THE DETERMINATION OF HEAVY METAL CONCENTRATION IN SEDIMENT FROM KERTEH RIVER, TERENGGANU

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Abstract: Concentrations of heavy metals accumulated in sediment from nine stations along the Kerteh River of Kemaman were measured using Inductively Coupled Plasma Optical Emission Plasma (ICP-OES) chemical analyses. The average concentration of heavy metals were; Pb (15.29 ± 4.44 μg g^{-1}), Cd (4.42 ± 0.27 μg g^{-1}), Cu (34.33 ± 14.73 μg g^{-1}), Cr (11.32 ± 3.92 μg g^{-1}), Zn (44.94 ± 13.29 μg g^{-1}), Ni (11.42 ± 5.20 μg g^{-1}). The trend of heavy metal concentration at the study area was Zn>Cr>Pb>Ni>Cu>Cd; indicating possible enrichment from anthropogenic sources such as oil refinery industry, boating, fishing and domestic waste. The concentration of Pb and Zn were most abundant at station A4 (Petronas outlets 2) while station A2 (Petronas outlets 1) was abundant with Cd and Cu. The highest concentration of Cr and Ni was found at station A9 (mangrove plant). The distribution of heavy metals at Kerteh River was much influenced by anthropogenic sources and human activities.

KEYWORDS: Sediments ; Kerteh River; Heavy metals; Physical parameters

Introduction

One of the most dangerous pollutants in sediment is heavy metals. High levels of metals in river and estuarine areas frequently result from anthropogenic activities both along estuarine shorelines and in upland watersheds. When particle-reactive pollutants, such as heavy metals, enter estuarine waters, many are quickly adsorbed on suspended matter and removed to bottom sediments (Valentina *et al.*, 2003).

In this study, the heavy metals content in the Kerteh River were determined using Inductively Coupled Plasma Optical Emission Plasma (ICP-OES). The study area is located near a petroleum refineries plant, an airport and highways. Other than that, many human activities are held here such as industrial, economical, agricultural and fisheries activities. All these activities may contribute to aquatic pollution by heavy metals. For example, the discharge from refineries may contain heavy metals that can affect the aquatic system surroundings. Many people do not realize the risk of contamination in aquatic systems and organisms and how this pollution can effect this organism population (Rozaini and Brimblecome, 2009).

This study was conducted to obtain a database for the Kerteh River's surroundings in order to monitor the impact of human activities around the study area to the aquatic system. Other than that, the level of pollution will be determined in the study area. If the result shows higher concentration of heavy metals, this information will be used to identify the possible sources of contamination in the study area.

Experimental

Sampling Locations

The sampling site is in the Kerteh River which is located in Kemaman, Terengganu. The sediment samples were taken from 9 sampling stations. The latitude and longitude of each sampling station was determined and recorded by using Global Positioning System (GPS) as shown in Table 1.

Table 1. Sampling locations during the present study

Station	*Longitude*	*Latitude*
A1 (upstream)	04° 33. 680′	103° 24. 555′
A2 (Petronas outlet 1)	04° 33. 024′	103° 26. 458′
A3 (waste discharge)	04° 32. 497′	103° 26. 485′
A4 (Petronas outlet 2)	04° 31. 594′	103° 26. 490′
A5 (dumping area)	04° 31. 372′	103° 26. 477′
A6 (aquaculture/highway)	04° 31. 452′	103° 26. 843′
A7 (jetty)	04° 31. 154′	103° 26. 968′
A8 (sandbank)	04° 33. 680′	103° 26. 680′
A9 (mangrove plants)	04° 29. 291′	103° 26. 835′

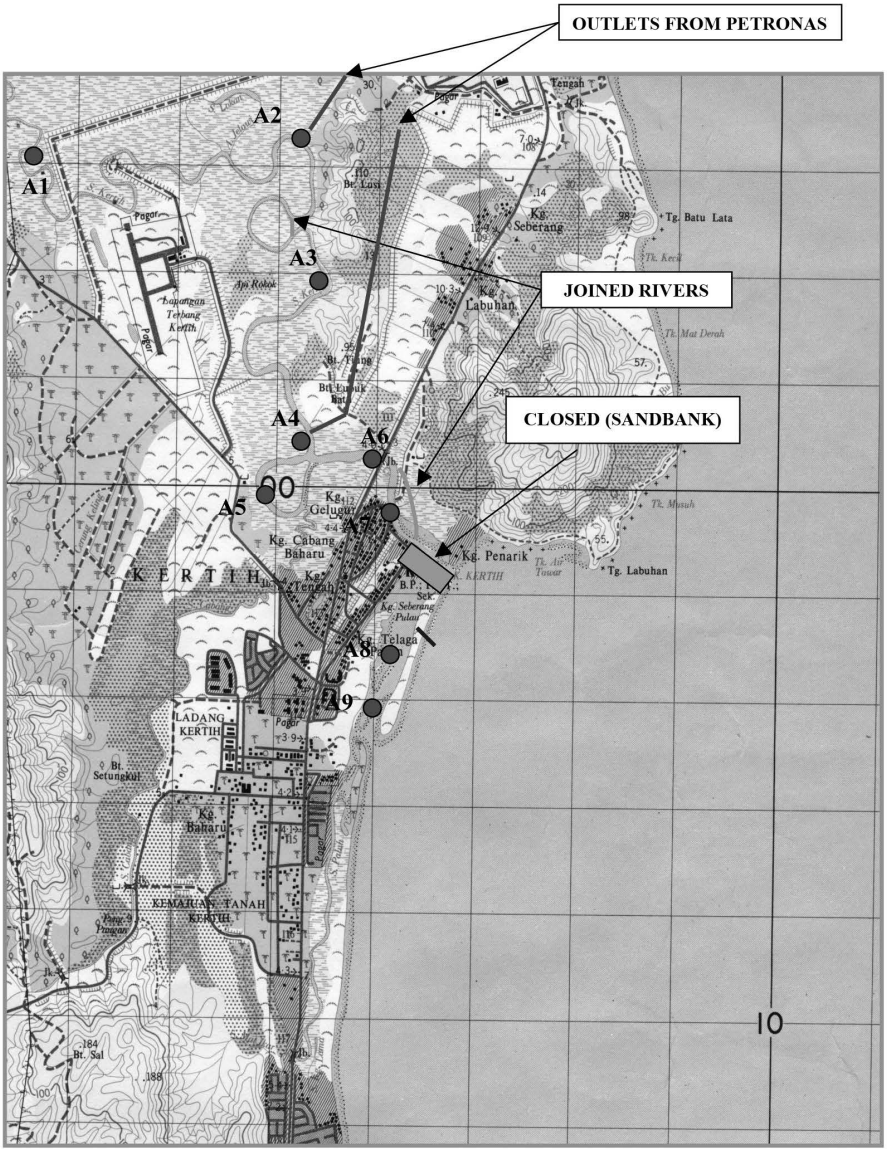

Figure 1. Map of sampling site during the present study

Apparatus and Sampling Equipment Preparation

Before the samples were analyzed, all the apparatus used must go through a pre-treatment stage. In this stage, all were washed in soap and soaked in 10% nitric acid for one week at room temperature to remove all the adhered impurities, and then rinsed with distilled water and deionized water before being dried in an oven at 50-60°C. The purpose of this procedure is to avoid contamination.

Sampling Collections

All surface sediment was sampled at 20 cm-depth using a Van Veen grab sampler. Approximately 2 kg wet weight of sediment from each sample point was collected in acid-washed polyethylene,

vacuum-sealed and labeled bags. Then, all the samples were transported to the laboratory at 4°C for analysis. In any sediment sampling, physical parameters are very important. Thus, physical parameters such as salinity and temperature was taken in-situ.

Sampling Preparations

All the samples were prepared by air-drying at room temperature (25 ± 2°C) for 3-4 days until a constant weight was attained. Then, the samples were crushed with a pestle and mortar. The mortar must be cleaned each time for every sample. After crushing, the samples were sieved using 63 µm siever for digestion purposes (Tam and Wong, 2000).

Heavy Metals Analysis

Sediment samples were weighed up to 0.3 g and the samples were transferred into a Teflon vessel. Then, 8 ml of 20% nitric acid, 5 ml of 2% hydrochloric acid and 2 ml of 5% hydrofluoric acid were added. The sample was put into a microwave for 30 minutes at 210°C. The samples were allowed to cool down to room temperature. Before transferring the sample into 50 ml volumetric flask, 10 ml of 1% boric acid was added to remove any excess flouride. Then, the sample was diluted with deionized water until 50 ml and the samples were ready for analysis using ICP-OES.

Results and Discussion

Concentrations of Heavy Metals in Sediments

The concentrations of 7 types of heavy metals in sediment were measured for each sampling station at the Kerteh River. These heavy metals were Pb, Cd, Cr, Zn, Cu, Ni, with Al as the normalizer. The concentrations of the heavy metals in sediment versus sampling station are depicted in Figures 2 until 7. Summarization results for heavy metal analysis is shown in Table 2 below:

Table 2. Summarization for heavy metal analysis in sediments from sampling stations

	Pb	Cd	Cr	Cu	Zn	Ni
				µg/g		
A1	16.00	4.70	13.00	6.30	16.00	7.00
A2	11.00	5.00	40.00	20.00	60.00	13.00
A3	21.00	4.00	32.00	12.00	40.00	10.00
A4	25.00	4.20	31.00	15.00	62.00	11.00
A5	14.00	4.20	22.00	7.00	41.00	7.00
A6	13.00	4.20	30.00	10.00	45.00	8.00
A7	15.00	4.18	29.00	11.50	44.00	8.00
A8	11.00	4.15	40.00	10.00	47.00	13.00
A9	14.00	4.20	67.00	9.00	48.00	24.00

Lead (Pb)

From Table 3, it shows that Pb ranged from 11.62-24.10 μg/g. Station A7 exhibited the highest level of Pb when compared to other sampling stations (Figure 2). When comparing the average concentration of Pb, 15.29 μg/g with an average shale value 12.5 μg/g from Devesa-Rey *et al.*, (2009) , it shows that Pb is higher than in the crust value which indicating the enrichment from the anthropogenic sources. The waste discharge from petroleum refinery outlet is believed to be the main anthropogenic source that contributes to the increase of Pb concentration at those stations while Kamaruzzaman *et al.* (2006) reported that the major sources of Pb at the Terengganu River were contributed from shipping and fishing activities. However, according to classification of sediment from Hong Kong Environmental Protection Department, cited by Tam and Wong (2000), the sediment at station A4 is considered class A, indicating it is uncontaminated with Pb as the concentration is less than 25 μg/g.

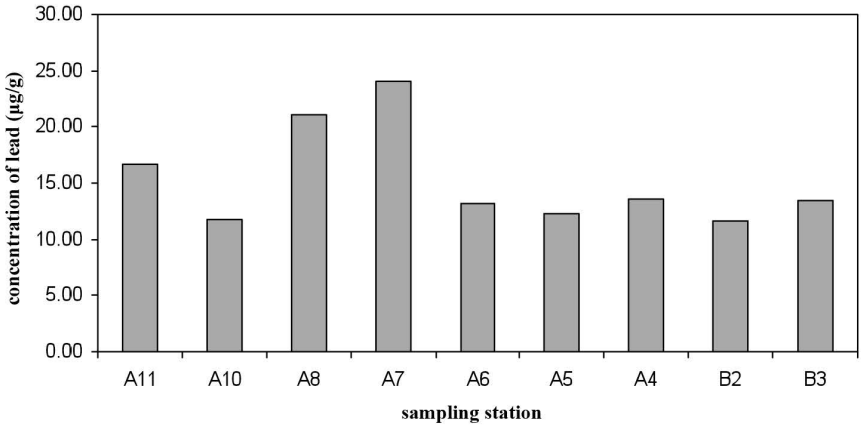

Figure 2. Distribution of Lead (Pb) in sediment

Cadmium (Cd)

Table 2, shows that the concentration of Cd ranges from 4.04-4.95 μg/g. The sampling station A2 presented the highest level of Cd compared to other sampling stations (Figure 3). When comparing the average concentration of Cd, 4.42 μg/g with the average shale value 0.2 μg/g from Devesa-Rey *et al.*, (2009), it shows that Cd is higher than the crust value which indicates enrichment from the anthropogenic sources. This is an expected result, as station A2 receives discharge from Petronas outlets. Subsequently, the concentrations of heavy metals may be dispersed by river water or absorbed by sediments, as the alkaline pH of river water would also facilitate the formation of heavy metal precipitation at the station because under alkaline conditions, Cd becomes less mobile (Redfern, 2006).

The cadmium concentration in sediments from the Kerteh River is considered higher when compared to the study by Kaushik *et al.* (2009) conducted at the Yamuna River, India which varies from 0.82 to 4.6 $mgkg^{-1}$. The comparison between Yamuna River was made because of the geographical similarity and also the antropogenic sources. In addition, the concentration of the Kerteh river also supported by the enrichment factor value of 23.35 which is relatively higher than in the Yamuna river with the EF value is 6.97. According to classification of sediment from Hong Kong Environmental Protection Department, cited by Tam and Wong (2000), the sediment at station A2 is considered class D, indicating serious contamination with Cd, as the concentration is higher than 1.5 μg/g.

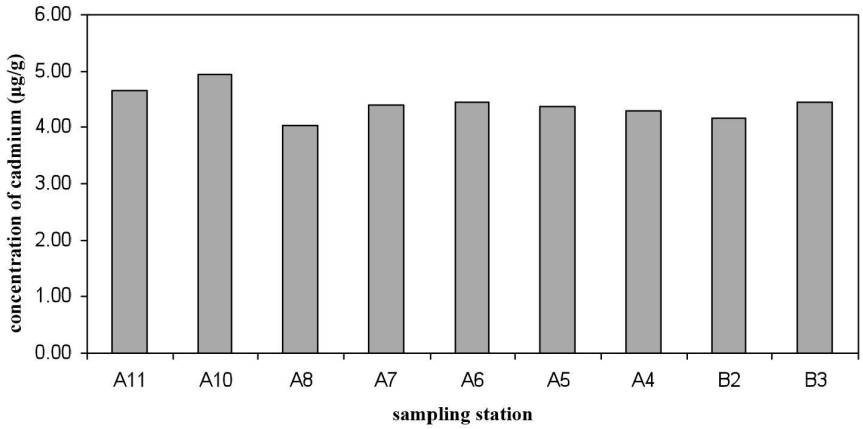

Figure 3. Distribution of cadmium (Cd) in sediment

Chromium (Cr)

The concentration of Cr from the Kerteh River sediment fluctuated very widely between the sampling stations (Figure 4). From Table 2, the Cr levels in the sediment varied from 14.01-66.02 µg/g. Comparing the present Cr concentration with the study reported by Kaushik *et al.* (2009), the concentrations in Kerteh River was higher than that in Yamuna, which ranged from 6.8-35.0 µg/g. From Figure 4, the maximum concentration of Cr is located at station A9. Generally, the source of Cr comes from industry such as electroplating, dyes and metallurgy-ferrochromium alloys (Redfern, 2006). However, the profile of this station shows that no such industry activity occurred. This station is a lagoon surrounded by mangrove plants. The water flow of this lagoon was hindered by a sandbank that is close to the station A8. This may have prevented the unidentified sources of Cr from incoming tides from flowing back out and accumulated instead in this lagoon, contributing to an increased enrichment of Cr concentration to the sediment. However, according to classification of sediment from Hong Kong Environmental Protection Department, by Tam and Wong (2000), the sediment at station A9 is class C, indicating moderate contamination with Cr, as the concentration is between 50 µg/g to 80 µg/g .

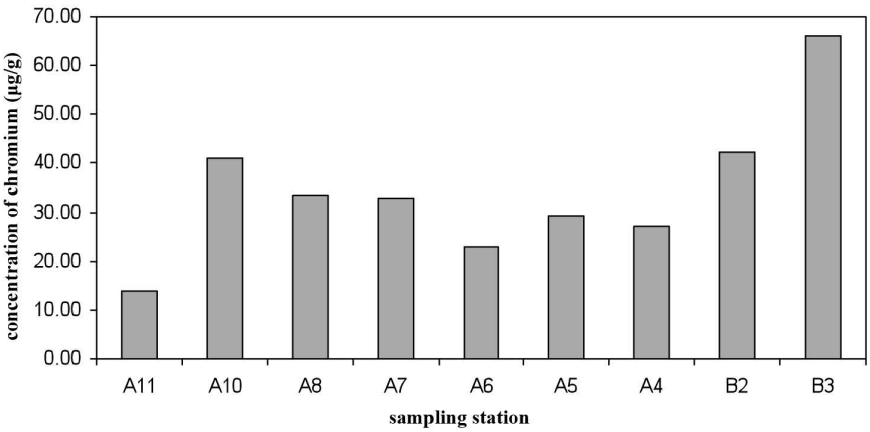

Figure 4. Distribution of chromium (Cr) in sediment

Copper (Cu)

The concentration of Cu at the Kerteh River ranges between 6.70-19.60 µg/g. Similar findings by Tam and Wong (1995) reported that Cu concentrations of surface sediments fluctuated from 1 to 42 mg/kg along transects lying from landwards to seaward regions of the Sai Keng mangrove which is located higher than the Kerteh River. The maximum concentration of Cu at the Kerteh River was located at station A2. Inputs of copper into the natural waters come from various sources including mining, smelting, domestic and industrial wastewaters, steam electrical production, incinerator emissions, and the dumping of sewage sludge (Redfern, 2006). However, the concentration of Cu at Kerteh River generally received input from Petronas outlets and atmospheric sources.

Based on a previous study by Kamaruzzaman *et al.* (2007), increased Cu readings can be caused by anthropogenic activities such as from fishing, and from industrial areas upstream, at Kerteh Mangrove forest. But, compared to the present study, the enrichment factor value of Cu at the Kerteh River is lower (0.22) than at the Kerteh Mangrove Forest (3.83). According to classification of sediment from Hong Kong Environmental Protection Department, editted by Tam and Wong (2000), the sediment at station A2 in Kerteh River is class B in nature, indicating slightly contaminated with Cu, as its concentration is between 10 µg/g to 54 µg/g.

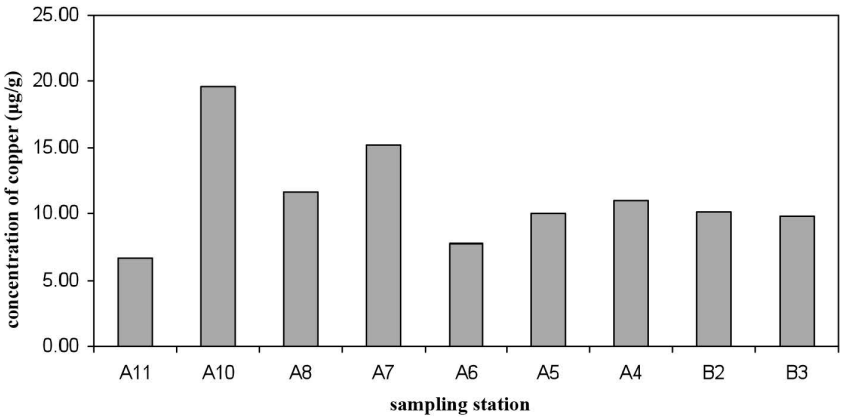

Figure 5. Distribution of copper (Cu) in sediment

Zinc (Zn)

Table 3, shows that the Zn ranged from 16.13-62.25 µg/g. The sampling station A4 recorded the highest level of Zn when compared to other sampling stations. When comparing the average concentration of Zn, 44.94 µg/g with the average shale value 70.0 µg/g from Devesa-Rey *et al.*, (2009) , it can be seen that concentration of Zn is lower than the crust value which indicates enrichment from natural sources. According to classification of sediment from Hong Kong Environmental Protection Department, cited by Tam and Wong (2000), the sediment at station A7 is class A, indicating no contamination as the concentration of Zn is less than 70 µg/g. Although station A4 was the closest to the discharge site, the mobility of zinc was controlled by the alkalinity of river water. Subsequently, the heavy metal was dispersed by river water, as the alkaline pH of river water facilitates the formation of heavy metal precipitation under the pH limits, which will decrease the adsorption ability and bioavailability of the metal, and then increase the mobility of heavy metal. This can be supported by previous study by Jian-feng *et al.* (2009) who reported that the pH limit value for Zn in sediments is 6.0-6.5.

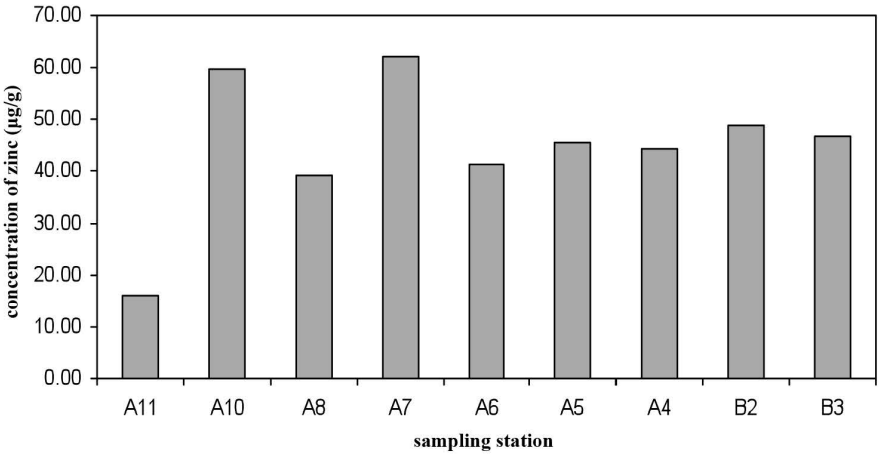

Figure 6.Distribution of zinc (Zn) in sediment

Nickel (Ni)

The concentration of Ni in the Kerteh River sediment was quite uniform and fluctuated very widely (Figure 7). Nickel levels in the sediment varied from 7.27-23.95 µg/g. Comparing the present Ni concentration with the study reported by Kaushik *et al.* (2009), the concentration in the Kerteh River was much lower than in Yamuna, where the concentration of Ni varied from 45.2-49.9 µg/g. Figure 7, shows that the maximum concentration of Ni is located at station A9. According to classification of sediment from Hong Kong Environmental Protection Department, cited by Tam and Wong (2000), the sediment at station A9 is considered class B indicating slight contamination with Ni, as the concentration is between 15 µg/g to 35 µg/g.

Commonly, major uses of Ni include its metallurgical use as an alloy, plating and electroplating, a major component of Ni-Cd batteries and as a catalyst for hydrogenating in petroleum refinery (Redfern, 2006). However, the profile of this station shows no occurrence of such activities. This station is considered a lagoon surrounded by mangrove plants. The water flow of this lagoon was hindered by a sandbank that is close to station A8. This may have prevented anthropogenic sources of Cr such as wastewater from hydrogenating in a petroleum refinery upstream, which flowed in with the incoming tides from flowing out and instead accumulated in this lagoon, contributing to an enrichment of Cr concentration in the sediment.

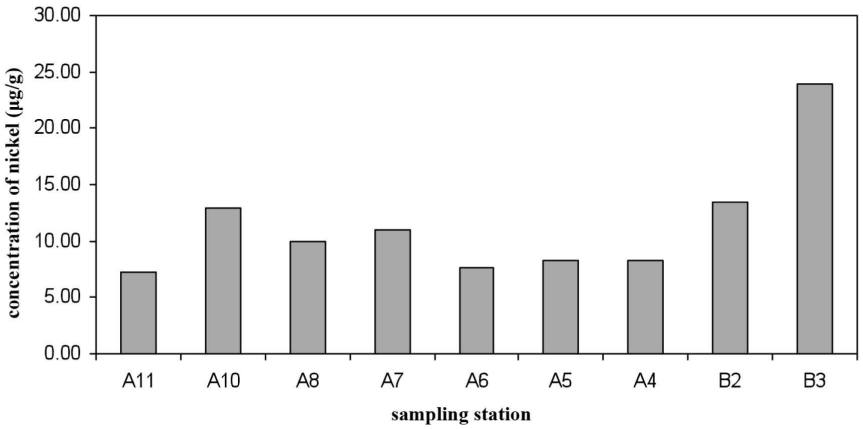

Figure 7. Distribution of nickel (Ni) in sediment

Comparison of Heavy Metal Concentration with previous studies from other sites

Table 3 shows the comparison of the mean concentration of heavy metals from other sites.

Table 3. Comparison of the mean concentration of heavy metals with other areas

	Concentration (µg/g)
Pb	
Gomti River, India (Singh *et. al.* 2005)	40.33
Terengganu River, Malaysia (Kamaruzzaman *et al.*, 2006)	123.63
This study (Kerteh River, Terengganu)	15.29
Cd	
Pahang River, Malaysia (Farah, 2005)	0.09
Gomti River, India (Singh *et. al.* 2005)	2.42
This study (Kerteh River, Terengganu)	4.42
Cr	
Terengganu River, Malaysia (Hazimin, 2002)	18.82
Gomti River, India (Singh *et. al.* 2005)	8.15
This study (Kerteh River, Terengganu)	34.33
Cu	
Terengganu River, Malaysia (Hazimin, 2002)	34.85
Kerteh Estuary, Malaysia (Kamaruzzaman *et al.*, 2007)	43.65
This study (Kerteh River, Terengganu)	11.32
Zn	
Larut Matang, Malaysia (Hasrizal *et al.*, 2006)	51.80
Terengganu River, Malaysia (Kamaruzzaman *et al.*, 2006)	52.80
This study (Kerteh River, Terengganu)	44.94
Ni	
Terengganu River, Malaysia (Hazimin, 2002)	5.10
Gomti River, India (Singh *et al.* 2005)	15.17
This study (Kerteh River, Terengganu)	11.42

Conclusion

In this study, the concentrations of heavy metals in the study area were determined. The trend of heavy metal concentration was Zn>Cr>Pb>Ni>Cu>Cd. It was found that Pb and Zn were most abundant at station A4 (Petronas outlets 2) while station A2 (Petronas outlets 1) was abundant with Cd and Cu. The highest concentration of Cr and Ni was found at station A9 (mangrove plants). The distribution of heavy metals at the Kerteh River was much influenced by anthropogenic sources such as fishing activities, thermal power plants, fertilizers, boating, municipal wastewater, waste discharge from petroleum refinery outlets and industrial areas upstream at Kerteh Mangrove.

References

Devesa-Rey, R., Diaz-Fierros, F . & Barral, M. T. (2009). Normalization strategies for river bed sediments: A graphical approach. *Microchemical Journal* **91**: 253–265.

Farah Akmal, I. (2005). Taburan Beberapa Logam Berat Dalam Sedimen Di Perairan Pahang dan Perkaitannya dengan Ferum dan Aluminium. Laporan Projek Tahun Akhir. Sm. Sn. (Kimia Analisis dan Persekitaran). Fakulti Sains dan Teknologi. Kolej Universiti Sains dan Teknologi Malaysia.

Hasrizal, S., Kamaruzzaman, Y., Jamil, T., Ong Meng Chuan & Willison Kung Yee See. (2006). Taburan elemen Cu, Mn, dan Zn di dalam sedimen dasar sungai hutan paya bakau Larut Matang, Taiping, Perak. *The Malaysian Journal of Analytical Sciences* 10: 211-216.

Hazimin, M. N. (2002). Penentuan Kandungan Beberapa Logam Berat dalam Sedimen di Sungai Terengganu. Laporan Projek Tahun Akhir. Sm. Sn. (Sains Samudera). Fakulti Sains dan Teknologi. Kolej Universiti Sains dan Teknologi Malaysia.

Jian-feng Peng, Yong-hui Song, Peng Yuan, Xiao-yu Cui, & Guang-lei Qiu. (2009). The remediation of heavy metals contaminated sediment. *Journal of Hazardous Materials* 161: 633–640.

Kamaruzzaman, Y., Jamil, T., Hasrizal, S., Willison Kung Yee See & Ong Meng Chuan. (2006). Interpretasi kemasukan sumber antropogenik di dalam sediment sungai Terengganu dengan menggunakan Al dan Li sebagai elemen rujukan. *The Malaysian Journal of Analytical Sciences* 10: 269-274.

Kamaruzzaman, Y., Antotina, A., Airiza, Z., Syalindran, S. & Ong M. C. (2007). The geochemical profile of Mn, Co, Cu and Fe in Kerteh mangrove forest, Terengganu. *The Malaysian Journal of Analytical Sciences* 11: 336-339.

Kaushik, A., Ankur, K., Santosh, M., Shiv, K. & Kaushik, C. P. (2009). Heavy metal contamination of river Yamuna, Haryana, India: Assessment by Metal Enrichment Factor of the Sediments. *Journal of Hazardous Materials* 164: 265–270.

Redfern, F. M. (2006). Heavy Metal Contamination from Landfills in Coastal Marine Sediments: Kiribati and New Zealand. Final Year Project for Masters of Science. University of Waikato.

Rozaini, M.Z.H. and Brimblecome, P.,(2009b). The Odd-Even behavior of dicarboxylic acids solubility in the atmospheric aerosols. *Water, Air and Soil Pollution*. 198:65-75.

Rozaini, M.Z.H. and Brimblecome, P. (2009a). The solubility measurement of dicarboxylate salts; sodium oxalate, malonate, succinate, glutarate and adipate in the water at 298.15 K: *Journal of Chemical Thermodynamic*. 41(9):980-983.

Singh, K. P., Mohan, D., Singh, V. K. & Malik, A. (2005). Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India. *Journal of Hydrology* 312: 14–27.

Tam, N. and Wong, Y. S. (1995). Retention and distribution of heavy metals in mangrove soils receiving wastewater. *Environmental Pollution* 94: 283-291.

Tam, N. and Wong, W. S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution* 110: 195–205.

Valentina, G. C., Frank, J. M. & Albert, P. (2003). The distribution of trace metals in Florida Bay sediments. *Marine Pollution Bulletin* 46:1420–1433.