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Geochemical Proxy of Some Chemical Elements in Sediments of Kemaman River Estuary, Terengganu, Malaysia

(Proksi Geokimia bagi Beberapa Unsur Kimia di Dalam Sedimen Muara Sungai Kemaman, Terengganu, Malaysia)

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ABSTRACT

The concentrations of heavy metals (Mn, Co, Cu and Cr) were determined in the surface sediments from Kemaman River estuary using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). The relationship of heavy metal content with sediment particles size was studied. The average concentration of heavy metals are 597.8 µg/g dry weight, 16.0 µg/g dry weigh, 48.8 µg/g dry weight and 100.4 µg/g dry weight for Mn, Co, Cu and Cr, respectively. All metals showed low Enrichment Factor (EF) values (EF<1) when compared with Al which indicates that the elements in the sediment originated predominantly from crustal material or terigenous in origin. This study shows that there is a positive correlation between the mean particle size and the studied elements.

Keywords: Enrichment factor; Kemaman River estuary; particle size; surface sediment

ABSTRAK

Kepekatan logam berat (Mn, Co, Cu dan Cr) di dalam sedimen permukaan muara Sungai Kemaman telah dianalisis dengan menggunakan Spektrometri jisim – Plasma gandingan teraruh (ICP-MS). Hubungan di antara kepekatan logam berat dan saiz partikel sedimen juga dikaji. Purata kepekatan logam berat bagi Mn adalah 597.8 µg/g berat kering, 16.0 µg/g berat kering bagi Co, 48.8 µg/g berat kering bagi Cu dan 100.4 µg/g berat kering bagi Cr. Nilai Faktor Pengayaan (EF) yang rendah (EF<1) bagi semua logam dibandingkan dengan kepekatan Al boleh dianggap sebagai mempunyai sumber terigenus yang dominan atau secara semulajadi. Kajian ini juga menunjukkan hubungan kolerasi yang baik di antara kepekatan logam dan saiz purata partikel yang dikaji.

Kata kunci: Faktor pengayaan; muara Sungai Kemaman; saiz partikel; sedimen permukaan

INTRODUCTION

Estuaries often act as efficient reservoirs of river-borne and marine-derived pollutants (Duinker 1989). This is because various hydrodynamic features of these water bodies result in long residence times of material deposited there. The capacity of estuaries to act as a sink for pollutant and, in particular, heavy metals, is related to the anaerobic conditions generally found in bottom sediment. The accumulation of heavy metals in the bottom sediments of a river mouth depends not only on the distribution of the various fluvial inputs, but also on the chemical interaction between metals and the constituents of the sediments. Pollutants associated with sinking sediment particles become bound to inorganic or organic matrices by adsorption processes. For metals, the main adsorption processes are co-precipitation and co-reaction with oxides and hydroxides of manganese and iron, humic, clay structures and sulphide. These chemical species eventually control the bioavailability of metals with which they may become associated (Luoma 1983; Perin et al. 1997; Kehrig et al. 2003).

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 (Schuurmann & Market 1998; MacFarlane & Burchett 2000). Heavy metals are of high ecological significance since they are not removed from water as a result of self purification, but accumulated in reservoirs and enter the food chain (Loska & Wiechula 2003). The elevation of metal levels in a reservoir is shown mainly by an increase in their concentrations in the bottom sediment. Their occurrence in the environment results primarily from anthropogenic activities. Also, natural process, such as weathering of rocks and volcanic activities plays a noticeable role in enriching the water of reservoirs with heavy metals (Forstner & Whittman 1983; Nriagu 1989; Veena et al. 1997).

A range of studies have been conducted on trace metal distribution in estuarine and plain sediments throughout the world. The majority of these studies, however have concentrated on polluted areas with the objective of describing trace metal concentration to identify sources of the pollutants (Owen & Sandhu 2000; Chen et al. 2001; De Carlo & Anthony 2002). Determining the background metal levels in unpolluted areas, however, has not been studied widely. Identifying naturally elevated metal concentration is important because some metals can appear to be enriched, although when compared to their source such as bedrock material, it is concluded that such elevation may still be natural. Some studies have examined background levels (McMurtry et al. 1995), and others have concentrated on identifying the major factors which influence the geochemical character of sediments, their mobility and transport processes (Forstner et al. 1984; Arakel and Honjun 1992).

METHODOLOGY

The sampling sites were located in the Kemaman district which is about 180 km south of Kuala Terengganu, capital city of Terengganu. The Kemaman River and Chukai River in this district flow to the South China Sea through the Kemaman River estuary. The Kemaman River has a comparatively large drainage area compared to the Chukai River. Kemaman River also has a larger discharge and mean annual outflow compared to the Chukai River. In this study, 16 and 10 sampling points were fixed along Kemaman River and Chukai River, respectively (Figure 1).

The sediment samples were digested and the analyses for heavy metal concentration followed the standard methodologies with some modifications (Noriki et al. 1980; Kamaruzzaman 1999). All the apparatus were acid washed with 5% nitric acid and were oven dried. A total 50 mg sediment was constantly weighted and then placed into the Teflon beakers. Sediment samples were digested with 1.5 mL of concentrated of mix acid (HF, HCl and HNO_3), and kept in 150°C oven for 5 hours. The samples were then cooled and added with 3 mL of mixed solution of boric acids and EDTA and kept in the oven at 150°C for another 5 hours. The samples were cooled in room temperature and transferred into 10 mL test tube and were meshed up to 10mL with 5% HNO_3. The samples were analyzed by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS).

RESULTS AND DISCUSSION

Figure 2 shows the concentration of Mn, Co, Cu and Cr at Kemaman and Chukai Rivers. In this study, the average concentration of Mn was 597.8 μg/g dry weights, varied from 500.8 μg/g dry weights to 775.1 μg/g dry weights. The concentration was higher near the river mouth compared to upstream. Kemaman River had the higher Mn concentration than Chukai River. The highest concentration of Mn was at K6 and the lowest at K11. From the graph, the Mn concentration was homogenous apparently where

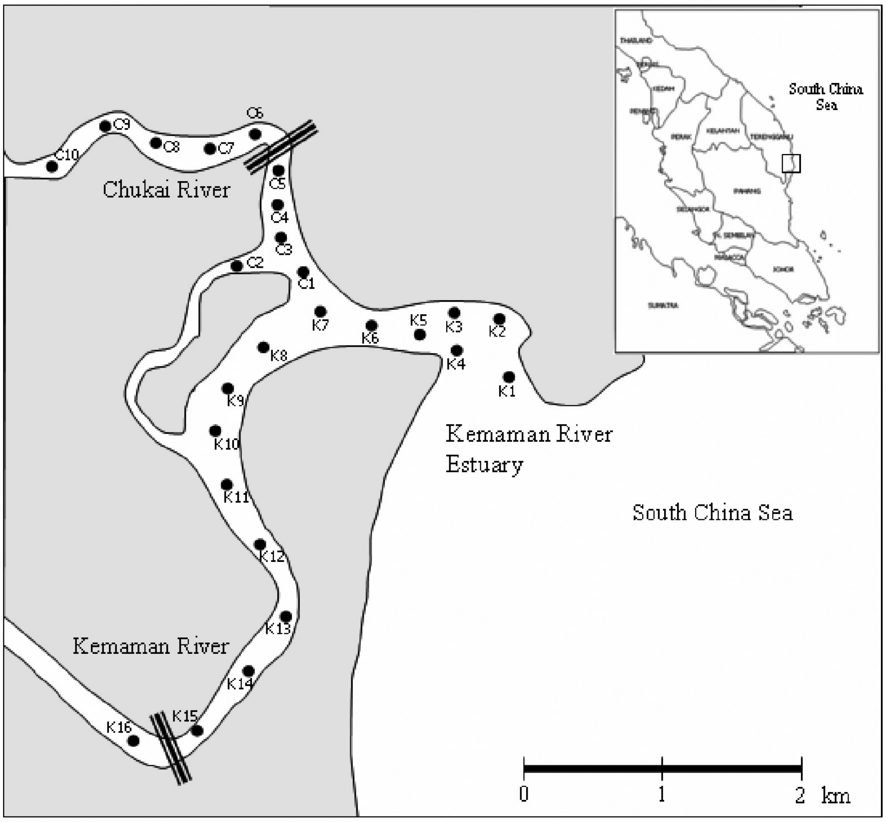

FIGURE 1. Location of study area showing the sampling point along Kemaman and Chukai River, Terengganu

the concentration was almost consistent. However, the $p<0.05$ calculated from the statistical test, ANOVA two way factor proved that Mn concentration of all the sampling point are significant different. For Co concentration, the highest stated at C1, 19.8 μg/g dry weights while the lowest at K10, 12.2 μg/g dry weights, and average concentration, 16.0 μg/g dry weights. Chukai River had the higher concentration compared to Kemaman River. From the statistical test, ANOVA two way factor showed that there was a significant difference in Co concentration of all the sampling points ($p<0.05$).

On the other hand, C4 had the highest Cu concentration, 73.7 μg/g dry weights while the lowest, 28.5 μg/g dry weights at K10 and the average Cu concentration, 48.8 μg/g dry weights. From the graph, concentration of Cu in Kemaman River was lower than Chukai River. Similar

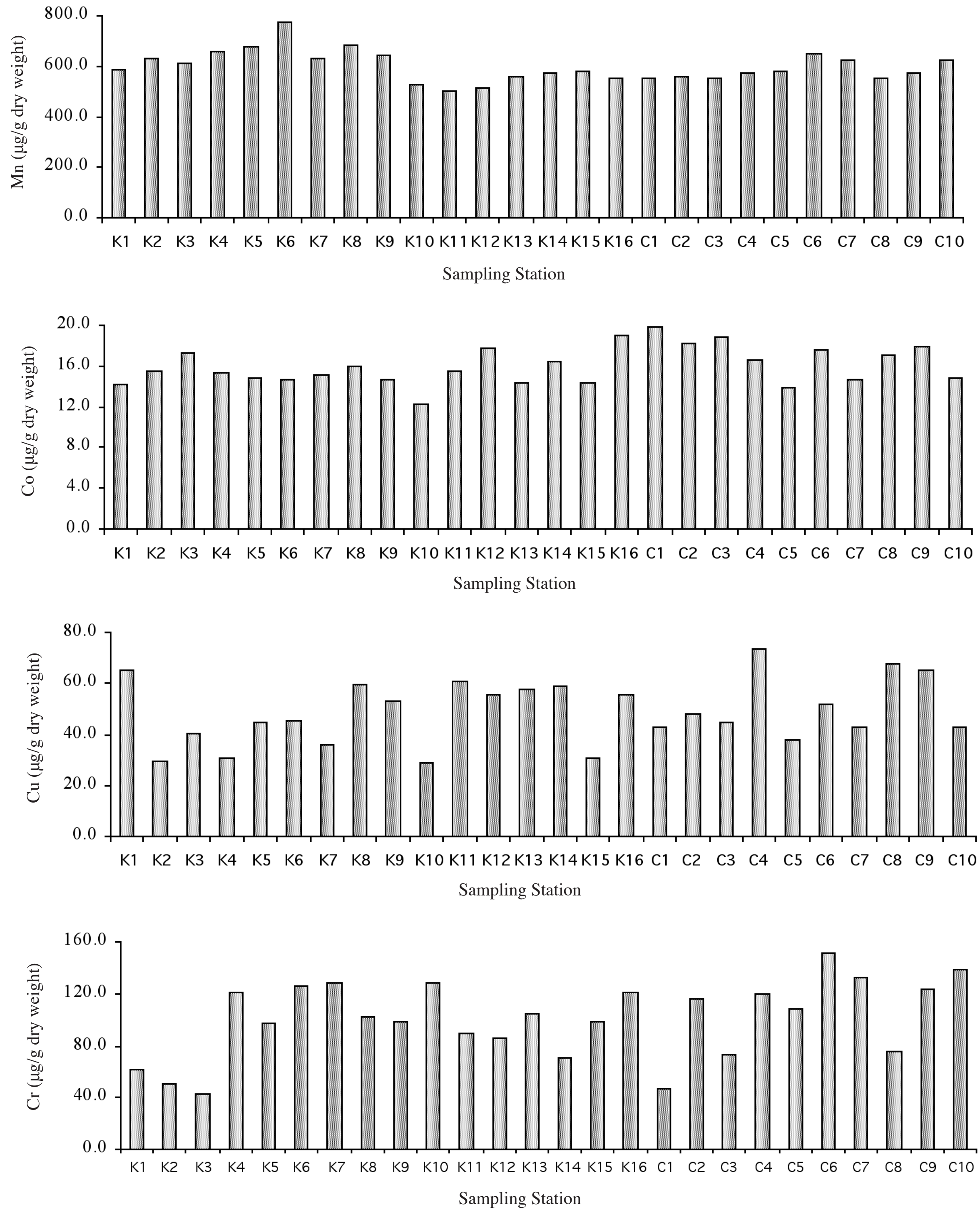

FIGURE 2. Concentrations of the Mn, Co, Cu and Cr in the surface sediments of Kemaman and Chukai River

with other metals, the statistical test, ANOVA two way factor also showed the significant difference among the sampling points with $p<0.05$. The average concentration of Cr was 100.4 μg/g dry weights, ranged from 42.3 μg/g dry weights at K3 to 150.8 μg/g dry weights at C6. The concentration was lower at the river mouth and higher toward the upstream. The $p<0.05$ from ANOVA two way factor proved that the concentration in each sampling points was significantly different.

From the study observation, the concentrations of Cu and Cr were higher compared to those in the average shale (Table 1) indicate that the main source of heavy metal enrichment came from anthropogenic and non-anthropogenic elements that were deposited directly or indirectly by human activities such as fisheries activities and city sewage effluents. The enhanced Cu concentration found in the surface sediments reflected the increase of concentration in the exchangeable fraction. Other sources of Cu in sediment of both the rivers are the usage of leaded gasoline in boats and also emissions from automobiles consuming leaded petrol from vehicles using the major road (Ong 2006). The concentration of Cr was influenced by the human activities and anthropogenic elements were deposited directly or indirectly such as mining operation, agricultural and burning fossil fuel via riverine influx which can be observed at the river banks of Kemaman and Chukai Rivers (Kennish 1994; Segura et al. 2006; Farkas et al. 2007). The average concentrations of Co and Mn were relatively lower with the average concentration of heavy metals in the earth's crust. Most of Co and Mn in the sediments were naturally origin, probably derived from the weathering of ultrametic rock. The geochemistry of Kemaman and Chukai River system was like most coastal environments via estuary or river, which were much dependence upon the combination of physical forces such as freshwater runoff, tidal currents and waves (Kamaruzzaman 1994; Sabine et al. 2006).

TABLE 1. Concentration of Mn, Co, Cu and Cr

	Kemaman and Chukai River	Mason and Moore 1982
Mn	597.8 μg/g dry weights	850 μg/g dry weights
Co	16.0 μg/g dry weights	19 μg/g dry weights
Cu	48.8 μg/g dry weights	45 μg/g dry weights
Cr	100.4 μg/g dry weights	90 μg/g dry weights

The sediment mean size value along the Kemaman and Chukai River ranged from 0.58 to 2.17 Ø or ranging from coarse sand to fine sand (Figure 3). The Kemaman estuary area (K1 to K9) and Chukai Rivers were dominated by fine sand, meanwhile the sampling station far from estuary (K10 to K16) were more dominated by the coarse sand. This can be explained by the high water velocity from the river flow which transport the fine sand and left the coarser sand on the river bed. The large amounts of suspended and fine sand were transported to the estuary, trapped and settle down during tidal (Kamaruzzaman et al. 2008).

The amount of heavy metals in sediment is also affected by the sediment characteristic, particularly, the type and quantities of organic matter, grain size, cation exchange capacity and mineral constituents (Tam & Wong 1995). Most heavy metals are bound in the fine-grained fraction (<63um) mostly because of its high surface area grain size ratio and humic substance content (Horowitz & Elrick 1987; Moore et al. 1989) where they have a potentially greater biological availability than those in the larger (2 mm-63 um) sediment fraction (Brayan & Langston 1992; Everaat & Fischer 1992). In this study, Mn showed significant correlation with the sediment mean size consistently ($r = 0.5444$) while the correlations of Co, Cu and Cr were not significantly with slightly lower r-values, 0.0875, 0.1968 and 0.0028, respectively.

For a better estimation of anthropogenic input, an enrichment factor (EF) was calculated for each metal by dividing its ratio to the normalising element by the same ratio found in the chosen baseline. Table 2 shows the calculated EFs of the analysed elements with respect to those determined in the crustal abundance (Grant & Middleton 1990), employing the equation

$$\text{Enrichment Factor (EF)} = \frac{(\text{Element concentration / Al})_{sediment}}{(\text{Element concentration / Al})_{crust}},$$

where $(\text{element concentration / Al})_{sediment}$ and $(\text{element concentration / Al})_{crust}$ are the relative concentrations of the respective element and Al in the sediment and in the crustal material, respectively (Molinari et al. 1993; Kremling & Streu 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 such as the weathering rocks and leaching of soils which are responsible for a portion of the concentrations of heavy metals in the sediments. It is clear from Table 2 that Mn, Co, Cu and Cr EF values were close to unity and may therefore be considered to be predominantly terrigenous in origin and not impacted seriously by an anthropogenic activity.

CONCLUSION

Generally metal concentrations in the sediment were much influenced by the natural processes. Their regional distribution of all elements showed relative enrichment near the upstream compared to the river mouth. The concentration of metals increased with the decreasing mean grain size, suggesting their association with the fine fraction of the sediments. From the EF calculation, it is clear that concentrations of the selected elements were not greatly caused by anthropogenic activities, but moderately occured naturally. Anthropogenic sources such as fishing activities and industrial estate may be the main reasons contributing insignificant heavy metal to

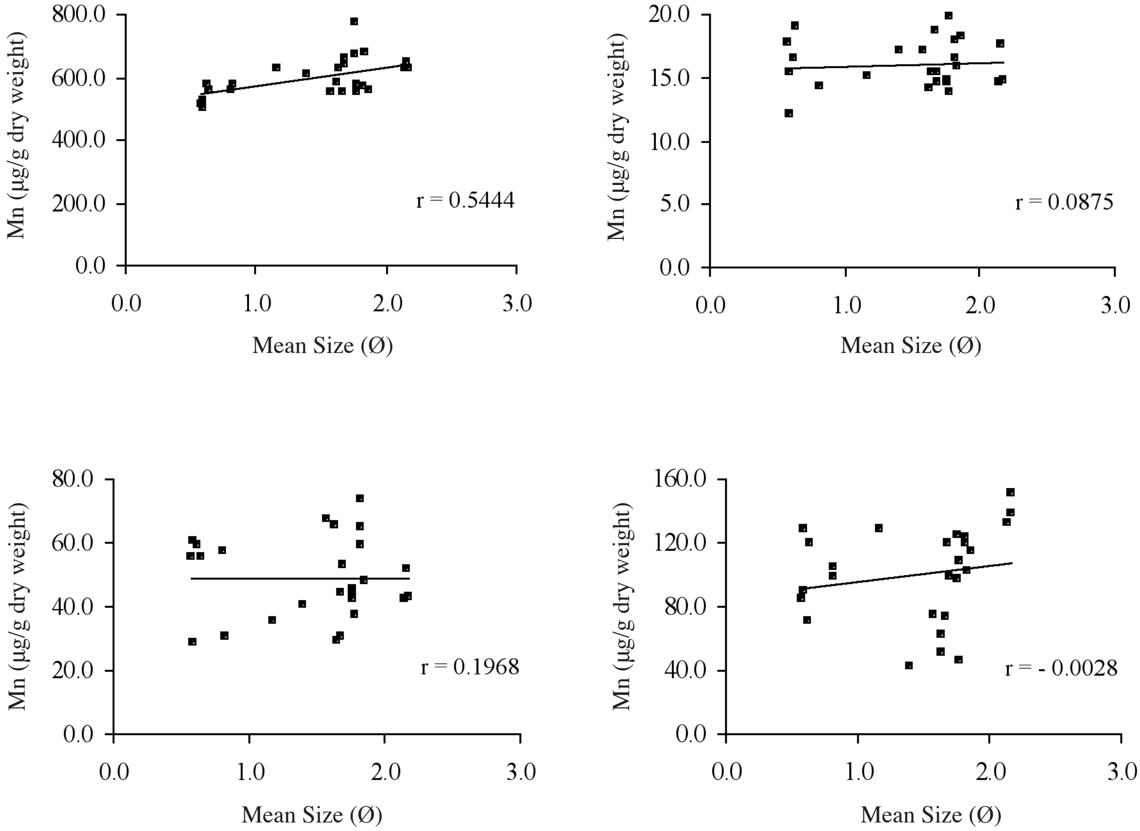

FIGURE 3. The correlation of Mn, Co, Cu and Cr concentration against sediment particle mean size at Kemaman and Chukai Rivers

TABLE 2. EF value with respect to crustal rations based on mean concentration determined at Kemaman and Chukai River sediment

Element	EF value
Mn	0.60
Co	0.73
Cu	0.94
Cr	0.95

the sediment of both rivers. In brief, it can be concluded that there were no serious heavy metal contaminations in Kemaman and Chukai Rivers in comparison with the world average shales.

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