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THE DISTRIBUTION OF Co, Pb AND Zn IN THE BOTTOM SEDIMENT OFFSHORE OF KEMAMAN, TERENGGANU, MALAYSIA DURING PRE- AND POST-MONSOON PERIODS

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Abstract: This study focussed on heavy-metal concentrations in sediment off the coast of Kemaman. Sampling was conducted at 21 stations during the pre-monsoon and post-monsoon seasons. Sediment was analysed for total concentration of Co, Pb and Zn using ICP-MS after total acid digestion. The grain size of the sediment samples were measured by dry sieving and using a particle-size analyser. In addition, organic carbon content in the sediment was determined using the wet dichromate-oxidation method. The average concentration of Co, Pb and Zn during the pre-monsoon season was 11.40±3.84 µg/g dry weight, 44.08±33.40 µg/g dry weight and 254.90±141.02 µg/g dry weight, respectively. The average concentration of Co, Pb and Zn during the post-monsoon season was 10.60±12.66 µg/g dry weight, 17.54±30.79 µg/g dry weight and 110.71±58.14 µg/g dry weight, respectively. Cu, Pb and Zn show poor correlation or negligible relationship with sediment particle size and organic carbon content. This study also found that all the elements have a mainly crustal origin rather than anthropogenic input with Geoaccumulation Index (I_{geo}) value of less than 1.0 and Enrichment Factors (EF) of 0.69-2.91which suggests minimal-to-moderate enrichment of the metals.

KEYWORDS: Cobalt, Lead, Zinc, Enrichment Factor, Geoaccumulation Index

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Introduction

Heavy metals are natural constituents of seawater and sediment and their occurrence in nature is controlled by weathering processes, including erosion of ore-bearing rocks, windblown dust and volcanic activity (Clark, 1992). The distribution of heavy metals in the marine environment varies widely from place to place. Some metals are mobilised by man to the atmosphere and hydrosphere at rates comparable and at times exceeding those by the weathering process. When a man-made input increases the concentration of substances above the natural background level for that particular area, this can lead to pollution (Clark, 1992).

Another important factor that influences heavy-metal concentration in sediment is the geochemical properties of the sediment. It has been shown that the amount of heavy-metal retention in sediment is affected by sediment characteristics, particularly, the type and quantities of organic matter, grain sizes, cation-exchange capacity and mineral constituents (Vertacnik *et al.*, 1995). Average contents of most elements increase with the decrease of grain size, mainly because of their high surface area-to-grain size ratio. Sediment-size characteristics provide information concerning the weathering phenomena about transport, sorting and sediment source. As a combined result, metal concentration in the sediment changes with space and time.

The east coast of Peninsular Malaysia, particularly the near-shore area has always been an interesting site for scientific studies since the area is likely to receive impacts from the sewage

disposal, mangrove-swamp conversion and land reclamation and fishing activities. In this study, the Dungun River, Paka River, Kertih River and Chukai-Kemaman River are the sources of pollutant input into the southern Terengganu waters. The study area lies in the wet tropics where highest rainfall is recorded during the northeast-monsoon season. The large volume of freshwater input, and with it lithogenic material via rivers into the Southern Terengganu waters during the monsoon season, is expected to have some influence on the geological, chemical as well as physical characteristics of the sediment. Therefore, this study was carried out to monitor the current status of Co, Pb and Zn concentrations in the sediment of southern Terengganu waters and to identify the possible sources of metals and the degree of enrichment.

Materials and Methods

Sampling

Surface sediments were collected during the pre-monsoon (September 2006) and post-monsoon (March 2007) seasons at 21 stations along the coastal waters of Dungun to Kemaman (southern Terengganu waters, South China Sea) as shown in figure 1 below. The sediment samples were collected using Smith McIntyre Grab and kept in clean labelled polyethylene bags. The samples were kept frozen until required for analysis in the laboratory.

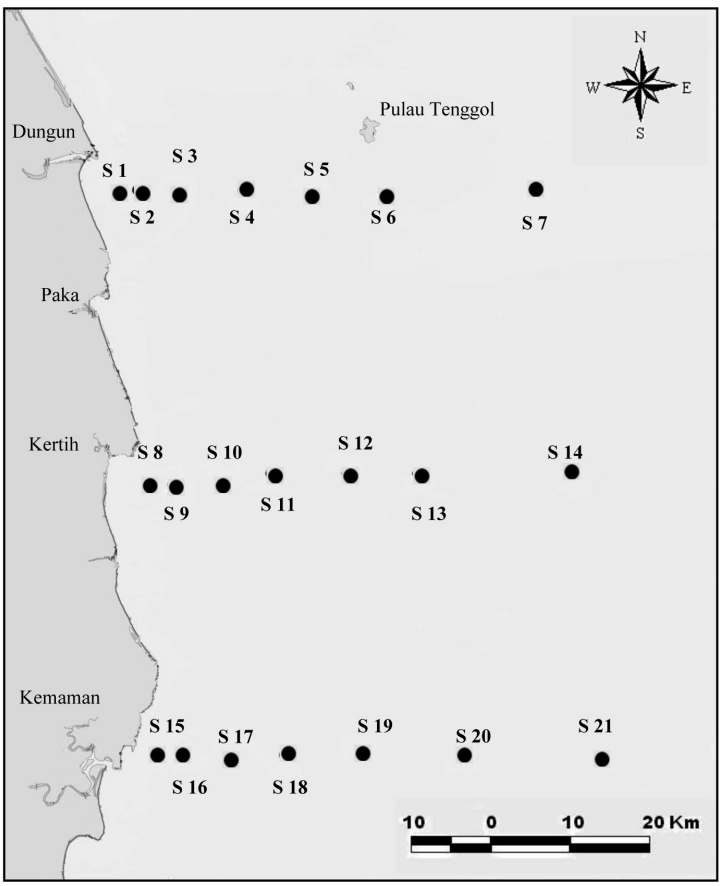


Fig. 2.1 Sampling stations at the Kemaman offshore, Terengganu.

Heavy-Metal Analysis

Sediment samples were digested and analysed for total Co, Pb and Zn following established methodologies with some modifications (Kamaruzzaman *et. al.,* 2001, Kamaruzzaman, 1999 and Noriki, *et.al.* 1980). The sediment samples were dried until constant weight and 50 mg of sediment added into Teflon vessels. Then, 1.5 mL of mixed acid (2HF: 2HCl: $4HNO_3$) was added to the Teflon vessels. The sealed Teflon vessels were then heated in an oven at 150°C for 6 hours, followed by a period of cooling before 3.0 mL of mixed solution of boric acid and EDTA (0.825 g of EDTA and 11 g of boric acid, dissolved in the 20 mL of ammonium solution, made up to 500mL with deionised water) was added. The samples were then heated again in the oven at 150°C for 6 hours. The digested samples were later cooled at room temperature, transferred into 10 mL polypropylene test tubes and the volume made up to 10 mL with 10% of HNO_3. Clear solutions with no residue were obtained and the heavy-metal concentrations in the samples were detected by Inductively-Coupled Plasma-Mass Spectrometer (ICP-MS). The precision and accuracy of the method were examined with replicates, blank samples and Marine Sediment Reference Material (MESS-3) from the National Research Council Canada. The metal concentrations were within ±5% of certified values (Table1).

Table 1. Recovery test result of certified reference material MESS-3 for Co, Pb and Zn

Elements	Certified value (% dry weight)	Analysed value (% dry weight)	Recovery (%)
Co	14.4±2.0	14.24±1.9	98.90
Pb	21.1±0.7	20.56±1.6	97.44
Zn	159±8	182.85±19	115.00

Total Organic Carbon Analysis

Wet dichromate-oxidation method (Holme and Mc Intyre, 1984) was used for the organic-carbon analysis. The samples were digested using potassium dichromate, sulfuric acid, phosphoric acid and diphylamine as an indicator.

The samples were then titrated using ferrous sulphate solution, ending when the blue colour turned green. The volume of ferrous sulphate used was recorded. The percentage of organic carbon was calculated using the formula:

$$\% \text{ organic carbon} = \frac{(V_1 - V_2) \times 0.003 \times 100}{\text{Sample weight (g)}}$$

Where; V_1 = volume of dichromate used (mL)
V_2 = volume of ferrous sulphate used (mL)
0.003 = Carbon content in 10 mL potassium dichromate

The precision and accuracy of the method were examined with replicates, blank samples and glucose solution and the results were in agreement with the certified value (Glucose, 36%) within a difference of about 3%.

Sediment-Size Analysis (Dry sieving)

Approximately 100g of dried sediment samples were transferred into a series of arranged sieves of mesh size ranging between 4000 µm, 2000µm, 1000µm, 710µm, 600µm, 425µm, 212µm, 150µm, 106µm, 90µm and 63µm and shaken for 20 minutes. After that, the weight of sample retained in each sieve was recorded. Residue samples with grain size below 63 µm having weights more than 10% of total sample weight were further subjected to particle-size analysis using a laser diffractometer (MALVERN Master Sizer particle-size analyser).

Particle-Size Analysis (PSA)

Approximately 10.0 g of sediment sample was weighed exactly, placed in a 100 mL beaker and 20mL of distilled water added. The sample was then placed on a hot-plate at a constant temperature of 60ºC. A few drops of hydrogen peroxide (H_2O_2) were added gradually until there was no formation of bubbles. This procedure was done to remove all the organic matter in the sample. The sample was then allowed to cool down to room temperature. After that, freshly-prepared dispersing agent Calgon solution (sodium hexametaphosphate) was added to aid in the break-up of flocks that may have formed by clay particles. The solution was then stirred, and subjected to ultrasonication for 10 to 15 second burst, before analysis by laser diffractometer.

All data collected from dry sieving and particle-size analyser were subjected to statistical analysis using the moment method as suggested by McBride (1971) and Folk (1980). The formula is as follows:

$$\text{Mean size, } Ø = \sum fm / n$$

Where; f = percentage weight of each grade of particle size
m = median of each particle size
n = total number of the samples in 100 when f is in percentage (%)

Statistical Analysis

Statistical differences in results between pre-monsoon and post-monsoon periods were assessed using one-way ANOVA test. Relationships of metal concentrations with particle mean size and organic-carbon content were examined using Pearson Correlation.

Index of Geoaccumulation (I_{geo}) and Enrichment Factor (EF) were used in order to determine the pollution status and the anthropogenic contribution to the concentration of heavy metals in the study area. I_{geo} describes the relationship between the measured elemental concentration in the sediment (C_n) and the average shale value of an element (B_n). A constant factor of 1.5 is introduced to include natural fluctuations in the content of a given substance in the environment (Muller, 1981). This relationship can be simplified in a formula as given below:

$$I_{geo} = \log_2 (C_n / 1.5\ B_n)$$

Meanwhile, EF is used to evaluate the dominant source of the elements and as indication of pollution effects (Szefer *et. al.* 1999). Values around 1 indicate that the element is primarily from lithogenous sources, whereas EF values greater than 10 indicate that the sources are more likely to be anthropogenic. EF is calculated using the equation below:

$$EF = (E/Al)_{sample} / (E/Al)_{crust}$$ (from Szefer *et. al.*, 1999).

in which $(E/Al)_{sample}$ and $(E/Al)_{crust}$ are the concentrations of the respective elements E and Al in the sediment and in the crustal material.

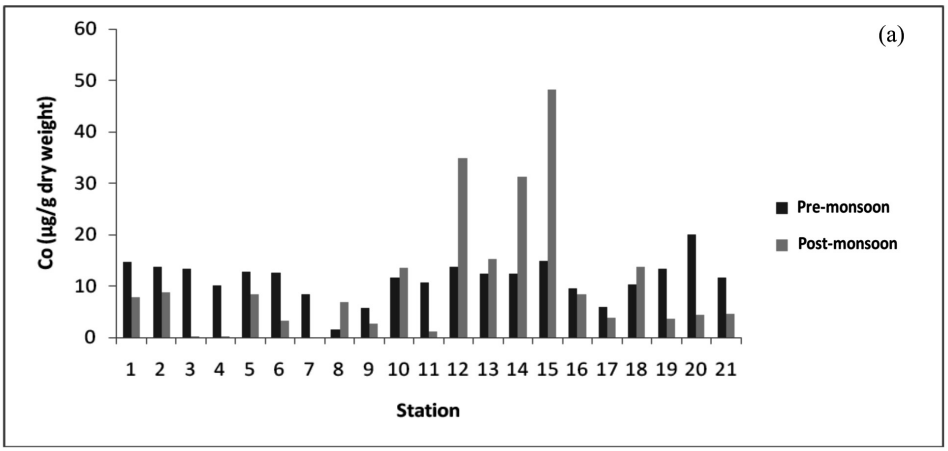
Results and Discussion

The average concentration of Co (Fig. 1a) in Kemaman offshore during pre-monsoon and post-monsoon season was 11.40±3.8 µg/g dw and 10.60±12.6 µg/g dw respectively, with no significant difference between the two seasons ($p>0.05$). These concentrations are also much lower than the Earth's crust average shale concentration of 19 µg/g (Turekian and Wedepohl, 1961). This is attributed to increased solubility of Co during intense chemical weathering in the humid tropical environment.

The average concentration of Pb of 44.08±33.4 µg/g dw (Fig. 1b) in Kemaman offshore during pre-monsoon season was higher than the Earth's crust average shale value of 20 µg/g or global mean sediment concentration of 19 µg/g (Salomons and Forstner, 1984). However, during post-monsoon, the average concentration of Pb was lower than average shales with 17.54±30.8 µg/g dw. Pb concentration was significantly higher during pre-monsoon than in post-monsoon ($p<0.05$). The higher concentrations of Pb during the pre-monsoon period and the much lower values post-monsoon suggests that Pb that was accumulated in the sediments during the pre-monsoon period was redistributed within the sedimentary environment of the study area during the post-monsoon period and also diluted with fresh sediment input via the rivers.

Meanwhile, the average concentration of Zn (Fig. 1c) in Kemaman offshore during pre-monsoon and post-monsoon season was 254.90±141.0 µg/g dw and 110.71±58.1 µg/g dw respectively with no significant difference between the two seasons ($p>0.05$). The Zn concentrations were significantly higher than the average Earth's crust shale (Turekian and Wedepohl, 1961) and global mean sediment value of 95 µg/g (Salomons and Forstner, 1984).

Metal concentrations were poorly correlated with grain size (Fig. 2, Fig. 3 and Fig.4) and not significantly correlated with total organic carbon (TOC) (Fig. 5, Fig. 6 and Fig. 7) for both monsoon periods. In this study, Co, Pb and Zn have calculated I_{geo} values less than 1.0 and therefore can be classified as practically uncontaminated to moderately contaminated (Figure 8). EF values lower than 10 are not significant as such small enrichments may arise from differences in the composition of local parent soil material and reference material used in the calculations (Pekey, 2006). The EF values (Table 2) found in this study ranged between 0.60 and 2.91, and analysis by this method alone would suggest that the source of heavy metals is solely natural, with minimal-to-moderate enrichment as categorised by Sutherland (2000). Moderate enrichment of Pb and Zn is notable in pre-monsoon sediments whereas in post-monsoon sediments metal concentrations were much lower.



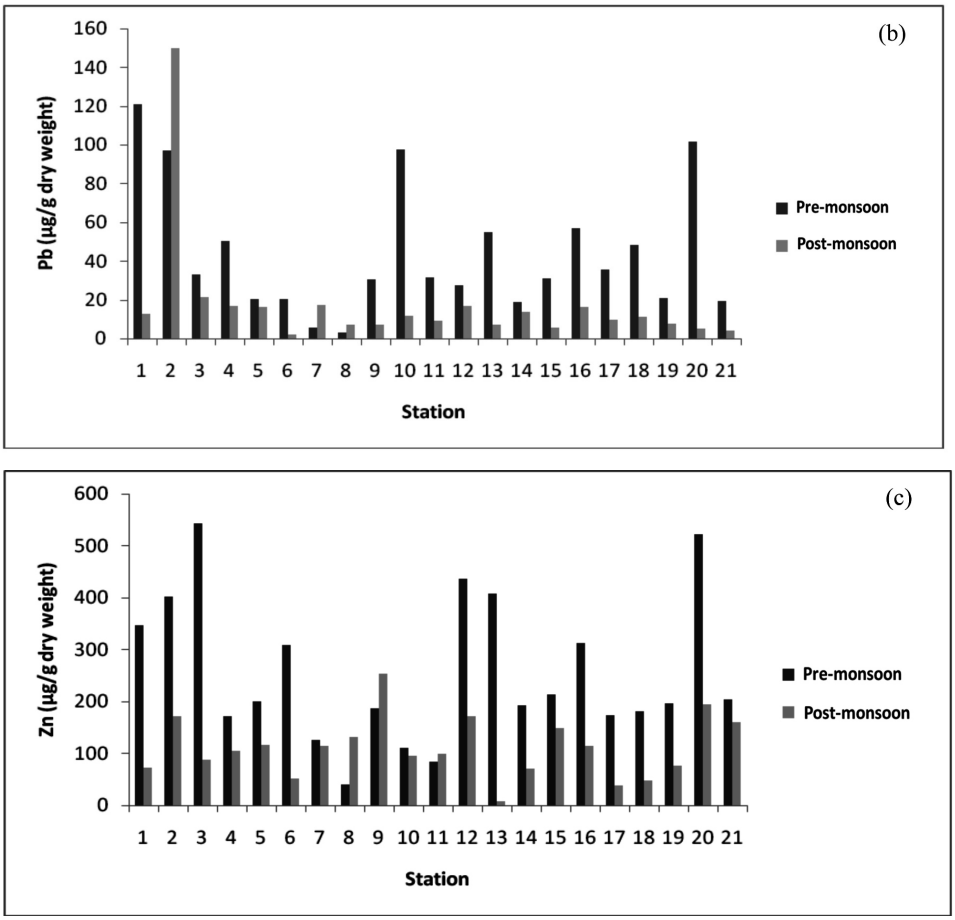


Figure 1. (a) Co, (b) Pb and (c) Zn distribution in Kemaman offshore during the pre- and post-monsoon periods.

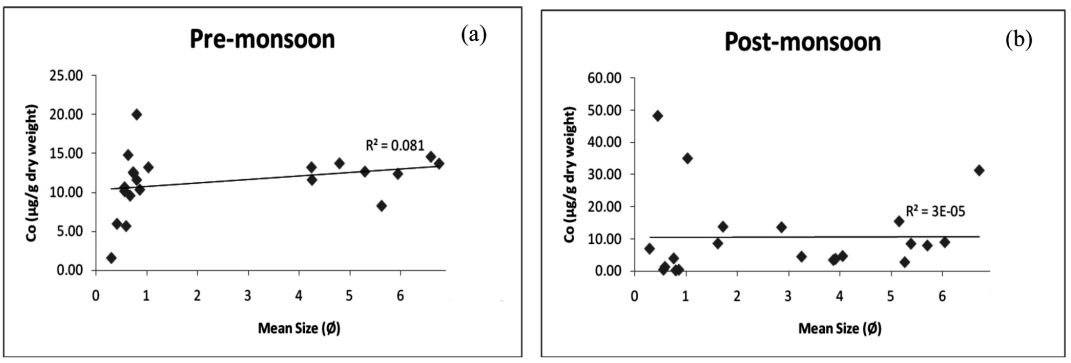


Figure 2. Correlation between Co and sediment size during the (a) pre-monsoon and (b) post-monsoon periods.

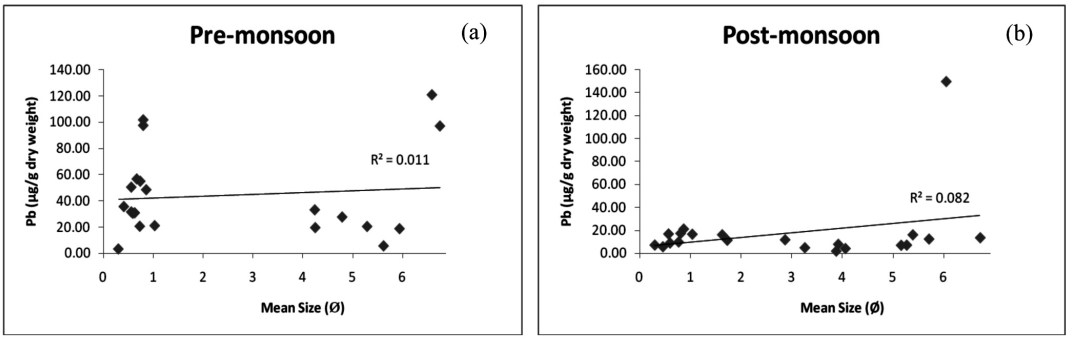


Figure 3. Correlation between Pb and sediment size during the (a) pre-monsoon and (b) post-monsoon periods.

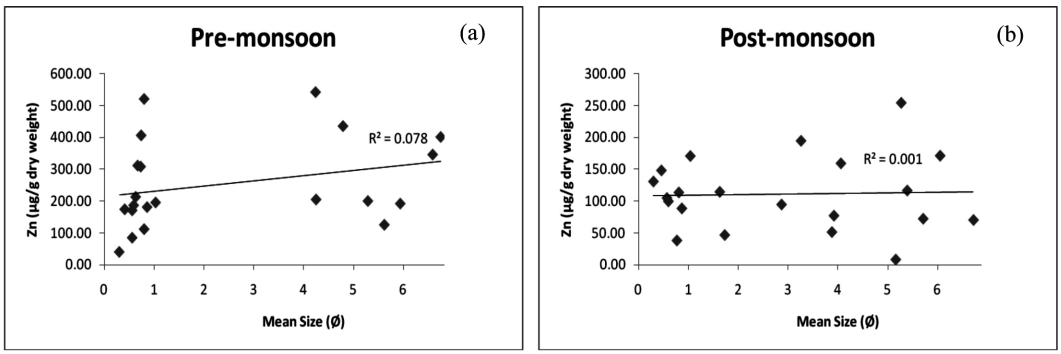


Figure 4. Correlation between Zn and sediment size during the (a) pre-monsoon and (b) post-monsoon periods.

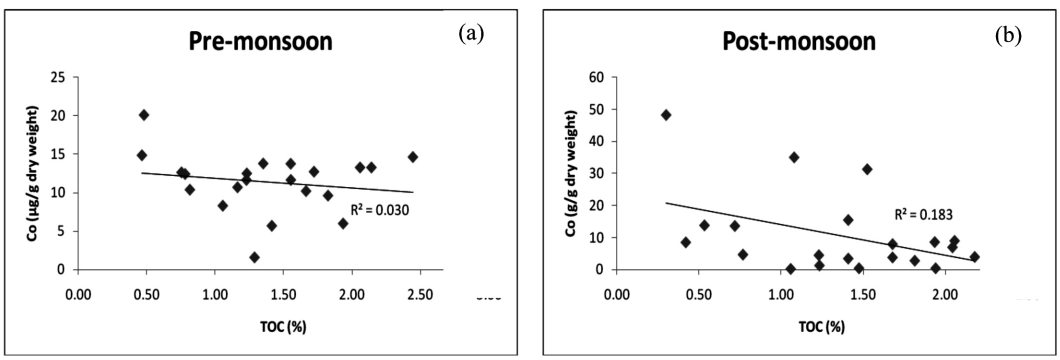


Figure 5. Correlation between Co and organic carbon during the (a) pre-monsoon and (b) post-monsoon periods

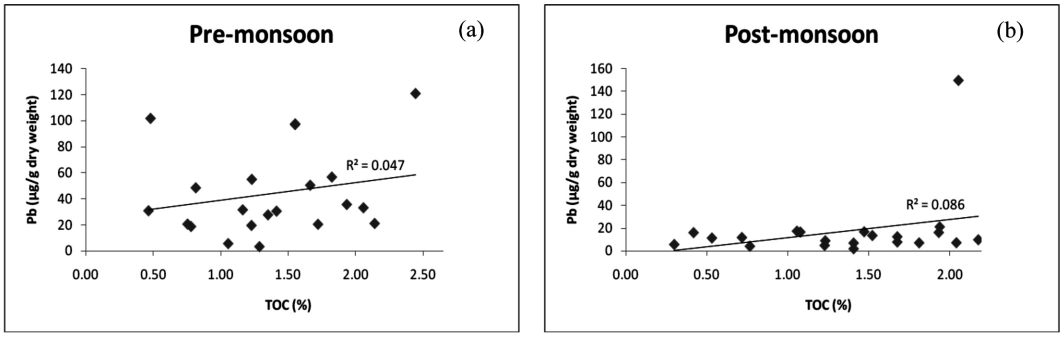


Figure 6. Correlation between Pb and organic carbon during the (a) pre-monsoon and (b) post-monsoon periods.

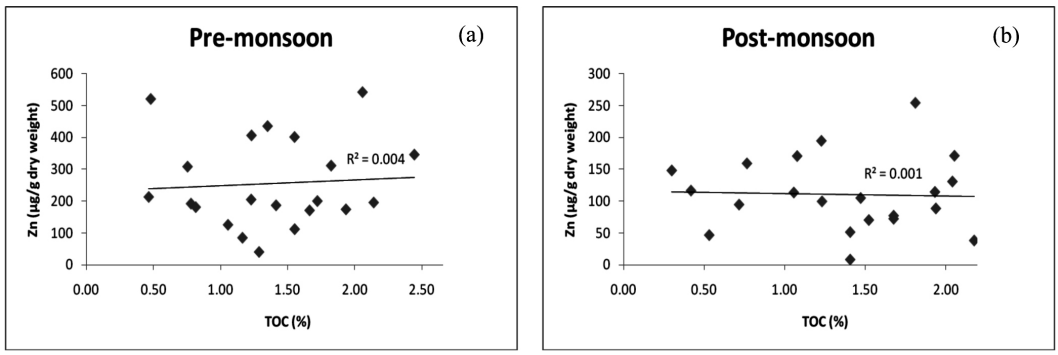


Figure 7. Correlation between Zn and organic carbon during the (a) pre-monsoon and (b) post-monsoon periods.

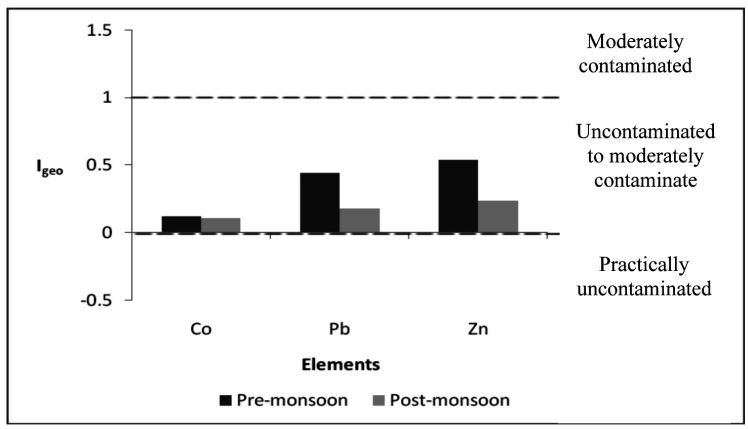


Figure 8. Contamination level using I_{geo} at Kemaman offshore during pre-monsoon and post-monsoon.

Table 2. EF values for elements in sediment of southern Terengganu waters.

Element	Pre-monsoon	Post-monsoon	Category	Source
Co	0.65	0.60	Deficiency-to-minimal enrichment	Natural
Pb	2.39	0.95	Moderate enrichment	Natural
Zn	2.91	1.26	Moderate enrichment	Natural

Conclusion

The concentration of Co in Kemaman offshore ranges from 0.12 µg/g dw to 48.25 µg/g dw. Pb concentration ranges from 3.18 µg/g dw to 150.01 µg/g dw while Zn concentration ranges from 8.27 µg/g dw to 543.12 µg/g dw. Generally, metal concentrations in the sediment were higher in the pre-monsoon than in the post monsoon sediment. The relatively high concentraton of metals observed at some stations were probably influenced by anthropogenic input from land. However, the Igeo and EF values indicate that the area is relatively uncontaminated with Co but moderately enriched with Pb and Zn in pre-monsoon sediments. The lower concentrations of metals in bottom sediments in the post-monsoon period is thought to be due to redistribution of the bottom-sediment environment and dilution of the sediment by fresh input of material via rivers. Continuous monitoring of these metals in the study area is recommended in future studies.

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References

Clark, R. B. (1992). *Marine Pollution*. 3rd ed. New York: Oxford University Press Inc 169pp.

Folk, R.L. (1980). *Petrology of sedimentary rocks*., Austin, Texas: Hemphill Publishing Company 184pp.

Holme, N.A. & Mc Intyre, A.D. (1984). *Method for the study of marine benthos*. IBP Handbook 16, Blackwell Scientific Publication, Oxford, London, Edinburgh, Boston, Palo Acto Melbourne. 387pp.

Kamaruzzaman, B.Y. (1999). Geochemistry of the marine sediments: Its paleoceanographic significance. Ph.D Dissertation, Hokkaido University, Japan.

Kamaruzzaman, B.Y., Cornel, J.M., Marcel, M. & Ju Maria C.B. (2001). The determination of ^{230}Th in marine sediments: A sediment dating method. *Oriental Journal of Chemistry* 17:335-360.

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

Muller, G. (1981). Index of geoaccumulation in sediments of the Rhine River. *Geojournal* 2:108-118.

Noriki, S., Nakanishi, K., Fukawa, T., Uematsu, M., Uchida, T. and Tsunogai, S. (1980). Use of a teflon vessel for the decomposition followed by the determination of chemical contituents of various marine samples. *Bull. Fac. Fish, Hokkaido Univ*. 31:354 – 465.

Pekey, H. (2006). Heavy metal pollution assessment in sediments of the Izmit Bay, Turkey. *Environ. Monit. and Assess.* 123:219-231.

Salomons. W. and Forstner, U. (1984). *Metals in the hydrocycle*, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo.

Sutherland, R.A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environ. Geol*. 39: 611-27.

Szefer, P., Glasby, G.P., Stqben, D., Kusak, A., Geldon, J. and Berner, Z. (1999). Distribution of selected heavy metals and rare earth elements in surficial sediments from the polish sector of the vistula lagoon. *Chemosphere* 39:2785–98.

Turekian, K.K. and Wedepohl, K.H. (1961). Distribution of the elements in some major units of the Earth's crust. *Geological Society of America Bulletin* 72:175-192.

Vertacnik, A., Probic, E., Kozar, S. and Juracec, M. (1995). Behaviour of some trace metal elements in alluvial sediment, Zagreb water-well field area, Crotia. *Water Research* 29:237-246.