

Concentration and Enrichment Factor of Trace Metals in the Coal Electric Power Station Sediments of Kapar, Selangor, Malaysia

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Received July 26, 2006; revised and accepted June 29, 2007

Abstract: The concentrations of trace elements such as Zn, Mn, Cu, Co, Pb, Cr, Fe and Al in the interval of three cm were detected using the Atomic Absorption Spectrometry in three sediment cores at Kapar coastal area, nearby the coal-fired power plant. The range of these metals were 14.0 ± 1.37 - 58.1 ± 4.94 $\mu\text{g g}^{-1}$ (Zn), 192 ± 13 - 350 ± 23 $\mu\text{g g}^{-1}$ (Mn), 4.5 ± 0.53 - 12.4 ± 0.79 $\mu\text{g g}^{-1}$ (Cu), 12.7 ± 0.35 - 40.4 ± 1.08 $\mu\text{g g}^{-1}$ (Co), 14.5 ± 0.22 - 59.1 ± 0.59 $\mu\text{g g}^{-1}$ (Pb), 3.5 ± 0.11 - 15.6 ± 0.52 $\mu\text{g g}^{-1}$ (Cr), 0.84 ± 0.03 - $1.91 \pm 0.06\%$ (Fe) and 1.2 ± 0.00 - $5.2 \pm 0.01\%$ (Al) in dry weight, where Al is used to normalize these metals in order to calculate the enrichment factors (EF). The EF values obtained were in the range of 0.26 to 1.23 for all metals and not exceeded the ratio of 1 : 3, which indicate that the equilibrium condition was due to the origin of crust material or natural processes. This proves that Kapar coastal was not affected by the contamination of heavy metals neither from the coal-fired power plant operations nor the river discharges.

Key words: Trace elements, enrichment factors, coal electric power plant.

Introduction

The contamination of trace metals in the coastal sediments always occurred from the external sources such as industrial, modern population activities, ship scrapping yards, fly ash discharges, atmospheric emissions as well as domestic waste discharges (Reddy et al., 2004; Selvaraj et al., 2004). Recently much attention has been paid to the chemical composition of marine sediments in the coastal area located near an industrial and urban area because it is associated with the deterioration of oceanic ecosystem. Pollution problems in such areas can increase heavy metal concentrations (e.g., Zn, Pb, Cd and Cu) to

five or 10 times higher than 50 or 100 years ago (Cardoso et al., 2001). According to Huai-yang et al. (2004) trace elements such as Zn, Ni and Cu have a wider area of contamination than TiO_2 , V and Cr in the Pearl River Estuary, China due to their chemical characteristics.

A significant quantity and variety of trace elements, some of them potentially toxic, resulting from the combustion of coal in thermal power plants, are transferred to the surrounding environment through different pathways (Chow et al., 1994). The importance of this transfer can be inferred from the fact that a conventional power plant of 1000 MW consumes 12,000 tonnes (t) of coal per day and produces about 1,000,000 t of wastes per year. The trace elements are released to the environment through two main pathways as atmospheric emissions and leaching of combustion byproducts i.e.,

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fly and bottom ashes (Llorens et al., 2001). The objective of this study is to measure the distribution of heavy metals affected by the coal-fired power plant operation using the enrichment factor (EF) values.

Site Description

Kapar coastal is located approximately 56 km from Kuala Lumpur and only a few kilometres from Klang Port (Figure 1). It is a semidiurnal tidal coastal area, humid with tropical weathering and fishery activity is done in a small scale. This study area was chosen in order to observe the effect from the coal-fired power plant operation to the heavy metals concentration and their enrichment in the marine environment. Sultan Salahuddin Abdul Aziz Power Plant (SSAAPS) nearby the Kapar coastal has been operating since 1985. Currently, its capacity extends to 2420 MW with coal oriented consuming 2.5 mtpa (million tonne per year) of raw charcoal, as main fuel and is the biggest power plant in Malaysia that contributes 23% of the electricity demand to the country. Raw charcoals are imported from Australia, Indonesia, South Africa, China and also from Sarawak, Malaysia. The power plant is occupied with ESP (Electrostatic Precipitators) and its efficiency is up to 99.2% (TNB Generation, 2003). Station 2 (St. 2) is located at the point of hot water discharge from the power plant cooling system. Station 3 (St. 3) is 2.5 km away from Station 2 and Station 7 (St. 7) is an estuary area

with salinity of 21.05 psu. The depth of water column at St. 2, St. 3 and St. 7 are 0.3 m, 1 m and 1.5 m, respectively.

Methods

Sampling

Three sediment cores were collected at the coast of Kapar coal power station on the 25th October 2003. The cores were sliced into 3 cm interval during sampling and stored frozen until further laboratory analyses. Sub-samples were dried at 60°C after the large shell fragments removed to a constant weight. Sediment porosity was calculated from the water content. Dried samples were lightly pestle with mortar and passed through 2 mm, 1 mm, 250 µm, 125 µm and 63 µm mesh mechanical sieves to get the grain size percentage for each sub-sample.

²²⁸Th Analysis

The activity of ²²⁸Th was determined in order to estimate the sedimentation rate of this area. About 0.5-1.0 g sample was taken from the above preparation and treated with 15 ml of 8 M HCl for partial (leaching) digestion and ²²⁹Th was spiked with known activity (0.258 Bq mL⁻¹) as chemical yield tracer. Thorium isotope extracted from the partial digestion procedure shows that it was from the organic matter (Krishnaswami and Sarin, 1976). Samples were heated for 2-3 hours at 100°C, cooled down and filtered through the 0.45 µm filter paper. The supernatant was then dried. Nitric acid was added and slightly heated if any black layer did exist with a few drops of H₂O₂, as an oxidized agent (Schwarcz, 1982). The separation of 30 ml sample solutions was carried out using an anion resin (Bio-Rad; 1 × 8; 100-200 mesh) procedures where the thorium isotope was eluted with 8 M HCl (Adam, 1998). Finally, the thorium isotope was electrodeposited onto the stainless steel disc (Buesseler et al., 1992) and counted for three days using the Alpha Spectrometry (Ortec EG & G, Model 676 A ALPHA KINGTM). The accuracy of analytical procedure was established using four replicates of standard reference materials (SRM IAEA-300 Baltic Sea Sediment) and the obtained results were in the range of standard reference materials.

Heavy Metals Analysis

Two replicates were used for each sample and eight replicates of analytical blanks were done for quality control in order to determine the uncertainty of determination. Eight analytical blanks were prepared to estimate the contribution of an element added to the sample as a contaminant (Hamilton, 1980). About 0.5 g

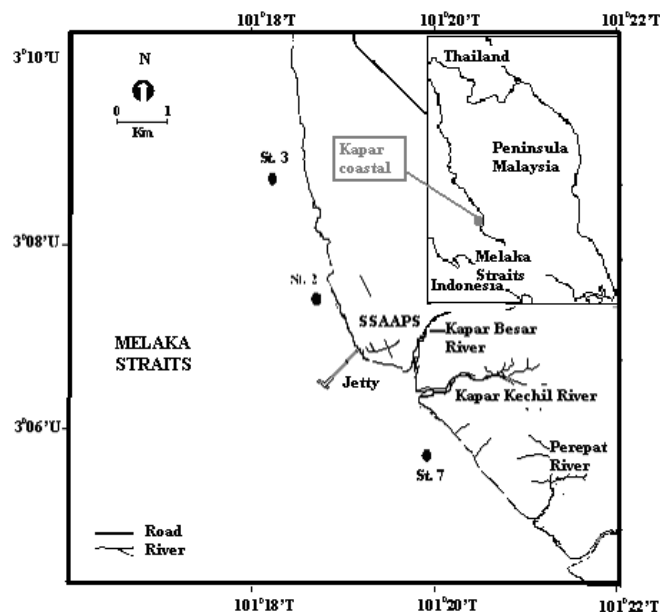


Figure 1: Location of three sediment cores at Kapar, Selangor, Malaysia.

of homogeny dried sediments were extracted with 20 ml of 8 M HCl at 100°C for 2–3 hours. Samples were filtered through the 0.45 µm filter paper and separate the supernatant. Samples were re-dissolved in 25 ml of 0.5 M HCl and analysed by Atomic Absorption Spectrometry (AAS) for heavy metals determination. Four replicates each of OR1 and OR2 were prepared in the Marine Chemical Oceanography Laboratory, Universiti Kebangsaan Malaysia and were used as a standard to calculate the coefficients of variation within the replicates with obtained uncertainties less than 10%.

Results and Discussion

Sedimentation Rate

Many aspects of human impact on the environment can be reconstructed by sediments in coastal areas, which can be regarded as good archives of environmental processes and their effects. Therefore, the environmental evolution can be recorded well in a relatively stable sedimentary environment. The estimation of sedimentation rate is of central importance to develop a continuum of insight into environmental processes (Xueqiang and Matsumoto, 2005), where the ^{228}Th generally provides a reliable method that the uppermost layers of ^{228}Th ($t_{1/2} = 1.91$ yr) deposit is indicative of material accumulation over the last ten years (Koide et al., 1973). The activities of ^{228}Th have been measured and estimation of sedimentation rate was calculated based on the published model (Ruiz-Fernández et al., 2003; Tee et al., 2003).

$$A_z = A_0 e^{-\lambda(Z/S)} \quad (1)$$

where the A_z is the activities of ^{228}Th at the depth Z (dpm g⁻¹), A_0 is the activities of ^{228}Th at the surface layer (dpm g⁻¹), λ is the decay constant of ^{228}Th (0.363 yr⁻¹), Z is the depth (cm) and S is the sedimentation rate (cm yr⁻¹).

The $^{228}\text{Th}_{\text{xs}}$ value was directly taken for calculation into the formula without deduction from the ^{232}Th value and the partial procedure was followed during sample analyses (Thomson, 1982). The sedimentation rate obtained at study site was to be 15.38 cm yr⁻¹, 5.69 cm yr⁻¹ and 5.07 cm yr⁻¹ at St 3, St 2 and St 7, respectively. But the year scale calculated was based on the average value of 5.6 for St 2 and St 7, except for St 3 (15.38 cm yr⁻¹).

Trace Element Concentrations

Trace element concentrations in sediments cores at the study site were in the range of 14.0±1.37 - 58.1±4.94

µgg⁻¹ (Zn), 192±13 - 350±23 µgg⁻¹ (Mn), 4.5±0.53 - 12.4±0.79 µgg⁻¹ (Cu), 12.7±0.35 - 40.4±1.08 µgg⁻¹ (Co), 14.5±0.22 - 59.1±0.59 µgg⁻¹ (Pb), 3.5±0.11 - 15.6±0.52 µgg⁻¹ (Cr), 0.84±0.03 - 1.91±0.06% (Fe) and 1.2±0.00 - 5.2±0.01% (Al). All values are reported in the weight unit.

All samples are considered as sand-rich (> 80% of sand materials) with an average of 41% and 42% for grain size of 0.250-1.0 mm and 0.125-0.25 mm, respectively (Figure 2). The studied samples are classified from fine sand to coarse sand as referred in the Wentworth description (Silvester and Hsu, 1993) and similarly with sediment samples obtained from Bay of Bengal, India (Selvaraj et al., 2004).

The vertical profiles of porosity values (Ooi, 2004) and trace elements were fluctuated at all stations especially at St 2 (Figure 3). These may be as a result of the disturbing and alteration of sediment from the power plant operation because St 2 is situated near hot water discharges. This phenomenon was confirmed by the turbidity measurement showing the extraordinary high value (391.1 NTU) at surface layer compared to St 3 (129.2 NTU) and St 7 (80.1 NTU). The concentration of Zn, Fe, Pb and Cr are enriched at the surface layer and decreasing until the depth of 15-18 cm especially at St 2. Surface enrichment is partly due to the scavenging effect of metals onto Fe hydroxides (Sirinawin and Sompochaiyakul, 2005). However, concentrations of metals at Kapar coast are not reaching maximum concentrations at zone with maximum water turbidity as obtained in previous study (Huai-yang et al., 2004; Windom et al., 1991). Even though the turbidity value is maxima at St 2, it does not show any maximum metals concentration at this station, it may be due to the disturbed sediment caused by the hot water discharges.

Meanwhile, St 3 shows a little enrichment at the 18-21 cm depth upward and is constantly distributed downward. It has a reverse pattern at St 3 (Figure 3b) compared with St 2 showing a small scale decreasing trend of trace elements with depth (except Mn), generally starting from 9-12 cm depth. Overall, the metal profiles at St 3 are quite similar to St 7 and the concentrations of metals are higher at most layers at St 3 and St 7 than St 2. New sediment at St 3 is expected to derive from the point of hot water discharge (St 2) that bring along the metals and resulting accumulation of metal concentrations. This is confirmed by the obviously higher sedimentation rates at this station (15.38 cm yr⁻¹) compared to other stations (Figure 4), reflecting the transport pathway of sediment from St 2.

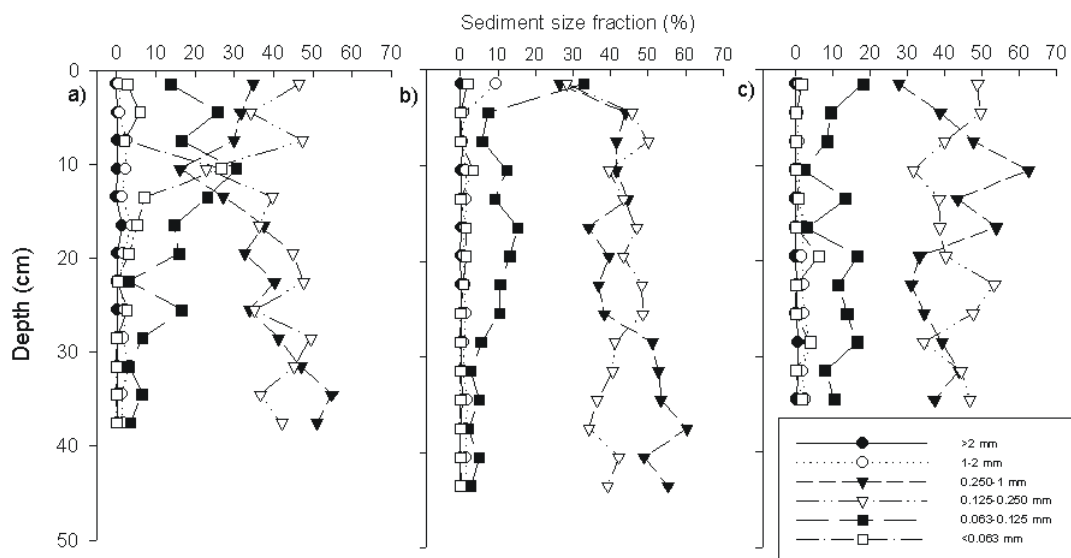


Figure 2: Percentage of sediment grain size at (a) St. 2, (b) St. 3 and (c) St. 7.

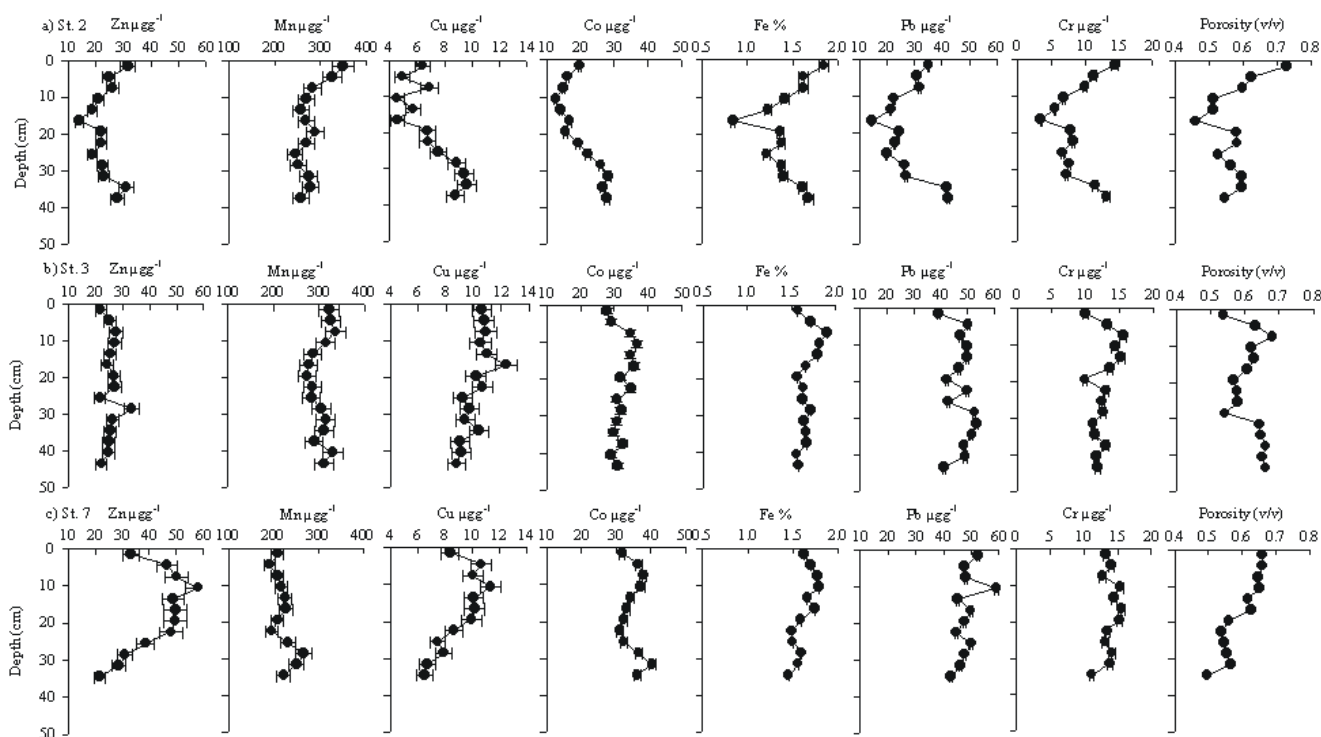


Figure 3: Vertical distribution of metal concentrations and porosity in sediment cores of Kapar coastal area.

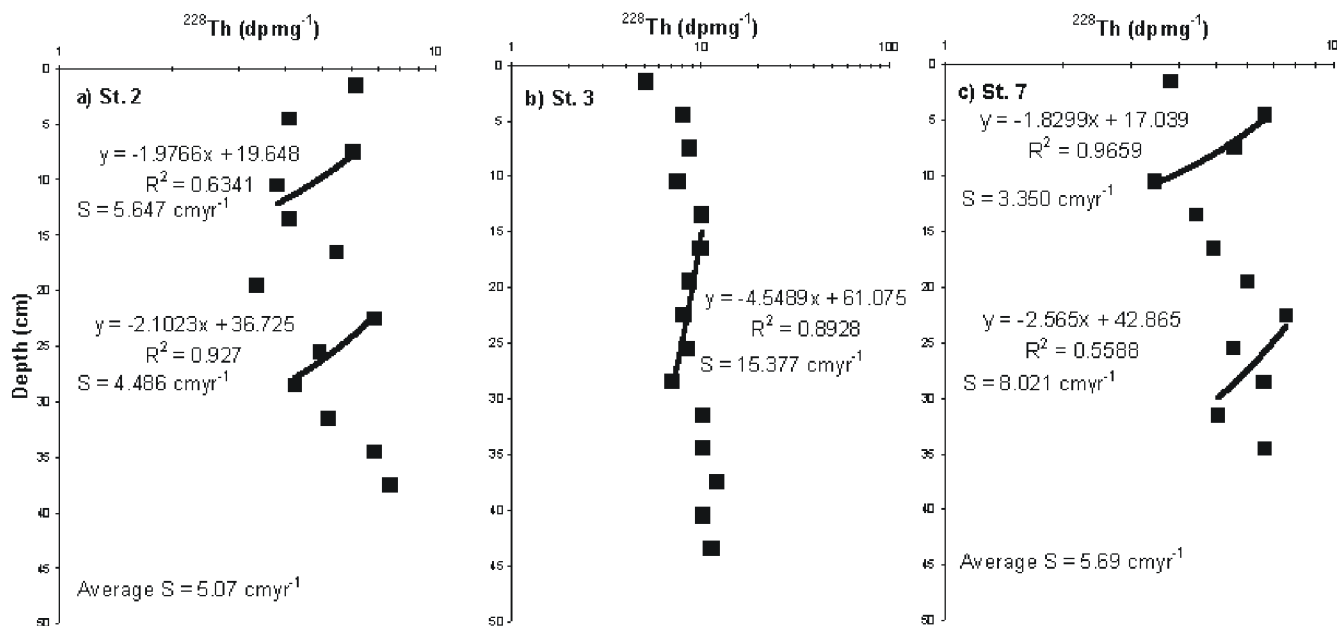


Figure 4: Sedimentation rates ($S = \text{cm yr}^{-1}$) calculated with partial ^{228}Th .

Trace elements at St 7 (Figure 3c) are higher than St 2 because the aggregation of metals onto particles occurs at the surface sediment at fresh-salt water mixing estuary condition and finally settle down (Bilinski et al., 1991). This fact is matched with the estuary salinity (21.05 psu) that increased the metals adsorption onto the particles. Station 7 is located near the river mouth of Kapar Besar River and Kapar Kechil River. During the ebb tide, some of the surface sediments are exposed to atmosphere and a small tidal flat exists at the north-west of St 7. Therefore, the entrance of river water at St 7 is more efficient and according to Zhang et al. (1992), river water usually contains large amount of trace elements. Minimum trace elements concentration level (except Mn and Co) at the deepest layer of the core is showing that the source of trace element is from natural crust.

Trace elements concentration at the Kapar sediments and some other previous studies are listed in Table 1. It shows that Zn, Mn, Cu and Fe concentrations in the Kapar sediments are quite similar with Songkhla Lagoon, Thailand (Maneepong, 1996). This is mainly due to the same geochemistry and chemical weathering of Thailand and Malaysia waters. However, in comparison with Tanjung Karang estuary, Juru and Straits of Johor in Malaysia, concentration of metals at Kapar are within the range or lower from the minimum value at these areas except for Co.

Low concentrations result from different digestion methods and detection levels. The metals concentration

in this paper are presented in partial fraction and not in total concentration. The partial procedure will remove metals held in ion exchange positions, easily soluble amorphous compounds of Fe and Mn, carbonates, and weakly held metals in organic matter (OM). It leaves the silicate lattices intact and does not attack the resistant Fe and Mn minerals or organic compounds. The Co and Pb concentrations are quite high in this study area compared to Tanjung Karang estuary, Juru and Straits of Johor. According to Huai-yang et al. (2004), both metals are representative of anthropogenic sources. Most of Co in estuarine sediments originates from the industrial drainage. The distribution of Co in the estuarine environment always reflects the characteristics of the source input. Previous studies showed a large amount of Pb supplied by the precipitation of aerosols in estuary. Cobalt and lead are strongly correlated with r value of 0.827 at $p < 0.01$ (Table 2) indicating that both metals are probably originated from the same sources (Huai-yang et al., 2004). Zinc, copper, cobalt, lead and chromium are positively correlated among each other. According to Valdés et al. (2005), these metals input are from anthropogenic activities and pollution sources. However, Zn, Cu, Co, Pb and Cr have also revealed a significant correlation with Al and Fe. Aluminium together with iron are major components of silica minerals that are produced from the weathering processes of rock and soil (Huai-yang et al., 2004). These indicate that the metals are also terrestrial and land derived.

Freshly precipitated solid Al hydroxide species have a potential for anion adsorption (Kabata-Pendias & Pendias, 1984) and these metals might be transferred to estuary and coastal system by colloid and mineral particulates (Peng et al., 2003).

Chromium is strongly correlated with Fe and Pb with r values of 0.862 indicating that the source of iron and lead are from the same ingredient that contains chromium (Table 2). These three metals are usually found to be enriched in soils close to the coal power station (Davies, 1980) and it is well known that many heavy metals tend to enrich in coal, fly and bottom ashes (Llorens et al., 2001; Waheed et al., 2001). Meanwhile, Zn is not correlated strongly ($r \leq 0.673$) with other metals as zinc usually exists in the dissolved form and enhanced its

mobility (Huai-yang et al., 2004). Manganese shows a weak correlation with all metals and an inverse correlation with zinc. This suggests rare presence of Mn-oxides at the study stations, which indicates that Mn-oxides in Kapar coast are not metal associate phases as reported by Selvaraj et al. (2004).

Assessment of the Pollution Status

The correlation between metal concentrations with the partial ^{228}Th will be useful to evaluate and elucidate an interpretation of the patterns of Al, Zn, Mn, Cu, Co, Fe, Pb and Cr contamination with time factor. Due to the sedimentation process, the recent settlement sediment should be the high activity of ^{228}Th compared to those buried some time ago. These analyses indicate that the

Table 1: Heavy metal concentrations determined in this study and some other areas

Area	Zn	Mn	Cu	Co	Fe	Pb	Cr	Al	Reference
Kapar	14.0-58.1	192-350	4.5-12.4	12.7-40.4	0.84-1.91	14.5-59.1	3.5-15.6	1.2-5.2	This study
Tanjung Karang estuary, Malaysia*	26.3-85.7	446-698	2.63-18.1		2.04-4.50	10.6-28.0			Mohamed et al (2002)
Juru, Penang & Straits of Johor, Malaysia*	36.7-83.7	118-442	9.3-43	3.0-6.5	0.92-2.90	17.3-35.5	11.5-59.6	2.6-8.1	Khalik et al. (1997)
Songkhla Lagoon (Thailand)	68.5-230.7	113-861	10.8-92.9	1.8-8.1	1.53-4.13	26.4-69.9	21.9-62.8	3.0-12.2	
Mai Po, Hong Kong [#]	22-136	90-520	4-15		0.83-2.80				Maneepong (1996)
Pearl River estuary*	130-308		51-87		0.04-0.33	69-220			Ong (1999)
Average shale*	28.4-237.16		11.2-75.7	16.2-99.9		49.3-78.9	58.1-117.8		Huai-yang et al. (2004)
	95	720	45	19		20	90	6.93	Turedian & Wedepohl (1961), Valdés et al. (2005)

Values in μgg^{-1} , except Fe and Al in %

*Total digestion method (HF) or INAA

[#] Digestion with HNO_3 and H_2SO_4

Table 2: Pearson correlations coefficient (r) between heavy metals, partial ^{228}Th and porosity in Kapar coastal cores

	Al	Zn	Mn	Cu	Co	Fe	Pb	Cr	^{228}Th	Porosity
Al	1									
Zn	0.364*	1								
Mn	0.141	-0.572**	1							
Cu	0.583**	0.429**	-0.002	1						
Co	0.735**	0.501**	-0.260	0.715**	1					
Fe	0.814**	0.512**	0.222	0.635**	0.559**	1				
Pb	0.854**	0.586**	-0.058	0.706**	0.827**	0.778**	1			
Cr	0.854**	0.673**	-0.74	0.599**	0.736**	0.862**	0.862**	1		
^{228}Th	0.482**	-0.223	0.434**	0.436**	0.359*	0.351*	0.430**	0.295	1	
Porosity	0.450**	0.342*	0.297	0.441**	0.293	0.736**	0.495**	0.577**	0.348*	1

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

concentrations of Al, Mn, Cu, Co, Fe and Pb have a good positive correlation at $p < 0.01$ and $p < 0.05$. Metal concentrations are increasing with the increased activity of partial ^{228}Th . This shows that these metals have been deposited with the new sediments or particles at this area. Overall, even though the input of metals studied are from the various sources, the concentration of metals at Kapar coast are still within the normal range and are much lower compared to the polluted area such as Mai Po, Hong Kong.

The enrichment factor (EF) can be used as an index to evaluate the anthropogenic influences of heavy metals in sediments and as a useful indicator reflecting the status of environmental contamination (Huan et al., 2004). Partial aluminium measured in this study is a conservative proxy for the variations of the loosely bound aluminosilicate fraction and its associate metals. According to Sirinawin & Sompongchaiyakul (2005), the proportion associated with aluminosilicate fraction will be estimated by the metal/Al ratios, where the constant metal/Al ratios would imply that the metals are associated with the aluminosilicate fraction. Although the extent of metal enrichment relative to Al is not directly known, the enrichment factors (EF) may be estimated indirectly by a formula below:

$$EF = \frac{\text{metal}/\text{Al}_{\text{enriched}}}{\text{metal}/\text{Al}_{\text{background}}} \quad (2)$$

where the $\text{metal}/\text{Al}_{\text{enriched}}$ is the metal/Al ratio in each interested sample and $\text{metal}/\text{Al}_{\text{background}}$ is the metal/Al ratio at the lowest Al concentration in each core. The enrichment factors then can be calculated to quantify significant heavy metal inputs above natural levels (Birch et al., 2001; Datta & Subramaniam, 1998; Singh et al., 1997).

However, any assessment of the pollution level at one area must take into account the geochemistry and geomorphological changes. Therefore, simple comparison with established background concentrations or quality objectives might not be sufficient (Woitke et al., 2003). To overcome the spatial variations in sediment composition, the $\text{metal}/\text{Al}_{\text{background}}$ in this study was derived from the level in these cores at which the Al concentration is the lowest (Table 3). Metals in this study are treated with the partial method, demonstrating that Al determined by partial digestion may be a better choice for normalizing heavy metal concentrations (Kersten & Smedes, 2002).

The results from this study show that enrichment factors of Zn, Mn, Cu, Co, Fe, Pb and Cr generally are less or unity (Table 3) with the EF values ranged from

0.38-1.08, 0.37-1.08, 0.26-1.09, 0.27-1.07, 0.49-1.04, 0.61-1.23 and 0.46-1.06, respectively. It seems that the depositional rate of these metals in the sediments core

Table 3: Heavy metals enrichment factors with depth at Kapar coastal area

Station	Depth (cm)	Enrichment Factor (EF)						
		Zn	Mn	Cu	Co	Fe	Pb	Cr
2	0-3	0.62	0.54	0.32	0.34	0.57	0.66	0.83
	3-6	0.51	0.52	0.26	0.29	0.53	0.61	0.67
	6-9	0.55	0.47	0.37	0.27	0.54	0.65	0.61
	9-12	0.66	0.66	0.36	0.34	0.69	0.67	0.61
	12-15	0.63	0.66	0.48	0.40	0.63	0.67	0.53
	15-18	0.66	0.95	0.53	0.66	0.60	0.63	0.46
	18-21	0.94	0.95	0.72	0.57	0.91	0.99	0.97
	21-24	0.95	0.89	0.73	0.70	0.92	0.93	1.01
	24-27	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	27-30	0.95	0.82	0.94	0.94	0.91	1.06	0.93
	30-33	0.88	0.82	0.91	0.93	0.84	0.99	0.80
	33-36	0.73	0.51	0.57	0.54	0.60	0.95	0.79
	36-39	0.52	0.37	0.41	0.44	0.49	0.75	0.71
3	0-3	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	3-6	0.89	0.79	0.79	0.81	0.85	0.99	1.03
	6-9	0.75	0.63	0.62	0.75	0.73	0.72	0.93
	9-12	0.71	0.56	0.57	0.76	0.67	0.73	0.83
	12-15	0.81	0.62	0.72	0.87	0.80	0.89	1.06
	15-18	0.79	0.61	0.83	0.91	0.75	0.85	0.97
	18-21	1.06	0.74	0.84	1.00	0.87	0.94	0.86
	21-24	0.84	0.61	0.69	0.86	0.71	0.87	0.89
	24-27	0.70	0.62	0.61	0.77	0.73	0.76	0.86
	27-30	1.03	0.65	0.63	0.79	0.75	0.91	0.86
	30-33	1.08	0.88	0.80	1.00	0.95	1.23	1.00
	33-36	0.98	0.91	0.83	0.87	0.89	1.11	0.96
	36-39	0.84	0.67	0.63	0.86	0.79	0.91	0.96
	39-42	0.97	0.88	0.74	0.89	0.85	1.07	1.00
7	42-45	0.89	0.84	0.72	0.97	0.88	0.91	1.03
	0-3	0.60	0.91	0.83	0.87	0.93	1.01	0.84
	3-6	0.77	0.78	0.98	0.93	0.90	0.85	0.82
	6-9	0.92	0.93	1.02	1.07	1.04	0.95	0.83
	9-12	1.00	0.92	1.09	0.99	1.00	1.10	0.94
	12-15	0.86	0.98	0.99	0.93	0.95	0.86	0.91
	15-18	0.86	0.96	0.97	0.88	0.97	0.93	0.95
	18-21	0.93	0.96	1.03	0.93	0.96	0.96	1.02
	21-24	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	24-27	0.72	1.05	0.77	0.92	0.89	1.00	0.87
	27-30	0.52	1.08	0.72	0.93	0.84	0.84	0.83
	30-33	0.49	1.04	0.63	1.06	0.85	0.84	0.83
	33-36	0.38	0.94	0.62	0.96	0.81	0.79	0.68

*Figures in bold represent sediment layer selected for metals/Al ratio as background for each station

from the water column occurred at a very high rate (Figure 5) and these metals could penetrate to the deeper layer. Sediment samples that were dominated by sandstone structures were characterized by the porosity values that are proportional to its permeability. Positive significance of the Pearson correlation coefficients r values obtained between Al, Zn, Cu, Fe, Pb and Cr versus porosity (Table 2), indicate that metal concentrations are increased with increasing the ability of fluid flow through the porous solid. These show that the metals in the sediments at Kapar are derived from the pore water. The equilibrium in permeable sediment solids in the tidal environments are repeatedly altered by the tidal flushing, which causes a partial renewal of pore waters and export the solution to the water column twice a day and could be a reverse process that pore waters derived chemical composition from the water column (Caetano et al., 2002).

The EF values of Cu and Co at St 2 from 15 cm depth upward and all metals (excluding Pb and Cr) at the deepest layers are less than 0.5 (Figure 5a). According to Huan et al. (2004), the EF values less than 0.5 indicate that the origin of metals is not from the crust materials or natural processes. These low EF values are strongly due to the actively resuspension and disturbed sediments by the power plant discharges. This disturbance only occurs in a short-time scale because the chemical compositions in sediments are frequently modified. Therefore, this will affect the natural EF metal. The EF values decreased from

the surface to 10 cm depth core and started to increase until 30 cm depth.

The erratic and not constant EF values were shown at St 3 with a 'zig-zag' profile and clearer pattern from the depth of 20 cm onwards. This profile matches with the highest sedimentation rates at this station compared to other stations. Years calculated show the historical EF values of metals from early 2000 (45 cm) until middle of 2003 (3-6 cm). The whole core length is true for three years record that is equal to the records of St 2 and St. 7 from 0 to 20 cm depth. If St 3 core is much longer, maybe a similar decreasing profile could be obtained as St 2 and St 7 show the decreasing EF before the year 2000 (20 cm downward).

Station 7 shows two small peaks which represent the year 2002 (10 cm depth) and 2000 (20 cm depth), which is similar with St 3 at 20 cm depth (2002). Figure 5c also shows the same pattern at the bottom layer like St 2, starting from 25 cm depth and downwards. The EF values show that heavy metals enrichment was quite constant at St 7 from 20 cm depth to the surface. It shows that settling contaminated flocs and aggregates formed due to the coagulation and metal scavenging that takes place at the freshwater-saltwater interface (Palanques et al., 1998).

The EF values for Zn, Mn, Cu, Fe and Pb at station located near the mouth of U-Tapao Canal (Sirinawin & Sompongchaiyakul, 2005) were higher than values obtained at Kapar especially for Pb. It was due to the

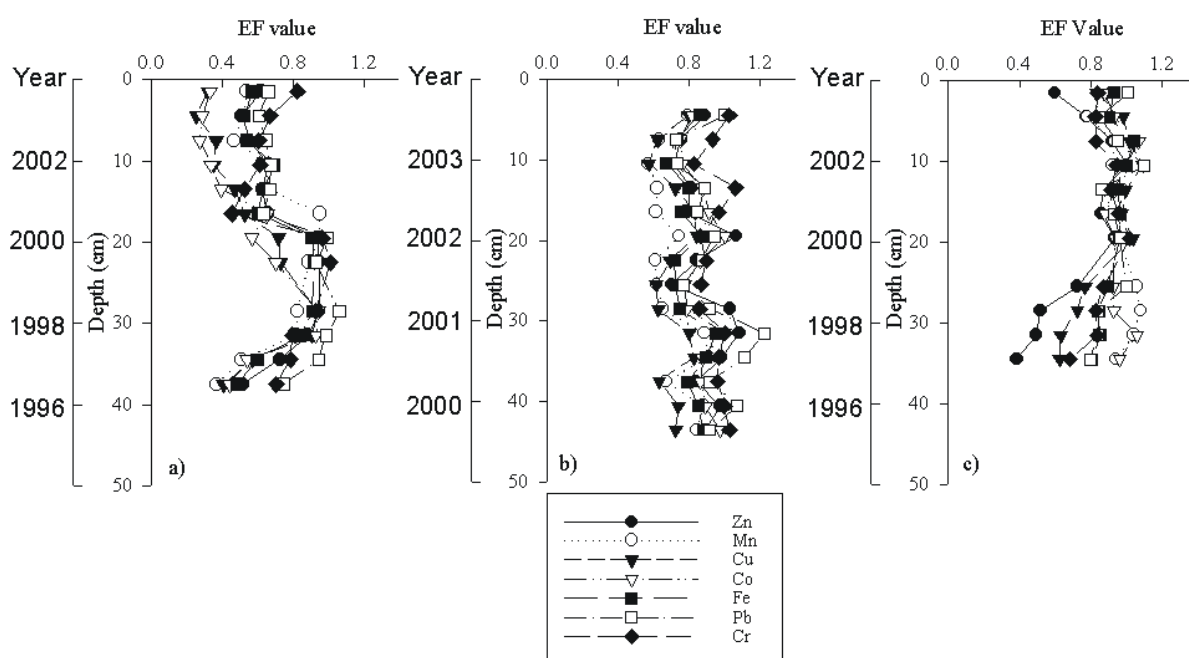


Figure 5: Enrichment factor (EF) profiles of heavy metals normalized with Al at (a) St. 2, (b) St. 3 and (c) St. 7.

effect of the scavenging of metals onto Fe and Mn hydroxides. However, the values and profiles of EF in their study are quite similar to this study and U-Tapao Canal was found having no anthropogenic contamination. These prove that metals at each station have the same sources. The EF values for all heavy metals at Kapar coast are close to one, indicating a crust origin of metals and the enrichment is only highlighted when the corresponding EF is higher than 1.3 (Valdés et al., 2005; Capilla et al., 2005). None of the EF value in this study reached or exceeded 1.3 ratio. These values become an evidence to show that Kapar coast is not polluted by the coal-fired power plant operation or other human activities nearby in recent years. Moreover, this power plant operation managed by Tenaga Nasional Berhad (TNB) meets strict regulations and is monitored by Malaysia's government environmental division (TNB Generation, 2003).

Conclusion

Distribution of Zn, Mn, Cu, Co, Fe, Pb and Cr show an erratic and not constant profile with the core depth and have fast metals deposition. The resuspension and transportation of particles play an important role in the redistribution and profile of heavy metals in Kapar coastal area due to the significant suspended solid volume and shallow water depth. Based on the EF values, Kapar coast was not affected by the contamination of heavy metals neither from SSAAPS operations nor the river discharges. The EF values of all the metals generally are less or reach 1.00 ratio, indicating an equilibrium condition due to the origin crust or natural processes.

Acknowledgements

Thanks to Universiti Kebangsaan Malaysia for their financial support for this work under the IRPA Grant No. 09-02-02-0045-EA141. The authors would like to thank all the laboratory staff of Marine Science Programme, Universiti Kebangsaan Malaysia and Malaysian Institute for Nuclear Technology Research for their assistance during sampling and sample analyses.

References

- Adam Khatir Sam, Mustafa, Ahamed, M.O., El Khangi, F.A., El Nigumi, Y.O. and E. Holm (1998). Radioactivity levels in the Red Sea coastal environment of Sudan. *Mar. Poll. Bull.*, **36**: 19-26.
- Bilinski, H., Kozar, S., Plavšić, M., Kwokal, Ž and M. Branica (1991). Trace metal adsorption on inorganic solid phases under estuarine conditions. *Mar. Chem.*, **32**: 225-233.
- Birch, G., Siaka, M. and C. Owens, (2001). The source of anthropogenic heavy metals in fluvial sediments of a rural catchment: Coss River, Australia. *Water, Air and Soil Poll.* **126**: 13-35.
- Buesseler, K.O., Cochran, J.K., Bacon, M.P., Livingston, H.D., Casso, S.A., Hirschberg, D., Hartman, M.C. and A.P. Fleer (1992). Determination of thorium isotopes in seawater by non-destructive and radiochemical procedures. *Deep-sea Research*, **39**: 1103-1114.
- Caetano, M., Vale, C. and M. Bebianno (2002). Distribution of Fe, Mn, Cu and Cd in upper sediments and sediment-trap material of Ria Formosa (Portugal). *J. Coastal Res.*, **36**: 118-123.
- Capilla, X., Schwartz, C., Bedell, J.P., Sterckeman, T., Perrodin, Y. and J.L. Morel (2005). Physicochemical and biological characterisation of different dredged sediment deposit sites in France. *Env. Poll.*, **xx**: 1-11.
- Cardoso, A., Boaventura, G., Silva, E. and J. Brod (2001). Metal distribution in sediments from the Ribiera bay, Rio de Janeiro, Brazil. *J. Brazilian Chemical Soc.*, **12**: 767-774.
- Chow, W., Miller, M.J. and I.M. Torrens (1994). Pathways of trace elements in power plants: interim research results and implications. *Fuel Process Technol.*, **39**: 5-20.
- Datta, D.K. and V. Subramaniam (1998). Distribution and fractionation of heavy metals in the surface sediments of the Ganges-Brahmaputra-Meghna river system in the Bengal Basin. *Env. Geol.*, **36**: 93-101.
- Davies, B.E. (1980). Trace element pollution. In: Davies, B.E. (ed.). Applied soil trace elements. John Wiley & Sons Ltd., Wales.
- Hamilton, E.I. (1980). Analysis for trace elements. I: Sample treatment and laboratory quality control. In: Davies, B.E. (ed.). Applied soil trace elements. John Wiley & Sons Ltd., Wales.
- Huai-yang Zhou, Xiao-tong Peng and Jian-ming Pan (2004). Distribution, source and enrichment of some chemical elements in sediments of the Pearl River Estuary, China. *Continental Shelf Res.*, **24**: 1857-1875.
- Huan Feng, Xiaofei Han, Weiguo Zhang and Lizhong Yu (2004). A preliminary study of heavy metal contamination in Tangtze River intertidal zone due to urbanization. *Mar. Poll. Bull.*, **49**: 910-915.
- Kabata-Pendias, A. and H. Pendias (1984). Trace elements in soils and plants. United States: CRC Press, Inc.
- Kersten, M. and F. Smedes (2002). Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. *J. Env. Monit.*, **4**: 109-115.
- Khalik Hj, Wood, A., Zaharudin Ahmad, Noor Azhar Md. Shazili, Rosnan Yaakob and R. Carpenter, (1997). Geochemistry of sediments in Johor Straits between Malaysia and Singapore. *Continental Shelf Res.*, **17**: 1207-1228.

- Koide, M., Bruland, K.W. and E.D. Goldberg, (1973). Th-228/Th-232 and Pb-210 geochronologies in marine and lake sediments. *Geochim. et Cosmo. Acta*, **37**: 1171-1187.
- Krishnaswami, S. and M.M. Sarin, (1976). The simultaneous determination of Th, Pu, Ra isotopes, ^{210}Pb , ^{55}Fe , ^{32}Si and ^{14}C in marine suspended phases. *Analy. Chim. Acta* **83**: 143-156.
- Krishnaswamy, D.L., Martin, J.M. and M. Meybeck (1971). Geochronology of lake sediments. *Earth Planet. Sci. Lett.*, **11**: 407-414.
- Llorens, J.F., Fernández-Turiel, J.L. and X. Querol (2001). The fate of trace elements in a large coal-fired power plant. *Environmental Geology*., **40**: 409-416.
- Maneepong, S. (1996). Distribution of heavy metals in sediments from outer part of Songkhla Lagoon, southern Thailand. *Songklanakarin J. Sc. Techno.*, **18**: 87-97.
- Mohamed, C.A.R., Faeiza Buyong, Mohd. Azmi Mohd Lila and Othman Hj. Ross. (2002). Trace element levels in the sediments of Tanjung Karang Estuary, Selangor, Malaysia. *Sains Malaysians*, **31**: 1-9.
- Ong Che, R.G. (1999). Concentration of heavy metals in sediments and mangrove root samples from Mai Po, Hong Kong. *Mar. Poll. Bull.*, **39**: 269-279.
- Ooi Chai Gaik (2004). Distribution of ferum, mangan and organic carbon in sediment cores of Redang Island, Langkawi Island, Selangor Estuary and Kapar. Degree bachelor of Sc. Thesis. Universiti Kebangsaan Malaysia.
- Palanques, A., Sanchez-Cabeza, J.A., Masque, P. and L. Leon, (1998). Historical record of heavy metals in a highly contaminated Mediterranean deposit: The Besòs prodelta. *Mar. Chem.*, **61**: 209-217.
- Peng, X.T., Zhou, H.Y., Weng, H.X., Pan, J.M. and C.Y. Hu (2003). Distribution characteristics, transfer mechanism and pollution assess of heavy metal vanadium, nickel and cobalt in sediment cores of the Pearl River estuary. *J. Zhejiang Uni. (Sc. Ed)*., **30**: 103-108.
- Reddy, M.S., Basha, S., Kumar, V.G.S., Joshi, H.V. and G. Ramachandraiah (2004). Distribution, enrichment and accumulation of heavy metals in coastal sediments of Alang-Sosiya ship scrapping yard, India. *Mar. Poll. Bull.*, **48**: 1055-1059.
- Ruiz-Fernández, A.C., Páez-Osuna, F., Soto-Jiménez, M.F., Hillaire-Marcel, C. and B. Ghaleb (2003). The loading history of trace metals and nutrients in Altata-Ensenada del Pabellón, lagoon complex, northwestern Mexico. *J. Env. Radioact.*, **69**: 129-143.
- Schwarcz, H.P. (1982). Applications of U-series dating to archaeometry. In: Ivanovich and Harmon, R.S. (eds). Uranium Series Disequilibrium: Applications to Environmental Problems. Oxford: Clarendon Press, pp. 302-324.
- Selvaraj, K., Mohan, V.R. and P. Szefer (2004). Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: Geochemical and statistical approaches. *Mar. Poll. Bull.*, **49**: 174-185.
- Silvester, R. and J.R.C. Hsu (1993). Coastal stabilization: Innovative concepts. Prentice Hall, New Jersey.
- Singh, M., Ansari, A.A., Müller, G. and I.B. Singh (1997). Heavy metals in freshly deposited sediments of the Gomati River (a tributary of the Ganga River): Effects of the human activities. *Env. Geol.*, **29**: 246-252.
- Sirinawin, W. and P. Sompongchaiyakul (2005). Nondetrital and total metal distribution in core sediments from the U-Tapao Canal, Songkhla, Thailand. *Mar. Chem.*, **94**: 5-16.
- Tee Lee Theng, Zaharudin Ahmad and Che Abd. Rahim Mohamed (2003). Estimation of sedimentation rates using ^{210}Pb and ^{210}Po at the coastal water Sabah, *Malaysia. J. Radioanal. Nuclear Chem.*, **256**. 115-120.
- Thomson, J. (1982). A total dissolution method for determination of the α -emitting isotopes of uranium and thorium in deep-sea sediments. *Analytica Chimica Acta.*, **142**: 259-268.
- TNB Generation (2003). Sultan Salahuddin Abdul Aziz Power Station, Kapar. Pamphlet. Selangor.
- Turekian, K.K. and K.H. Wedepohl (1961). Distribution of the elements in some major units of the earth's crust. *Bull. Geological Soc. of America*, **72**: 175-192.
- Valdés, J., Vargas, G., Sifeddine, A., Ortieb, L. and M. Guíñez (2005). Distribution and enrichment evaluation of heavy metals in Mejillones Bay (23°S), Northern Chile: Geochemical and statistical approach. *Mar. Poll. Bull.* **50**: 1558-1568.
- Waheed, S., Ahmad, S., Zaidi, J.H., Rahman, A., Qureshi, I.H. and M. Saleem (2001). Utilisation of a low power reactor for instrumental neutron activation analysis of 40 elements in coal. *Radiochim. Acta.*, **89**: 425-431.
- Windom, H., Byrd, J., Smith, R.Jr. and F. Huan (1991). Inadequacy of NASQUAN data for assessing metal trends in the Nation's river. *Env. Sc. Techno.*, **25**: 1137-1142.
- Woitke, P., Wellmitz, J., Helm, D., Kube, P., Lepom, P. and P. Lithraty (2003). Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. *Chemosphere.*, **51**: 633-642.
- Xueqiang Lu and E. Matsumoto (2005). Recent sedimentation rates derived from ^{210}Pb and ^{137}Cs methods in Ise Bay, Japan. *Est., Coastal and Shelf Sc.*, **65**: 83-93.
- Zhang, J., Huang, W.W., Liu, S.M., Liu, M.G., Yu, Q. and J.H. Wang (1992). Transport of particulate heavy metals towards the China Sea: A preliminary study and comparison. *Mar. Chem.* **40**: 161-178.