Int. J. Environ. Res., 4(4):877-886, Autumn 2010
ISSN: 1735-6865

Vertical Distribution of Heavy Metals and Enrichment in the South China Sea Sediment Cores

Rezaee, Kh.[1*], Saion, E. B. [2], Yap, C. K. [3], Abdi, M. R.[4] and Riyahi Bakhtiari, A.[5]

[1]Department of Nuclear Engineering, Faculty of Modern Sciences and Technologies, University of Isfahan, Isfahan 81747-73441, Iran

[2] Universiti Putra Malaysia, Physics Department, 43400 UPM SERDANG, Selangor, Malaysia

[3]Universiti Putra Malaysia, Biology Department, 43400 UPM SERDANG, Selangor, Malaysia

[4]Department of physics, Faculty of Science, University of Isfahan, Isfahan 81747-73441, Iran

[5]Department of Environmental Science, Faculty of Natural Resources and Marine Sciences, Tarbiat Modares University, Noor, Mazandaran, Iran

Received 17 Nov. 2009; Revised 10 June 2010; Accepted 25 June 2010

ABSTRACT: Forty seven sediment cores recovered from the South China Sea coasts along the east coast of Peninsular Malaysia were analysed for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn using instrumental neutron activation analysis. The results indicate a homogeneous distribution except for As and Pb in all stations. Assessment of heavy metal pollution in marine sediments requires knowledge of pre-anthropogenic metal concentrations to act as a reference against which measured values can be compared. Primitive values for the cored sediments were determined from shale average metal. Various methods for calculating metal enrichment and contamination factors are reviewed in detail and a modified and more robust version of the procedure for calculating the degree of contamination is proposed. The revised procedure allows the incorporation of a flexible range of pollutants, including various organic species, and the degree of contamination is expressed as an average ratio rather than an absolute summation number. Comparative data for normalized enrichment factors and the modified degree of contamination show that the South China Sea sediments are in uncontaminated to moderately contaminated level of heavy metal contamination. Compared to obtained values the Kelantan and Pahang big rivers mouth show higher enrichment averaged across other sites.

Key words: Heavy metals, Enrichment factor, Degree of contamination, Sediment cores pollution, South China Sea, Peninsular Malaysia

INTRODUCTION

The pollution of aquatic ecosystems by heavy metals has assumed serious proportions due to their toxicity and accumulative behavior (Milenkovic et al., 2005; Nirmal Kumar et al., 2005). Like soils in the terrestrial ecosystem, marine sediments in aquatic ecosystem are the sources of substrate nutrients and become the basis of support to living aquatic organisms (Abdullah et al., 2007). Their origins may be classified into various sources including terrigenous derived from continents (weathering and erosion), biogenic derived from organism decays (skeletal parts, carbonaceous or siliceous), authigenic derived from seawater (chemical or biochemical precipitation and Fe-Mn nodules), volcanogenic, extraterrestrial or cosmogonies, and anthropogenic derived from human activities. Industrialization, urbanization, agriculture (food production), and natural resources exploitation (mining and energy exploration) are basic activities associated with the modern living and vibrant society (Fçrstner, 1989; Fowler 1990; Tatasukawa et al., 1990; Leach et al., 1985; Enell and Wennberg, 1991; Gribble, 1994). However, these anthropogenic activities can contribute to the environmental impacts of sedimentation such as loss of aquatic habitat, decrease in fishery and aquatic plant resources, fish migration, and human health concerns (Young et al., 2007). Anthropogenic sources of elemental contamination and pollution released into the environment have been summarized by many researchers (Harrison, 2001; Morrisey et al., 2003; Malin et al., 2003).

This paper is concerned with a study on contamination and pollution of heavy metals in coastal marine sediments off the South China Sea along the

---

*Corresponding author E-mail: rezaee.nucl@gmail.com east coast of Peninsular Malaysia, as determined by the Instrumentation Nuclear Activation Analysis (INAA) and the Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) techniques. The data undergo several experimental procedures including statistical analyses, normalization, and estimating anthropogenic impact factors to establish the concentration and identify the status of each heavy metal under investigation.

The study area is the coastal marine ecosystem of the South China Sea along the east cost of Peninsular Malaysia shown Fig.1. The sea has an area 3.8 million km^2 by considering the Gulfs of Thailand and Tonkin. About 270 million people live in the coastal sub regions of the South China Sea that have had some of the fastest developing and most vibrant economies on the globe (Morton, 2001). The east coast of Peninsular Malaysia is 957 km, stretching from Kota Baharu in the north to Johor Bahru in the south and has the population of about 5 million people. There are major rivers such as Endau, Kuantan, Rompin, Sungai Besar, Pahang, Terengganu, Kelantan rivers flow into the South China Sea. Among these rivers, Pahang River in the state of Pahang with 459 km long is the longest river in the Peninsular Malaysia that begins at the confluence of Jelai and Tembeling rivers on the mountain ranges of Titiwangsa. Moreover, Kelantan River in the state of Kelantan has a catchment area about 11,900 km in northeast Malaysia including part of Taman Negara National Park. Other rivers are small rivers that flow through the states of Johor, Pahang, Terengganu, and Kelantan.

MATERIALS & METHODS

The core sediment samples were collected at a sea water depth about 42.0-51.6 m using a standard box corer sampler and taken to a sediment depth of 60 cm by the sampler own weight. However, the core sediment samples used in this work were from depth ranges of 18-20 cm, 22-24 cm, 26-28 cm, 30-32 cm, 34-36 cm, 38-40 cm, 42-44 cm, 46-48 cm and 50-52 cm for each site, except for EC1 and EC2 stations where the layer extended to 54-56 cm. Information about temporal changes in the deeper layer is the reason of this selection. The least and the most deep did not use in this analysis. The sampler has a cross sectional area of 20×30 cm^2 and was designed to take undisturbed samples from the top layer of the sea floor. When the box frame reached the seafloor, a weight was taken off the hoist cable and the trigger mechanism released the core box. The box then penetrated the seafloor to a maximum of 70 cm because of its own weight hydrostatic pressure. A piston with a handle on its upper end passed through the sampler frame. The piston was retracted when the cylinder pressed into the bed material. The suction created by the piston holds the sample in the cylinder. After collecting the core sediment samples, they were cut into strata between 2-3 cm intervals and the thickness of each sample section was about 2 cm layer (Wood et al., 1997). The samples were transferred into pre-cleaned and pre-weighed polyethylene bottles and refrigerated at -5 °C for analysis later.

The samples were weighted approximately 0.05 to 0.1 g for short irradiation and 0.15-0.20 g for long irradiation. The samples and the standard reference material IAEA-Soil-7 were then irradiated with thermal neutron flux of 4×10^{12} n cm $^{-2}$s^{-1} at the MINT TRIGA Mark II research reactor operated at 750 kW where a pneumatic transport facility was used. The irradiation, decay and counting times for short irradiation were 1 minute, 20 minutes and 5 minutes respectively. For long irradiation, the samples were irradiated for 6 hours and counted for 1 hour after a cooling time of 3-4 days and 21-28 days.

About 0.5 g of dried and grounded samples were placed in Teflon vessels with 3 mL of $HClO_4$ (MERK, 64%) and 10 mL of HF (MERK, 60%) and heated for 3-4 hours at 160° C until the white smoke of HF throw out. Then 1 mL of HCl (MERK, 36%) and 1-2 mL deionized water added and heated for 5 minute at 200° C. The resulting solution was transferred to polypropylene tubes and diluted up to 50 mL with deionized water. The concentration of heavy metals was determined by ICP-AES. A blank sample together with three reference standard material used to calibrate ICP-AES equipment. Reading time for each sample takes long about 2 minute and after twenty reading one standard sample used to trust to the calibration.

A number of calculation methods have been suggested to quantify the degree of metal enrichment in sediments, e.g. Ridgway and Shimmield (2002). Three methods are discussed in the following sections along with proposed modifications. A common approach to estimating the anthropogenic impact on sediments is to calculate a normalized enrichment factor (*EF*) for metal concentrations above uncontaminated background levels (Salomons et al., 1984; Dickinson et al., 1996; Hornung et al. 1989; Hernandez). The *EF* method normalises the measured heavy metal, trace elements, rare earth elements and actinides content with respect to a sample reference metal such as Fe, Sc or Al (Ravichandran et al., 1995). In this work, the *EF* is calculated according to the following equation:

$$\frac{\left(\frac{C_x}{C_{ref}}\right)_{Sample}}{\left(\frac{C_x}{C_{ref}}\right)_{Average\ shale}} \qquad (1)$$

Table 1. Muller's classification for geo-accumulation index

I_{geo} value	Class	Qualification of sediment
≥ 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately polluted to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly polluted to extremely polluted
>5	6	Extremely polluted

where $(C_x / C_{ref})_{Sample}$ is the sediment sample concentrations ratio of the heavy metal and Sc (or other normalising element), while $(C_x / C_{ref})_{Average\ shale}$ is their concentrations in a suitable background or baseline reference material such as average shale (Salomons et al., 1984). In this manner, if the enrichment factor for each element is equal or less one it showing that the main source is natural and originally came from the crustal or marine. Otherwise, if the enrichment factor is much greater than one, it indicates that the main source is anthropogenic contribution. A common approach to estimate the enrichment of metal concentrations above background or baseline concentrations is to calculate the geoaccumulation index (I_{geo}) (Müller, 1969). The method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index. This index is calculated as follows:

$$\log_2[C_n/(1.5 \times B_n)] \qquad (2)$$

where C_n is the concentration of the element in the enriched samples, and the B_n is the background or pristine value of the element. The factor 1.5 is introduced to minimise the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Stoffers et al. 1986). Therefore, if the concentration of element in a sample be five times greater than the concentration of it in the background the sample is extremely polluted. Müller proposed the following descriptive classes for increasing I_{geo} values in Table (1). Modified degree of contamination (mC_d) is based on the calculation for each pollutant of a contamination factor (*Cf*). However, the *Cf* requires that at least five surficial sediment samples are averaged to produce a mean pollutant concentration which is then compared to a baseline pristine reference level, according to the following equation:

$$Cf = \frac{C_{Sample}}{C_{Background}} \qquad (3)$$

where C_{Sample} and $C_{background}$ respectively refer to the mean concentration of a pollutant in the contaminated sediments and the pre-industrial "baseline" sediments or average shales. The numeric sum of the *k* specific contamination factors expressed the overall degree (Hakanson, 1980) of sediment contamination (C_d) using the following formula:

$$C_d = \sum_{i=1}^{k} Cf^i \qquad (4)$$

The C_d is aimed at providing a measure of the degree of overall contamination in surface layers in a particular core or sampling site. Furthermore, all n species must be analysed in order to calculate the correct C_d for the range of classes defined (Hakanson, 1980). A modified and generalised form of the (4.14) equation for the calculation of the overall degree of contamination are presented by equation (4.16) at a given sampling (Abrahim, 2005). The modified formula is generalised by defining the degree of contamination (mC_d) as the sum of all the contamination factors (*Cf*) for a given set of estuarine pollutants divided by the number of analysed pollutants. The modified equation for a generalised approach to calculating the degree of contamination is given below:

$$mC_d = \frac{\sum_{i=1}^{n} Cf^i}{n} \qquad (5)$$

where *n* is number of analysed elements and *i* is i_{th} element (or pollutant) and *Cf* is contamination factor. Using this generalised formula to calculate the mC_d allows the incorporation of as many metals as the study may analyse with no upper limit. For the classification

Table 2. Hakanson (1980) classification of the modified degree of contamination (Abrahim *et al.*, 2007)

mCd values	Qualification of sediment
$mCd < 1.5$	Nil to very low degree of contamination
$1.5 \leq mCd < 2$	Low degree of contamination
$2 \leq mCd < 4$	Moderate degree of contamination
$4 \leq mCd < 8$	High degree of contamination
$8 \leq mCd < 16$	Very high degree of contamination
$16 \leq mCd < 32$	Extremely high degree of contamination
$mCd \leq 32$	Ultra high degree of contamination

Table 3. Heavy metal concentrations, in mg/kg, measured in the core sediments of the east coast of Peninsular Malaysia

Station	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
EC1								
18-20	5.8	0.3	53.1	9.3	0.08	27.2	25.1	41.3
22-24	7.7	0.3	48.2	9.5	0.08	32.5	18.6	42.9
26-28	6	0.3	52.1	9.8	0.06	25.5	19.3	39.8
30-32	7.5	0.3	49.9	8.9	0.08	30.3	17.9	39.9
34-36	9.2	0.4	48.1	8.1	0.09	29.4	17.5	39.5
38-40	10.5	0.4	50	8.6	0.09	29.4	15.4	39.5
42-44	9.3	0.4	52.2	7.9	0.11	28.5	16.3	38.9
46-48	15.8	0.5	49.8	7	0.12	26.6	29.7	38
50-52	11	0.4	45.7	7.7	0.11	31.1	15	41
54-56	9.3	0.5	51.8	8.7	0.11	28.8	28.5	42.1
EC2								
18-20	0.2	0.2	51.2	11	0.05	28.6	17.1	43.3
22-24	5.6	0.2	53.1	11.2	0.06	30.9	14.1	44.8
26-28	12.1	0.3	49.3	10.2	0.07	28.1	11.1	43.6
30-32	5.7	0.3	45	9.5	0.08	28.3	23.9	39.8
34-36	7.2	0.3	52.8	9.4	0.11	25	19.7	39.2
38-40	9.4	0.3	49	9	0.06	24	14.3	38.3
42-44	7	0.3	43.6	9.1	0.06	18.9	15.2	36.3
46-48	6.4	0.3	46.4	8.7	0.06	20.8	12.6	37.1
50-52	11.5	0.3	39.3	8.8	0.08	28.2	19.7	37.6
54-56	6.3	0.3	47	10	0.08	24	22.2	40.2
EC3								
18-20	15.7	0.2	36.6	8.8	0.07	22	29	46.6
22-24	15.4	0.3	33.8	9.2	0.1	18.8	28.2	50.2
26-28	20.3	0.3	37.1	7.9	0.07	17.8	21.9	45.8
30-32	21.3	0.3	30.9	9	0.08	24	27.7	46.3
34-36	20.2	0.3	34.4	9	0.08	17.4	28.8	47.4
38-40	21	0.2	29.9	7.3	0.06	22.3	22.8	43.9
42-44	27.2	0.2	29.3	6	0.06	20.2	23.7	40.2
46-48	14.9	0.2	27.6	6.1	0.07	20.3	19.4	39.7
50-52	18.7	0.2	23.4	5.4	0.06	17	29.7	37.5
EC4								
18-20	2.2	0.2	29.9	4.2	<0.05	17.6	13	23.2
22-24	0.8	0.2	25.8	3.8	<0.05	19.3	7.9	22.5
26-28	1.6	0.2	31.5	3.2	<0.05	18.7	6.1	21.5
30-32	2.9	0.2	28.1	3.3	<0.05	18.7	20.1	22.2
34-36	9	0.2	23.3	4	<0.05	21.1	15.9	20.8
38-40	3.8	0.2	27.4	3.2	<0.05	17.9	17.2	20.7
42-44	2.9	0.1	23	4.4	<0.05	23.6	17	22.1
46-48	4.5	0.2	28.9	3.3	<0.05	20.2	-	24.3
50-52	4.6	0.2	23.9	4.4	<0.05	13.7	6.2	26
EC5								
18-20	7.1	0.2	34	6.6	<0.05	22.5	22.1	31.2
22-24	10.3	0.2	33.1	6	<0.05	22.2	18.3	90.1
26-28	8.8	0.2	33.5	7.1	<0.05	20.4	27.8	98.3
30-32	9	0.2	25.8	5.6	<0.05	19.1	26.6	82.6
34-36	10	0.2	30.9	5.2	<0.05	17.9	17.8	80.4
38-40	10.1	0.2	31	5.4	<0.05	18.9	24.8	83.8
42-44	9.7	0.2	34.8	5.3	<0.05	18.4	22	86.1
46-48	7.1	0.2	35.6	4.9	<0.05	24	19.6	74
50-52	9.6	0.2	36.3	5.6	<0.05	18.7	15.6	84.2
Average	9.6	0.3	38.2	7.2	0.1	22.9	19.6	45
CV	61.3	38.2	26.4	31.9	19.1	20.5	31.1	44.7
Max	27.2	0.5	53.1	11.2	0.1	32.5	29.7	98.3

and description of the modified degree of contamination *(mC_d)* in estuarine sediments the following gradations are proposed in (Table 2).

RESULTS & DISCUSSION

Table 3 shows concentrations, mean values, coefficient variation and maximum values of *As*, *Cd*, *Cr*, *Cu*, *Hg*, *Ni*, *Pb* and *Zn* (mg/kg) obtained in sediment profiles of the five sampling sites. The distribution profile of heavy metal concentrations in the five sampling stations is shown in Figure 5.13. As it can be seen, in general the heavy metals show a homogeneous distribution profile except *As* and *Pb* in all stations. The distribution of *Zn* also is homogeneous except for EC5 that the concentration decreases in the upper layer. In station EC3 the *As* concentration increases from the bottom to the top until 42-44 centimetre. Above this depth there is an inversion of its behaviour and it decrease with very slow sleep. Most of heavy metals show significant correlation with Fe and Al, except As, Pb and Zn. This may be is attributed to that organic carbon and silicates are not the main geochemical carriers of these metals in the five sampling stations (Chatterjee et al., 2006). The lake of association of As, Pb and Zn with those carriers proposes that these elements have a different origin. This is supported with obtained enrichment factor values in section 3.3. These elements probably come from anthropogenic activities such as agriculture because in the past, arsenic was commonly used as a poison to kill rodents, insects, and plants.

The maximum mean concentration values for *Cd* (0.4 mg/kg); *Cr* (50.1 mg/kg) and *Ni* (28.9 mg/kg) were obtained at EC1 in the core sediment samples. Moreover, by averaging concentration of these heavy metals between layers in each station their mean concentration increase from east south (close to the Johor) to east north (close to the Kelantan). Intensive agriculture, sewage drainage from the Kelantan River and other commercial activities are proposed to be potential sources for the enrichment of these heavy metals in EC1 rather than the other four stations. The concentration of all heavy metals revealed variations between the elements, between stations and bottom and upper layers. An overall decreasing value from bottom to top core is also noticed that may be connected to ground water infiltration derived from multifarious sources (Chatterjee et al., 2006). Although for most elements (e.g. *Cr, Cu*) there is important fluctuation in distribution along to the core, the trend shows consistent between sites. The element *Pb* revealed similar trend of irregular distribution in the sediment profiles except in station EC5 that there is a clearly decreasing in the 18-20 cm layer. The precipitated in the form of oxyhydroxide has the affinity to scavenge other metals namely *Cu*, *Zn* and *Pb* as they pass through the water to the sediments (Waldichuk, 1985).

Approximately the elevated levels of most elements is observed at EC1 station which may be attributed to multiple factors like use of mechanized boat for fishing and agriculture activities by the local inhabitants. Moreover approximately the lower values of most heavy metals (except for *As*) are observed in EC4 station which there is no important river discharges to the South China Sea in this region.

To distinguish the heavy metals originating from human activities and from natural weathering calculating enrichment factor is an essential part of geochemical studies (Praveena et al., 2010). One such technique greatly applied is normalizing of metal concentration to a texture or compositional characteristic of sediments. For these heavy metals, normalizing heavy metals relative to Sc is used since its concentration is generally not influenced by anthropogenic activities and specially used for elements that are marine origin (IAEA-TCS-4, 1992). Normalizing heavy metals relative to *Fe* is not suggested because of most heavy metals in the core sediments have positive correlation factor with *Fe*. The values of EFs can be calculated using the equation $\text{EF}= (\text{metal/Sc})_{\text{sediment}} / (\text{metal/Sc})_{\text{shale}}$. EFs close to unity point show crustal origin whiles those greater than one are related to non-crustal source (Nolting et al., 1999). The EFs obtained for most heavy metals (*Cr*, *Cu*, *Hg*, *Ni*, *Se* and *Zn*) are less than unity that reveals these elements are depleted in some of the phases relative to crustal abundance in the study area (Chatterjee et al., 2006). *Cr*, *Cu*, *Hg*, *Ni* and *Zn* are known as non-anthropogenic heavy metals in the core sediments. However, heavy metals with an EF value greater than unity show excess these elements relative to crustal abundance that may attributed to the sediment contamination, for example the higher EF values for *Cd* for all layers and *As* and *Pb* in some layers at five stations. *Cd*, *As* and *Pb* are known as anthropogenic heavy metals in the core sediments. Gasoline residues source of the *Pb* increases and urban refuse incineration is a major source of the *Cd* increase (Nriagu and Pacyna, 1988). Moreover, *Cd* has received a wide variety of uses in industries with the largest being electroplating and battery manufacture. Its emission from natural sources (erosion and volcanic activity) is negligible (Lollar, 2004). Domestic waste is the primary source of the generation of solid wastes as a result the high concentration of *Cd* in Malaysia and its coasts (Manaf et al., 2009). Also, the combinations of *As* are used in agriculture industries (e.g. Sodium arsenile is used essentially in agriculture;

Methylarsinic acid is employed as a weedkillerin cotton cultivation, and dimethylarsinic acid or cacodylic acid as a weed-killerand insecticide against ants; Arsenic anhydride or arsenic pentoxide (As_2O_5), obtained through controlled oxidation of arsenics anhydride by nitric acid, is used in large quantities to protect wood from insects) (Datta et al., 2004; Lollar, 2004). The enrichment factor for *As* in stations EC3 and EC5 at all layers is greater than one and in the EC1 station at layers 34-36, 38-40, 42-44, 46-48 and 50-52 is greater than one. By considering the obtained enrichment factors for these layers in the stations EC1, EC3 and EC5, the numeric values of the enrichment factor does not have salient difference in different layers (Table 4). Therefore, the results show in during sedimentation in this area had not any important events to release heavy metals to the aquatic environment in the east coast of Peninsular Malaysia. In fact, this east coast of Peininsular Malaysia is an area under agriculture industry as a result the relatively high values of *As* in the bottom sediment of this area may be attributed to agriculture. However, decrease concentration of *As* in the upper sediments due to good management and improving agriculture industry in recreantly years.

The I_{geo} method was used to calculate the heavy metal contamination levels for the recovered cores from the east coast of Peninsular Malaysia. The average I_{geo} class are 0 and 0–1 indicating uncontaminated and uncontaminated to moderately contaminated levels respectively. Details of the I_{geo} values for individual

Table 4. Enrichment factors (EF) of anthropogenic heavy metals in the core sediments of the east coast of peninsular Malaysia, normalized with respected to the scandium content in the continental shales

	EC1	EC2	EC3	EC4	EC5
			Cd		
18-20	2.0	1.3	1.3	2.1	1.6
22-24	1.8	1.2	2.0	2.1	1.5
26-28	1.9	2.0	2.2	2.1	1.6
30-32	2.3	2.1	2.0	2.1	1.5
34-36	2.8	1.8	2.2	2.0	1.3
38-40	2.6	1.9	1.5	2.0	1.4
42-44	2.7	2.0	1.5	1.0	1.5
46-48	3.4	1.9	1.5	2.0	1.4
50-52	2.4	1.9	1.6	2.1	1.3
			As		
18-20	<1	<1	1.7	<1	<1
22-24	<1	<1	1.7	<1	1.3
26-28	<1	<1	2.5	<1	1.2
30-32	<1	<1	2.4	<1	1.1
34-36	1.1	<1	2.5	<1	1.1
38-40	1.1	<1	2.6	<1	1.2
42-44	1.1	<1	3.3	<1	1.2
46-48	1.8	<1	1.8	<1	<1
50-52	1.1	<1	2.6	<1	1
			Pb		
18-20	1.5	1	1.7	1.3	1.7
22-24	1.1	<1	1.8	<1	1.3
26-28	1.2	<1	1.5	<1	2.1
30-32	1.3	1.5	1.7	1.9	2
34-36	1.2	1.1	2	1.5	1.1
38-40	<1	<1	1.6	1.6	1.6
42-44	1	<1	1.6	1.6	1.5
46-48	1.9	<1	1.3	<1	1.3
50-52	<1	1.2	2.3	<1	<1

Table 5. Index of Geoaccumulation (I_{geo}) in core sediments of the east coast of Peninsular Malaysia

			I_{geo} values				
Core	**EC1**	**EC2**	**EC3**	**EC4**	**EC5**	**I_{geo} class**	**Sediment quality**
			As				
18-20	-1.7	-6.6	-0.3	-3.1	-1.4		
22-24	-1.3	-1.7	-0.3	-4.6	-0.9		
26-28	-1.7	-0.8	0.1	-3.6	-1.1	0-1	From unpolluted to moderately polluted
30-32	-1.3	-1.7	0.1	-2.7	-1.1	0-1	From unpolluted to moderately polluted
34-36	-1	-1.4	0.1	-1.1	-0.9	0-1	From unpolluted to moderately polluted
38-40	-0.9	-1	0.1	-2.3	-0.9	0-1	From unpolluted to moderately polluted
42-44	-1	-1.5	0.5	-2.7	-1	0-1	From unpolluted to moderately polluted
46-48	-0.3	-1.6	-0.3	-2.1	-1.4		
50-52	-0.8	-0.7	0	-2	-1	0	unpolluted
			Cd				
18-20	-0.1	-0.7	-0.7	-0.7	-0.7		
22-24	-0.1	-0.7	-0.1	-0.7	-0.7		
26-28	-0.1	-0.1	-0.1	-0.7	-0.7		
30-32	-0.1	-0.1	-0.1	-0.7	-0.7		
34-36	0.3	-0.1	-0.1	-0.7	-0.7	0-1	From unpolluted to moderately polluted
38-40	0.3	-0.1	-0.7	-0.7	-0.7	0-1	From unpolluted to moderately polluted
42-44	0.3	-0.1	-0.7	-1.7	-0.7	0-1	From unpolluted to moderately polluted
46-48	0.6	-0.1	-0.7	-0.7	-0.7	0-1	From unpolluted to moderately polluted
50-52	0.3	-0.1	-0.7	-0.7	-0.7	0-1	From unpolluted to moderately polluted
			Pb				
18-20	-0.4	-1	-0.2	-1.4	-0.6		
22-24	-0.9	-1.2	-0.3	-2.1	-0.9		
26-28	-0.8	-1.6	-0.6	-2.4	-0.3		
30-32	-0.9	-0.5	-0.3	-0.7	-0.3		
34-36	-0.9	-0.8	-0.2	-1.1	-0.9		
38-40	-1.1	-1.2	-0.5	-1	-0.4		
42-44	-1	-1.1	-0.5	-1	-0.6		
46-48	-0.2	-1.4	-0.8	-	-0.8		
50-52	-1.2	-0.8	-0.2	-2.4	-1.1		

Table 6. Modified degree of contamination using shale average baseline values for heavy metals in core sediments from the east coast of Peninsular Malaysia

			mCd		
	EC1	**EC2**	**EC3**	**EC4**	**EC5**
18-20	0.6	0.5	0.7	0.4	0.5
22-24	0.6	0.5	0.7	0.3	0.6
26-28	0.6	0.6	0.7	0.3	0.6
30-32	0.6	0.6	0.8	0.4	0.6
34-36	0.7	0.6	0.8	0.4	0.6
38-40	0.7	0.6	0.6	0.4	0.6
42-44	0.7	0.5	0.7	0.3	0.6
46-48	0.9	0.5	0.6	-	0.5
50-52	0.7	0.6	0.6	0.3	0.5
54-56	0.8	0.6	-	-	-

elements in the nine cores at five sampling are presented in Table 5. The negative I_{geo} values found in the table are the results of relatively low levels of contamination for some metals in some cores and the background variability factor (1.5) in the I_{geo} equation.
In the core sediments of the east coast of Peninsular Malaysia, the revised Hakanson equation (5) is used to calculate the modified degree of contamination (mC_d) for the all analysed trace elements. The results for each core are presented in Table 6. The mC_d for the individual cores lie in the range 0.3-0.9 that is less than 1.5 showing nit to very low degree of contamination in the east coast of Peninsular Malaysia sediments. The mC_d data indicate non-anthropogenic impact in all cores.

The results of the various methods for calculating heavy metal enrichment in the east coast of Peninsular Malaysia sediments showed approximately same obtained results in difference methods. Moreover, is used of the core deepest as a reference concentration and averagely results demonstrate that, using the continental shale as a reference concentration the enrichment factor is relatively high. The results of all methods enrichment factor, geoaccumulation index and modified degree of contamination of this study showed there is not any important pollutant in the east coast of Peninsula Malaysia.

Clearly, in any survey of marine, estuarine or freshwater sediments, the best approach is to penetrate below the present day surface contamination and sample the pristine or least contaminated sediments available at depth in cores from the target survey area. This will allow the determination of realistic baseline values for the target area. This approach will work best in areas that have only suffered relatively recent contamination such as in countries that have relatively young industrial histories such as Malaysia where it is possible in most cases to get below the level of first anthropogenic impact.

Moreover, the result was also compared to US NOAA's sediments quality guidelines for estimating the possible environmental consequences of metals analyzed. In this study, just Effect Range-Low (ER-L) and Effect Range-Medium (ER-M) are considered. The ER-L shows chemical concentrations below which hostile biological effects were rarely observed and the ER-M shows concentrations above which effects were more frequently observed (Long et al., 1995 and 1997). By considering the concentration values of the heavy metals at each layer in five stations, the majority of the elements revealed low values.

CONCLUSION

The impact of anthropogenic heavy metal pollution on the South China Sea along the east coast of Peninsular Malaysia was evaluated using Enrichment Factors (EF), geoaccumulation indices (I_{geo}) and modified degrees of contamination (*mCd*) for As, Cd, Cr, Cu, Hg, Pb and Zn in marine sediments in nine cores at five sites.

The geoaccumulation indices (I_{geo}) are distinctly variable and suggest that marine sediments in the various the east coast of Peninsular Malaysia cores range from uncontaminated to moderately contaminated with respect to the analysed heavy metals. The uncontaminated I_{geo} designation is clearly supported by the other methods for calculating heavy metal pollution impact in the east coast of Peninsular Malaysia.

Normalised enrichment factor (EF) values for eight heavy metals were calculated for the east coast of Peninsular Malaysia using the continental shale abundance of Fe. The results show that using the Fe concentration in the continental shale as a normaliser produces higher than two EF values for Cd for all core samples and higher than one for As and Pb in some core samples that indicate anthropogenic activity for these heavy metals. The enrichment factor method is however the most relevant to the east coast of Peninsular Malaysia. With regard to an overall measure of heavy metal contamination applicable to estuarine or coastal sediments, the present study proposes a modified and generalised form of the Hakanson (1980) pollution impact equation. A modified degree of contamination (mCd) is proposed in which the sum of the individual contamination factors is divided by the number of analysed pollutants. Overall, the range of mCd values indicates nil to very low degree of marine sediment contamination in the east coast of Peninsular Malaysia cores.

ACKNOWLEDGEMENTS

The authors are thankful to the staff of TRIGA Mark II research reactor especially to Dr. Abdul Khalik Wood at Nuclear Institute in Malaysia for their assistance during the execution of work.

REFERENCES

Abdullah, M. H., Sidi, J. and Aris, A. Z. (2007). Heavy Metals (Cd, Cu, Cr, Pb and Zn) in Meretrix meretrix Roding, Water and Sediments from Estuaries in Sabah, North Borneo, International Journal of Environmental & Science Education, **2 (3)**, 69- 74.

Abrahim, G. M. S., Parker, R. J. and Nichol, S. L. (2005). Distribution and Assessment of Sediment Toxicity in Tamaki Estuary, Auckland, New Zealand. Environmental Geology, **52**, 1315-1323.

Abrahim, G. M. S. and Parker, R. J. (2007). Assessment of Heavy Metal Enrichment Factors and the Degree of Contamination in Marine Sediments from Tamaki Estuary, Auckland, New Zealand, Environ Monit Assess, **136**, 227-238.

Chatterjee, M., Silva Filho, E. V., Sarkar, S. K., Sella, S. M., Bhattacharya, A., Satpathy, K. K., Prasad, M. V. R., Chakraborty, S. and Bhattacharya, B. D. (2006). Distribution and Possible Source of Trace Elements in the Sediment Cores of a Tropical Macrotidal Estuary and Their Ecotoxicological Significance, Environment International, **33**, 346-356.

Dickinson, W. W., Dunbar, G. B. and McLeod, H. (1996). Heavy Metal History from Cores in Wellington Harbour, New Zealand. Environmental Geology, **27**, 59–69.

Datta, P. K., Ray, A. K. Sharma, V. K. and Millero, F. J. (2004). Adsorption of Arsenate and Arsenic on Titanium Dioxide Suspensions. Journal Colloid Interface Sci., **278**, 270-275.

Enell, M. and Wennberg, L. (1991). Distribution of Halogenated Organic Compounds (AOX)—Swedish Ttransport to Surrounding Sea Areas and Mass Balance Studies in Five Drainage Systems. Wat. Sci. Tech., **24,** 385-395.

Forstner, U. (1989). Contaminated Sediments: Lectures on Environmental Aspects of Particle-Associated Chemicals in Aquatic Systems (Lecture Notes in Earth Sciences, 21. Springer, Berlin, Germany.

Fowler, V. M. (1990). Tropomodulin. A Cytoskeletal Protein that Binds to the End of Erythrocyte Tropomyosin and Inhibits Tropomyosin Bbinding to Actin. J. Cell Biol, **111**, 471-482.

Hakanson, L. (1980). Ecological Risk Index for Aquatic Pollution Control. A Sedimentological Approach. Water Research, **14**, 975-1001.

Hernandez, L., Probst, A., Probst, J. L. and Ulrich, E. (2003). Heavy metal distribution in some French forest soils: evidence for atmosphere contamination. The Science of Total Environment, **312**, 195-210.

Hornung, H., Karm, M. D., and Cohen, Y. (1989). Trace Metal Distribution on Sediments and Benthic Fauna of Haifa Bay, Israel. Estuarine, Coastal and Shelf Science, **29**, 43-56.

Leach, J. M., Howard, T. E. and Lanz, H. E. (1985). Chlorinated Organics in Shellfish from Coastal Waters. Pulp and Paper Canada, **86,** 12, T398-T401.

Lollar, B. Sh. (2005). Environmental Geochemistry. First Edition. Elsevier Science: Amesterdam, Netherlands.

Long, E. R., MacDonald, D. D., Smith, S. L. and Calder, F. D. (1995). Incidence of Adverse Biological Effects Within Ranges of Chemical Concentrations in Marine and Estuarine Sediments, Environm. Manage., **19,** 81-97.

Long, E. R. and Wilson, C. J. (1997). On the Identification of Toxic Hot Spots Using Measures of the Sediment Quality Triad. Marine Pollution Bulletin, 34, 373-374.

Malin, E. K., Rauch, S., Morrison, G. M. and Andam, K. (2003). Impact of automobile emissions on the levels of platinum and lead in Accra, Ghana. Journal of Environmental Monitoring, **5**, 91-95.

Manaf, L. A., Samah, M. A. A. and Zukki, N. I. M. (2009). Municipal Solid Waste Management in Malaysia: Practices and Challenges. Waste Management, **29**, 2902–2906.

Morrisey, D. J., Turner, S. J., Mills, G. N., Williamson, R. B. and Wise, B. E. (2003). Factor affecting the distribution of benthic macrofauna in estuaries contaminated by urban runoff. Marine Environmental Research, **55 (2)**, 113-136.

Milenkovic, M., Damjanovic, M. and Ristic, M. (2005). Study of Heavy Metal Pollution in Sediments from the Iron Gate (Danube River), Serbia and Montenegro. Polish Journal of Environmental Studies, **14 (6)**, 781-787.

Morton, B. and Blackmore, G. (2001). South China Sea, Journal of Marine Pollution Bulletin, **42**, 1236-1263.

Müller, G. (1969). Index of Geoaccumulation in the Sediments of the Rhine River. Eojournal, 2, 108-118.

Nirmal Kumar, J. I., Soni, H. and Kumar, R. N. (2007). Evalution of Biomonitoring Approach to Study Lake Contamination by Accumulation of Trace Elements in Selected Aquatic Macrophytes: A Case Study of Kanewal Community Reserve, Gujarat. India. Apploed Ecology and Environmental Research, **6 (1)**, 65-76.

Nolting, R. F., Ramkema, A. and Everaarts, J. M. (1999). The Geochemistry of Cu, Cd, Zn, Ni and Pb in Sediment Cores from the Continental Slope of the Banc d' Arguin (Mauritania), Continental Shelf Research, **19,** 665-691.

Nriagu, J. O. and Pacyna, J. M. (1988). Quantitative Assessment of Worldwide Contamination of Air, Water and Soils by Trace Metals. Nature, **333,** 134-139.

Praveena, S. M., Aris, A. Z. and Radojevic, M. (2010). Heavy Metals Dyanamics and Source In Intertidal Mangrove Sediment of Sabah, Borneo Island. EnvironmentAsia, **3**, 79-83.

Ravichandran, M., Baskaran, M., Santschi, P. H. and Bianchi, T. S. (1995). History of Trace Metal Pollution in Sabine-Neches Estuary, Beaumont, Texas. Environ. Sci. Tech., **29,** 1495–1503.

Ridgway, J., and Shimmield, G. (2002). Estuaries as Repositories of Historical Contamination and Their Impact on Shelf Seas. Estuarine, Coastal and Shelf Science, **55**, 903-928.

Salomons, W., and Förstner, U. (1984). Metals in the Hydrocycle. Springer, Berlin Heidelberg Tokyo.

Stoffers, P., Glasby, G. P., Wilson, C. J., Davis, K. R. and Watter. P. (1986). Heavy Metal Pollution in Wellington Harbour. New Zealand Journal of Marine and Freshwater Research, **20**, 495-512.

Tatasukawa, R. and Kurokawa, A. (1990). Distribution of Heavy Metals in Soils of Vellar River Estuary, South

India. In Proc. Ann. Symp. of the Society of Environmental Science, Japan Tokyo: Toranomon, 152.

Gribble, G. W. (1994). The Natural Production of Chlorinated Compounds. Environ. Sci. Technol., **28 (7),** 310-319.

IAEA-TCS-4. (1992). Sampling and Analytical Methodologies for Instrumental Neutron Activation Analysis of Airborne Particulate Matter. International Atomic Energy Agency (IAEA), Vienna, Austria.

Waldichuk, M. (1985). Biological Availability of Metals to Marine Organisms. Mar. Pollut. Bull., **16,** 7-11.

Wood, A. K. H., Ahmed, Z., Shazili, N. A. MD., Yaakob, R. and Carpenter, R. (1997). Geochemistry of Sediments in Johor Straits between Malaysia and Singapore. Continental Shelf Research, **17 (10)**, 1207-1228.

Young, E. (2007). Can 'Fertilizing' the Ocean Combat Climate Change? Companies are Planning to Boost the Ocean's Plankton, Hoping they will Harvest more CO2 from the Air. But will it work? New Scientist, **15**, 42-45.