

Geochemical proxy of sediment cores from Terengganu coastal water, Malaysia

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ABSTRACT

Two 40 cm sediment cores were sampled at the Terengganu coastal water within TR1 and TR2. The concentration of heavy metals (Co, Cu and Pb) was analyzed using the Inductively Coupled Plasma Mass Spectrometry (ICPMS). The average concentration of Co in core TR1 and TR2 were of $11.2 \pm 1.03 \mu\text{g/g}$ dry weights and $8.38 \pm 2.08 \mu\text{g/g}$ dry weights, and the average concentration of Cu were of $11.3 \pm 0.88 \mu\text{g/g}$ dry weights and $8.06 \pm 2.14 \mu\text{g/g}$ dry weights, respectively. The average concentration of Pb in TR1 and TR2 were $30.48 \pm 6.91 \mu\text{g/g}$ dry weight and $18.85 \pm 5.57 \mu\text{g/g}$ dry weights, respectively. The calculated enrichment factor (EF) values for the metals were close to 1 and may therefore be considered to be predominantly terrigenous in origin.

Key words: Cobalt, copper, lead, organic carbon; enrichment factor.

INTRODUCTION

Rapid increasing of human population, industrial and tourism activity in East-Coast of Malaysia can affect the quality of the ecological system especially coastal area. Through human activities, namely suburban, sewage disposal and city runoff are the main human discharge into coastal that can harmed marine environment. According to Förstner & Wittmann¹, urban effluents may carry important metals load, mostly in the colloidal and particulate fractions. Residential effluents are usually enriched by organic matter, suspended matter, detergent, synthetic organics and metals including Cd, Cu, Pb and Zn^{1,2,3}. Furthermore, city runoff may also contain high contents of metals (including Cd, Cu, Pd and Zn) due to the 'washing' of the city surfaces (building and streets). Metal sources in the city runoff include

may include loss of motor oils, decomposition of tires, vehicle exhaust, and street corrosion, weathered paint of building surfaces, corroded cars and metallic surfaces and atmospheric pollutants^{4,5}. In the marine environment, following flocculation and settling⁶, the effluent-born metals are finally accumulated into the harbour sediments thus creating important toxic metal deposits^{6,7}. Metal can also derived from the geological process; however the concentration can be very low and cannot harm the environment. The purpose of this study is to determine the distribution of metal in cores sediment and its relation to organic carbon in Terengganu coastal area.

MATERIAL AND METHOD

Sampling sites

Two sediment cores, TR1 and TR2 (Fig.1),

were collected at longitude 5° 40.4' N and latitude 103° 13.0' E and longitude 5° 37.6' N and latitude 103° 26.3' E, respectively. The outfall of the study area was usually influenced by the north-east monsoon seasons which prevailed from October to March. In this study, a 40 cm sediment core were collected with a plegger corer and was cut into segments of approximately 5 cm interval, labeled and stored in acid cleaned bottle for analysis. To avoid contamination, all plastic and glassware like beakers, volumetric flasks, spatulas and pipettes were soaked with nitric acid 5% over night, rinsed with distilled water and oven-dried.

Heavy metal analytical methods

The sediment samples were digested according to the published methods^{8,9,10}. An inductively-coupled plasma mass spectrometer (ICP-MS) was used for the quick and precise determinations of Co, Cu, and Pb in the digested marine sediment. Briefly, the digestion method involved the heating of 50 mg of a < 63 µm size sample in a sealed teflon vessel with a mixed concentrated acids of HF, HNO₃ and HCl in the ratio of 2.5: 3.5: 3.5. The teflon vessels were kept at 150 °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 °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 (NBS 1646) and the results coincided with the certified values within a difference of ± 3% (Table 1).

RESULTS AND DISCUSSION

Depth distribution

Depth profiles of Co, Cu and Pb are shown in Fig.2. Although some of these profiles show an increase in concentration toward the surface layer, this is not necessarily an indication for anthropogenic input. It is more likely that early diagenetic processes are responsible for this phenomenon^{11,12}. In this study, the average concentration of Co was consistent for both cores with 8.44 ± 2.11 µg/g dry weights and 8.36 ± 2.08 µg/g dry weight in TR1 and TR2, respectively. On the other hand, the average concentration of Cu was relatively higher in TR1 (11.3 ± 0.88 µg/g dry weight) compared to TR2 (8.07 ± 2.14 µg/g dry weight). The average concentration of Pb were also higher in TR1 (42.5 µg/g dry weights) compared to TR2 (18.9 µg/g dry weights). The vertical distribution of organic carbon content also having a similar trend (Table 2) with relatively higher average value in TR1 ($1.82\% \pm 0.64$) compared with TR2 ($1.08\% \pm 0.11$). The concentration of Co in both cores ranged from 10.6 µg/g dry weights to 13.2 µg/g dry weights (Fig.2). However, their average concentrations were much lower than the values of the average shales and the mean crustal materials¹³. Both cores depth profiles were almost constant even though TR1 has relatively higher average concentration compared to TR2. The difference of mean concentration in both transects could be due to the location of study area, where TR1 was located near the mainland or island that strongly effluence by human activities. The major removal processes for Co in sediment are the uptake of plants and chemical reaction activities in the sediment such as oxidation-reduction reactions, organic decay and excretion¹⁴. Therefore, the vertical variations in the depth profile might be due to temporal changes in biological

Table 1: The percentage recovery of metals analyzed in standard reference material (NBS 1646)

Element	Analytical Value (ug/g dry weights)	Certified Value (ug/g dry weights)	Recovery Test (%)
Co	4.81 ± 0.43	5.00 ± 0.42	96.20
Cu	9.58 ± 0.65	10.01 ± 0.34	95.70
Pb	12.30 ± 0.23	11.70 ± 1.2	105.13

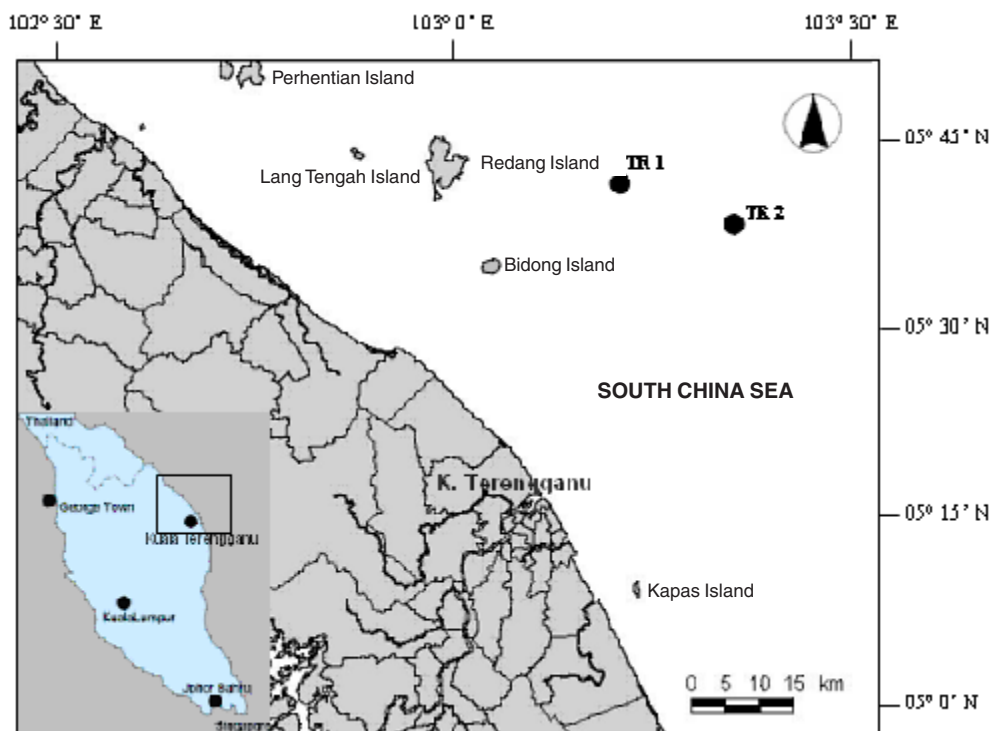


Fig. 1: Location of the core (%) study area in Terengganu coastal, east coast of Peninsular Malaysia.

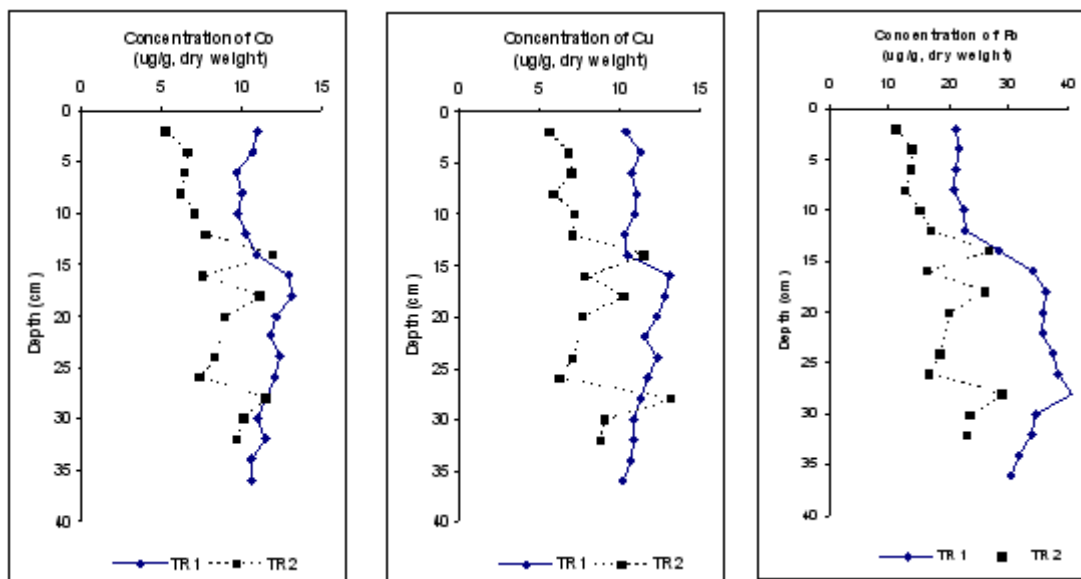


Fig. 2: Vertical distribution of Co, Cu and Pb in both cores TR1 and TR2

productivity. In this study, lower concentration of Co observed at upper depth can be considered to be primarily derived from the increased productivity as Co play an important role in biological processes where it is considered essential for the proper functioning of biological system of plants. In an other study at Kemaman mangrove forest¹⁵, Co has a fairly good correlation with organic matter, suggesting that the sedimentation of Co is controlled largely by the biogenic matter, although the detrital fraction was dominant in the sediments.

The concentration trend of Cu depth profile was similar with that of Co. As for Co, the average concentration of TR1 (11.32 µg/g dry weights) was also found relatively slightly higher than TR2 (8.06 µg/g dry weights). In this study, Cu ranged from 10.2 µg/g dry weights to 13.1 µg/g dry weights in TR1 and 5.2 µg/g dry weights to 11.9 µg/g dry weights in TR2. The mean concentration TR2 was lower than TR22 could be due to the elevated levels of toxic bivalent metals such as Cd and Pb competing with Cu as far as binding with organic matter, which may increase its solubility and

consequently uptake by plants. However, the average concentration in both cores was 7 times lower than the values of the average shales and the mean crustal materials¹³. Some higher concentrations at several depths can be related to the content of smectite¹⁶. However, the relative low concentration of Cu in the surface area might be due to the fact that it is been taken away intensely by plants during heavy vegetation. Loska *et al.*,¹⁷ reported that Cu is indispensable to the proper growth of plants and its deficiency in plants results in certain disturbances. However, Cu compounds from anthropogenic sources are more available to plants than the ones from natural sources

Lead ranged from 20.9 µg/g dry weights to 91.6 µg/g dry weights in TR1 and 11.1 µg/g dry weights to 26.6 µg/g dry weights in TR2. The slight decreased of Pb in the surface layer may be due to the early diagenetic loss of Pb, being a common phenomenon in the sediments. TR1 has higher value due to their location which was situated adjacent to the coastline near Terengganu River. The Pb saturation in TR1 might be caused by the

Table 2a: Calculated enrichment factors (EF) of Co, Cu and Pb for TR1, based on the mean concentrations determined in the whole sub-cores

TR1 Depth (cm)	Co	Cu	Pb
2	0.220	0.112	0.406
4	0.216	0.096	0.417
6	0.195	0.091	0.404
8	0.200	0.094	0.399
10	0.197	0.093	0.431
12	0.206	0.087	0.437
14	0.221	0.089	0.544
16	0.260	0.111	0.650
20	0.246	0.105	0.686
22	0.236	0.098	0.680
24	0.248	0.105	0.718
26	0.242	0.100	0.734
28	0.232	0.095	0.775
32	0.231	0.092	0.646
34	0.214	0.091	0.606
36	0.212	0.087	0.579
Average	0.226	0.097	0.581
	±0.021	±0.008	±0.132

Table 2b: Calculated enrichment factors (EF) of Co, Cu and Pb for TR2, based on the mean concentrations determined in the whole sub-cores

TR1 Depth (cm)	Co	Cu	Pb
2	0.1300	0.058	0.261
4	0.164	0.071	0.325
6	0.158	0.073	0.318
8	0.154	0.061	0.296
10	0.174	0.076	0.359
12	0.192	0.074	0.398
14	0.296	0.120	0.626
16	0.186	0.081	0.382
18	0.275	0.107	0.610
20	0.221	0.081	0.476
24	0.206	0.074	0.435
26	0.184	0.065	0.395
28	0.347	0.138	0.683
30	0.251	0.094	0.552
32	0.241	0.092	0.544
Average	0.212	0.084	0.444
	±0.060	±0.022	±0.131

direct anthropogenic contribution from the activities of settlement, industrial, agriculture and mining near the coastal areas. The average concentration in TR1 was close to the values of the average shales and the mean crustal materials but the average concentration in TR2 was more than 2 times lower the average shales and the mean crustal materials¹⁹. The enormous amounts of finer sediments at some depths may also increase the adsorbing surface of trace metals.

Sources of Elements

Since metals are naturally occurring and distributed in the environment, the above distributions are a combination of both natural background concentrations and whatever anthropogenic inputs occur within the region. Depending on the relative size of these two components, the anthropogenic inputs may be masked by background distributions. In order to reduce the masking effects of background distributions, metal concentrations measured in sediments may be normalized against the identified effects of specific partitions. Normalizing elements relative to Al is widely used to compensate for differences in grain size variations and carbonate content. This method is also a powerful tool for the comparison of trace metal contents in sediments in different areas around the world and can also be applied to determine enrichment factors (EF). In the present study the EF values are applied to evaluate the dominant source of the sediments and as indicators for pollution effects. Table 3 shows the calculated EFs of the analyzed elements with respect to those determined in the crustal abundance¹⁸, employing the equation:

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

In which $(E/Al)_{sed}$ and $(E/Al)_{crust}$ are the concentrations of the respective element E and Al in the sediment and in the crustal material^{19,20}. Enrichment factors close to 1 point to a crustal origin, while those with a factor more than 10 are considered to have a non-crustal sources. It is clear from Table 2a and 2b, all elements in both cores have values significantly about unity and are considered to be dominantly terrigenous in origin. Furthermore, there was no enrichment of Co, Cu and Pb found in all core sections, and therefore can be assumed to have no influence of anthropogenic input.

CONCLUSION

Generally metals concentrations in the sediment were much influenced by the natural processes. Anthropogenic sources such as fishing activities, urban and river runoff and industrial estate may be the main reasons contributing insignificant heavy metal to the coastal sediment. In conclusion, even though the study areas are rapidly developing, the activities at present are not widespread enough as to have much influence on pollution of the area.

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