ORIENTAL JOURNAL OF CHEMISTRY
An International Open Free Access, Peer Reviewed Research Journal
www.orientjchem.org
Est. 1984
ISSN: 0970-020 X
CODEN: OJCHEG
2012, Vol. 28, No. (2):
Pg. 725-732

The Distribution of Selected Metals in the Surface Sediment of Langkawi Coast, Malaysia

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(Received: May 11, 2012; Accepted: June 14, 2012)

ABSTRACT

Surface sediment samples were collected from five stations covering 25 sampling points from the Langkawi coastal waters. Concentration of metals such as Zn, Cu, Pb, Cd, and Cr were determined using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The detected concentration range of Zn, Cu, Pb, Cd, and Cr were 41.02-137.1 μgg^{-1}, 14.36-46.32 $\mu g.g^{-1}$, 14.4-38.6 $\mu g.g^{-1}$, 0.6-2.4 $\mu g.g^{-1}$, and 40.5-84.5 $\mu g.g^{-1}$ dry weight respectively. Enrichment factors (EF) analysis showed that the source of Zn, Cu and Cr in the sampling areas were predominantly of terrigenous in origin while the source of Pb and Cd were slightly of anthropogenic in nature.

Key words: Enrichment Factor, Langkawi Island, Zinc, Copper, Lead, Cadmium, Chromium.

INTRODUCTION

The coastal zone is an important area as it affects the global environments through the interaction between land and ocean (Kremer *et al.,* 2005). Metal concentrations in sediments usually exceed those of the overlying water column (Caroline *et al.,* 2002). As a consequence, metals originating from human activities can often be identified more readily by analysis of sediment than by the quantification of metal concentrations present in water (Haynes *et al.,* 2006). Kevin *et al.,* (2006) has reported the ability of the sediments in integrating the temporal variability of metals that are originating from human sources. He also observed the remobilization of metals during the early stages of post-depositional transformations of the sediments. Sediments have high physical-chemical stability and their characteristics usually represent the average condition of the system, often being representative of the average water quality (Isaac *et al.,* 2005).

Estuarine and coastal environments are primarily being used as a sinks of river borne metals originating through natural weathering and anthropogenic sources (Hung and Hsu, 2004). Due to the industrialization and urbanization processes, a considerable number of anthropogenic activities such as smelting, mining, electroplating, and other related industrial processes, releases their effluents containing heavy metals into the aquatic water body that ultimately interfere with the natural and ecological equilibrium of the surrounding environment. It should also to be noted that some essential metals (light metals) such as Mn, Fe, Zn, and Cu, are required by aquatic organisms for their proper physiological and biochemical functions. On the other hand, lethal metals such as Hg, As, Cd and Pb, can be toxic to aquatic organisms, even at their trace concentrations. Therefore, types and amounts of metals entering the environment must be considered in assessing possible toxic effects. Hence, the present study was aimed to investigate the metal bioavailability in the surface sediments of Langkawi coastal waters.

MATERIALS AND METHODS

Sampling sites

Langkawi is one of the major tourist islands in Malaysia and located in the west coast of Peninsular Malaysia. It is part of Kedah state and governed by the Langkawi Development Authority (LADA). The shores around the main island which consist of soft, silty, and fine sand are protected by several smaller islands surround it. The mean daily temperature in this study area varied from 26.6°C to 29.3°C. Meteorological and bathymetric data showed that the numbers of rain days in a month ranged from none (0) to 27 days and the tides along the Langkawi Island are semi-diurnal type (twice daily) and wind speed was mostly prevailed at 0.3 m/s to 3.3 m/s. Langkawi island is influenced by a wind system (South West Monsoon which blows from May to Sep.) that blown from the Indian Ocean which bring monsoon season to Langkawi Island and its adjacent areas.

Samples collection

Five sampling sites were selected along the Langkawi coast covering its entire coast which includes Kuah, Kuala Triang, Pantai Kok, Datai and Tanjung Rhu (Fig 1). The bottom sediment samples were collected using Ekman Grab method (Kamaruzzaman *et al.,* 2011). In order 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

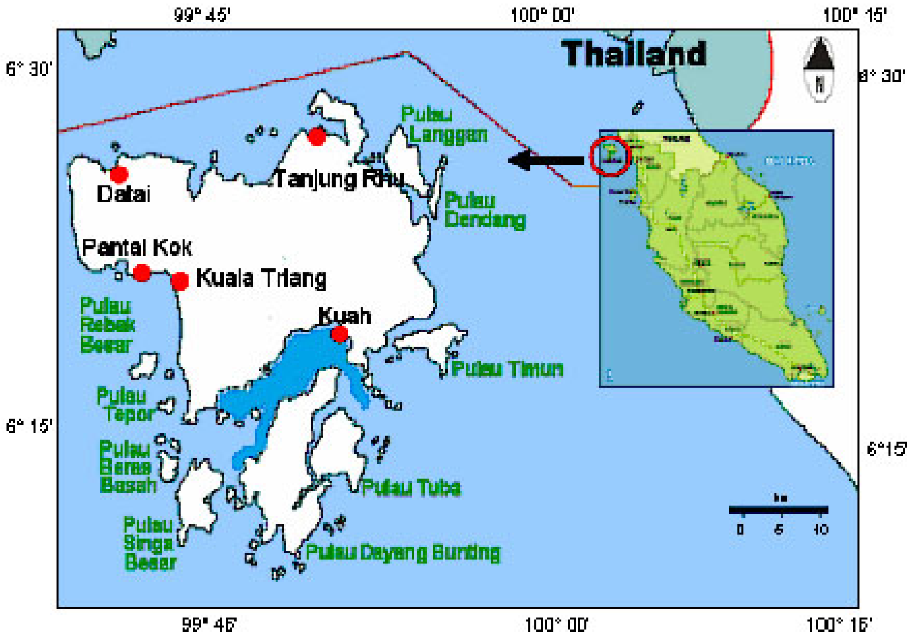

Fig 1. Map of study area and sampling point at Langkawi Coastal Waters

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 analyzed for the selected metal contents (Zn,Cu, Pb,Cd, and Cr) by followed the published methods (Tsunogai and Yamada, 1979; Noriki *et al.,* 1980; Sen Gupta and Bertnard, 1995; Kamaruzzaman, 1999) with some modifications. Sediment sample (0.05 g) was weighted and heated at 60 °C overnight. Then, the sample was kept in a desiccator to cool down. The weight of sample was recorded. These processes were repeated three times to get the constant weight. The sediment sample was transferred into Teflon bomb for closed digestion. 1.5 mL of mixed acid with the ratio of 3.0 (HF): 3.5 (HNO_3): 3.5 (HCl) was added and heated at 150 °C for 5-7 hours. After heating, the Teflon bomb was cooled down at room temperature. Then, 3.0 mL of boric acid and EDTA were added and heated again at 150 °C for 5-7 hours. This mixture was then cooled down at room temperature and a clear solution with no residue was transferred into 10 mL test tube and backed up to 10ml using Milli-Q water. A laboratory standard reference material (Estuarine sediment, SRM 1646a) and a blank reagent were also subjected to the same procedures, in order to determine the precision of the analytical method. The samples then analyzed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Data analysis

The enrichment factors (EFs) were calculated to evaluate the actual level of elemental contamination by using the earth crust as reference matrix. This analysis would indicate whether the metals are from natural weathering processes of rocks or from anthropogenic sources and reflect status of the environmental contamination. The enrichment of selected heavy metals was calculated using the following formula:

$$EF \quad \frac{(C_x / C_{Al})_S}{(C_x / C_{Al})_C}$$

where, C_x and C_{Al} refers to the concentration of elements from the present study (S), and C refers to the crustal value (Taylor, 1964). In this study, the value of earth crust from (Turekian and Wedepohl, 1961; Bowen, 1979; Mason and Moore, 1982) was used as a reference and Al was used as normalizing elements.

RESULTS AND DISCUSSION

The concentrations of Zn in surface sediment of Langkawi island ranged from 41.02 to 137.1 µg/g dry weight. The maximum concentration of Zn was found in the Tanjung Rhu samples (132.20 ± 4.62 µg/g dw) while the minimum concentration was recorded at station Kuah (50.12 ± 6.65 µg/g dw). Zn concentration in Pantai Kok, Datai and Kuala Triang was found 102.60 ± 6.82 µg/g dw, 96.30 ±

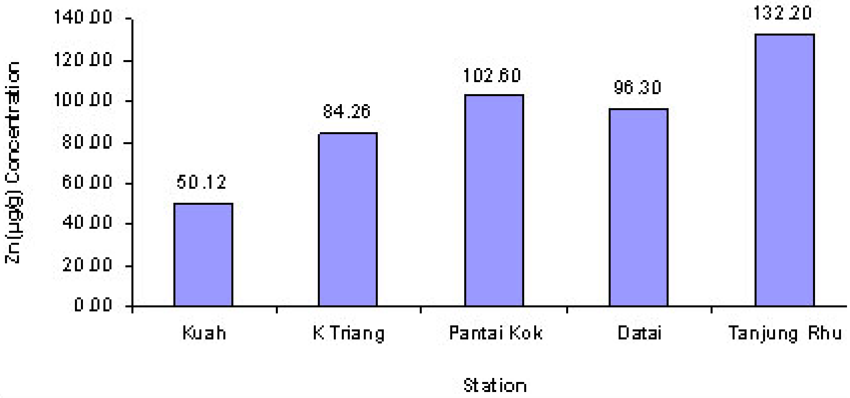

Fig. 2: Distribution of Zn at Langkawi Coastal Waters.

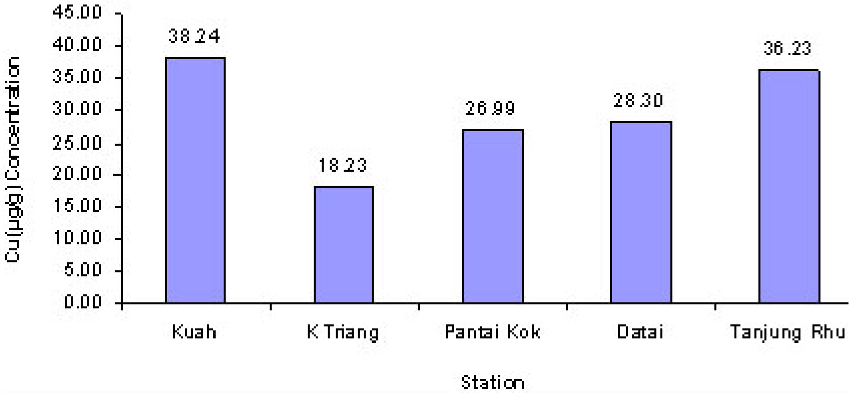

Fig. 4: Distribution of Cu at Langkawi Coastal Waters.

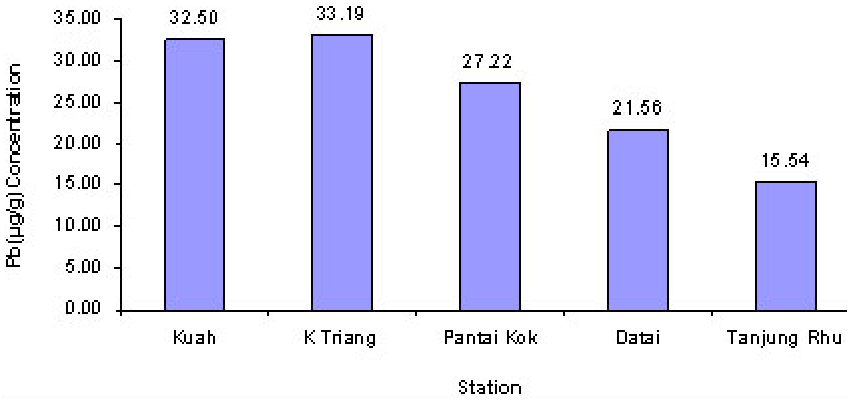

Fig. 5: Distribution of Pb at Langkawi Coastal Waters.

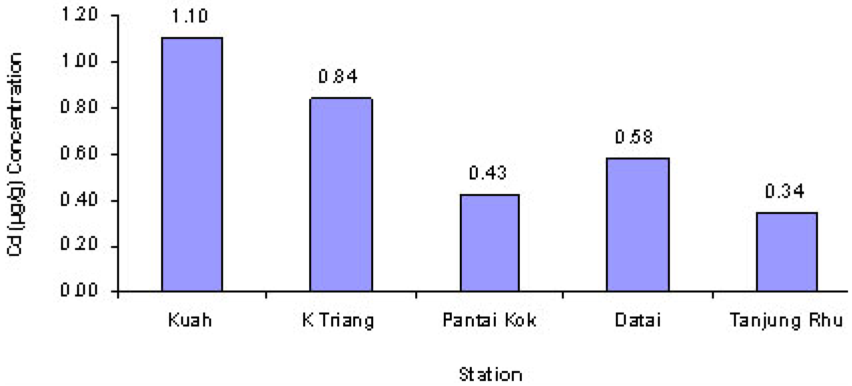

Fig. 6: Distribution of Cd at Langkawi Coastal Waters

2.72 µg/g dw and 84.26 ± 3.88 µg/g dw respectively (Fig 3). In general, higher concentrations of Zn in the study areas might be due to its application as an anticorrosive agent in boat paint (Deya *et al.,* 2003), and used as antifouling paint (Konstantinou and Albanis, 2004). Many tourist boat as well as fishing boats in the study areas might also enhanced the Zn level in the environment. Similar observation was noted by (Ismail *et al.,* 1995), who found that heavy metal like Zn in the sediment was higher in the area where boats and shipping activities were dominant. Kamaruzzaman *et al.,* (2006) stated that painting activities of fishing boats and the used of antirust paint in fishing and shipping industries may affect the levels of Zn in the sediments.

Sediment at Kuah station had highest Cu concentration (38.24 ìg/g dw). The lowest concentration of Cu was found at Kuala Triang station (18.23 ìg/g dw) as shown in Figure 4. The higher concentration of Cu in Kuah was probably due to the following activities being carried out in Kuah station 1. Loading and offloading fishes from fisherman, 2. Cleaning of boats and maintenance, antifouling paint applications, and fuelling activity. WHO, (1998) has reported that these activities would substantially increase the Cu load in an aquatic environment (WHO, 1998). However, in sediment, Cu could be found since it is one of the essential metals for biota, being associated with numerous metalloenzymes and metalloproteins (Kamaruzzaman *et al.,* 2011). However, high level of Cu in the sediment could be potentially toxic and this may pose concern because of bioaccumulation once in the food chain. The high level of Cu found in the sediment could be due to both natural origins and man-induced activities which are widely reported in the literature (Christensen and Juracek, 2001).

Lead (Pb) concentration was highest in Kuala Triang (33.19 ìg/g dw) and lowest at Tanjung Rhu (15.54 ìg/g dw). Concentration of Pb in Kuah and Kuala Triang stations were comparable with the previous study carried out by Wan Mohd Razi *et al.,* (2009), who recorded the Pb concentration of 35 ± 16.17 ìg/g dry weights. Compared to our study, there is a slight reduction in the Pb concentration in Kuah station was apparent during 2009 though it is not statistically significant ($p > 0.05$). Higher concentrations of Pb as the consequence of the usage of leaded gasoline in ships and boats as well as spillage during shipment and other operations that had took place along the area (Kamaruzzaman *et al.,* 2008). Activities such as cleaning and painting of boats would also contribute higher concentrations of Pb into the environment. Beside that, emissions from automobiles that consume leaded petrol are the major source of the atmospheric Pb, as the atmospheric route may represent a major source of Pb into the marine environment (Jalal *et al.,* 2009).

Station Kuah had the highest concentration of Cd (1.10 ± 0.47 µg/g dw), followed by Kuala Triang (0.84 ± 0.30 µg/g dw), Datai (0.58 ± 0.16 µg/g dw), Pantai Kok (0.43 ± 0.12 µg/g dw) and Tanjung Rhu (0.34 ± 0.12 µg/g dw) (Fig 6). Cadmium concentration in Langkawi coastal sediments ranged between 0.6 and 2.4 µg/g dry weights. According to Lindsey *et al.,* (2004), levels of Cd depend on industrial activities, fishing landing ports, domestic sewage and Cd concentrations are usually high in the estuary region. Field observation showed that a lot of boats that bring passengers and tourist pass through the area everyday which might influence the Cd load in the environment. Besides this fact, Cd is a component of petrol's, diesel fuels and lubricating oil. Seepage as well as spillage of fuel during shipment process would also results in increasing of Cd levels into the adjacent area such as Kuah station.

The concentrations of Cr in Langkawi coastal sediment ranged from 40.5 - 84.5 µg/g dry weights. The highest and lowest concentration of Cr was found at Kuala Triang station (76.15 ± 6.48 µg/g dw) and Datai (45.65 ± 3.41 µg/g dw) respectively (Fig 7). Higher concentrations of Cr are most probably caused by anthropogenic activities. According to Ahmed *et al.,* (2007) and Lindsey *et al.,* (2004), a variety of anthropogenic activities could contribute to the release of Cr to the environment. Cr released by the electroplating activities, steel manufacturer, leather tanning, and textile industries is also a large responsible of contamination in this study area. However, the absence of such industries along the Langkawi

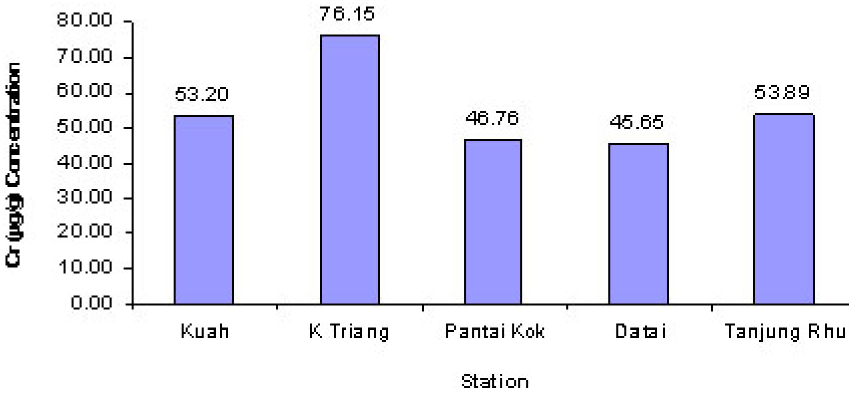

Fig. 7: Distribution of Cr at Langkawi Coastal Waters.

Table.1: Mean EF value determined in sediment of Langkawi coastal water

Element	EF value	Contamination category
Cr	1.83 ± 0.23	Deficiency to minimal enrichment
Cu	1.34 ± 0.41	Deficiency to minimal enrichment
Zn	1.89 ± 0.08	Deficiency to minimal enrichment
Cd	2.77 ± 0.41	Moderate enrichment
Pb	4.95 ± 0.47	Moderate enrichment

Island proved that the source of Cr is from various inshore fishery activities. This observation was well corresponded with the recent study conducted by Cuong *et al.,* (2008), who noted that the inshore marine activities such as shipment, discharge of oil at the sea, application of antifouling paint and anti corrosive paint, oil spills during shipment to the residence also will results in higher concentrations of Cr. High concentration of Cr in the study area might be due an intensive usage of an antirust paint and anticorrosive paint that contains Cr element

(Kamaruzzaman *et al.,* 2008). In addition, higher concentrations of Cr obtained from this study might also caused by the applications of fertilizers that were used in agriculture activities (Teck *et al.,* 2010).

Table 1 shows the enrichment factor (EF) values of selected heavy metals in Langkawi coastal water. In this study, the enrichment of the metals over the crustal values was in the order of Pb > Cd > Zn > Cr > Cu. The slightly higher proportion of Pb and Cd implies that the sediments are contaminated by the atmospheric deposition of finer particles, domestic effluent discharges and the extensive use of paints along the study area (Selvaraj *et al.,* 2004). Though the sources of other metals such as Zn, Cr and Cu are high in the study area, their minimal enrichment value showed that these metals concentration in Langkawi coastal sediment probably do not cause much effect on the organisms living in the coastal sediment bed. Nevertheless, long term environmental monitoring program would give crucial details on the quality of the Langkawi coastal areas as these metals affects the distribution of sensitive fauna along the coastal region.

ACKNOWLEDGEMENTS

This research was conducted with joint funding from the International Islamic University Malaysia under the Research Matching Grant Scheme (RMGS) and Grant from the Sultan Qaboos University, Oman. The authors wish to express their gratitude to the laboratory teams of both the universities for their invaluable assistance throughout the sampling period.

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