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Distribution of Chromium, Manganese and Cobalt in the Bottom Sediment of Pahang River-Estuary, Pahang, Malaysia

[1]B.Y. Kamaruzzaman, [1]A. Siti Waznah, [1]M.S. Mohd Zahir, [2]M.C. Ong, [1]S. Shahbudin, [1]K.C.A. Jalal, [1]Z. Rina Sharlinda, [1]A.T. Shuhada, [1]B. Akbar John, [2]B. Joseph, [3]S.M. Al-Barwani and [3]J.S. Goddard
[1]Institute of Oceanography and Maritime Studies, International Islamic University Malaysia, Bandar Indera Mahkota, 25200 Kuantan, Pahang, Malaysia
[2]Faculty of Maritime Studies and Marine Science, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia
[3]Department of Marine Science and Fisheries, Sultan Qaboos University, P.O. Box 34, Al-Khod 123, Sultanate of Oman

Abstract: Bottom sediments from 62 stations at Pahang river-estuary were analyzed for the concentrations of Chromium (Cr), Manganese (Mn) and Cobalt (Co). Heavy metal concentrations were analyzed by using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The average dry weight concentrations of Cr, Mn and Co were 62.80±20.04, 416.21±127.41 and 7.93±3.25 $\mu g\ g^{-1}$, respectively. The observed concentrations of the studied metals were significantly higher near the estuary and declining as the sampling points were further away from the estuary. The Enrichment Factors (EFs) were calculated and all elements showed metal contamination was predominantly of terrigenous in origin.

Key words: Pahang river-estuary, shale value, metal accumulation, pekan river, enrichment factor (EF)

INTRODUCTION

Sediments can be sensitive indicators for monitoring contaminants in aquatic environments. The sediments were polluted with various kinds of hazardous and toxic substances (Kamaruzzaman *et al*., 2011). Heavy metals are one of the main pollutant classes which gets accumulate in bottom sediments primarily due to the urban developmental practices. Sources of heavy metal contamination are numerous and tend to be associated with urban runoff, sewage treatment plants, industrial effluents and wastes, mining operations, boating activities, domestic garbage dumps and agricultural fungicide runoff etc. Sediment in the estuary plays an important role as a carrier of trace metals in the hydrological cycle, where they can react as traps for trace elements especially the pollutant elements (Chester *et al*., 1994). Sediments can also act as a scavenger agent for heavy metal and an adsorptive sink in aquatic environment. It is therefore considered to be an appropriate indicator of heavy metal pollution (Idris *et al*., 2007). These phenomena were described by previous study in the river watershed where the sediment load is significant in the transport of pollutants (Olsen *et al*., 1989). Sediments in estuaries have multiple sources with the main sources being rivers, offshore and littoral areas and the banks of estuaries themselves (Burton, 1988). Their secondary sources such as from the sediment flocculation that occurs at low-high salinity contact is also an important phenomenon with regard to elemental behavior (Olivarez and Owen, 1991). The transportation and mixing of those different sources of input can be explained largely through the measurement of the chemical composition in the sediments (Idris *et al*., 2007).

Concentrations of trace metals in estuaries can be elevated due to high inputs from natural as well as anthropogenic sources (Alemdaroglu *et al*., 2003; Heyvaert *et al*., 2000). Recently Yap *et al*. (2002, 2003) reported the existing Pb and Cu concentration in the sediments of Malaysian west coast. The studies regarding geochemical profile of sediments in east coast of Malaysia is still scanty. In recent years, Pahang River 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 activities in this area and is the catalyst for other supportive industries to develop around the area. In view of the

Corresponding Author: B.Y. Kamaruzzaman, Institute of Oceanography and Maritime Studies, International Islamic University Malaysia, Bandar Indera Mahkota, 25200 Kuantan, Pahang, Malaysia

importance of the estuary to various aspects of the environment, research on the concentration of heavy metals as well as their distribution pattern in sediment was carried out.

MATERIALS AND METHODS

Sampling sites and samples collection: The study was carried out at Pahang River estuary which located at Pekan and situated 50 km south of Kuantan, Malaysia (Fig. 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 and 3071 mm. The Pekan river is mostly influenced by the semidiurnal tides and the riverbanks provides suitable habitat for mangroves at downstream but dominated by Nypa at upstream due to low salinity and soft bottom sediment. A total of 62 bottom sediments were collected using a Smith McIntyre at Pahang river-estuary during 2008. Collected samples were transferred to the polyethylene bags and labelled properly and transported to the laboratory prior to the analysis. Samples were kept in hot air oven at 60°C for 7 days to remove the moisture content and finely powdered for further analysis.

Heavy metal analysis: Acid digestion method were adopted to determine the total Cr, Mn and Co levels in the sediment samples following the published methods with some modifications (Defew *et al*., 2005; Munksgaard *et al*., 1998; Yuan *et al*., 2004). An inductively-coupled plasma mass spectrometer (ICP-MS) was used for the precise determination of Cr, Mn and Co in the digested sediment. The digestion processes involved heating up 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, 3.0 mL of mixed solution of EDTA and boric acid were added and the vessels were heated again at 150°C for 5 h. After cooling, the content of the vessels were transferred into a 15 mL polypropylene test tube and were dilute to 10 mL with deionized water. The precision were assessed by the replicate analysis which was less than 3%.

RESULTS AND DISCUSSION

In general, the distributions pattern of Cr, Mn and Co in the sediments of Pahang river-estuary showed an increased concentration towards the downstream area. This phenomenon might be due to the effects of prevailing water salinity that has apparent influence on the distribution of selected metals. Similar observation was also reported by Callaway *et al*. (1998), who stated that the water salinity could influence in changing the heavy metals from insoluble form to a soluble form that

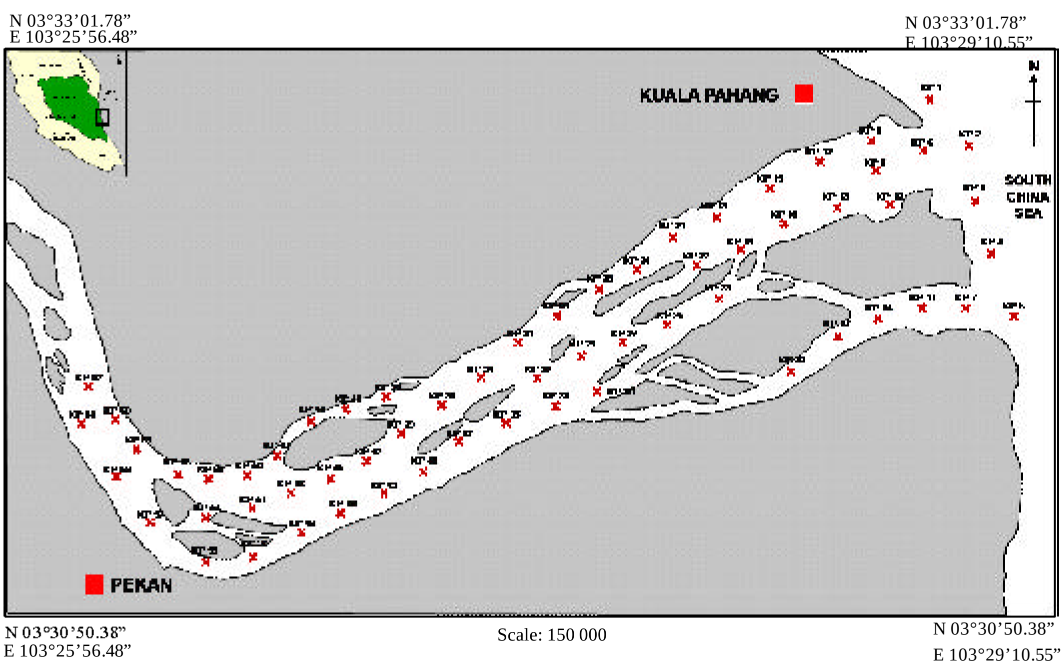

Fig. 1: Location of the study area showing sampling site along Pahang River-Estuary

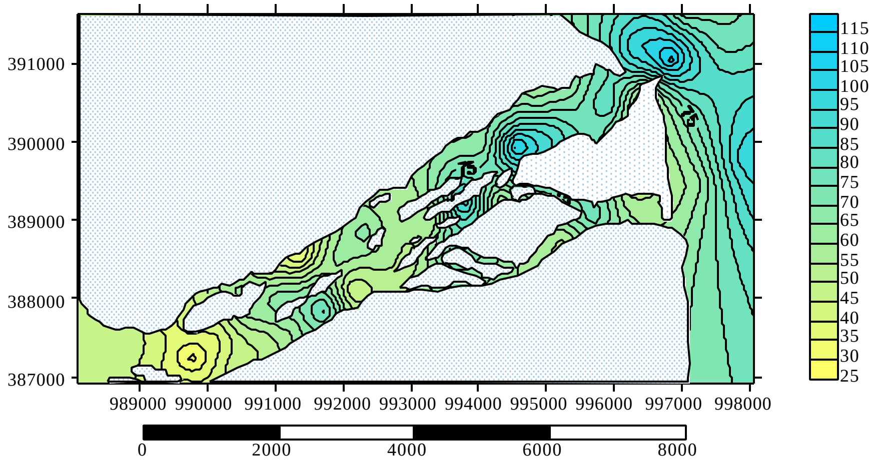

Fig. 2: The distribution pattern of Chromium (Cr) in Pahang River-estuary, Pahang, Malaysia

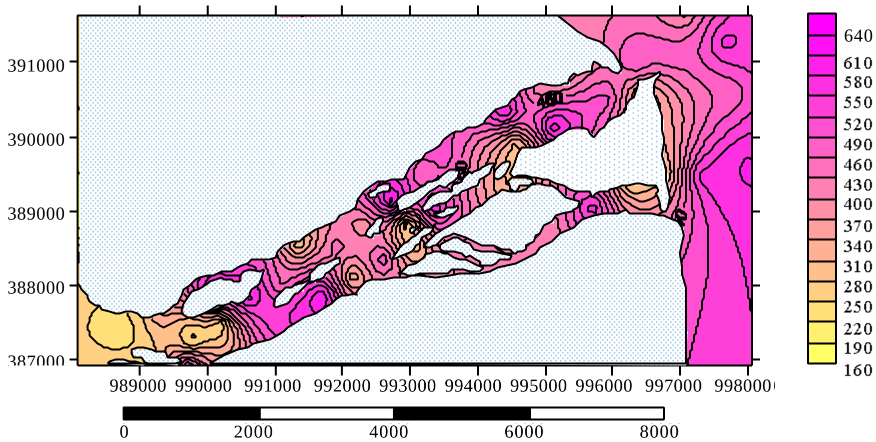

Fig. 3: The distribution pattern of Manganese (Mn) in Pahang River-estuary, Pahang

might be easily trapped by fine sediments. Besides, the complex sediment-water system, speed of water current, sediment matrix, availability and possible toxicity of contaminants are influenced by physic-chemical factors such as redox gradient, pH, salinity and temperature which in-turn determine the amount of heavy metal absorption by the superficial sediments (Ankley *et al*., 1992; Leivouri, 1998; Maher and Aislabie, 1992) .

The concentration of Cr in the bottom sediment ranged between 26.80 and 114.13 μg g^{-1} dry weights with mean concentration of 62.80±20.04 μg g^{-1} dry weights (Fig. 2). For Mn, the average concentration observed was 416.21±127.41 μg g^{-1} dry weights, which varied between 160.59 and 633.43 μg g^{-1} dry weights (Fig. 3). The concentration of Co was relatively low, ranging between 3.06 and 15.23 μg g^{-1} dry weights, with mean concentration value of 7.93±3.25 μg g^{-1} dry weights (Fig. 4). Overall, the concentration of the selected heavy metals was relatively lower when compared with their respective average shale values (Table 1). The observed concentration of Cr, Mn and Co from the present study were comparable with other estuarine and coastal sediments such as more intensely developed areas of Penang on the west coast of Malaysia and Terengganu River (Kamaruzzaman *et al*., 2004; Khalik *et al*., 1997).

It was report that the change in chemical composition of sediment from different sampling stations had direct influence on the absorption of different heavy metals at different rates (El-Nemr *et al*., 2007; Liu *et al*., 2003). The variations in heavy metal accumulation at different stations also depend on the rate and sources of contaminations, hence it is necessary do determine the pollution level of the study area. The Enrichment Factors

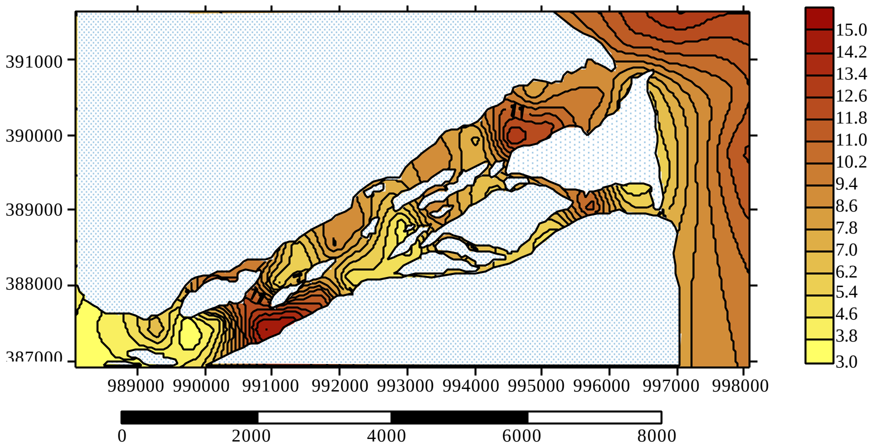

Fig. 4: The distribution pattern of Cobalt (Co) in Pahang River-estuary, Pahang

Table 1: The observed concentration of Cr, Mn and Co in the present study were compared with available data from previous studies

Element	Present study	Terengganu river (Kamaruzzaman *et al.*, 2004)	Juru, Penang (Khalik *et al.*, 1997)	Average Shale (Mason and Moore, 1982)
Cr	62.80±20.04	82.0±44	46.6±15.7	90
Mn	416.21±127.41	517.9±161.8	305.0±86	850
Co	7.93±3.25	15.1±7.4	5.1±1	25

Table 2: EF-value with respect to crustal ratios based on mean concentration determined in bottom sediments of Pahang river-estuary

Element	EF-value	Contamination Category
Cr	0.86±0.21	Deficiency to minimal enrichment
Mn	0.62±0.25	Deficiency to minimal enrichment
Co	0.42±0.14	Deficiency to minimal enrichment

(EF) for all the elements were calculated to determine the pollution status of the study area. Enrichment Factors (EFs) values lesser than 1.0 are considered to be non-significant, because such small enrichments might arise from difference in the composition of local soil material and reference soil used in EFs calculations (El-Nemr *et al.*, 2007; Liu *et al.*, 2003). The Efs value was calculated by the equation below:

$$EF = \frac{(C_X/C_{Al})_{sample}}{(C_X/C_{Al})_{crust}}$$

where, $(C_X/C_{Al})_{sample}$ is the ratio of concentration of the element being tested (C_X) to that of (C_{Al}) in the sediment sample and $(C_X/C_{Al})_{crust}$ is the same ratio in unpolluted reference baseline (Szefer *et al.*, 1996). Mason's soil composition was used as the reference and Al was used as normalizing element (Weijden, 2002; Tanner *et al.*, 2000). The calculated EF values showed that the heavy metal accumulation in the sediments was not due to anthropogenic activities (Table 2).

CONCLUSION

The Chromium (Cr), Manganese (Mn) and Cobalt (Co) distributions in Pahang river-estuary showed lower concentrations in the upstream and become higher towards the downstream sampling points. The calculated EF values showed that the sediments distribution occurs naturally and not greatly caused by anthropogenic and human activities. Anthropogenic sources from the fishing activities and industrial area at the upstream might be the major reason contributing insignificant heavy metal accumulation at the estuarine system and thus it can be conclude that there were no serious heavy metal contaminations in the study area. It is also to be noted that study related to heavy metal contamination along the coastal areas of Malaysia is still scanty. A detailed and comprehensive study could be carried out to explore the existing status of various heavy metal contamination along the coastal waters of Peninsular Malaysia.

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