CHAPTER 4: RESULTS AND DISCUSSION

Fishermen village in Matang, Perak.

CHAPTER 4

RESULTS AND DISCUSSION

4.0 Introduction

This chapter presents results and discussion of four sampling times that spanned almost a year for analysis of water quality parameters and heavy metals in water, sediment and tissues of fish, prawn and cockles obtained from Larut river and Sangga Besar river. Physico-chemical parameter analysis in water and concentrations of heavy metals in surface water were reported. The water quality is then compared to the DOE Marine Water Quality Criteria and Standards Class E. For sediments, concentrations of heavy metals in surface sediments and distribution of heavy metals profiles in sediment at the depth between 0-20 cm were reported. The heavy metals concentrations in sediments from the river will also be compared with the Dutch Standards and other studies from different areas. For tissue, concentrations of heavy metals in gills, liver and muscle of fish species *Scaptophagus argus* were reported. Analysis of heavy metals in cockles (*Anadara granosa*) and tissue (muscle, shell and head) of prawns (*Penaeus merguiensis*) were also discussed. The results of heavy metals in tissue were then compared with the Malaysian Food Act 1983 and Food Regulations 1985 Fourteen Schedule. The discussion also includes trend of heavy metals in water, sediment and tissues of fish, cockles and prawns.

4.1 Physico-chemical Parameter Analysis

The *in situ* water quality parameter data for eight sampling stations were summarized in Table 4.1. The physico-chemical parameters of the water column such as DO, pH, temperature, are important because they have a significant effect on the water quality. Furthermore, aquatic life will also suffer due to degradation of river water quality and rivers will be unsuitable for supporting healthy aquatic life. Thus, it is important that the physico-chemical parameters of a river have to be studied. As for the water quality studies, water samples were taken for laboratory tests and also done *in-situ* to get the existing environmental information.

Table 4.1: Results of *in-situ* water parameters

Sampling Sites	Station	pH	Temperature (ºC)	DO (mg/l)	Salinity (ppt)
Larut river	P1	6.62	28.51	1.58	16.25
	P2	6.59	28.53	1.21	12.73
	P3	6.73	29.32	2.84	14.77
	P4	6.87	30.68	3.43	18.73
Sangga Besar river	P5	6.78	29.02	2.58	24.23
	P6	7.33	30.41	8.05	24.55
	P7	7.13	30.31	4.79	24.24
	P8	8.03	33.93	6.58	25.35

4.1.1 pH

The pH is an important variable in water quality assessment as it influences many biological and chemical processes within the water body and all processes associated with water supply and treatment. The pH is a measure of the acid balance of a solution and is defined as the negative of the logarithm to the base 10 of the hydrogen ion concentration. The pH scale runs from 0-14 (very acidic to very alkaline), with pH 7 representing a neutral condition. In unpolluted waters, pH is controlled by the balance between the carbon dioxide, carbonate and bicarbonate ions as well as other natural compounds such as humic and fulvic acids. The natural acid-base balance of a water body can be affected by industrial effluents and atmospheric deposition of acid-forming substances. Changes in pH can indicate the presence of certain effluents, particularly when continuously measured and recorded, together with the conductivity of a water body. The pH of most natural waters is between 6.0 and 8.5, although lower values can occur in dilute waters high in organic content and higher values in eutrophic waters, groundwater brines and salt lakes. All the water samples at Larut river showed neutral pH with the pH values varied from 6.62 to 6.87. The mean pH value for Larut river was found to be 6.7 (Table 4.1 and Figure 4.1). For Sangga Besar river, the pH of the surface water varied from neutral at station P5 to slightly alkaline at station P8 showing some marine water intrusion at the mouth of Sangga Besar river. The mean pH value for Sangga Besar river was found to be 7.3 (Table 4.1 and Figure 4.2).

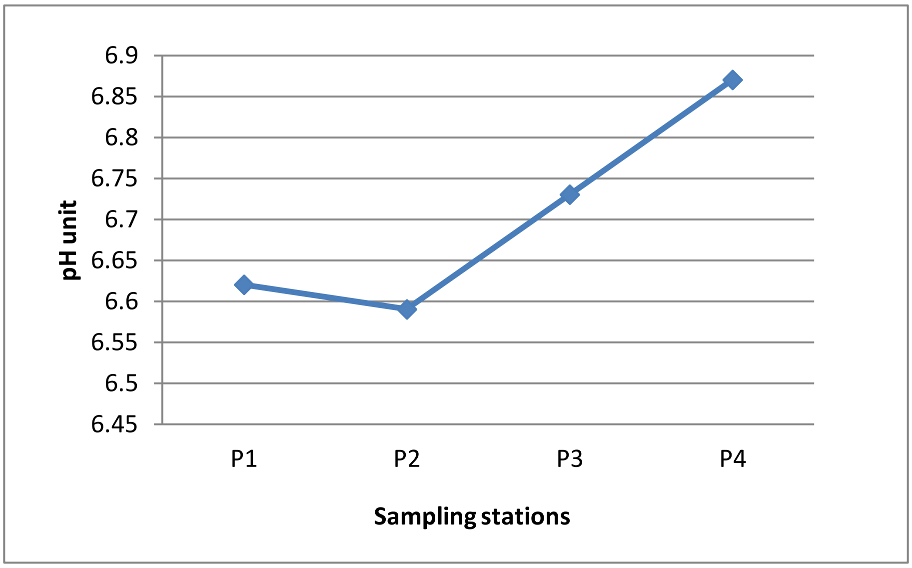

Figure 4.1: pH value from Larut River

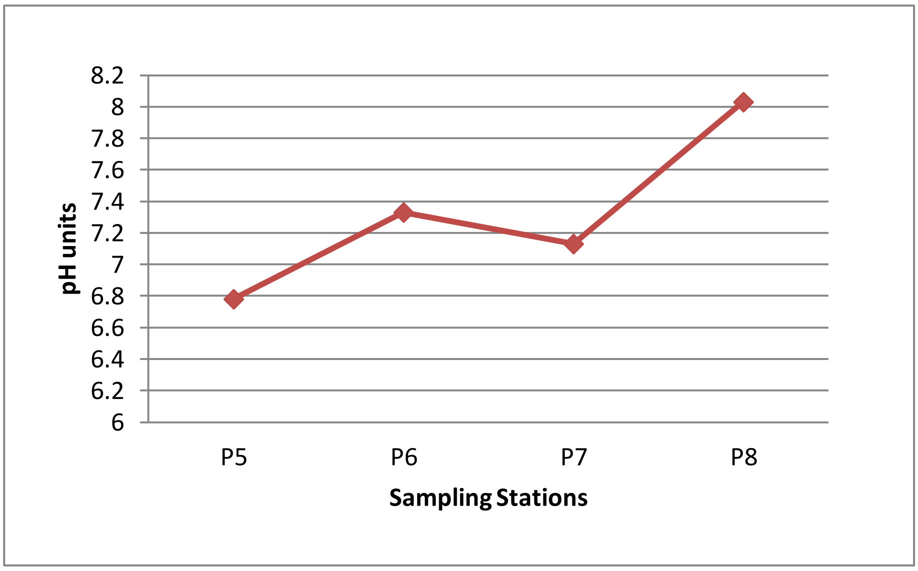

Figure 4.2: pH value from Sangga Besar River

4.1.2 Temperature

The temperature of surface waters is influenced by latitude, altitude, season, time of day, air circulation, cloud cover and the flow and the depth of the water body. Temperature affects physical, chemical and biological processes in water bodies. As water temperature increases, the rate of chemical reactions generally increases together with the evaporation and volatilization of substances from the water. The metabolic rate of aquatic organisms is also related to temperature, and in warm waters, respiration rates increase leading to increased oxygen consumption and increased decomposition of organic matter. Surface water is usually within the temperature range of 0°C to 30°C. For Larut river, the surface water temperature varied between 28.5 ºC to 30.6 ºC (Figure 4.3). The mean value of temperature measured along the rivers of Larut river was 29.3 ºC. For Sangga Besar river, the surface temperature varied from 29.0 to 33.9 ºC (Table 4.1 and Figure 4.4).

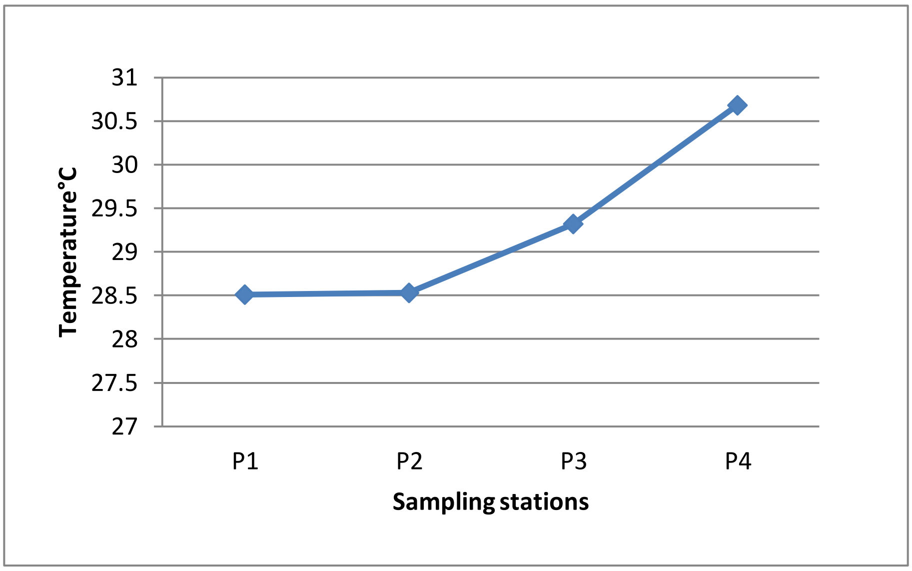

Figure 4.3: Surface water temperature from Larut River

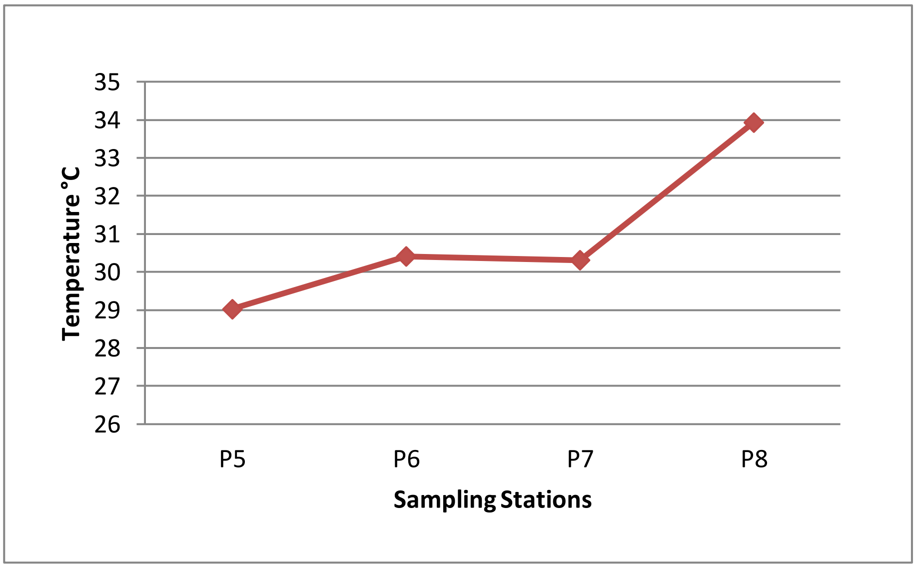

Figure 4.4: Surface water temperature from Sangga Besar River

4.1.3 Dissolved Oxygen (DO)

Oxygen is essential to all forms of aquatic life, including those organisms responsible for the self-purification processes in natural waters. The oxygen content of natural waters varies with temperature, salinity turbulence, the photosynthetic activity of algae and plants and atmospheric pressure. The solubility of oxygen decreases as temperature and salinity increase. In freshwaters the dissolved oxygen (DO) at sea level ranges from 15mg/l at 0°C to 8 mg/l at 25°C. Concentrations in unpolluted waters are usually closed to, but less than 10 mg/l. Biological respiration, including that related to decomposition processes, reduces DO concentrations. Waste discharges with high organic matter and nutrients can lead to a decrease in DO concentrations as a result of the increased microbial activity occurring during the degradation of the organic matter. Concentrations below 5mg/l may adversely affect the functioning and survival of biological communities and below 2 mg/l may lead to the death of most fish. For Larut river, the level of dissolved oxygen was low in the range of 1.21 mg/l to 3.43 mg/l (Figure 4.5). The average levels of DO were 2.26 mg/l. For Sangga Besar river, the dissolved oxygen content ranged between 2.58 mg/l to 8.05 mg/l (Figure 4.6). The average level of DO was 5.5 mg/l.

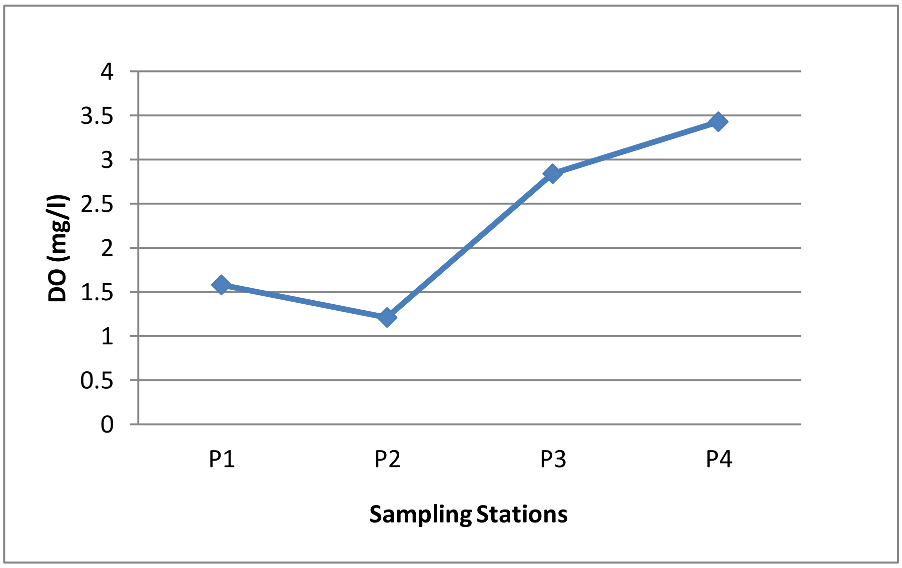

Figure 4.5: Dissolved oxygen level in Larut River

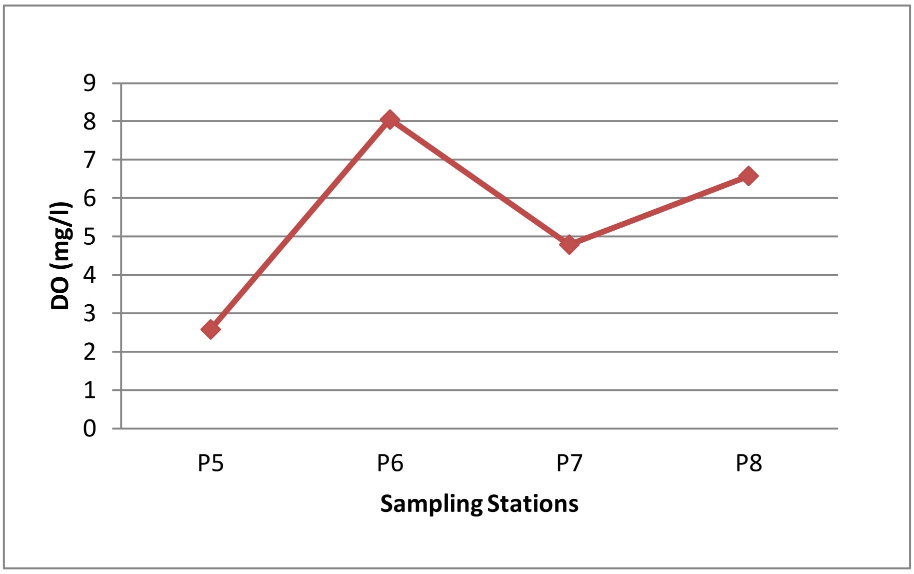

Figure 4.6: Dissolved oxygen level in Sangga Besar River

4.1.4 Salinity

Salinity is a measure of the salt content of the water. The salinity of seawater is approximately 35%, tending to be lower in tropical waters. The salinity of freshwater is always less than 0.5%. Thus the salinity of estuarine waters is between 0.5% and 35%. This range of salinity is generally termed brackish as distinct from marine or freshwaters. The salinity values for P1 to P4 varied between 12.73 ppt to 18.73 ppt, showing greater marine water intrusion at station P4 (Figure 4.7). Higher salinity values were found for station P5 to P8 and varied between 24.23 ppt to 25.35 ppt , with an increase from estuary to offshore (Figure 4.8).

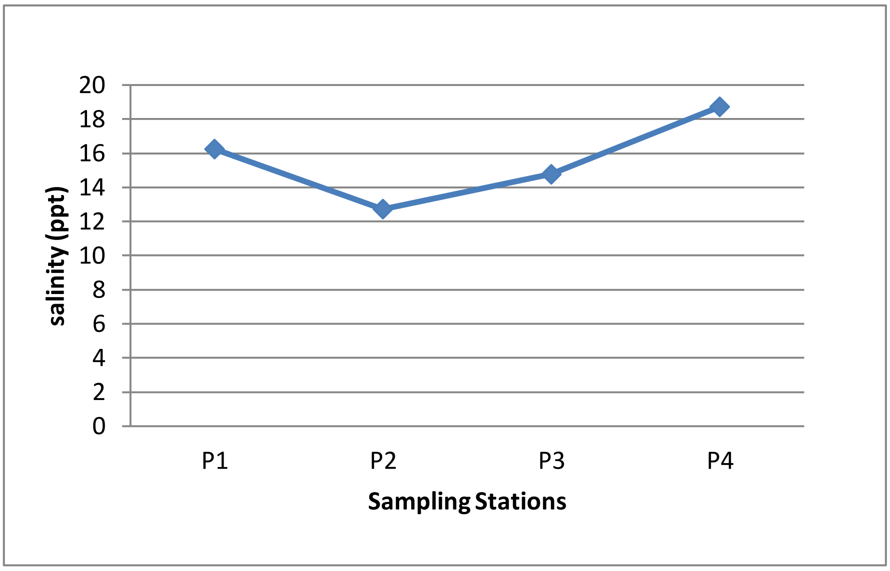

Figure 4.7: Salinity level in Larut River

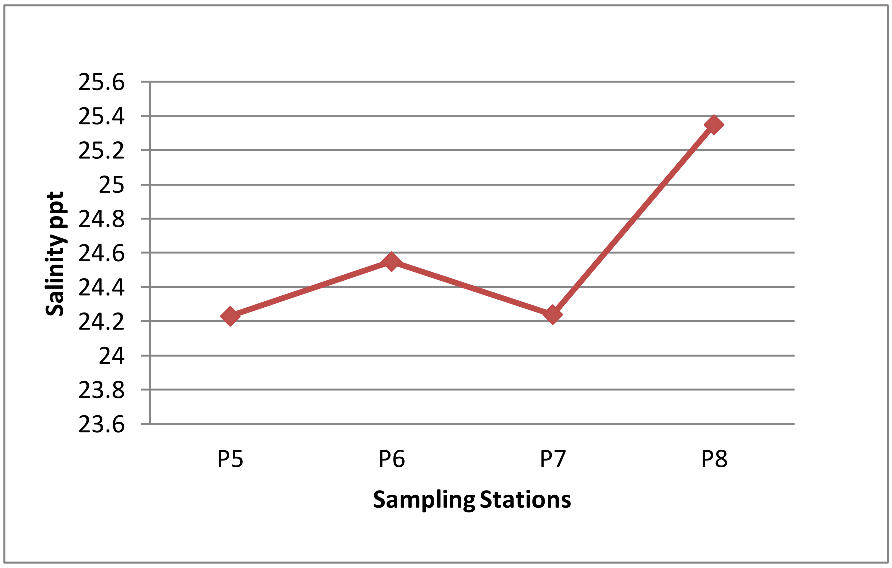

Figure 4.8: Salinity level in Sangga Besar River

4.2 Analysis of Standard Reference Material

The accuracy and precision of the results were checked by analyzing standard reference material. Standard reference materials are commonly used for assessing analytical accuracy. The quality of metal analytical methods in water was checked by using the certified reference water of the Community Bureau of Reference (BCR):CRM 505 (trace elements in estuarine water). The quality of total acid digestion of the sediment was checked by using a certified reference material of the National Institute of Standard and Technology (NIST) 1646a (estuarine sediment). For tissues, the accuracy of the analytical method was evaluated through the analysis of certified DORM-3-Fish protein from National Research Council Canada.

Precision is defined as relative standard deviation (RSD) which is calculated as a percentage using the standard deviation divided by the mean of replicate samples. Accuracy is determined by comparing the measured concentrations with the certified value and is expressed as percentage recovery (% Recovery). Based on a Florida Department of Environmental Protection, approved research quality plan, satisfactory precision and accuracy were required to be within ≤20% and 80-120% for all elements, respectively which corresponded to the uncertainty of the certified values (Chen, 1997). Accuracy of the analytical method was given as percent recoveries for each of the elements. The results for these SRM’s were given in Tables 4.2, 4.3 and 4.4.

According to Tables 4.2, 4.3 and 4.4, replicate analysis of these reference materials showed good accuracy, with recovery rates for metals between 82% and 116% for sediment, 88% and 120% for tissue and 84% and 116% for water.

Table 4.2: Observed and certified values of elemental concentrations in standard reference material NIST- Estuarine sediment (n=6)

Heavy Metals	Observed values (mg/kg)	Certified values (mg/kg)	% Recovery
Cu	9.53 ± 0.45	10.0 ± 0.340	105
Zn	47.40 ± 0.66	48.9 ± 1.90	97
Cd	0.12 ± 0.02	0.148 ± 0.007	82
Cr	47.50 ± 1.31	40.9 ± 1.90	116
Pb	10.80 ± 0.92	11.7 ± 1.20	92

Table 4.3: Observed and certified values of elemental concentrations in standard reference material NIST- tissue (n=6)

Heavy Metals	Observed values (mg/kg)	Certified values (mg/kg)	% Recovery
Cu	16.18 ± 0.71	15.5 ± 0.63	104
Zn	59.96 ± 0.77	51.3 ± 3.1	116
Cd	0.32 ± 0.05	0.290 ± 0.020	120
Cr	1.66 ± 0.36	1.89 ± 0.17	88
Pb	0.44 ± 0.13	0.395 ± 0.050	112

Table 4.4: Observed and certified values of elemental concentrations in standard reference material BCR-Fluka- estuarine water (n=6)

Heavy Metals	Observed values (μg/l)	Certified values (μg/l)	% Recovery
Cu	1.58 ± 0.26	1.87 ± 0.095	84
Zn	13.05 ± 0.32	11.24 ± 0.719	116
Cd	0.08 ± 0.04	0.09 ± 0.005	96
Cr	0.22	0.2	109
Pb	0.04 ± 0.002	0.05 ± 0.03	97

4.3 Concentrations of Heavy Metals

Heavy metals are natural trace components of the aquatic environment, but have increased due to industrial wastes, agricultural and mining activities. Heavy metals have been introduced into rivers through land surface runoff, rainfall precipitation and factory waste outlet point discharge. Anthropogenic metals may consistently retain within the water bodies or may be taken up by organisms such as plankton, benthos, or fish and finally transferred to humans. Therefore it is important that a baseline study is conducted to determine the background of heavy metal concentrations in the study area. This is necessary to understand the source of heavy metal pollution for future environmental planning strategies.

This study reports the concentrations of Cu, Zn, Cd, Cr and Pb in water, sediments and tissues of fish, prawns and cockles obtained from the Matang Mangrove, Perak. These metals are selected because of their potential for human exposure may increase health risk. Metals of major interest in bioavailability studies, as listed by the

US Environmental and Protection Agency (EPA), are aluminium, beryllium, arsenic, cadmium, copper, chromium, mercury, nickel, lead, selenium and antimony. Other metals that are presently of lesser interest to the EPA are silver, barium, cobalt, manganese, molybdenum, sodium, thallium, iron and zinc. The results obtained from the metallic analysis were expressed in mg/kg for sediment and tissues. While for water results were expressed in µg/l. The results from previous findings in literature were listed in the table as a comparison study.

4.3.1 Heavy metals in water

Table 4.5 shows the concentrations of total dissolved metals in water at the eight sampling points of Larut river and Sangga Besar river. For Larut river, the concentrations of metals varied within a range of 35-40 µg/l for Cu, 37-75 µg/l for Zn, 4-6 µg/l for Cd, 20-25 µg/l for Cr and 30-41 µg/l for Pb. Sangga Besar river recorded concentrations between 28-34 µg/l of Cu, 22-40µg/l of Zn, 2-6µg/l of Cd, 43-51µg/l of Cr and 23-40µg/l of Pb (Figure 4.10). Between these two rivers, Larut river had the highest concentrations of heavy metals with the exception of Cr. The Department of Environment reported higher concentrations of heavy metals in the waters off the west coast of Peninsular Malaysia compared to other areas because of the greater extensive land use and industrialization.

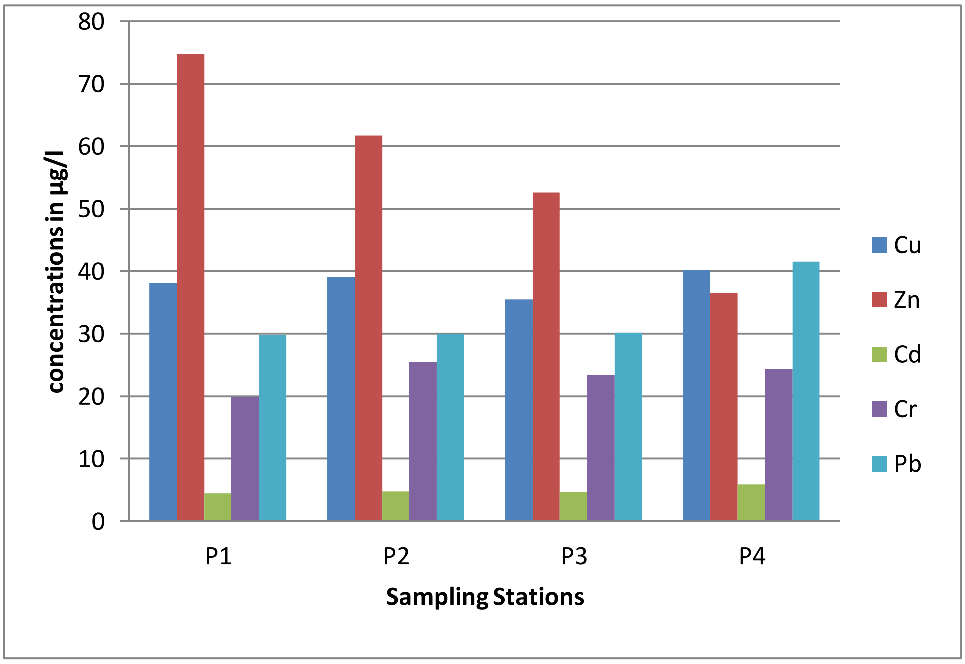

Figure 4.9: Heavy metal concentrations in water from Larut river

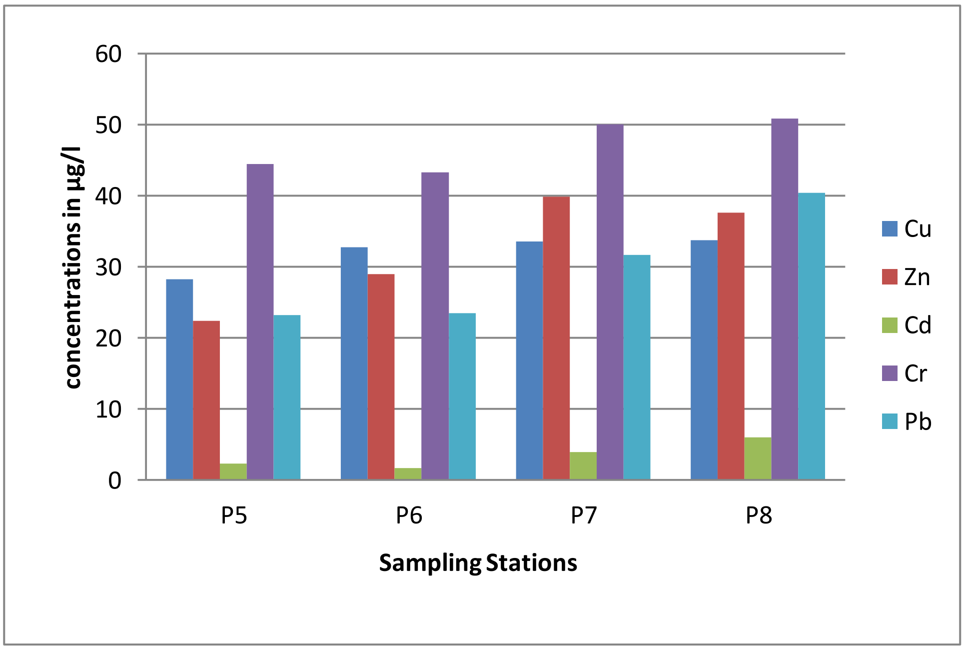

Figure 4.10: Heavy metal concentrations in water from Sangga Besar river

Table 4.5 Average concentrations of Heavy Metals in water (μg/l)

Sampling sites		Cu	Zn	Cd	Cr	Pb
	P1	38.17 ± 1.24	74.72 ± 0.28	4.49 ± 0.45	19.89 ± 1.06	29.71 ± 4.16
	P2	39.03 ± 2.09	61.71 ± 2.37	4.79 ± 0.55	25.46 ± 2.18	29.95 ± 4.31
Larut River	P3	35.47 ± 1.32	52.60 ± 2.24	4.69 ± 0.15	23.35 ± 2.88	30.17 ± 3.34
	P4	40.19 ± 0.47	36.53 ± 0.72	5.92 ± 0.20	24.33 ± 1.65	41.48 ± 3.62
	Average	38.22 ± 2.18	56.39 ± 14.59	4.93 ± 0.69	23.05 ± 2.93	32.83 ± 6.18
	P5	28.28 ± 1.27	22.38 ± 0.51	2.35 ± 0.06	44.43 ± 5.52	23.19 ± 2.73
	P6	32.72 ± 1.44	28.97 ± 2.55	1.71± 0.06	43.30 ±3.04	23.49 ±0.18
Sangga Besar River	P7	33.54 ± 4.20	39.86 ± 1.57	3.93 ± 1.11	50.04 ± 4.67	31.63 ± 1.39
	P8	33.70 ± 1.36	37.63 ± 2.23	5.99 ± 0.04	50.84 ± 1.0	40.44 ± 0.44
	Average	32.53 ±3.56	32.44 ±7.72	3.49 ±1.79	47.15 ± 4.84	29.69 ±7.50

Zinc

From all metals studied in both rivers, Zn showed the highest mean concentration value of 56 µg/l in Larut river (Figure 4.9). The highest concentration was observed at station P1. The recommended MWQS threshold level of zinc for Malaysian is 50 µg/L (Appendix 1). Thus, the average concentration of Zn is within the MWQS value. Total zinc concentrations in natural freshwaters are quite variable and may range from approximately 1 µg/l to as high as 1000 µg/l. Most waters have concentration less than 100 µg/l. Intensive fishing and industrial activities, weathering of minerals and rocks are possible sources for the enrichment of these metals.

There have been a number of studies of zinc speciation in Malaysian rivers. The present study indicates an increase of concentrations of zinc in water of Kuala Sepetang compared with the study carried out in 1995 by Ahmad Ismail *et al.* (1995) which recorded 0.05 µg/l of zinc in water. The study conducted in Langat River in Malaysia recorded concentrations of zinc in water varied between 32-75 µg/l. The concentrations of zinc from Qua Iboe estuary in Nigeria was found to be almost the same, i.e., 30 µg/l (Essien *et al.*, 2009). However, in Gao-ping River Taiwan, the concentration of zinc varied between 5-354 µg/l .The high concentrations of zinc was attributed to the emission of atmospheric deposits and wastewater discharge from factories located near the mouth of Gao-Ping River (Ruey-an Doong *et al.*, 2008).

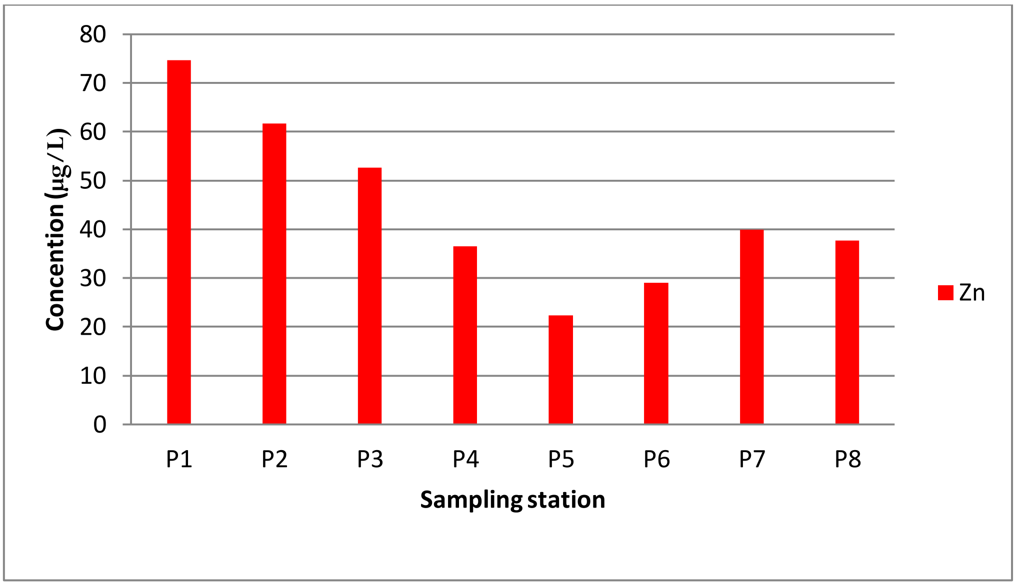

Figure 4.11: Concentration of Zn in water

Copper

The concentrations of copper in water from larut river and Sangga Besar river were found to range from 28-40 µg/l for the eight sampling points as shown in Figure 4.12. The average concentration of copper found in Larut river and Sangga Besar river was 38.2 µg/l and 32.5 µg/l, respectively For Larut river, the highest level of copper was obtained at sampling point P4. Meanwhile, in Sangga Besar river the highest concentration of copper was found at sampling point P8. These sampling points P4 and P8, are located at the mouth of both rivers. The recommended MWQS level of copper for Malaysian rivers is 2.9 µg/l. The copper concentrations for all sampling points were higher than the permissible limit. The highest concentrations of copper in this study may be contributed to the industries and factories at Hilir Sg Larut, a sub-basin of Larut river basin. The results was comparable to that found in Likas estuary, Sabah i.e., 41-43 µg/l (Abdullah *et al*. (2007). Another study done in Sg Juru had reported the concentration of copper as 2.0 µg/l (Mat and Maah, 1994). In other countries the concentration of copper from Gao-ping River, Taiwan ranged from 0.90 µg/l to 34.3 µg/l presumably attributed to the discharge of untreated industrial and wastewater into Gao-ping river, Taiwan (Doong *et al.*, 2008). On the other hand, Chale (2002) reported that the concentration of copper in Lake Tanganyika being less than 6 µg/l.

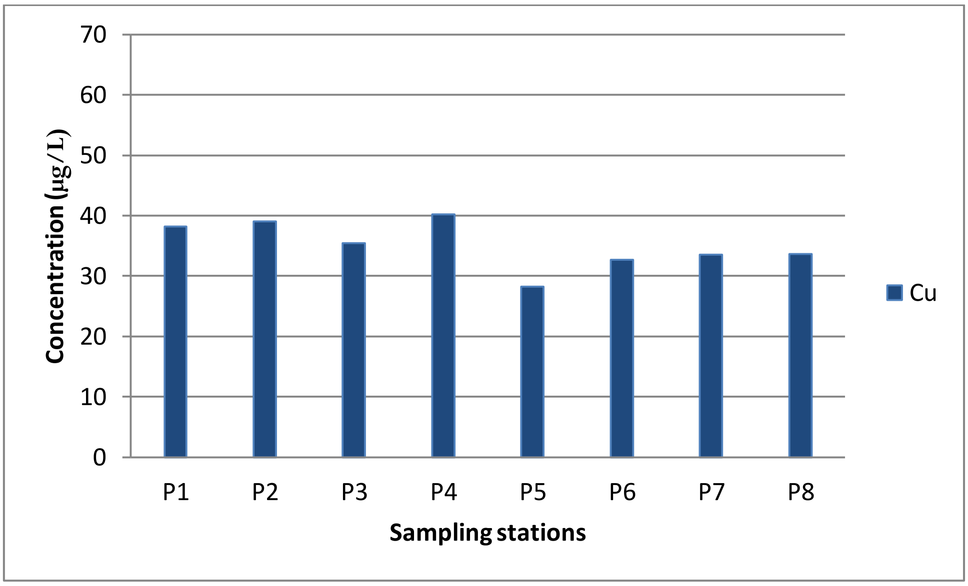

Figure 4.12: Concentration of Cu in water

Lead

The lead concentrations were found in the range of 29-41 µg/l and 23-40 µg/l for Larut river and Sangga Besar river respectively (Figure 4.13). For Larut river, the highest concentration of lead was found at station P4, the station nearest to the river mouth. Meanwhile for Sangga Besar river the highest concentration of lead was found at station P8 also nearest to the river mouth. The mean concentration level of lead from both rivers was higher than the MWQS level of 8.5 µg/l for Malaysian estuarine water and mangrove. In Malaysia, the impact of heavy metal pollution in the Juru River, Penang (northern Malaysia) during the 1970's was well documented. Analysis of water sampled adjacent to the Prai Industrial estate revealed high lead concentration up to 1.5 ppm (Ruddle, 1981). High value of lead was also found in Likas estuary, Sabah (94-108µg/l) indicating pollution of the estuarine water bodies. Elsewhere, it was reported that the lead concentration in brackish water ponds of Sunderban India ranged from 30-

200 µg/l (Himadri *et al*., 2000). In the water body of the Yellow River China, the concentration of lead varied within a range of 0.1-20 µg/l (Yimin *et al*., 2009).

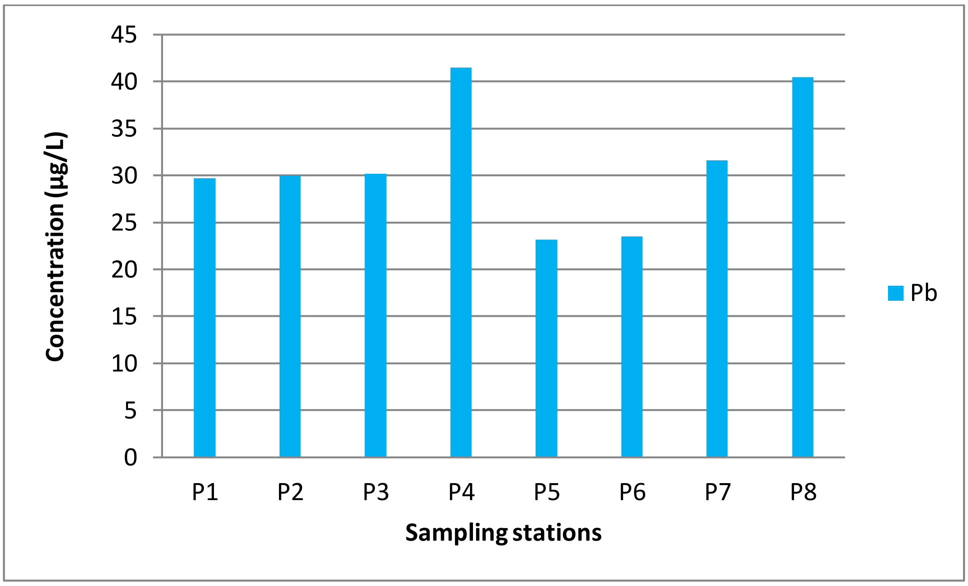

Figure 4.13: Concentration of Pb in water

Chromium

The concentrations of chromium determined in the water samples from this study ranged from 20-25µg/l and 43-50µg/l for Larut River and Sangga Besar River, respectively (Figure 4.14). The recommended MWQS threshold level of chromium for Malaysian rivers is 10 µg/L. The average concentrations of Cr for all sampling points from both river were higher than the MWQS limit. The levels of Cr from both rivers were much higher than other study done in Likas and Kota Belud estuaries Sabah, with concentrations range from 2-13µg/l. These two estuaries may have less industrial pollution. Meanwhile researchers had reported level of chromium in water ranging from 0.47 to 33.8µg/l in other countries (Doong *et al*., 2008 and Essien *et al*., 2009).

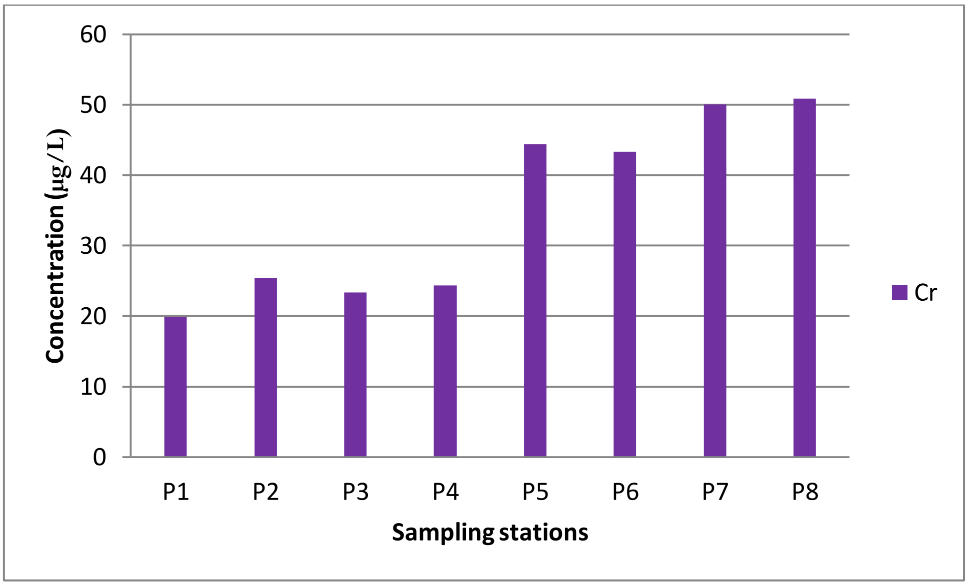

Figure 4.14: Concentration of Cr in water

Cadmium

The concentration of cadmium showed little fluctuation in the Sangga Besar river as shown in figure 4.15 ranging from 1.71-5.99 µg/l. The metal concentration in Larut river was shown to increase from P1 to P4 with values of 4.49-5.92 µg/l. The recommended MWQS level of cadmium for Malaysian rivers is 2 µg/L. The average value of cadmium for all the sampling points of the river system is higher than the MWQS level for class E. In another study, the level of cadmium concentration was found to be 1-10 µg/l in the Likas estuary, Sabah. Elsewhere, it was reported that the level of cadmium in water from Kolleru Lake India, were much higher (36µg/l) (Adhikari *et al*., 2009).

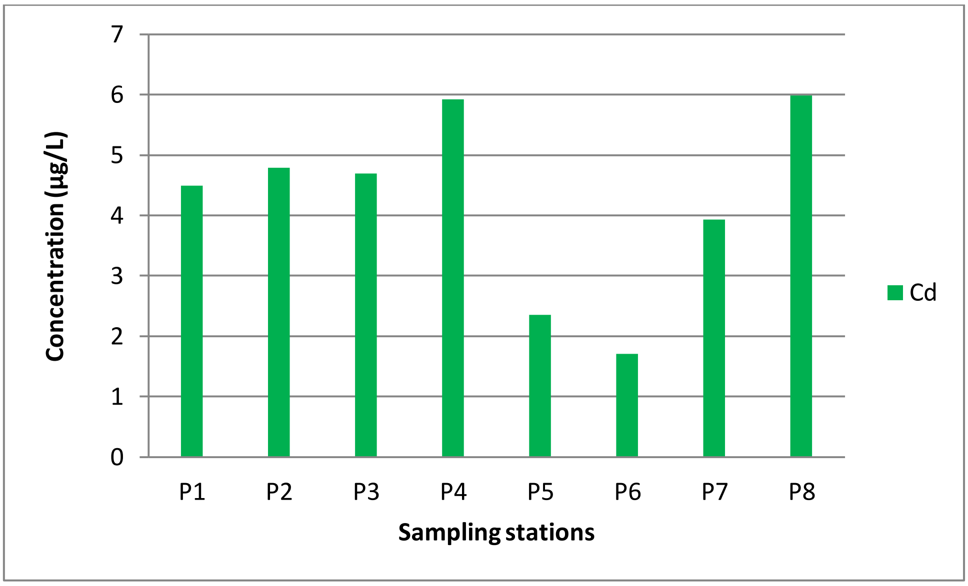

Figure 4.15: Concentration of Cd in water

The concentration of cadmium, zinc and copper, were certainly very much lower than the optimum values for aquaculture water quality recommended by Stickney (2000). The recommended values for aquaculture, for the three heavy metals are: Cd (<150 ppb), Zn (<250 ppb), and Cu (<100 ppb), respectively.

The results obtained were analysed using analysis of variance (ANOVA) to check whether the concentrations of heavy metals are difference among the sampling stations. To complete the hypothesis test, the calculated *F*-value was compared with the critical value obtained from the *F*-value table (Appendix) at the 95% confidence level. The results of ANOVA test were summarized in Table 4.6 for Larut River and Sangga Besar River, respectively. ANOVA statistics demonstrates that there is significance difference of all heavy metal levels between each station in Larut River. However, for Sangga Besar River, there is significant difference for Zn, Cu and Cd.

Table 4.6: Analysis of variance (ANOVA) of Cu, Zn, Cd, Cr and Pb concentrations in water at different sampling points in Larut and Sangga Besar rivers

Larut River	***F*-Value**	***p-value***	**F-crit**
Cu	6.05	<0.05	4.07
Zn	269.42	<0.001	4.07
Cd	9.64	<0.001	4.07
Cr	4.78	<0.01	4.07
Pb	6.66	<0.05	4.07
Sangga Besar River	***F*-Value**	***p-value***	**F-crit**
Cu	3.03	*ns*	4.07
Zn	58.77	<0.001	4.07
Cd	35.03	<0.001	4.07
Cr	2.83	*ns*	4.07
Pb	83.38	<0.001	4.07

p – significant level, *ns*- not significant

4.3.2 Heavy metals distribution in surface sediments

The range and average metal concentrations for each sampling site found in the sediment from this study area were shown in Table 4.7. The metals were ranged for the followings, Cu: 24.04-38.82 mg kg^{-1}; Zn: 59.74-179.01 mg kg^{-1}; Cd: 0.38-3.76 mg kg^{-1}; Cr: 29.89-65.42 mg kg^{-1}; Pb: 24.74-52.20 mg kg^{-1}. For Larut river, the highest Zn concentration was observed in Station P1 and the highest Cu concentration was found in station P4 as shown in Figure 4.16. The highest Cd and Pb concentrations were observed in station P2 and P3 while the highest Cr concentration was observed at station P3. The maximum concentrations of Cu, Zn, Cd, Cr and Pb in Larut river were 38.82, 179.01, 3.76, 65.42 and 52.20 mg kg^{-1}, respectively.

For Sangga Besar river the maximum concentrations of Cr and Pb were at P6 (Figure 4.17). The highest metal concentration was 42.3 mg kg^{-1} for Cr and 43.41 mg kg^{-1} for Pb. The results for Cu and Zn at Sangga Besar river were found to be 24.40 mg kg^{-1} to 31.97 mg kg^{-1} and 59.74 mg kg^{-1} to 84.44 mg kg^{-1}, respectively. For Cd, Cr and Pb, the highest concentration was found at station P6. Basically the concentrations of heavy metals in Larut river decreased in the order of Zn > Cr > Pb > Cu > Cd whereas in Sangga Besar river the order was Zn > Pb > Cr > Cu > Cd.

Table 4.7 Heavy Metal concentrations in surface sediments (mg kg^{-1})

Sampling sites		Cu	Zn	Cd	Cr	Pb
Larut River	P1	24.04 ± 0.99	179.01 ± 4.24	1.87 ± 0.46	37.8 ± 2.09	43.50 ± 6.85
	P2	25.49 ± 4.44	87.31 ± 6.04	3.76 ± 0.64	35.66 ± 3.70	51.60 ± 2.62
	P3	35.83 ± 3.42	89.41 ± 2.56	2.16 ± 0.34	65.42 ± 1.97	52.20 ± 1.73
	P4	38.82 ± 1.41	89.29 ± 1.09	2.13 ± 0.34	61.10 ± 4.63	48.17 ± 2.53
	average	28.51 ± 0.73	111.25 ± 3.48	2.48 ± 0.42	50.03 ± 1.38	48.9 ± 3.20
Sangga Besar River	P5	31.97 ± 2.96	84.44 ± 4.93	0.81 ± 0.18	36.88 ± 5.17	38.17 ± 4.25
	P6	26.96 ± 2.85	76.80 ± 6.27	2.34 ± 0.29	42.26 ± 6.27	43.41 ± 3.30
	P7	26.85 ± 3.05	59.74 ± 5.62	0.38 ± 0.04	29.89 ± 4.76	33.37 ± 3.23
	P8	24.40 ± 3.63	63.87 ± 3.41	1.08 ± 0.15	30.60 ± 2.95	24.74 ± 2.82
	average	27.55 ± 3.12	71.21 ± 5.06	1.15 ± 0.17	34.91 ± 4.79	34.92 ± 3.40
Dutch Criteria		190	720	12	380	530

It could be seen that the concentrations of heavy metals in the surface sediment from Larut river was much higher than that in the Sangga Besar river. It has been reported by many authors that the content of metals in sediment of estuary is higher than that in the rivers. Estuaries are zones of complex interaction between fluvial and marine processes that act as a geochemical trap for heavy metals bonded in the fine-grained sediments. Estuarine mixing can lead to a depositional acceleration of clay mineral due to salinity change, favouring the entrapment and accumulation of metal adsorbed on clay particles (Vicente *et al.*, 2009).

It is noteworthy that higher concentrations of Cr and Pb were found at station P3. This station is located at the mouth of Larut river. The mixing of river water and sea water causes a change in salinity. Trace metals are usually associated with fine particles. When fine particles move downstream to the mouth of Larut river, the changes in salinity enlarge the particle diameters by flocculation, resulting in the deposition of metal concentrations in the sediments of estuary (Doong *et al.,* 2008). Mackey *et al*. (1995) have determined the concentrations of trace metals along 12 transects laid down a mangrove woodland near the mouth of Brisbane River Australia and reported that metal concentrations tended to increase from land to sea. This is attributed to the role of tidal deposition in determining the spatial distribution of metals in sediments (Ong Che, 1999).

The total concentrations of various heavy metals were compared with those reported from Asia and Australia. The data in Matang mangrove estuary were still in the range when compared with those reported from Hong Kong, Taiwan, China and Australia (Table 4.8).The concentration of zinc in the sediments of Larut river and Sangga Besar river ranged from 59.7 mg kg^{-1} to 179.0 mg kg^{-1}. Higher concentrations of

Zn were observed at site P1. This might be related to nearby residential activities. However, comparing the results of this study with that in other areas. The Zn content in this study was lower than reported in other sites (Table 4.8). In Likas Sabah, the Zn content ranged from 286-420 mg kg^{-1}. (Mohd *et al.,* 2007). The high concentrations of Cr, Cu, Pb and Zn at this area can be related to the boat traffic, due to increased traffic of fishing vessels traveling to Kuala Sepetang for landings of fish, prawns and cockles.

Most studies from Malaysia were reported along the west coast of the Peninsular Malaysia with concentration of lead ranging from 1-180 µg/g. At Bintulu, on the east coast of Sarawak, Ismail (1993) reported that the lead concentration ranging from 11-36 µg/g in sediments. The low content clearly showed off-shore petroleum activity in South China Sea may not affect sediment quality. Although the Pb content in sediment in Matang mangrove estuary may be slightly higher or comparable to that reported in the west coast of Peninsular Malaysia, it is certainly low compared with China, where boat traffic was extremely high (Zheng *et al*., 2008).

The Cu ranges (24.04-31.97 mg/kg) found in the sediments in the Matang mangrove estuary were low compared to the other reported Malaysian studies. For examples, Mohd Harun Abdullah *et al*. (2007) reported total Cu concentrations ranged from 45.5-142.5 mg kg^{-1} in Bintulu whereas Ismail *et al.* (1995) had reported 41.5 mg kg-^{1} in sediments from Kuala Juru, Penang. The study by Abdullah (2007) on the heavy metals in the *Meretrix meretrix roding*, water and sediments from the estuaries in Sabah has reported Cu content in the sediments ranged from 45.5 mg/kg to 142.5 mg/kg. The higher concentration of copper in the sediment were possibly contributed by the natural geological and sedimentation of the area where Mountain Kinabalu and copper mining areas are located at the upstream of the river (Abdullah, 2007). In Mai Po Hong Kong, the Cu in the sediment had been reported ranged from 18.8 mg/kg to 86.6 mg/kg (Liang *et al*., 2003).

The results of the sediment taken from this study were also assessed against the Dutch Criteria for Assessment of Soil Pollutants. The values found in this study are very much lower than the guidelines values.

Table 4.8 Heavy metal concentrations mg kg^{-1} dry weight in surface sediments reported in this and other studies.

	Reference	**Cu**	**Zn**	**Cd**	**Cr**	**Pb**
This study (2009) Larut River Sangga Besar River		24-38 24-31	87-179 59-84	1.8-38 0.38-2.34	35-61 29-42	43-52 24-43
Darwin Harbour Australia (1989)	Peerzada and Rohoza (1989)	16-32	103-270	0.9-3.0	85-275	24-91
Mai Po Hong Kong mudflat (1998)	Ong Chee (1999)	51-87	130-308	1.1-1.4	20-75	69-220
Wuli river, China (2008)	Zheng et al. (2008)	56.63	525.2	7.947	-	80.5
Gao Ping River, Taiwan (2008)	Ra Doong et al. (2008)	14.5-197	65.9-1535	0.01-1.0	35.7-2714	18.3-92.9

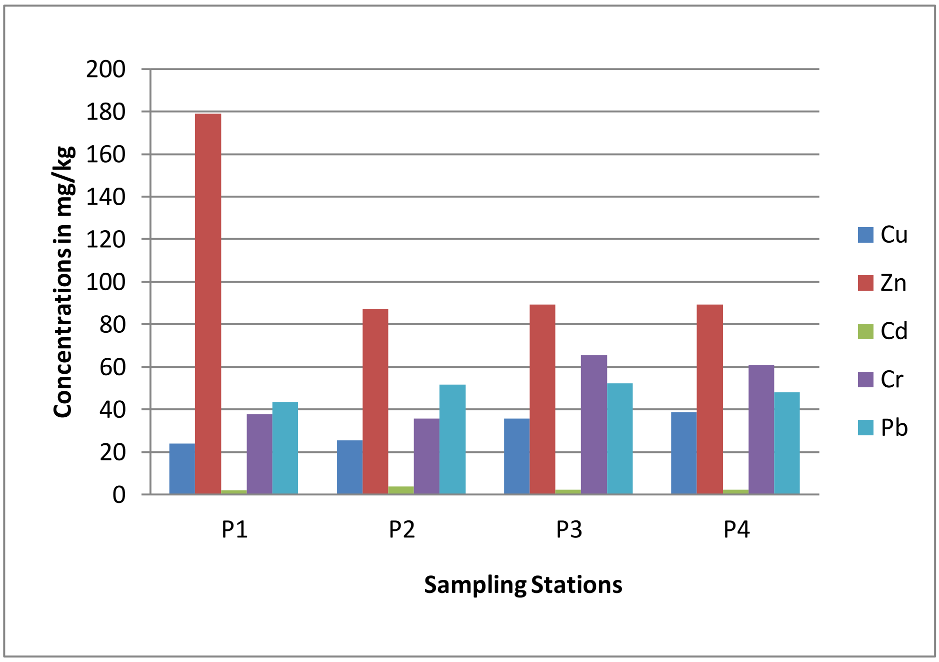

Figure 4.16: Heavy metal concentration in surface sediments from Larut river

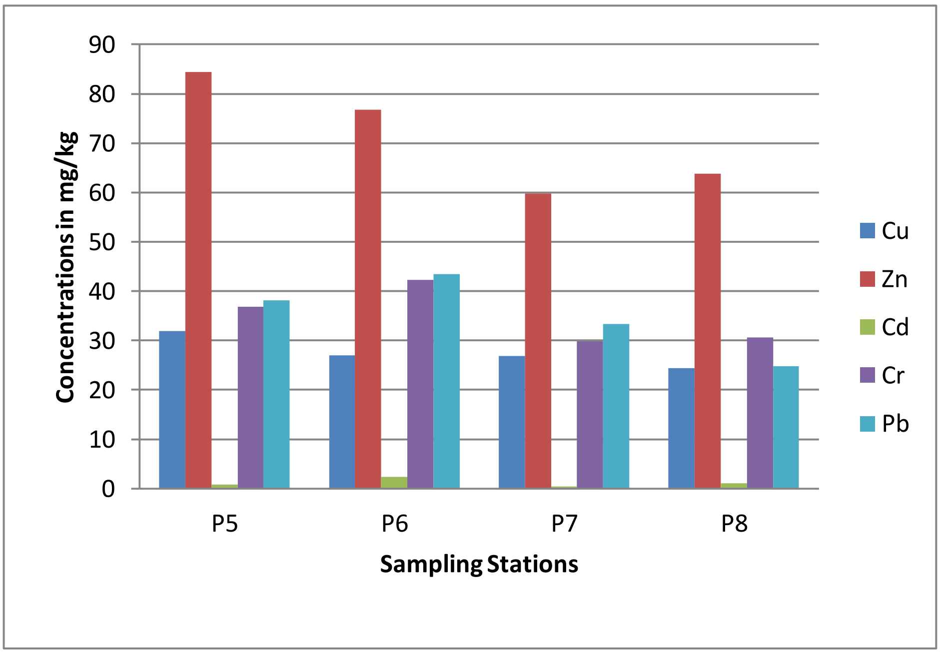

Figure 4.17: Heavy metal concentration in surface sediments from Sangga Besar river

4.3.3. Heavy metal distribution in typical sediment profiles

The distribution of heavy metals in sediment profiles at Larut river and Sangga Besar river were shown in Table 4.9 and Table 4.10. The average metal concentrations in the surface or subsurface sections were generally higher than that in the deeper layers although the differences were small. The vertical distribution of metal concentrations is commonly affected by many factors, such as sediment properties, hydrodynamic conditions and dredging activities. Vertical sections of the sediments can give a record of the level of contamination over time, provided that the pollutants are persistent and the sediment stratum has not been seriously disturbed by human activities such as dredging (Fung, 1993).

The distribution profile of metal concentrations in Larut river were shown in Figures 4.18 – 4.21. Most of the heavy metals had accumulated at the depth of 0-5cm and 5-10 cm. At 10-15 cm the concentrations of various heavy metals were low compared with the surface sections. Other studies also reported that the concentrations of Cd, Cu, Cr, Fe, Pb and Zn were more enriched in the upper 5-10 cm of the topsoil as compared to that in the 21-30 cm core of the mudflat sediments (Tam and Wong, 2000). The heavy metal concentrations in the surface sediments from Mai Po mangrove were 4-25% higher than those found in the deeper sediment (Ong Chee, 1999). Figure 4.21 shows large variation in metal concentrations within different sediment core depth. The concentrations of all heavy metals were highest at 5-10cm depth. The metal concentrations were then found to be lower at 10-15cm. As for P1 station, most of the heavy metals were accumulated at the top of sediment core (<10cm) except Cu. The distribution pattern was found to be similar in P2 except Cr which was accumulated in a higher concentration at 10-15cm. As for P3 station, Cd, Cr and Pb showed higher concentration at 5-10cm while the Cu and Zn content were higher at 10-15cm and 15-

20cm sediment core sections, respectively. However, for P4 station all the heavy metals showed higher concentrations on the top sediment cores (< 10cm).

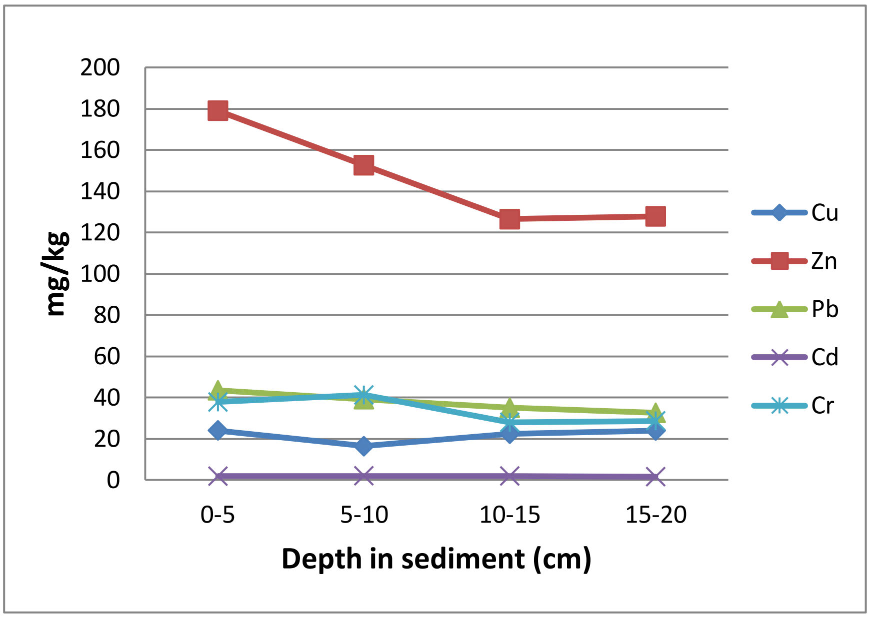

Figure 4.18: Heavy Metals profiles at P1

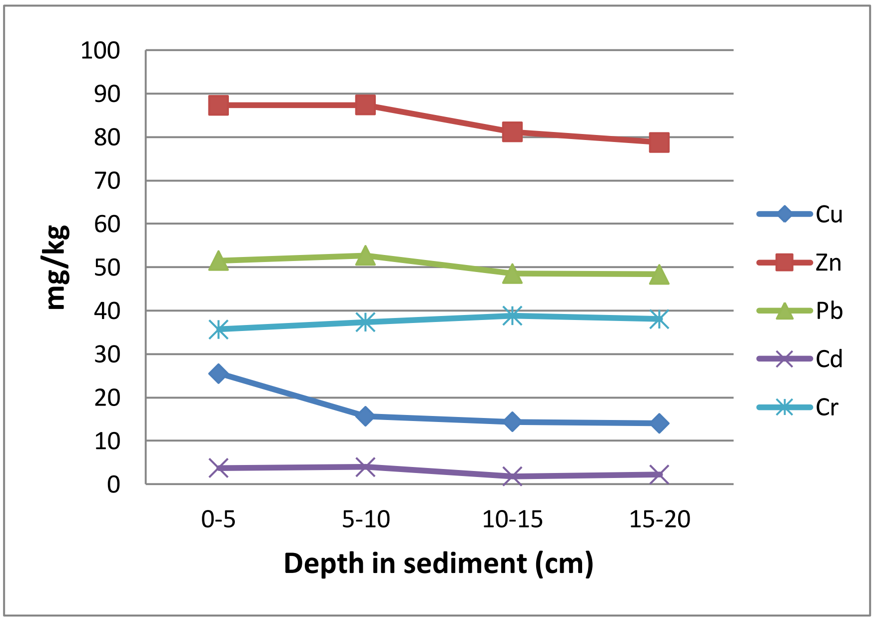

Figure 4.19: Heavy Metals profiles at P2

Table 4.9: Concentrations of heavy metal (mg kg^{-1}) in sediment profile from Larut River

		P1	P2	P3	P4
Cu	0-5cm	24.04 ± 0.99	25.49 ± 4.44	35.83 ± 3.42	38.82 ± 1.41
	5-10cm	16.36 ± 0.48	15.67± 1.31	36.19 ± 0.65	80.83 ± 1.87
	10-15cm	22.42 ± 1.40	14.41 ± 0.87	39.88 ± 0.90	25.91 ± 4.45
	15-20cm	23.99 ± 1.15	14.03± 2.04	37.72 ± 2.31	27.66 ± 4.38
Zn	0-5cm	179.01 ± 1.38	87.31 ± 6.04	89.41 ± 2.56	89.29 ± 1.09
	5-10cm	152.57 ± 1.33	87.42 ± 2.09	100.79 ± 3.01	100.91 ± 3.78
	10-15cm	126.41 ± 1.52	81.21 ± 5.76	101.90 ± 0.82	70.19 ± 4.19
	15-20cm	127.79 ± 1.79	78.75 ± 2.28	110.61 ± 3.98	73.73 ± 2.11
Pb	0-5cm	43.50 ± 7.84	51.56 ± 2.65	52.20 ± 1.73	48.17 ± 2.53
	5-10cm	39.19 ± 5.11	52.76 ± 1.66	55.18 ± 6.54	50.93 ± 1.57
	10-15cm	35.02 ± 2.39	48.56 ± 3.00	52.08 ± 2.63	42.94 ± 1.31
	15-20cm	32.56 ± 1.34	48.36 ± 1.70	50.29 ± 2.67	41.57 ± 3.06
Cd	0-5cm	1.87 ± 0.46	3.76 ± 0.64	2.16 ± 0.34	2.13 ± 0.34
	5-10cm	2.06 ± 0.49	3.95 ± 0.80	2.21 ± 0.37	1.87 ± 0.17
	10-15cm	1.96 ± 0.11	1.83 ± 0.41	1.54 ± 0.45	1.39 ± 0.17
	15-20cm	1.62 ± 0.26	2.23 ± 0.36	1.65 ± 0.37	0.72 ± 0.18
Cr	0-5cm	37.80 ± 2.09	35.66 ± 3.70	65.42 ± 1.97	61.10 ± 4.63
	5-10cm	41.23 ± 1.73	37.36 ± 1.36	66.79 ± 3.95	64.36 ± 3.83
	10-15cm	27.97 ± 1.68	38.85 ± 3.36	61.58 ± 1.61	35.40± 3.63
	15-20cm	28.70 ± 1.79	38.05 ± 2.52	56.87 ± 3.59	42.25 ± 6.34

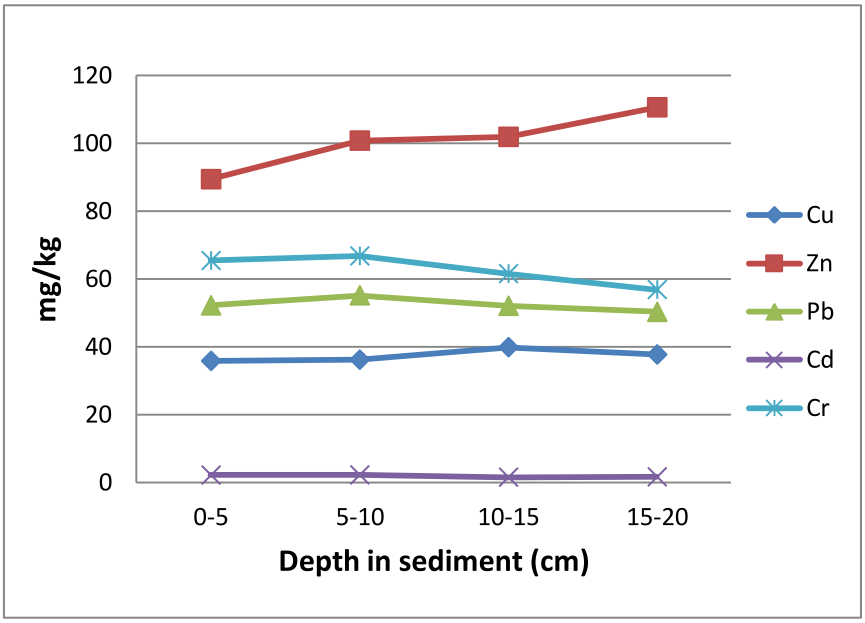

Figure 4.20: Heavy Metals profiles at P3

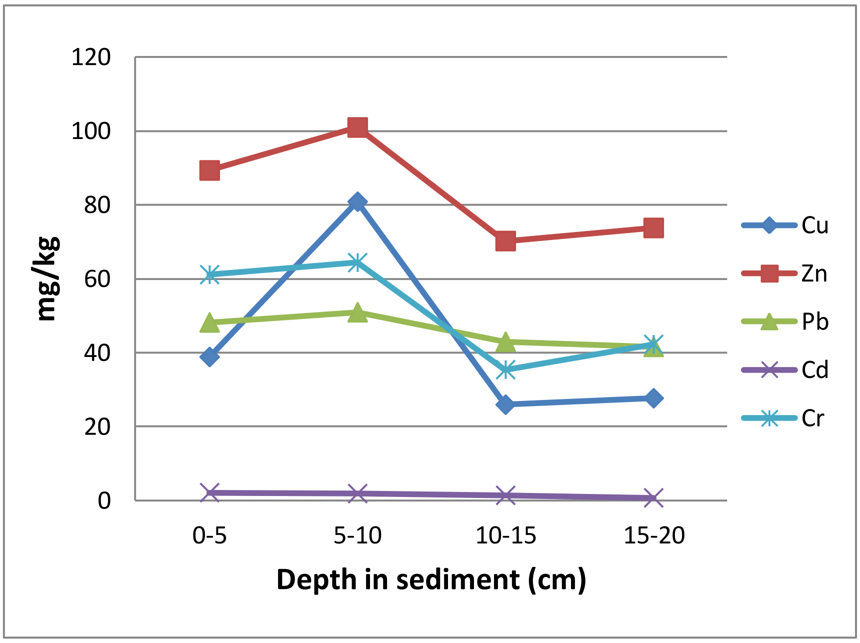

Figure 4.21: Heavy Metals profiles at P4

In Sangga Besar river, the distribution profiling of heavy metals in the sediment cores were shown in Figures 4.22 – 4.25. Most of the heavy metals showed higher concentrations at the top sediment cores (<10 cm). As for station P5, the metal concentrations were high at the depth of 5-10cm except Cd which was high at 0-5cm.

The similar situation was found at station P6 except Cd interchanged with Pb. However, at station P7, copper was found to be high at 0-5 cm while the other heavy metals were accumulated at the depth of 5-10 cm.

The concentrations of all heavy metals showed variations between the elements, between the sampling station and between depths. Overall the concentrations of all heavy metals were higher on the top sediments compared to the bottom sediments from both rivers. Cr showed similar distribution pattern of heavy metals from both rivers. Zn also showed similar trend of distribution in sediments profile for all sampling stations in Sangga Besar river. Lau and Chu (2007), studying on the significance of sediment contamination in a coastal wetland Hong Kong, also revealed the enrichment of Zn in the upper sediment compared to the bottom sediment.

The adsorption of heavy metals by soil involves a series of complex chemical and biological interactions. The four major processes of metal retention include cation exchange, complex with organics, precipitation as oxides, oxyhydroxides and carbonates and precipitation as sulphides (Dunbabin & Bowmer, 1992). The last process is extremely important in mangrove swamp, because this ecosystem is subjected to periodic exposure to the air and submersion in water during a single tidal cycle which produces alternating aerobic and anaerobic conditions in the uppermost layer of the soil column. The lower layers are anaerobic. Under anaerobic environment, sulphate-reducing bacteria produce H_2S that may precipitate metal as metal sulphides. (Lacerda *et al.,* 1993). Furthermore sedimentation and coagulation of particulate and colloidal matter also result in metal fixation in bottom sediments (Dunbabin and Bowmer, 1992).

Table 4.10: Concentrations of Heavy Metals (mg kg^{-1}) in sediment Profiles from Sangga Besar River

		P5	P6	P7	P8
Cu	0-5	31.97 ± 2.96	26.96 ± 2.85	26.85 ± 3.05	24.40 ± 3.63
	5-10	37.57 ± 5.08	32.49 ± 5.87	15.41 ± 2.45	26.71 ± 2.04
	10-15	23.68 ± 3.65	29.36 ± 5.30	3.53 ± 0.53	34.90 ± 3.01
	15-20	24.34 ± 4.12	27.07 ± 1.29	2.44 ± 0.17	26.36 ± 2.03
Zn	0-5	84.44 ± 4.93	76.80 ± 6.27	59.74 ± 5.62	63.87± 3.41
	5-10	93.68 ± 13.00	82.85 ± 7.49	68.75 ± 5.78	76.05 ± 3.96
	10-15	81.40 ± 4.68	64.59 ± 7.32	57.97 ± 2.16	66.90 ± 2.28
	15-20	76.05 ± 1.35	60.43 ± 4.67	54.73 ± 1.69	65.51 ± 1.62
Pb	0-5	38.17 ± 4.25	43.41 ± 3.30	33.37 ± 3.23	24.74 ± 2.82
	5-10	41.72 ± 3.33	38.38 ± 4.28	50.68 ± 3.87	34.07 ± 4.94
	10-15	13.66 ± 1.90	36.43 ± 2.68	37.80 ± 4.33	29.84 ± 1.59
	15-20	16.46 ±2.53	37.43± 6.00	26.72 ± 2.70	29.66 ± 1.80
Cd	0-5	0.81± 0.18	2.34 ± 0.29	0.38 ± 0.04	1.08 ± 0.15
	5-10	1.36 ± 0.38	1.60 ± 0.17	0.89 ± 0.11	1.33 ± 0.24
	10-15	0.94 ± 0.39	1.26 ± 0.17	0.35 ± 0.05	0.17 ± 0.01
	15-20	1.22 ± 0.37	1.664 ± 0.24	0.34 ± 0.04	0.28 ± 0.16
Cr	0-5	36.88 ± 5.17	42.26 ± 6.27	29.89 ± 4.76	30.60 ± 2.95
	5-10	53.14 ± 4.68	56.19 ± 5.09	43.91 ± 4.73	40.79 ± 4.84
	10-15	30.95 ± 5.01	35.39 ± 4.10	23.72 ± 1.40	27.08 ± 4.01
	15-20	30.26 ± 1.26	42.06 ± 5.81	32.16 ± 4.62	34.74 ± 4.99

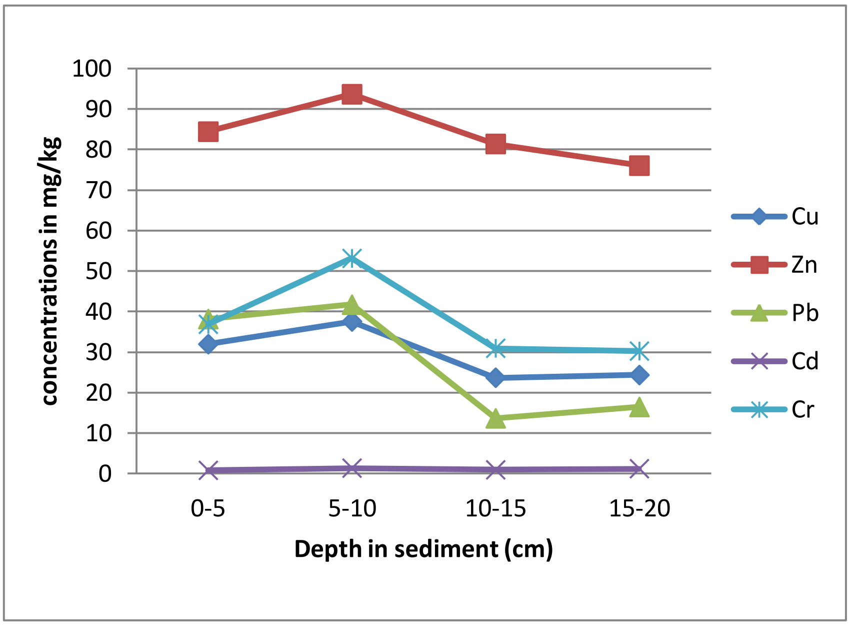

Figure 4.22: Heavy Metals profiles at P5

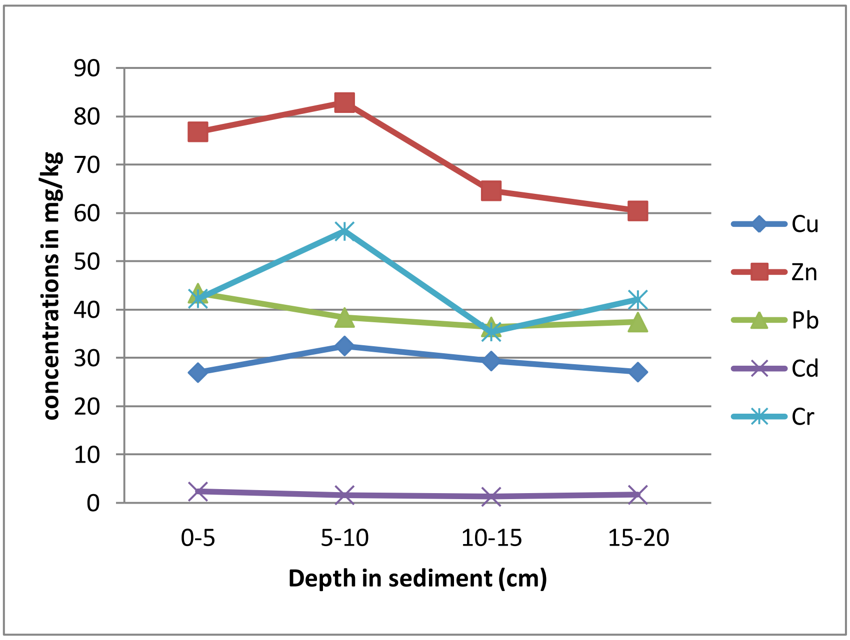

Figure 4.23: Heavy Metals profiles at P6

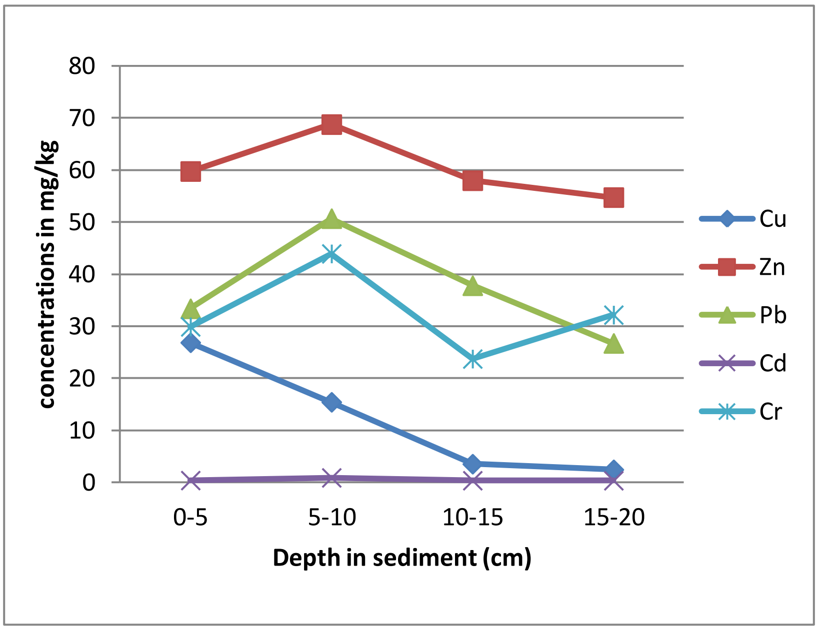

Figure 4.24: Heavy Metals profiles at P7

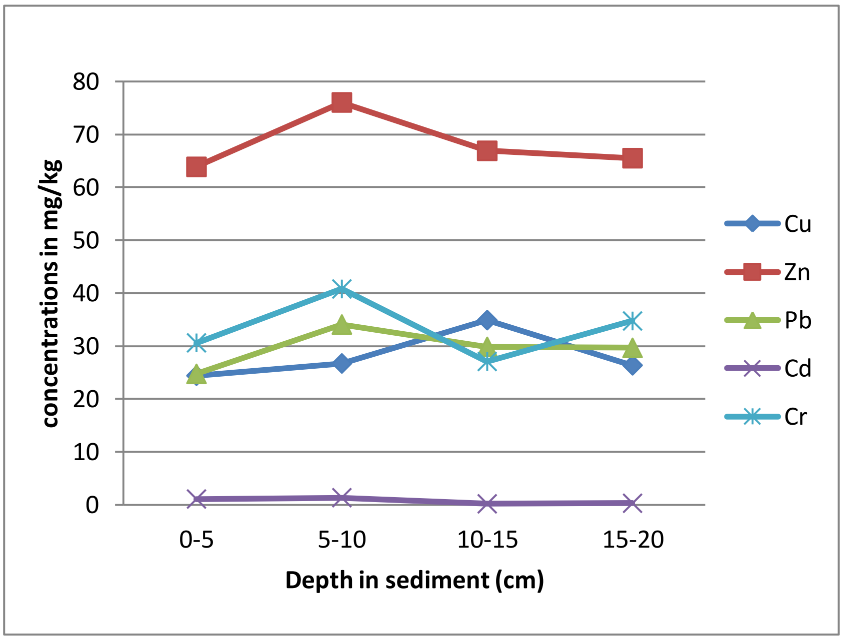

Figure 4.25: Heavy Metals profiles at P8

4.3.4 Correlation coefficient analysis in sediment

The correlation matrixes between heavy metals in sediments obtained from the two rivers were examined. The correlation data for Larut river and Sangga Besar river were presented in Tables 4.11 and 4.12, respectively. For Larut river a positive relationship was exhibited between Cr and Pb with Cu. For Sangga Besar river, Cr, Zn and Pb correlated positively with Cu. Other positive relationship was also found among Cd, Cr and Pb.

Table 4.11: Pearson correlation coefficient matrix between heavy metals in sediment of Larut river at sites P1-P4 (n=36)

	Cu	Zn	Cd	Cr	Pb
Cu	1				
Zn	-0.8842*	1			
Cd	0.2579	-0.4331*	1		
Cr	0.5077*	-0.4816*	-0.4055*	1	
Pb	0.5817*	-0.5711*	0.3272	0.2378	1

*Correlation is significant at 0.05

Table 4.12: Pearson correlation coefficient matrix between heavy metals in sediment of Sangga Besar river at sites P5-P8 (n=36)

	Cu	Zn	Cd	Cr	Pb
Cu	1				
Zn	0.5846*	1			
Cd	-0.0894	0.3574*	1		
Cr	0.3483*	0.6679*	0.6705*	1	
Pb	0.3965*	0.5940*	0.4809*	0.6970*	1

*Correlation is significant at 0.05

4.4 Metal concentrations in different aquatic species

From the results it was found that the content of metals varies among the species. This may be explained mainly in terms of the chemical forms of the elements, their concentrations in the local aquatic environment, microbiological activity and differences in fish size. Furthermore, different feeding habit of these fishes also contributes to the variation in metal accumulation (Adhikari *et al*., 2009).

In this study, a total number of 40-60 specimens of cockles (*Anadara granosa*) and prawns (*Penaeus merguiensis*) were collected from two rivers namely, Larut river and Sangga Besar river. The concentration of heavy metals in the cockles and prawns from two rivers were compared. The overall content of heavy metals in prawns and cockles were shown in Table 4.13. The content was expressed as mg kg^{-1} of dry weight. For Larut river, heavy metal contents in prawns and cockles were in the order: Zn>Pb>Cu>Cr>Cd and Zn>Cu>Cr>Pb>Cd, respectively. For Sangga Besar river the heavy metal contents in prawns and cockles were in the order: Pb>Cu>Zn>Cr>Cd and Zn>Cu>Pb>Cr>Cd, respectively.

Among all the heavy metals tested for Larut river and Sangga Besar river in both specimens, zinc content was found to be the highest (83.67 mg kg^{-1} and 67.82 mg kg^{-1} , respectively) and cadmium was the lowest (0.45 mg kg^{-1} and 1.63 mg kg^{-1}, respectively) as shown in figure 4.26 and 4.27. No previous data is available on heavy metals in prawns and cockles from this region. Based on the data, the content of metals varied within the estuarine marine species. Different species tends to accumulate different amount of heavy metals.

Table 4.13: Average content of Heavy Metals in tissue of prawns and cockles (mg kg^{-1} d.w)

Sampling site	Sample	Cu	Zn	Cd	Cr	Pb
Larut	prawns	29.05 ± 2.82	83.67 ±1.96	0.62 ± 0.26	13.33 ± 1.94	58.92 ± 4.36
River	cockles	19.70 ± 3.57	61.34 ± 8.51	0.45 ± 0.24	15.67 ± 2.10	6.11 ± 0.71
Sangga	prawns	37.3 ± 1.01	22.21 ± 3.55	1.63 ± 0.33	13.76 ± 1.32	43.03± 10.50
Besar river	cockles	31.54 ± 4.84	67.82 ± 6.51	1.81 ± 0.49	15.51 ± 2.38	3.33 ± 0.24

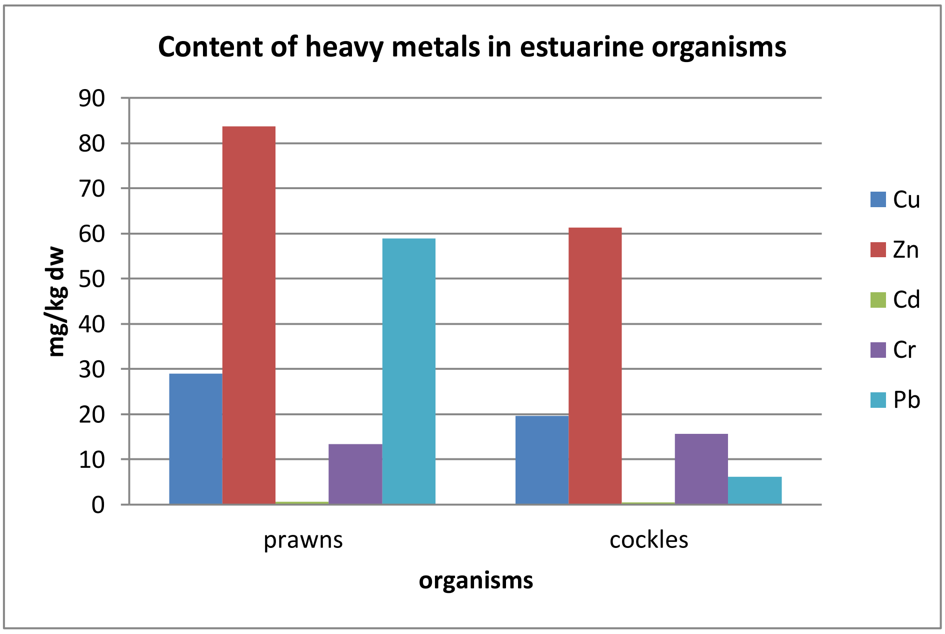

Figure 4.26: Content of heavy metals in estuarine organisms from Larut river

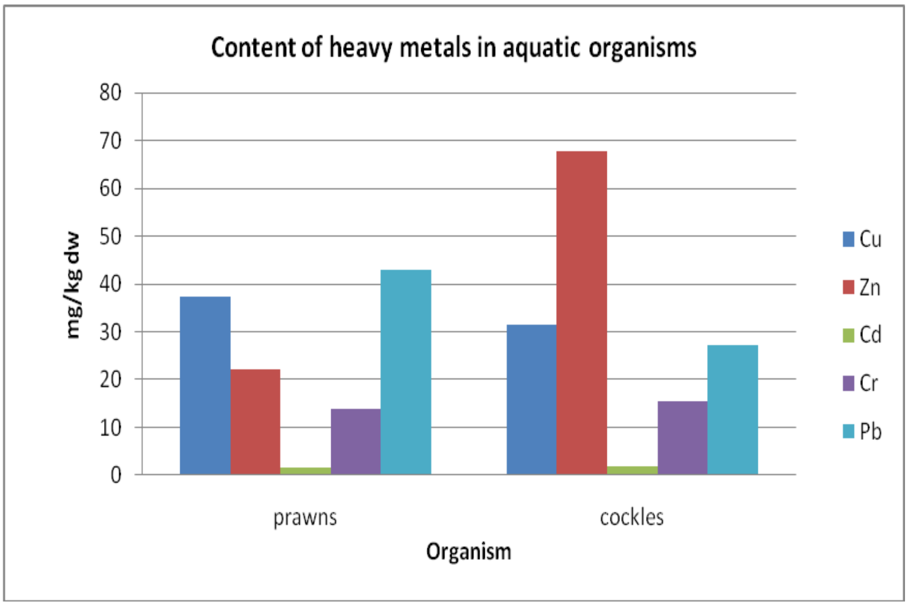

Figure 4.27: Content of heavy metals in estuarine organisms from Sangga Besar river

4.4.1 Heavy metals contents in various parts of prawns

The mean content and standard deviation of copper, zinc, cadmium, chromium and lead in the muscle, shells and heads of shrimp *Penaeus merguiensis* harvested from both from Larut river and Sangga Besar river were shown in Table 4.14.

Higher content of copper and zinc were observed in the head position of shrimp followed by shell and muscle. The content of Cu and Zn accumulation in tissues of shrimp were similar for both rivers. The concentration of copper in head, shell and muscle of shrimp from Larut river were 61.89 mg kg-^{1}, 31.45 mg kg^{-1} and 29.05 mg kg^{-1}, respectively (Figure 4.28). While in Sangga Besar river, the copper content was found to be 73.91 mg kg^{-1}, 47.06 mg kg^{-1} and 37.30 mg kg^{-1} in head, shell and muscle of shrimp, respectively (Figure 4.29).

High value of Pb was found in prawns from both rivers. This value in the tissues of prawns were higher than those reported by Awaludin *et al*. (1992) and Patimah & Dainal (1993). The study done by Mohd Ismail (2002) on trace metal concentrations in marine prawns off the Malaysian coast had reported most of the samples studied contained low metal concentrations, except for a few samples which were collected from Kuala Sepetang and Melaka on the west coast of Peninsular Malaysia. The high levels of certain metals in samples from Kuala Sepetang and Melaka may be related to elevated concentrations of metals in local sediments.

The prawn caught from Larut river had higher concentrations of Zn and Pb. On the other hand, prawns obtained from the Sangga Besar River exhibited higher levels of Cu, Cd and Cr. It is difficult to establish a general pattern of relationship between heavy metals in water and tissue of prawns. Obviously, Zn and Pb concentrations were higher in the water as well as prawns tissues in Larut river while Cr was higher in water and in tissues of prawn from Sangga Besar River. Other metals such as Cu and Cd existed as a higher concentration. However, these metals were found to be in lower amounts in the prawn tissues. Kang *et al.*, (1999) who worked on Asian periwinkles *Littorina brevicula*, noticed that certain toxic metals, Cd and Pb in the tissue, reflected environmental levels, whereas Cu and Zn were regulated by these marine gastropods.

Table 4.14: Mean concentrations and standard deviation in the muscle, shell and heads of prawn (mg kg^{-1} d.w)

Sampling sites	Sample	**Cu**	**Zn**	**Cd**	**Cr**	**Pb**
Larut River	muscle	29.05 ± 2.82	83.67 ± 2.66	0.62 ± 0.26	13.33 ± 1.94	58.92 ± 4.36
	shell	31.45 ± 0.86	69.86 ± 1.45	2.18 ± 0.48	29.38 ± 4.90	80.20 ± 5.33
	head	61.89 ± 5.52	92.30 ± 0.87	2.14 ± 0.72	39.42 ± 2.08	101.50 ± 1.28
Sangga Besar River	muscle	37.30 ± 1.01	22.21 ± 3.55	1.63 ± 0.33	13.76 ± 1.32	43.03 ± 10.50
	shell	47.06 ± 1.34	18.30 ± 3.44	4.08 ± 0.94	14.25 ± 0.99	46.66 ± 3.61
	head	73.91 ± 8.22	65.77 ± 9.93	2.69 ± 0.87	10.67 ± 0.77	34.35 ± 6.27
Iskanderum Bay Turkey (Penaeus semisulcatus 2007)	muscle	27.18 ±10.75	6.74±2.27	-	8.97±3.02	0.41±0.17
Awaluddin et al. 1992	muscle	12.8-159	-	1.6-6.1	-	4.6-32

In Turkey, study done by Yilmaz, A. B. and Yilmaz, L. (2007) found that heavy metal content varied with types of metal, seasons and sex. Accumulation of different metals also differed significantly in certain organs. The metals content was found to be the highest in male gonad whereas the metal contents in the muscle of all shrimp species were found to be the lowest.

The correlations of heavy metal contents in tissue of prawns were examined. For Larut river, Cu and Zn were negatively correlated while other heavy metal contents did not show significant relationship between them. For Sangga Besar river, a strong positive relationship was exhibited between Cd and Cu. No significant relationships were found for other heavy metals

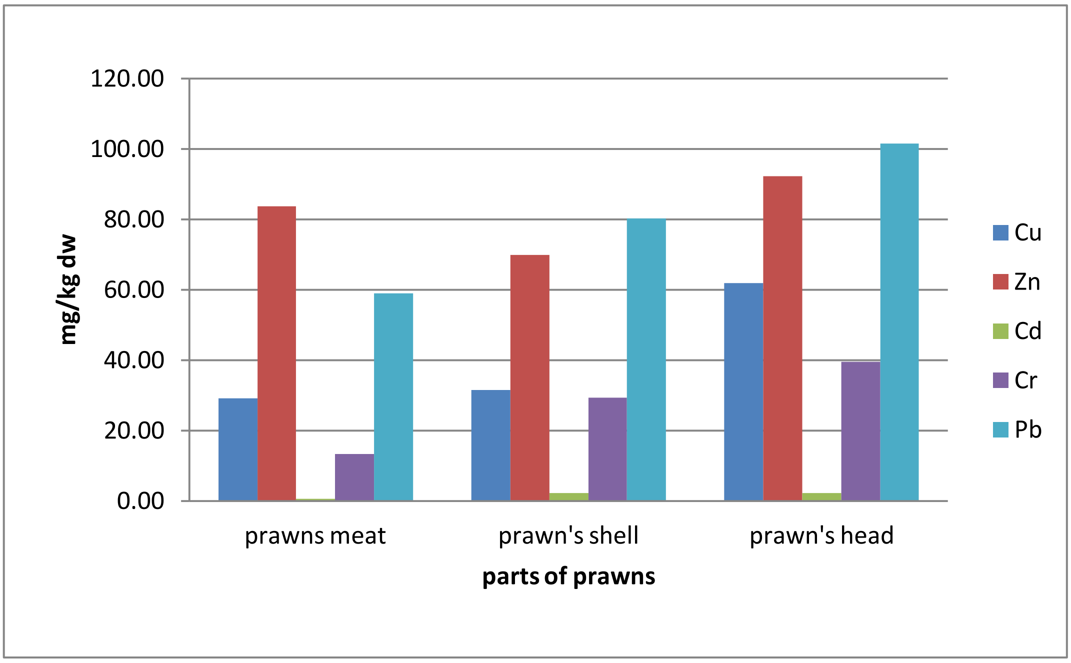

Figure 4.28: The content of heavy metals in the prawn harvested from Larut river

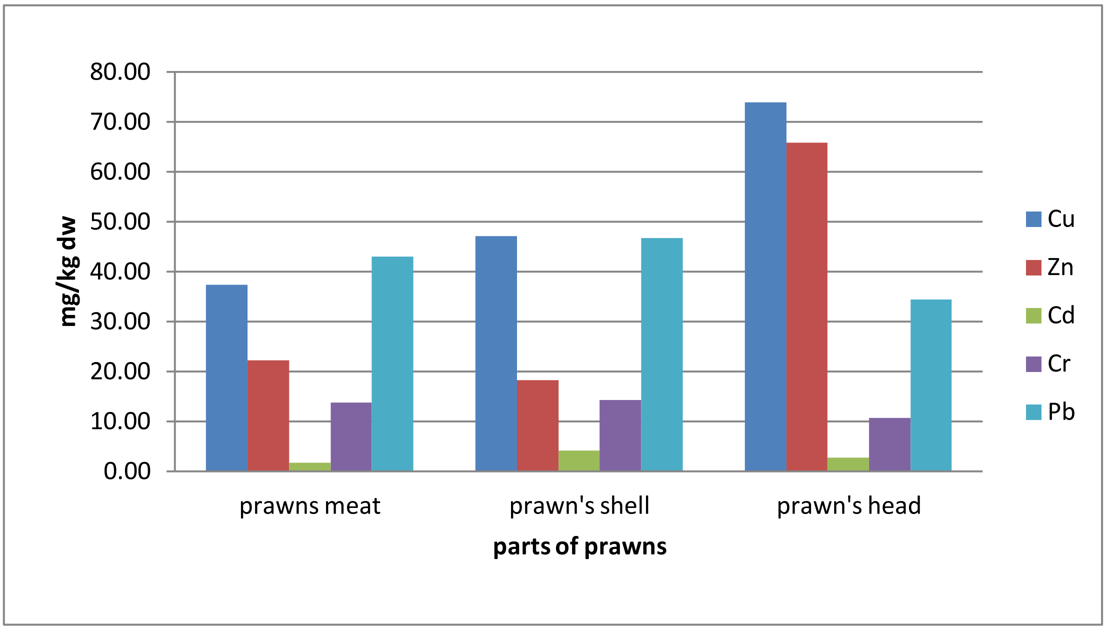

Figure 4.29: The content of heavy metals in the prawn harvested from Sangga Besar River

4.4.2 Heavy metal contents in cockles (*Anadara granosa*) species

The mudflats adjacent of the Matang Mangrove Forest are suitable cultural areas for cockle production. The soft flocculent mud of at least 45-75cm thick and salinity level of 18-30ppt are ideal for cockle culture. The Matang Mangrove Forest Reserve produces about 50% of the cockles in Malaysia. The scientific name of cockles is *Anadara granosa.* It is a bivalve mollusc in the family Arcidae, subfamily Anadarinae. The bivalves in this family are of considerable importance as a source of cheap protein and iron in tropical areas, especially in the Indo-Pacific. Since *Anadara granosa* is a filter feeding organism, contamination of heavy metals in the highly productive mudflats may be absorbed and accumulated in the whole body tissue.

Zinc was shown to be present at the highest content harvested from both rivers with the average values of 61.34 mg kg^{-1} and 67.82 mg kg^{-1} dry weight for Larut river and Sangga Besar river, respectively. This was followed by Cr and Pb while Cd showed the lowest content in cockles from both rivers. It was found that zinc recorded the highest concentrations of heavy metals in cockles for both rivers. It was found that zinc content in *meretrix meretrix roding* from Likas estuary, Sabah were in the range 50.3-223.6 mg kg^{-1} dry weight. Filter feeding bivalve molluscs are generally shown to accumulate highest level of Zn from the marine environment. Although zinc is not particularly toxic to humans, the levels in some seafoods may be high enough to be harmful. For this reason, the National Health and Medical Research Council have specified a maximum zinc concentration of 1000 µg/g (wet weight) in molluscs and 150 µg/g in other seafoods. The mean value of Zn in A. *granosa* in the present study was also found to be within the mean content observed in the previous study on heavy metals in the bivalve *Anadara senilis (Senilia)* from Nigeria (Joiris *et al*., 1999).

A. *granosa* has accumulated cadmium in the range of 0.25-0.73 mg kg^{-1} and 1.11-2.56 mg kg^{-1} dry weight from Larut river and Sangga Besar river, respectively. There are many reports of aquatic organisms accumulating cadmium. This is particularly true of molluscs which appear able to accumulate quite high concentrations. The mean content of Cd in the cockles harvested from both rivers were slightly lower than that of Kuala Selangor (Maah *et al*., 1994). The content of cadmium in cockles harvested from Kuala Selangor (5.2 mg/kg) were two orders of magnitude higher than those obtained from the Matang mangrove forest.

The mean content of Cr in A. *granosa* for both rivers were almost similar (15 mg kg^{-1} d.w). The mean content was slightly higher than those mean content obtained in *meretrix meretrix roding* another bivalve species from Likas estuary. These aquatic organisms might be exposed to chromium through ambient water, sediment and food. Toxic effects may occur when excretory, metabolic, storage and detoxification mechanisms are no longer capable matching uptake rates.

The mean content of Pb in *A. granosa* harvested from both rivers was very much lower than that had been reported in other various bivalve spp. (Table 4.15). The mean content of 6.11 mg kg^{-1} dry weight of Pb in cockles from Larut river and 3.33 mg kg^{-1} dry weight of Pb in cockles from Sangga Besar river were obtained in this study. The industrial and other anthropogenic activities in the surrounding areas are always positively associated with the elevated level trace metals, such as Pb in marine or estuarine biota. Molluscs can accumulate lead in two ways, directly from the water and from food such as algae.

Table 4.15: Mean heavy metal concentrations in cockles from Matang Mangrove comparison with literature data

Origin (River)	Species	Cu	Zn	Cd	Cr	Pb	Reference
Larut River	*Anadara granosa*	19.70±3.57	61.34±8.51	0.45±0.24	15.67 ±2.10	6.11±0.71	This study
Sangga Besar River	*Anadara granosa*	31.54±4.84	67.82±6.51	1.81±0.49	15.51±2.38	3.33±0.24	This study
Juru	*Anadara granosa*	-	205.2±19.6	-	3.58±0.93	-	Noorddin Ibrahim (1995)
Bonny River estuary, Nigeria	*Anadara senilis*	5.45±2.00	76.40±12.63	0.16±0.05	-	0.19±0.03	Joiris & Azokwu (1999)
Curimatau estuary, Brazil	*Anadara ovalis*	6.61±0.09	79.3±2.5	1.35±0.01	-	-	Silva *et al*. (2006)

4.4.3 Heavy metal contents in various organ of fishes

The content of Cu, Zn, Cd, Pb and Cr were expressed in mg kg^{-1}, wet tissue for liver, skin, gills and muscle of *Scaptophagus argus* fish species as shown in Table 3.0. The distribution pattern of Zn, Cd, Cr and Pb in *Scaptophagus argus* follows the order: skin> liver>gills>muscle while Cu follows the sequence: liver>gills>skin>muscle. Higher content of metals was found in liver, skin and gills while lower content was detected in muscle tissues. This brief pattern of the accumulation behavior of metals in fish shows very distinctly that the liver, skin and gills may accumulate heavy metals at a faster rate than muscle tissue. Due to functional difference between the organs, the relative accumulation values can vary depending on the types of metal present in the water. For certain elements, the liver is a better indicator of an elevated metal load, while for others it is the skin (Galindo *et al.*, 1986). In aquatic systems, metal ions or compounds in solution are available for biota by adsorption on the surface of organisms and by translocation into the cells. One of the most important pathways is the uptake through the skin and gills.

Liver tissues in fish are often recommended as an environmental indicator of organism of water pollution as compared to any other fish organs. This is because liver tends to accumulate various kinds of pollutants from the environment at a higher concentration as previously reported by Galindo *et al*. (1986). The accumulation of heavy metals in liver could be based on the greater tendency of the elements to react with oxygen carboxylate, amino group, nitrogen and sulphur of the mercapto group in the metallothionines protein which is at the highest level in liver (Kendrick *et al*. 1992, El-shahawi, 1996). Liver also plays an important role in contaminant storage, redistribution, detoxification or transformation. Liver acts as an active site of pathological effects induced by contaminants. Yilmaz *et al*. (2007) found higher content of Cu, Cd and Pb in the liver of fish from Saricay, South-West Anatolia, Turkey.

Gills are central in the uptake of dissolved substances from the water and thus may also uptake some of dissolved components of heavy metals, such as Cd, Cu and Zn (Soto *et al*., 2003). The highly branched structural organization of the gill and the resultant highly increased surface area, along with the large volume of water passing through the gill surface and the highly vascular physiological state and relatively small biomass when compared to their surface area (Mayer *et al*., 1991) make the gill a prime site for trace metals accumulation. The content of metals in gills could be due to the element complexing with the mucus, which is impossible to remove completely from between the lamellae, before tissue is prepared for analysis. Thus, high concentrations of certain metals can be observed in gills (Yilmaz *et al*., 2007). The content of metals in gills often reflects the concentrations of metals in the waters where the fish live.

In general, relative accumulation of zinc in tissue was in the order of liver>gills>skin>muscle. The results supported the opinion that the main route of zinc entry is through water. The lowest zinc concentrations were found in muscle. In other study, the content of zinc was reported to be the lowest in muscle (Birungi *et al*., 2007) The mean content of Zn was slightly lower than the legislative limits (100 mg kg^{-1}, wet weight) stated in the Malaysian Food Act 1983 and Food Regulations 1985 Fourteen Schedule.

The high content of copper in liver (3.29 mg kg^{-1} w.w) may be due to the binding of copper to metallothioneins which serves as a detoxification mechanisms (Birungi *et al*., 2007). The specific metabolism process, and the enzyme catalyzed reaction taking place in liver involving Zn, Cu and Cd may also account for this behavior. In liver, the copper content is in a good agreement with the result reported by Al Yousuf *et al*. (2000). They reported that the average copper level in skin, muscle, gills and liver were found to be 0.90 ± 0.08, 0.19 ± 0.026, 2.16 ± 0.05, 3.29 ± 0.01, respectively.

The average content of heavy metals was tabulated in Table 4.16 together with the Malaysian Food Act 1983 and Food Regulations 1985 Fourteen Schedule. The average content of Cu in muscle tissues was 0.19 mg kg^{-1} wet weight. This value was very much lower than the permissible limit (30 mg kg^{-1}, wet weight) established by the Malaysian Food Act 1983 and Food Regulations 1985 Fourteen Schedule. The content of heavy metals in fish muscle was much lower than that reported in various species from Portugal and Luxembourg (Pereira *et al*., 2010 and Boscher *et al*., 2010).

Bioconcentration factor (BCF) was calculated in order to characterize the accumulation of heavy metals through chemical partitioning from water into fish tissues. Tissues with BCF greater than 1,000 considered high, and under 250 considered low, with those between classified as moderate. The results found that BCF for all the elements are below 250 (Table 4.16).

Very significant content of Pb (six times higher) was found in liver, gills and skin of *Scaptophagus argus* harvested from Matang. The Pb content in various fish tissues was in the range 0.50-3.53 mg kg^{-1}, wet weight. However in muscle tissues, the mean content was 0.50 mg kg^{-1}, wet weight and was very much below the permissible limit of the Malaysian Food Act 1983 and Food Regulations 1985 Fourteen Schedule. The accumulation of lead in different fish species has been reported in the international literature.

The cadmium content in fish is of considerable interest because fish consumption is an important source of cadmium for general population. Most of the cadmium content in fish or other seafood is highly absorbable in $CdCl_2$ form. In humans, the efficiency of gastrointestinal absorption of cadmium has been reported to be approximately 3-8% of the ingested load. Cadmium is particularly accumulated in kidney whereas in muscle the concentrations remain low (ATSDR, 2003). Cadmium has a long biological half-life from 17 to 30 years in humans. It affects adversely a number of organs and tissues such as kidney, heart and brain.

Several studies have demonstrated the variability in concentrations of cadmium in fish. In river Neretva Croatia, the concentration of cadmium is high in the kidney of carp, sval and mullet. This study indicates that liver tends to accumulate cadmium. (Has-Schon et *al*., 2006). High concentration of cadmium was found in liver, gills and muscles in samples fish (*Mugil cephalus* and *Mallus barbatus*) from the Mediterranean Sea (Cogun et al., 2006).

Muscle was found to contain the lowest concentration of heavy metals among all tissues investigated in the study. According to Miller *et al*., 1992, muscle was a poor indicator of low level copper and zinc contamination. Muscle does not come into direct contact with the metals as it is totally covered externally by the skin. It is not an active site for detoxification and therefore transport of trace metals from other tissues to muscle does not seems to arise (Adhikari *et al.*, 2009).

Table 4.16: Average content of heavy metals in fish (*Scaptophagus Argus*) obtained from Matang mangrove with comparison to the Malaysian Food Act 1983 and Food Regulations 1985 Fourteen Schedule in mg/kg, wet weight.

	Cu	**Zn**	**Cd**	**Cr**	**Pb**
Skin	0.90 ± 0.08	15.88 ± 0.71	0.56 ± 0.11	7.53 ± 1.02	3.53 ± 0.24
Muscle	0.19 ± 0.026	3.19 ± 0.26	0.14 ± 0.02	1.46 ± 0.13	0.50 ± 0.17
Gills	2.16 ± 0.05	4.05 ± 0.08	*nd*	3.54 ± 0.38	3.31 ± 0.30
Liver	3.29 ± 0.01	4.06 ± 0.08	*nd*	5.67 ± 0.38	3.45 ± 0.12
BF	6	100	46	31	17
Malaysian Food Act Standard	30	100	1	Not mentioned	2

nd- not detected, BF- *bioconcentration factor*

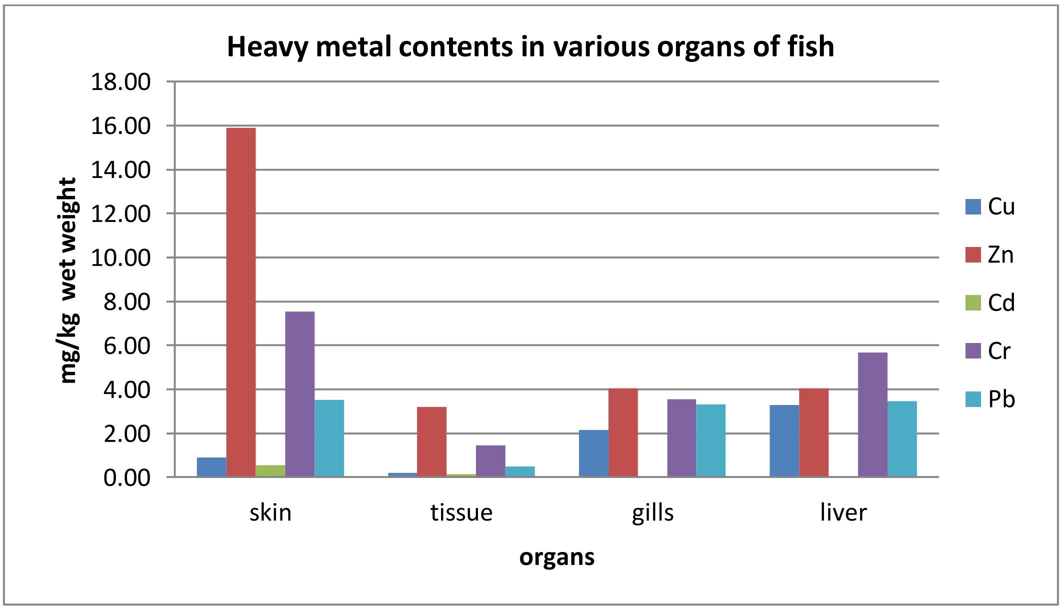

Figure 4.30: Heavy metals content in various organs of fish (*Scaptophagus Argus*)

4.4.5 Correlation coefficient analysis in tissues of fish

The correlations of heavy metal contents in various tissues of fish organs were examined. The heavy metal correlation data were presented in Tables 4.17-4.20 for skin, muscle, gills and liver, respectively. For skin, a strong positive relationship was exhibited between Cd and Cr, while Cu and Cd were significantly negatively correlated. Zn and Cd also showed positive relationship while Cu and Zn exhibited negative correlation. Other heavy metals content in skin did not show significant relationship between them. In muscle, a correlation matrix shows that the Zn, Pb and Cu are highly correlated with each other showing a strong positive association. Other significant relationship was shown between Pb and Zn in gills while Cr correlated with zinc negatively in liver.

Table 4.17: Linear correlation coefficient for heavy metals in skin (n=9)

Metal	Cu	Zn	Cd	Cr	Pb
Cu	1				
Zn	-0.79094*	1			
Cd	-0.9194*	0.779266*	1		
Cr	-0.71951*	0.529219	0.883458*	1	
Pb	-0.12787	-0.16833	-0.15393	-0.03295	1

* Correlation is significant at the 0.05

Table 4.18: Linear correlation coefficient for heavy metals in muscle (n=9)

Metal	Cu	Zn	Cd	Cr	Pb
Cu	1				
Zn	0.913961*	1			
Cd	-0.90799*	-0.87567*	1		
Cr	0.538139	0.353056	-0.22849	1	
Pb	0.99382*	0.912516*	-0.86221*	0.57878	1

* Correlation is significant at the 0.05

Table 4.19: Linear correlation coefficient for heavy metals in gills (n=9)

Metal	Cu	Zn	Cr	Pb
Cu	1			
Zn	0.464261	1		
Cr	-0.51665	-0.66684*	1	
Pb	0.606598	0.946887*	-0.63643	1

* Correlation is significant at the 0.05

Table 4.20: Linear correlation coefficient for heavy metals in liver (n=9)

Metal	Cu	Zn	Cr	Pb
Cu	1			
Zn	0.216922	1		
Cr	-0.59925	-0.89296*	1	
Pb	-0.29785	0.326462	-0.10001	1

*Correlation is significant at the 0.05

CHAPTER 5

CONCLUSION

Heavy metals constitute a significant potential threat to human health because they are associated to many adverse effects on health (Castro-Gonzales and Mendez-Armenta, 2008). The heavy metals from industries and agriculture from the Sepetang river basins may pollute the estuarine water and sediments in the Matang Mangrove Forest. The Matang Mangrove Forest produces large amount of marine and estuarine resources such as fish, prawns and cockles. Therefore, it is very important to investigate the content of heavy metals in water, sediments, fish, cockles and prawns to ensure the safety levels for human health.

The concentrations of heavy metals in water, sediment and tissue of fish, prawns and cockles from Larut river and Sangga Besar river were investigated in this study. Concentrations of heavy metals were compared with the guideline values and certain elements were found to exceed the guidelines value.

In surface sediments, the concentration of Zn was higher compared with that of other heavy metals. The heavy metals distribution in sediment profiles showed variations between the elements, between the sampling stations and between depths. Overall, the concentrations of all heavy metals were higher in the top sediments compared to the bottom sediments from both rivers. By comparing the results of this study with other areas in Malaysia as well as other parts of the world, the concentrations of heavy metals in sediments from Matang mangrove, were still within the range.

In the tissue of fish (*Scaptophagus argus*), the accumulation of zinc, copper, chromium and cadmium in liver tissue were found high compared to gills and muscle tissues. The concentration levels of the elements reported in this present study do not constitute a risk factor for human health and appear to be below the permissible limits issued by FAO.

In cockles concentrations of metals were in the order of Zn>Cu>Cr>Pb>Cd. Zinc was shown to be present at the highest content in cockles obtained from both rivers. In prawns species of *Penaeus merguiensis*, results showed that zinc content was the highest in various tissues followed by copper, chromium, lead and cadmium. The accumulation of copper and zinc in prawn's head of *Penaeus merguiensis* were found high compared to shell and muscle. The concentration levels of the element as reported in this study appear to be below the permissible limits for human consumption.

In order to have sustainable growth of marine estuarine bio-resources as well as active aquaculture activities, the water quality at upstream of the Matang Mangrove forest, such as Larut and Sangga Besar river basins must be well managed to maintain at an average or good level of water quality. Furthermore, selected water sampling points in the Matang Mangrove Forest should be monitored to ensure that fish, prawn and cockles produced in this estuarine environment are suitable for human consumption. In addition, these marine produces will certainly generate huge annual income for the State of Perak and Malaysia as well as the people living near the coastal areas. The results of this study provide valuable information about the metal contents in water, sediment and tissue of fish, prawns and cockles from various sampling sites in Larut and Sangga Besar river.