C. & Willison K.Y.S. 2004a. Trace metal concentration in the surface sediments of Paka mangrove forest, Terengganu, Malaysia. *Malaysian Journal of Science* 23(2): 55-60.

Kamaruzzaman B.Y., Ong M.C. & Willison K.Y.S. 2004b. Taburan Kepekatan Kobalt, Kuprum, Zink dan Plumbum di dalam Sedimen Dasar Muara Sungai Terengganu, Terengganu, Malaysia. *Sains Malaysiana* 33(2): 147-156.

Kamaruzzaman B.Y., Ong M.C., Norr Azhar M.S., Shahbudin S. & Jalal K.C.A. 2008. Geochemistry of Sediment in the Major Estuarine Mangrove Forest of Terengganu Region, Malaysia. American *Journal of Applied Science* 5(12): 1707-1712.

Kamaruzzaman B.Y., Willison K.Y.S. & Ong M.C. 2006. The concentration of Manganese, Copper, Zinc, Lead and Thorium in Sediments of Paka Estuary, Terengganu, Malaysia. *Pertanika Journal of Science and Technology* 14(1): 53-61.

Karageorgis A., Anagnostou C.H., Sioulas A., Chronis G. & Papathanassiou E. Sediment geochemistry and mineralogy in Milos bay, SW Kyklades, Aegean Sea, Greece. *Journal of Marine Systems* 16: 269-281.

Liaghati T., Micaela P. & Malcolm C. 2003. Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek catchment, southeast Quennsland, Australia. *Environment International* 29: 935-948.

Lua X.Q., Werner I. & Young T.M. 2005. Geochemistry and bioavailability of metals in sediments from northern San Francisco Bay. *Environment International* 31: 593-602.

Mason, B. & Moore, C.B. 1982. *Principles of Geochemistry*. 4th edition, New York: J. Wiley and Sons.

Masson M., Blanc G. & Schafer J. 2006. Geochemical signals and source contributions to heavy metal (Cd, Zn, Pb, Cu) fluxes into the Gironde Estuary via its major tributaries. *Science of the Total Environment* 370: 133-146.

McBride, E.F. 1971. Mathematical treatment of grain size distribution data. In *Procedure in Sedimentary Petrology,* edited by R.A. Davies Jr. (ed.) New York: Wiley Interscience.

Meade, R.H. 1972. Transport and deposition of sediments in estuaries. *The Geological Society of American Members* 133: 91-117.

Mendil D.O. & Uluozu O.D. 2007. Determination of trace metal levels in sediment and five fish species from lakes in Tokat, Turkey. *Food Chemistry* 101: 739-745.

Mudroch, A. & J. M. Azcul, 1995. *Manual of Aquatic Sediment Sampling*. Boca Raton: Lewis Publishers.

Noriki, S.K., T. Nakanishi, M. Fukawa, T. Uematsu, H. Uchida & S. Tsunogai, 1980. Use of a Teflon *vessel* for the decomposition followed by determination of chemical constituents of various marine samples. *Bull. Fac. Fish., Hokkaido Uni*. 31: 354-465.

Pekey H. 2006. The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. *Marine Pollution Bulletin* 52: 1197-1208.

Prudencioa M.I., Gonzalezb M.I., Diasa M.I., Galanb E. & Ruizc F. 2007. Geochemistry of sediments from El Melah lagoon (NE Tunisia): A contribution for the evaluation of anthropogenic inputs. *Journal of Arid Environments* 69: 285-298.

Sen Gupta J.G & Bertrand N.B. 1995. Direct ICP-MS determination of trace and ultratrace elements in geological materials after decomposition in a microwave oven. I. Quantitation of Y, Th, U and the lanthanides. *Talanta* 42(11): 1595-1607.

Tam, N.F.Y. & Wong, Y.S. 2000. Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution* 110: 195-205.

WHO. 1998. *Copper: Environmental Health Criteria Monograph 200*. International Program on Chemical Safety (IPCS).

Zhang L.P., Ye X., Feng H., Jing Y.H., Ouyang T., Yu. X.T., Liang R.Y., Gao C.T. & Chen W.Q. 2007. Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Marine Pollution Bulletin* 54: 974-982.

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Received: 12 June 2009
Accepted: 22 December 2009