ISSN: 0970-020 X; CODEN: OJCHEG
Oriental Journal of Chemistry
2011, Vol. 27, No. (2): Pg. 505-510

http://www.orientjchem.org

Concentrations of Lead, Copper and Zinc in the Bottom Sediments of Tuba Island Waters of Langkawi, Malaysia

B.Y. KAMARUZZAMAN[1]*, N.T. SHUHADA[1], M.S. ZAHIR, B. AKBAR JOHN[1], S. SHAHBUDIN[1], K.C.A. JALAL[1], S.M. AL-BARWANI[2] and J.S. GODDARD[2]

[1]Institute of Oceanography and Maritime Studies, International Islamic University Malaysia, Bandar Indera Mahkota, 25200 Kuantan, Pahang (Malaysia).
[2]Department of Marine Science and Fisheries, Sultan Qaboos University, P.O. Box 34, Al-Khod 123 (Sultanate of Oman).
E-mail: kama@iium.edu.my

(Received: March 10, 2011; Accepted: May 13, 2011)

ABSTRACT

Surface sediments were collected from Pulau Tuba (9 sampling points) has been analyzed for Pb, Cu and Zn by using the sensitive Inductively Coupled Plasma Mass Spectrometer (ICP-MS). In this study, the average concentration of Pb, Cu and Zn were 43.28±8.95 $\mu g.g^{-1}$ dry weights, 8.79±2.72 $\mu g.g^{-1}$ dry weights and 63.5 $\mu g.g^{-1}$ dry weights, respectively. In this study, the statistical analysis for Pearson correlation matrix has proved that there are significant relationship between the metal concentration and the grain size. The concentration of Pb, Cu and Zn increased with the decreased of mean size particles, suggest that there are association with the fine fraction of the sediments. In order to assess the influence of heavy metals pollution precisely, enrichment factor (EF) were calculated. In this study, all elements are about unity and considered to be dominantly terrigenous in origin.

Key words: surface sediments, lead, copper, zinc, enrichment factor.

INTRODUCTION

Sediment quality has been recognized as an important indicator of water pollution (Larsen and Jensen, 1989) since they act as sink of contaminants (Balls *et al.,* 1997). This fact converts the sediments in a permanent record of anthropogenic pollutants inputs (Baker and Harris, 1991; Andersen, 1992). The examination and study of sediment quality can reveal the pollutant variations, degradations and cycles, and their chronic effects on water pollution. In addition, the accumulation of heavy metals in sediment can produce harmful effects on the biota living in them (Long, 1992). Surface sediment play 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; Seyler, and Martin , 1990). These fenomena were described by previous studies in the river watershed where the sediment load are significant in the transport of pollutants (Presley *et al.,* 1980; 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; Meade, 1972). Their secondary sources such as from sediment flocculation which occurs at low-high salinity contact is also an important phenomenon with regard to elemental behaviour (Goldstein and Jacobsen, 1988). The transportation and mixing of those different sources of input can be explained largely through the measurement of the chemical composition in the sediments.

In recent years, the study area especially in the vicinity of Tuba Island waters 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. Fisheries activities and industrial are the main industry in the area and is the catalyst for other supportive industries to develop around the same area. The aim of this work was to study the geochemical behaviour of metals, their source and mode of incorporation in their sediments with regards to the sedimentological conditions of the area.

MATERIAL AND METHODS

Sample Collection

Langkawi Island is one of the most attractive ecotourism spot in Malaysia with well diverse marine lives hence attracting thousands of tourists every year. To support the increasing number of tourists every year, more development was made along the shore line such as hotels, resorts and marine recreational facilities. This extensive type of development contributes to the direct impact on the productivity of the marine environment ecosystem and would also cause pollution such as heavy metals pollution into the coastal and adjacent area. The bottom samples of 9 different sampling stations (Figure 1) were collected using Ekman Grab. To prevent contamination, the sediments at the top were gently scrapped out and only inner parts were taken. Then, the sediments were transferred into the plastic bottle which has been soak in 5 % nitric acid and were deep freezer prior to analyses. Samples that brought back the laboratory were dried to a constant weigh at 60°C and then sieved under 63µm stainless steel sieves.

Analytical procedure

The sediment samples were digested and the analyses for the total Pb, Cu and Zn following published methodologies with some modifications. An inductively Coupled plasma mass spectrometer (ICP-MS) was used for a quick and precise determination of Cu and Pb. The digestion method involve heating of 0.05 g of finely powdered sediments in a sealed Teflon vessels with a mixture of 1.5mL mixed acids solution (HF; HNO_3: HCL). The Teflon vessels were kept in the oven at 150° for 5 hours. After cooling to room temperature, the content of the beaker was throughly transfered into a 50 ml volumetric flask with deionized distilled water. A clear solution with no residue should be obtained at this stage. An estuarine sediment reference material (NBS 1646) and a reagent blank were also subjected to the same procedure. Precision of the entire analytical sample was assessed by doing replicate analyses of a sample. The precision assessed by the replicate analyses was less than 3 %. The accuracy was also examined by analyzing duplicate a Canadian Certified Reference Materials Project standard and the result coincided with the certified values within a different of ±3%.

RESULTS AND DISCUSSION

The distribution concentrations of Pb, Cu and Zn for Tuba Island are given in Figure 2. The spatial variations of total Pb, Cu and Zn concentrations between the sampling points of each transects were found to be significantly different ($P<0.05$). It is noted that the concentrations of Pb, Cu and Zn near the river were comparably high and declined towards the open sea (Fig. 2a, 2b and 2c). Although these elements show an increase in concentration near the river, this is not necessarily an indication for anthropogenic input. It is more likely that the much higher rates of sedimentation near the riverbank, the presence of organic matter and the high ion-exchange capacity of the silt-clay sediment type, will greatly affect the ability of these sediments to retain metals ions via adsorption, chelation and ion-exchange mechanisms.

Pb varies from 22.8 $\mu g.g^{-1}$ dry weights to 51.7 $\mu g.g^{-1}$ dry weights with average concentration of 43.28 $\mu g.g^{-1}$ dry weights (Fig 2a). Their concentrations are two times higher than the mean crustal materials (Mason and Moore, 1982). A study reported by Kamaruzzaman *et al.* (2010) in Pahang River estuary was also about two times higher than the mean crustal materials. Station 1 shows the highest Pb concentration; meanwhile station 9 has the lowest concentration. The most plausible explanation for the elevated Pb at station 1 is the congregation of anthropogenic activity (such as residential sewage outfall and industrial effluents) at the nearby areas which provides a variety of sources of metals to intertidal sediments. This indicates that local factors may play an important role in determining sediment metal concentrations.

Copper (Cu) was generally consistent, ranging from 8.15 $\mu g.g^{-1}$ dry weights to 10.64 $\mu g.g^{-1}$ dry weights and averaged at 8.79 $\mu g.g^{-1}$ dry weights (Fig. 2b). The concentration of Cu in this study was comparable as reported by Yap *et al.,* (2003) in Pulau Langkawi to Johore and Shazili *et al.,* (1986) in South China Sea. The mean value was much lower when compared with the average shale. Cu clearly indicates that their main source is from the city sewage and the industrial effluents (near station 5, 7 and 8), with an average concentration of 10.8 $\mu g.g^{-1}$ dry weights, 11.2 $\mu g.g^{-1}$ dry weights and 12.4 $\mu g.g^{-1}$ dry weights, respectively. Station in the inner parts of Tuba Island are a zone of enhanced deposition with extensive mangrove trees and their depositional environment may promote rapid incorporation of heavy metals from localized sources to sediments. The relatively low average Cu and some other metals in station 1 and 2 might be due to the solubilization of Cu from suspended matter that occurs as a result of physicochemical factors during the mixing of freshwater and seawater (Thompson, 1990).

Zinc (Zn) was generally constant ranging 37.6 $\mu g.g^{-1}$ dry weights to 78.4 $\mu g.g^{-1}$ dry weights and averaged at 63.5 $\mu g.g^{-1}$ dry weights (Fig. 2c). The average highest Zn values occur in station 3 (72.5 ppm), followed by station 5 (62.9 ppm) and station 6 (42.6 ppm). The relatively high values probably result from a combination of factors including industrial discharges to the river, inputs from weathering and the effects of local activities near Tuba island. However, it is not possible at this stage to assess the relative importance of the study areas as the sources of pollution. Elevated Zn values also occur at other study areas (Waldichuk, 1974), although the source of this is not clear. The areas of lower Zn values extended near the estuary and this may indicate the important role of the physicochemical factors and the less ability of sandy type sediment to retain metal ions.

For a better estimation of any anthropogenic inputs, an enrichment factors (EF) was calculated by dividing its ration to the normalizing element by the same ration found in the chosen baseline. Table 1 shows the calculated EFs of the analyzed elements with respect to those determined in the crustal abundance employing the equation:

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

An enrichment factors close to 1 would indicate a crustal origin, while those with factors greater than 10 are considered to have non-crustal sources.

From table 1, Cu and Zn in sediments were about unity and it resistant in sediments would probably due to natural sources such as chemical weathering of igneous and metamorphic rocks and decomposition of biota detritus (Badri and Aston,

Table 1: Average enrichment factor (EF) values for Pb, Cu and Zn in Tuba Island

Element	EF value	Contamination Category
Pb	11.56 ± 1.9	Significant Enrichment
Cu	0.56 ± 0.04	Deficiency to minimal enrichment
Zn	0.66 ± 0.05	Deficiency to minimal enrichment

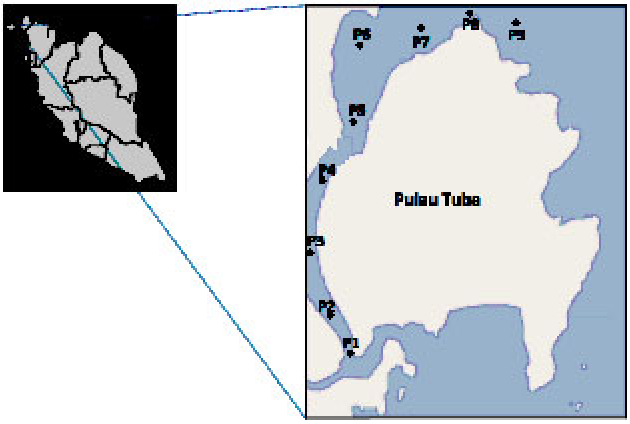

Fig. 1: Location of the 9 sampling station of Tuba island, Langkawi

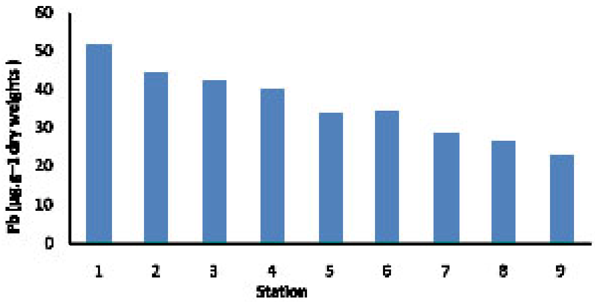

Fig. 2(a): Concentration of Pb at sampling stations of Tuba Island

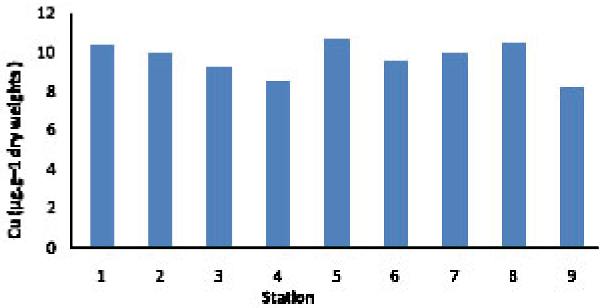

Fig. 2(b): Concentration of Cu at sampling stations of Tuba Island

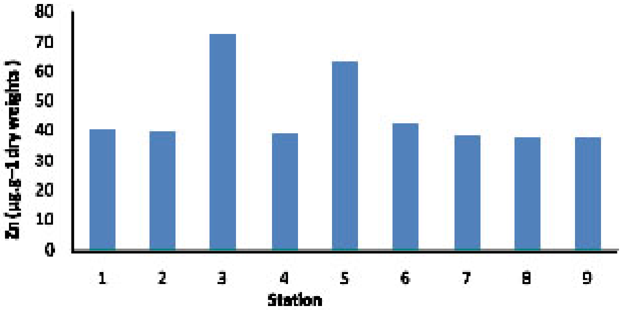

Fig. 2(c): Concentration of Zn at sampling stations of Tuba Island

1983). This natural fraction of sediments contains Cu that strongly incorporated into the crystalline lattice positions of minerals (Badri and Aston, 1983). A higher value of Pb may attribute to anthropogenic input. Consequently, in the area of Pulau Tuba waters, one of the most important transports is by boat. The used of leaded gasoline in the boats as well as spillage during shipment and other operations will inevitably results in higher lead levels in the environment. Activities such as cleaning and painting of boats will also contribute higher concentrations of Pb into the environment. Paint relies on lead compounds for its color, and this compound may give environmental effects if it enters the ecosystem in a higher concentrations. Besides that, prehistoric boating activities also would probably give some effects to present Pb value today.

REFERENCES

1. Andersen, H. E., The expansion of mercury contamination, five years after discovery. *Mar Pollut Bull* **24**: 367-369 (1992).
2. Badri; M. A and S. R. Aston, Observation of heavy metal geochemical associations I polluted and non-polluted estuarine sediments. *Environmental Pollution* (Series B), **6**: 181-193 (1983).
3. Baker, E. K. and Harris, P. T., Copper, lead and zinc distribution in the sediments of the Fly River Delta and Torres Strait. *Mar Pollut Bull* **22**: 614-618 (1991).
4. Balls, P. W., Hull, S., Miller, B. S., Pirie, J. M. and Protor, W., Trace metal in Scottish estuarine and coastal sediments. Mar *Pollut Bull* **34**: 42-50 (1997).
5. Burton, J. D., Riverborne materials and the continent-ocean interface, In: *Physical and Chemical Weathering in Geochemical Cycles* (Lerman and Meybeck, M., eds.). Kluver, Amsterdam, 201-225 (1988).
6. Chester, R., Lin, F. G. and Basaham, J. J., Trace metal solid state speciation changes associated with the down-column fluxes of oceanic particulates, *Journal of the Geological Society of London* **151**: 351-360 (1994).
7. Goldstein, S. J. and Jacobsen, S. B. 1988. REE in the Great Whale River estuary, Northwest Quebec, *Earth and Planetary Science Letters* 88, 241-252 (1988).
8. Kamaruzzaman, B. Y., Siti Waznah, A., Ong, M. C. and Joseph, B., Spatial distribution of Lead and Copper in the bottom sediment of Pahang River Estuary, Pahang, Malaysia. *Sains Malaysiana*, **39**(4): 543 -547 (2010).
9. Larsen, B. and Jensen, A., Evaluation of the sensitivity of sediment monitoring stationary in pollution monitoring. *Mar Pollut Bull* **20**: 556-560 (1989).
10. Long, E. R., Ranges in chemical concentrations in sediment associated with the adverse biological effects. *Mar Pollut Bull* **24**: 38-45 (1992).
11. Mason, B. and Moore, C. B., Principal of geochemistry, 4th edn. J. Wiley and Sons, New York. 344 pp (1982).
12. Meade, R. H., Transport and deposition of sediments in estuaries, *The Geological Society of American Members* **133**: 91-117 (1972).
13. Olivarez, A. M. and Owen, R. M., The Europium anomaly of seawater: implications for fluvial versus hydrothermal REE inputs to the oceans, *Chemical Geology* **92**: 317-328 (1991).
14. Olsen, C. R., Thein, M.and Larsen, I. L., Plutonium, Lead-210 and carbon isotopes in the Savannah estuary: river-borne versus marine source, *Environmental Science and Technology* **23**: 1475-1481 (1989).
15. Presley, B. J., Trefry, J. H. and Shokes, R. F., Heavy metals inputs to Mississippi delta sediments, a historical view, *Water, Air and soil Pollution* **13**: 481-494 (1980).
16. Seyler, P. and Martin , J. M., Distribution of arsenite and total dissolved arsenic in major French estuaries: Dependence on biogeochemical processes and anthropogenic inputs, *Marine Chemistry* **29**:

277-294 (1990).

17. Shazili, N. A., Husain, M. L. and Yaacob, Y., Heavy metal content of sediments in the South China Sea. In: *Ekspedisis Matahari'* 85. eds. A.K.M. Mohsin,M.I. Mohamed and M.A. Ambak, Occasional Publication, Faculty of Fisheries and Marine Sciences. University Putra Malaysia, **3**: 112-116 (1986).
18. Thompson, D. R., Metals levels in Marine Vertebrates. In:Heavy Metal in the marine environment, eds. R. W. furness and P. S. Rainbow, CRC Press, Boca Raton, FL., pp: 143 -182 (1990).
19. Waldichuk, M., Some biological consencion heavy metal pollution. In: Pollution and Physiology of Marine Organism, Eds. F.S. Vernberg and W.B Vernberg. Academic press, New York, pp: 1-57 (1974).
20. Yap, C. K., Ismail, A. and Tan, S. G., Concentration, Distribution and Geochemical Speciation of Copper in surface sediments of the Straits Malacca, *Pakistan J. Biological Science* **6**(12): 1021-1026 (2003).