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Spatial Concentrations of Lead and Copper in Bottom Sediments of Langkawi Coastal Area, Malaysia

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ABSTRACT

Surface sediment samples were collected from 5 different zones of the Langkawi coastal waters, Malaysia to determine the concentration of Lead (Pb) and Copper (Cu) by using the sensitive Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The concentration of heavy metals was compared with the world average concentration of shale values. It was found that the total concentration of Pb was between 12.25 and 71.38 μg g^{-1} dw with mean concentration value of 41.87±7.30 μg g^{-1} dw which was two fold higher than the average shale value (20 μg g^{-1}). Statistical analysis showed that the significant variation in Pb concentration between different sampling stations ($p<0.05$). Copper (Cu) concentration was ranged between 0.40 and 30.95 μg g^{-1} dw with mean concentration of 11.19±5.2 μg g^{-1} dw which was lower than the average shale value (45 μg g^{-1} dw). Enrichment Factor (EF) showed that source of Pb concentration in the study area was partially due to anthropogenic activities and the source of Cu was dominantly from terrigenous in origin. Results of the analysis showed that a coastal area of Langkawi is facing moderate metal pollution with increased rate of deposition.

Key words: Lead, copper, enrichment factors, Langkawi coastal waters, Shale value

INTRODUCTION

Sediments can be sensitive indicators for monitoring contaminants in aquatic environments. The sediments were polluted with various kinds of hazardous and toxic substances, including heavy metals. These accumulate in sediments via several pathways, including disposal of liquid effluents, terrestrial runoff and leachate carrying chemicals originating from numerous urban, industrial and agricultural activities, as well as atmospheric deposition. They also provide a useful archive of information on changing lacustrine and watershed ecology (Cohen, 2003). The sediment history broadly reflects the contamination history of an area. Currently, environmental pollution because of urbanization and industrial development is a major concern (Alemdaroglu *et al.*, 2003; Heyvaert *et al.*, 2000; Sadiq, 1992).

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 tourist visiting Langkawi Island, more development were made along the shore line such as hotels, resorts, jetties, shopping mall 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 (White, 1988).

Sediments can act as a scavenger agent for heavy metal and an adsorptive sink in aquatic environment. It is therefore considered to be an appropriate indicator of heavy metal pollution (Idris *et al.*, 2007). The very fine silt/clay sediment in particular has often grain-size less than 63 μm and is considered the most geochemically active fraction of sediment particles. Therefore, these particles are eminently suitable to gauge potential pollution of sediment by heavy metal (Idris *et al.*, 2007). Besides, it is an important component of ecosystem in which toxic compound accumulate through complex physical and chemical adsorption mechanisms depending on the properties of the adsorbed compounds and the nature of the sediments matrix (Ankley *et al.*, 1992; Leivouri, 1998; Maher and Aislabie, 1992).

Recent studies showed that elevated levels of Pb and Cu concentration in the coastal areas adjacent and urban areas (Ismail, 1993; Ismail *et al.*, 1993; Ismail and Yap, 2001) and ports (Ismail *et al.*, 1993; Ismail and Rosnia, 1997). On the other hand, the total of Pb and Cu in the sediment of the West coast of Peninsular Malaysia ranged from 3.59 to 25.36 μg g^{-1} dw, 0.25 to 13.8 μg g^{-1} dw and 4 to 79.05 μg g^{-1} dw, respectively (Yap *et al.*, 2009). The source of heavy metals input in the west coast of Peninsular Malaysia includes manufacturing industries, agro-based industries and urbanization activities (DOE, 1998). The concentration of most heavy metals studied in coastal sediments is important and can be regarded as a baseline values. There are only limited information regarding the geochemical profile of sediments in Malaysia and only some initial research were carried out by Khalik *et al.* (1997). It is also to be noted that the distinguishing features of metals from other toxic pollutants is that, they are not biodegradable. Sediments can incorporate and accumulate many metals added to a body of natural water. The favorable physic-chemical conditions of the sediment can remobilize and release the metals to the water column. Thus, it is an important to determine the pollution status of any coastal area in order to access the heavy metal contaminations. Based on this perspective, a study was conducted to determine the spatial distribution of Pb and Cu from the sediments collected from Langkawi coastal waters.

MATERIALS AND METHODS

Samples collection: Five zones were selected from the study area which include the Kuah coastal area (zone A), Cenang coastal area (zone B), Datai River (zone E), Kilim River (zone D) and Pulau Tuba waters (Zone E) (Fig. 1). A total of 51 surface sediment samples were collected by using Ekman Grab during 2008. The top samples which had the direct contact with the grab were gently scrapped out to prevent contamination. Samples were then placed in the labelled bottle and frozen prior to laboratory analyses. Samples were brought to the laboratory and dried to constant weight at 80°C and sieved through 63 μm stainless steel sieve.

Analytical procedure: Samples were digested to obtain the concentrations of Pb and Cu by using Teflon bomb digestion method and heavy metal detection was carried out by using

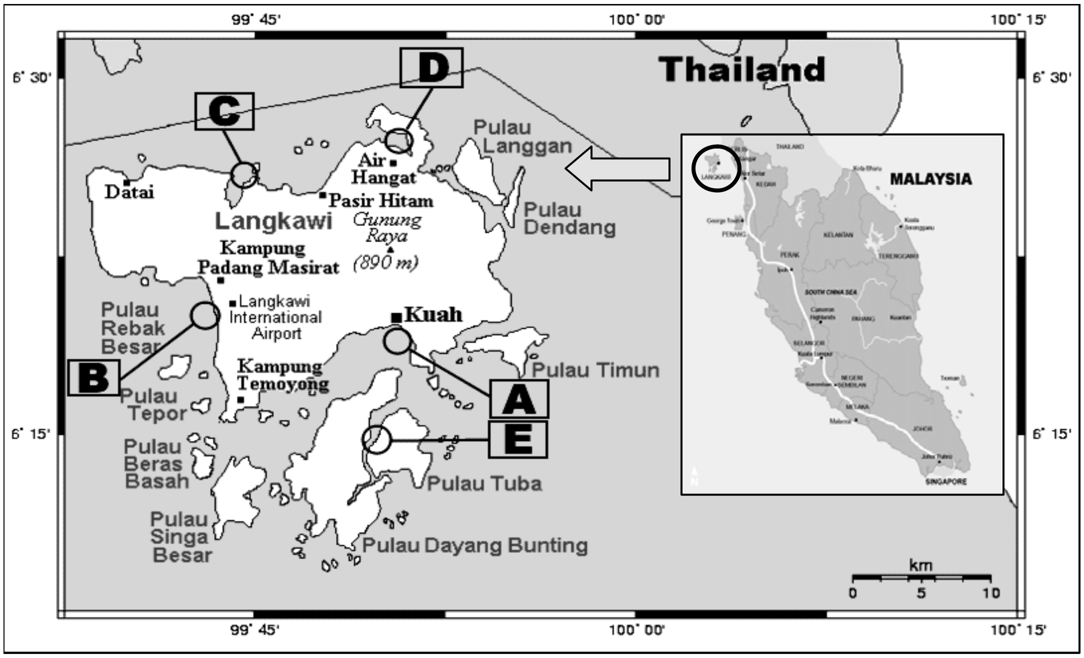

Fig. 1: Location of the sediment sampling sites at 5 different zones of Langkawi Island

Inductively-Coupled Plasma Mass Spectrometer (ICP-MS). About 0.05 g of dried sediments sample (<0.63 μm) were digested with 2 mL of mix acids (3.5 HCL: 3.5 HNO_3: 3 HF) in a Teflon jacket. Samples were then heated at 150°C for 5 h in the oven followed by cooling down to the room temperature and 3 mL of mix EDTA and Boric acid were added. Samples were then heated again at 150°C temperature for 5 h for complete digestion. The obtained clear solutions were then transferred in an acid washed falcon tube and diluted to 10 mL with 5% nitric acids. The digested samples were analyzed for heavy metals by using ICP-MS.

RESULTS AND DISCUSSION

The concentration of Pb in Langkawi waters exhibit in a variable concentrations with a range of 12.25 to 71.38 μg g^{-1} dw. The mean concentration of Pb for whole Langkawi coastal waters was 41.87±7.30 μg g^{-1} dw which was two fold higher than the average shale value (20 μg g^{-1}). The highest mean concentration of Pb was identified in zone C (52.75±12.31 μg g^{-1} dw) followed by zone E (43.28±8.95 μg g^{-1} dw), B (42.86±21.21 μg g^{-1} dw) and D (36.49±14.04 μg g^{-1} dw). The low mean concentration of Pb was recorded in zone A (33.99±11.93 μg g^{-1} dw). Statistical analyses of two way ANOVA showed that there is a difference in Pb concentrations between sampling stations ($p<0.05$) (Fig. 2).

The concentration of Cu in Langkawi coastal waters varied between 0.40 and 30.95 μg g^{-1} dw with an average concentration of 11.19±5.2 μg g^{-1} dw. The average of Cu concentrations in sediments collected reflects that it is lower than the respective average shale value (45 μg g^{-1} dw). The highest mean concentration of Cu in dry season was identified in zone C (20.28±6.6 μg g^{-1} dw), followed by zone D (11.93±7.74 μg g^{-1} dw), E (8.79±1.12 μg g^{-1} dw) and zone A (7.91±2.78 μg g^{-1} dw) and lower level was observed in zone B (7.41±3.95 μg g^{-1} dw) (Fig. 3).

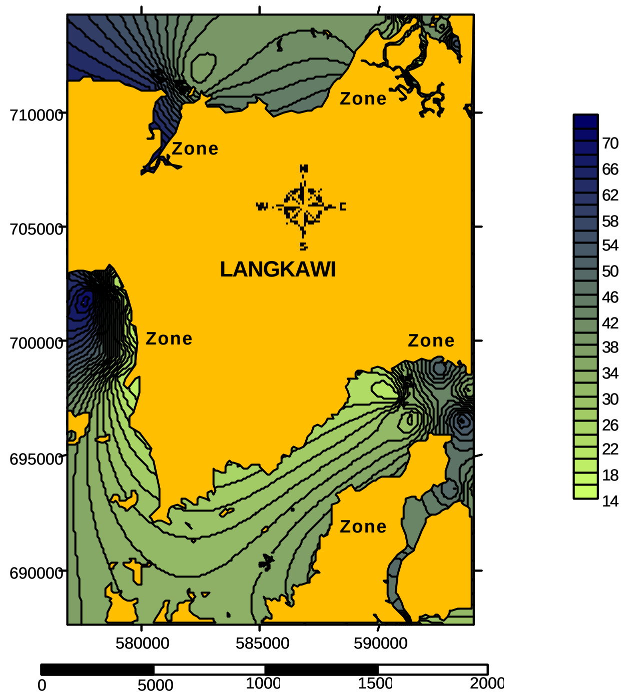

Fig. 2: Distributions of Pb along the five different zones of coastal waters of Langkawi

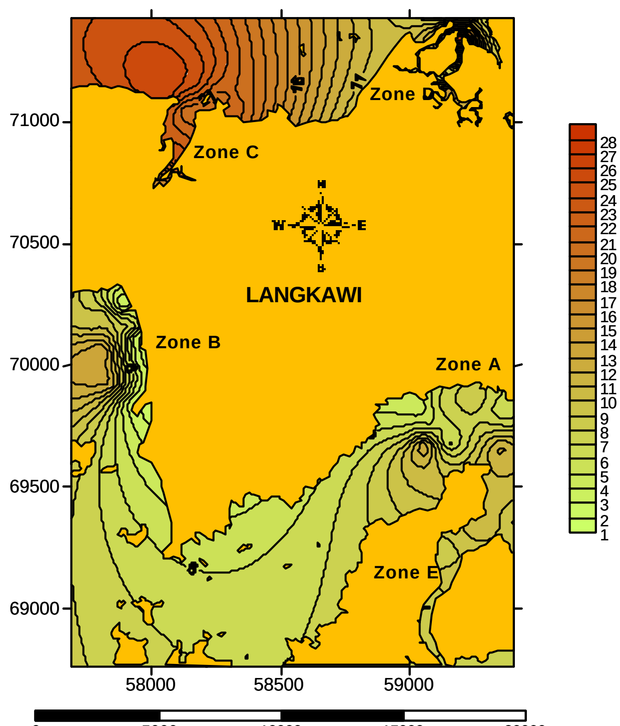

Fig. 3: Distributions of Cu along the five different zones of Langkawi coastal water

The higher concentrations of Pb in zone C might be due to frequent used lead rich gasoline in ships and boats as well as spillage during shipment and other operations that had took place along this area (Kamaruzzaman *et al.*, 2002). Although, unleaded petrol had been used recently, prehistoric activities also could results in higher concentrations of lead levels in the area as metals accumulates and retained in sediments for time due to its non biodegradable nature. Besides this, the continuous use of zone C waters for fishery activity and fishery product transport might cause high accumulation of Pb level in this area. Higher levels of lead might also came from several cargo ships that were hauled in this area. Activities such as cleaning and painting of boats would increase the higher concentrations of Pb into the environment.

Lead compounds are being used as a colouring agent in paint which may produce or accelerate environmental disturbances if the level is higher than the ambient level. According to San Francisco Maritime National Park Association, lead ballast is still used in some of boat vessels and lead based paints were preferred for marine used for many years. Contamination of Pb in this area is mostly from these activities and its applications. Similar findings were observed by Ismail and Yap (2001), who found that heavy metals (Cu, Zn, Pb and Cd) level in sediments were much higher at Port Klang and Port Dickson areas which ships and boats pass through the causeway everyday.

Besides that, during dry season, in zone A, D and E, it was also identified that these zones had higher concentration of lead compared with the average shale (20 $\mu g\ g^{-1}$). In zone A, a lot of boats and ferries passing through the pathways everyday in the area of Kuah town and also Pulau Langkawi main jetties where situated here. Leaking as well as spillage oil from these areas might enhanced the Pb concentration in the marine ecosystem. In addition, emissions from automobiles that consume leaded petrol are also the major source of the atmospheric Pb (Huntzicker *et al.*, 1975) and the atmospheric pathways may represent a major source of Pb into the offshore sediments. This was supported by other study which stated that elevated level of Pb concentrations near the causeway are most likely due to exhaust emissions from large volume of vehicles passing daily over the causeway, since leaded gasoline are still sold in Malaysian (Khalik *et al.*, 1997). The observed concentration of Pb and Cu is shown in Table 1.

Copper is an essential micronutrient to both plants and animal. In was found in large variations in concentrations which do occur in water and sediments (Waldichuck, 1974). Besides that, Cu has become among the most abundant metals in urban areas and especially in industrial waste and sewage, both of which directly contribute to the aquatic ecosystem in the form of particulate and dissolved materials.

According to Thompson (1990), Cu in sediments could be found since it is one of the most essentials metals from biota, being associated with numerous metalloenzymes and metalloproteins. However, high level of Cu in sediments could cause toxic and could also bioaccumulate in the food chain. The high level of Cu found in the sediments could be due to both natural and anthropogenic origins as reported by Christensen and Juracek (2001).

Cu found in some of the sampling locations could be partially attributed from the increasing levels of Cu from ports activities and jetties around Zone A. According to Kamaruzzaman *et al.* (2006) cleaning of boats and ships, ballasting, painting and repairing boats would proportionally increase Cu levels in the coastal environment. It is often difficult to separate Cu inputs from boating and shipping sources and urban run off. It was found that the anti-fouling paint for ships hulls is one of the major sources of Cu pollution in an aquatic environment (Clark, 2001). Boats and ships which are particularly old may be introducing Cu contents into the environment in form of the scrapping of the old boat paint that contains Cu and organo tin elements. This phenomenon also can be noted in the area of Zone C which exhibits the highest concentrations of Cu.

Table 1: Concentration of Pb and Cu from five different zones of Langkawi coastal waters

Elements	*Zone ($\mu g\ g^{-1}$ dw) A	B	C	D	E
Pb	58.15	21.18	68.62	49.38	22.88
	32.30	26.43	67.82	29.28	51.77
	38.67	22.27	59.95	12.25	45.42
	52.98	19.66	54.29	40.33	50.24
	35.81	28.64	38.95	35.86	42.63
	21.93	22.14	45.90	56.23	43.71
	18.44	69.48	61.06	45.98	44.41
	38.16	71.38	39.67	20.03	51.18
	26.62	62.61	38.50	39.04	37.30
	24.84	59.62	-	-	-
	33.12	47.97	-	-	-
	26.85	62.88	-	-	-
Cu	12.53	3.68	18.52	16.53	7.11
	6.98	4.29	24.35	5.60	8.34
	6.28	3.74	3.84	8.08	8.29
	9.02	2.77	19.98	30.95	7.96
	7.61	8.26	19.59	10.72	9.76
	4.25	2.82	22.22	9.23	8.15
	5.90	9.84	25.90	9.69	9.94
	7.20	9.30	24.08	7.36	10.64
	5.51	9.36	24.08	9.22	8.91
	7.02	14.10	-	-	-
	13.75	13.22	-	-	-
	8.80	7.54	-	-	-

*A total of 12 samples were collected from zone A and B. Zone C, D and E were represented with 9 samples from each sampling zones

Table 2: Enrichment factor value for Pb and Cu along the five different zones of Langkawi coastal waters

Element	Estimated EF value	Contamination categories
Pb	10.82±2.73	Significant enrichment
Cu	0.66±0.24	Deficiency to minimal enrichment

In zone A and B, the area are nearer to the mainland and this would partially attribute to the increasing in Cu levels from port activities and small jetties as the area is one of the most attractive tourist area and have several shore activities. Besides that, loading and off loading of fishes, cleaning of boats and ships, ballasting, painting and repairing boats as well as large ships and cargo also would proportionally increase the Cu levels in the coastal environment (Kamaruzzaman *et al*., 2008). Yap *et al*. (2003) suggested that Cu levels would also be higher in productive areas especially in muddy bottom (due to benthic action in decomposition of dead aquatic organisms). In addition, this reason can be applied to this area where most of the sediments are dominated by fine silt sediments.

Estimation of enrichment factors: For a better estimation of anthropogenic input, an enrichment factors was calculated for both the metals using average shale as reference matrix (Table 2). EFs around 2.0 indicate that the element in sediment is originated predominantly from lithogenous material. However, for those which is larger indicate that the element is of anthropogenic origin (Szefer *et al*., 1996). It was found that Pb were considered to have enrichments caused by anthropogenic activities (EF>1.00). However, both Cu and Zn existence are considered as a metal which is predominantly terrigenous in origin. Data obtained provides a scientific discovery and also can be referred as a baseline data for a better understanding and proper management of our marine coastal area.

Heavy metal contamination is an environmental problem in both developing and developed countries throughout the world. Human activities increase the release of heavy metals to natural environment because most metals are widely used in a variety of industrial and agricultural applications (Narval *et al*., 1992). In Malaysia, study related to heavy metals contamination is still inadequate. A more detailed and comprehensive study on heavy metals contamination in Malaysia coastline is essentials in order to support and established more baseline information in sediments in order to control and monitor the pollutions in our coastal area.

CONCLUSIONS

To summarise, the sediment samples collected from Langkawi coastal waters showed high concentration of Lead (Pb) which is primarily due to anthropogenic activities. As reported by various studies, lead can bioaccumulate in the higher quantity in the benthic community and ultimately reach higher trophic level through food chain. Hence, detailed study need to be carried out to check the bioaccumulation level of heavy metals in the benthic community of Langkawi coastal waters. It is also necessary to conduct detailed study to know the various physiological changes undergone by the benthic fauna during different concentration of heavy metal exposure since it influence in the physiology of any animal.

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