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CADMIUM, CHROMIUM, COPPER, LEAD, FERUM AND ZINC LEVELS IN THE COCKLES (*Anadara granosa*) FROM KUALA SELANGOR, MALAYSIA

(Tahap Kadmium, Kromium, Kuprum, Plumbum, Ferum dan Zink di dalam Kerang (*Anadara granosa*) dari Kuala Selangor, Malaysia)

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Abstract

The aim of this study is to provide information on the concentration of metals in cockles (*Anadara granosa*) from Kuala Selangor, Malaysia. Cockles in this study area were taken by local people as part of their diet, therefore necessary to determine metal concentrations in the cockles. Sample collection activity was conducted at Kuala Selangor (03°20'N - 101°15'E) between the month of March, and April 2012. About two kilograms of samples were purchased from local fish market at Kuala Selangor. The concentration of Cd, Cr, Cu, Pb, Fe and Zn in the samples were analysed using Inductively Coupled Plasma Optical Emission (ICP-OES). The observed mean concentration of Cd, Cr, Cu, Pb, Fe and Zn is 1.48 ± 0.33, 1.43 ± 0.91, 15.78 ± 5.28, 1.11 ± 0.46, 875.55 ± 343.43 and 94.17 ± 7.91 mg/kg respectively. From the public health point of view, these metal concentrations were below the maximum permissible levels set by the Malaysian Food Act (1983) and Regulations (1985). Therefore, cockles from Kuala Selangor are safe for human consumption.

Keywords: Kuala Selangor, Heavy Metals, *Anadara granosa*, ICP-OES

Abstrak

Tujuan kajian ini dijalankan, adalah untuk memberi maklumat terhadap kepekatan logam berat di dalam kerang di Kuala Selangor, Malaysia. Kerang di kawasan ini telah digunakan oleh penduduk setempat sebagai sebahagian daripada makanan mereka. Oleh itu, adalah perlu untuk menentukan kepekatan logam berat di dalam kerang. Aktiviti persampelan dijalankan di Kuala Selangor diantara bulan Mac dan April 2012.Sebanyak dua kilogram sampel telah dibeli daripada penjual di pasar tempatan di Kuala Selangor. Kepekatan Cd, Cr, Cu, Pb, Fe dan Zn di dalam sampel telah dianalisis dengan menggunakan kaedah Spektrometer Plasma Gandingan Aruhan Pancaran Optik (ICP-OES). Purata kepekatan yang didapati bagi Cd, Cr, Cu, Pb, Fe dan Zn adalah1.48 ± 0.33, 1.43 ± 0.91, 15.78 ± 5.28, 1.11 ± 0.46, 875.55 ± 343.43 dan 94.17 ± 7.91 mg/kg masing-masing. Dari pandangan sudut kesihatan untuk orang awam, kepekatan logam berat adalah di bawah tahap bahaya yang telah ditentukan oleh Akta Makanan Malaysia (1983) dan Peraturan (1985). Oleh itu, kerang dari Kuala Selangor adalah selamat untuk di makan.

Kata kunci: Kuala Selangor, Logam Berat, *Anadaragranosa*, ICP-OES

Introduction

Anadara granosa is a major cockle species and important protein source in Southeast Asia that is commercially cultured in the tidal mudflats along the western coast of Peninsular Malaysia. This cockle is a good revenue source for the local population [1]. An investigation of global contaminant patterns in this oceanic organism is required, especially for this region of Malaysia. Kuala Selangor is a coastal town about 70 km away from Kuala Lumpur, perched next to a large river mouth that feeds into the sea. Hence, its name means 'Confluence of the Selangor River'. Once Kuala Selangor was the centre for a tin mining industry that helped defines the early history of Malaysia. For this reason, Kuala Selangor was chosen as a study area. The location is shown in Figure 1 below.

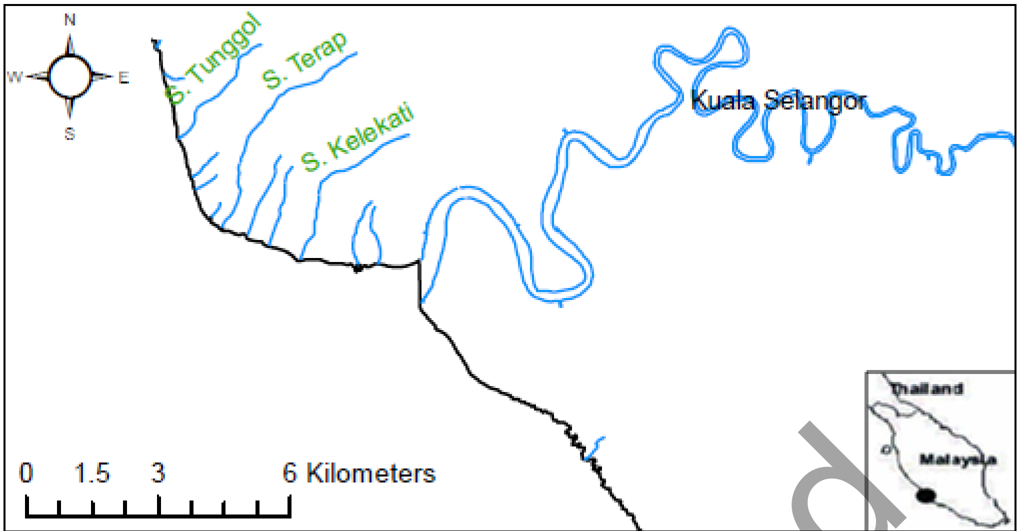

Figure 1. Location of study area

Heavy metal is defined as metallic chemical element that has a relatively high density and is toxic even at low concentrations. The common heavy metals that can be found in the cockles are Pb and Cd [2]. The presence of these heavy metals in the environment, especially aquatic ecosystems, could lead to health problems if being consumed by living organisms such cockles over a long period of time. The metals in the aquatic biota such as cockles are in constant interaction with the metals in the surface water, suspended matter, sediment and the interstitial water [3]. The data from this study will be used as a reference for future research on determination of source of heavy metals in cockle from Kuala Selangor (03°20'N - 101°15'E).

Materials and Methods

Sample Collection

Sample collection was conducted at Kuala Selangor between the months of March - April 2012. Two kilograms of samples were purchased from local fisherman, and were kept in a refrigerator at temperature below 4^{o}C to reduce all the activities and metabolism of the organism in the water.

Sample Preparation

The cockles were grouped into four ranges of sizes (A, B, C and D). Sample A with size range below 25 mm, sample B with size range from 25 to 30 mm, sample C with size 30 to 40 mm and sample D for size greater than 40 mm. Total of 20 similar size samples were separated from all cockles samples. Prior to analysis, cockle samples were cleaned with running tap water to remove the sand particles. Cockles' tissues were separated from the shell and washed with deionised water [4]. All the samples were made in triplicate and kept in oven at 60 ºC until a constant weight was obtained [5].

Sample analysis

A constant weight of 0.5 g dried tissue was weighed and transferred to the beaker for acid digestion process. Blanks was digested in beakers containing 8 mL of concentrated HNO_3 (65 % A.R. Grade) overnight digestion. After digestion was complete, the solution was cooled at room temperature then the solution was filtered using cellulose filter paper (0.45 µm). Deionised water was added until it reached 100 mL mark of volumetric flask. This solution was stored in plastic bottles at temperature 4°C until analysis was performed to determine the contents of heavy metals (Cu, Fe, Zn, Cd, Cr, and Pb) in the sample. The working standard solutions are from 0.05 to 5 ppm. Then, the heavy metal concentrations in cockles were determined by using ICP-OES.

Results and Discussion

Heavy metals contents

Sizes of 4 samples that were analysed in this study are shown in Table 1. The concentration of metals in the cockles is summarized in Figure 1. Knowledge on the living habitats is very important as it may represent the basis for the accumulation of heavy metals and other trace metals in bivalves.

Table 1. List of samples blood cockle (*Anadara granosa*) with narrow range of weight and length

Sample	Length (mm)	Width (mm)
A	21.1 - 24.6	15.0 – 18.3
B	23.1 – 27.9	18.2 – 20.8
C	34.0 – 38.5	21.5 – 28.9
D	33.0 – 39.5	25.0 – 31.0
E	40.0 – 49.0	29.0 – 38.0

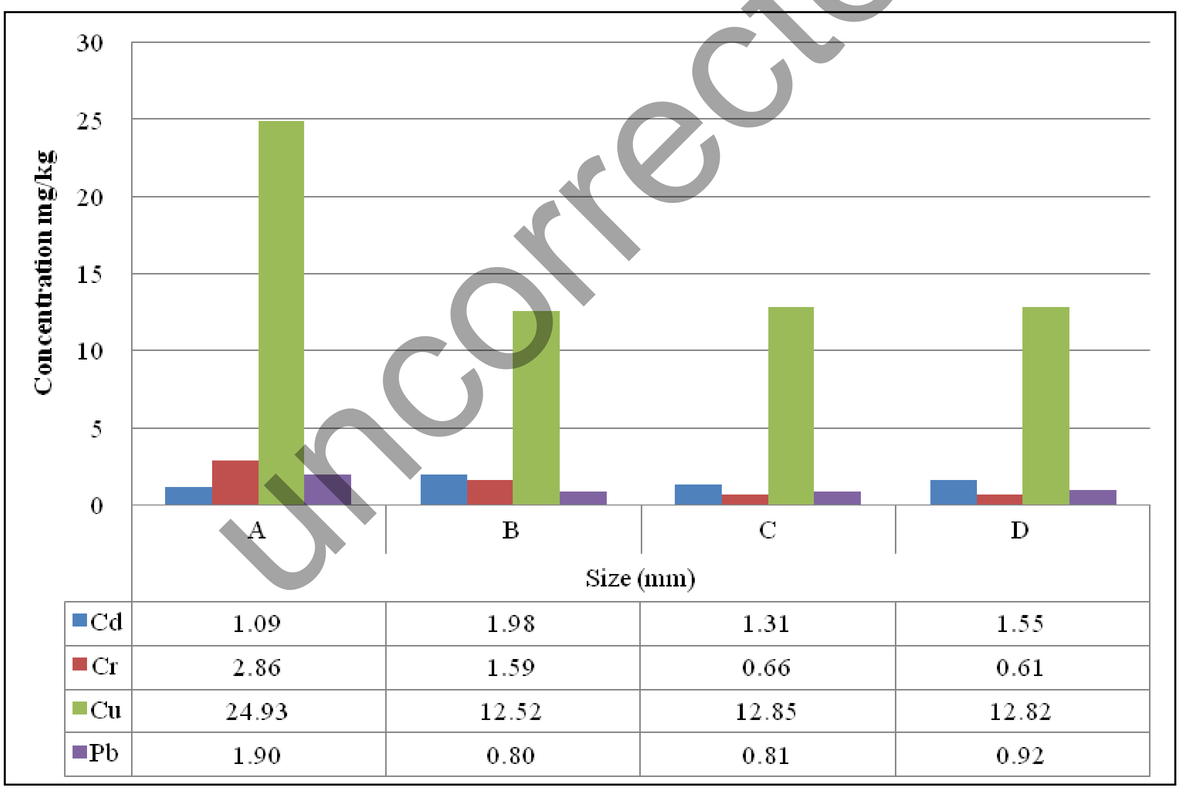

Figure 2. Concentration of Cd, Cr, Cu and Zn in cockles

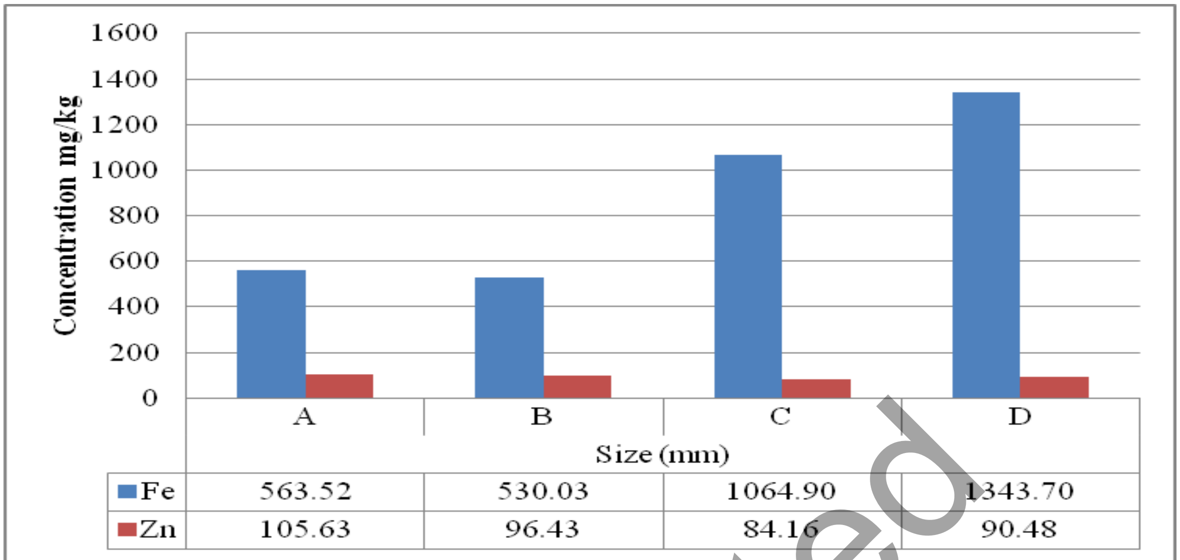

Figure 3. Concentration of Fe and Zn in cockles

Cadmium

Concentrations of Cd in this study are 1.09, 1.98, 1.31 and 1.55 mg/kg for samples A, B, C and D, respectively. The average concentration of Cd in all samples is 1.48 ± 0.38 mg/kg. The highest concentration of Cd was found in sample size between 25 to 30 mm with concentration of 1.98 mg/kg. The lowest concentration of Cd in this study is in sample size less than 25 mm or sample A, with concentration 1.09 ± 0.19 mg/kg. All samples were exceeding the permissible level set by Malaysian Food Act 1983and Regulation 1985 and FAO/ WHO 2004. The limit for Cd set by Malaysian Food Act 1983 and Regulation 1985 is 1.00 mg/kg and for WHO/FAO is 0.05 mg/kg.

Table 3 shows the comparison concentration of heavy metals in blood cockles from previous study. The concentration of Cd from previous study was range from 0.20 to 6.90 mg/kg [4, 6, 7, 8]. The highest reported concentration of heavy metal in blood cockles in the range of 8.25 - 12.20 mg/kg was reported by [4 and 9]. In this study the concentration of Cd in blood cockle is almost the same with others researcher [2, 6, 7, 8].

Figure 2 shows distribution of Cd in cockles' sample. The concentration of Cd is the highest due to the ability of Cd that can accumulate in shellfish in the form of Cd binding peptides [9]. Human activities may contribute to the higher level of Cd in the cockles. Cockles' aquaculture area is located near estuaries which receive sewage and waste deposits from the mainland [4]. Cd is present in rock and soil along with other metals.

Chromium

The concentration of Cr in sample A, B C and D is 2.86, 1.59, 0.66 and 0.61 mg/kg respectively. The average concentration of Cr in blood cockle is 1.43± 1.05 mg/kg. The highest concentration of Cr in this study is in sample A or sample length below 25 mm, the concentration is 2.86 mg/kg. The lowest concentration of Cr in blood cockles in sample D or sample size 30 to 40 mm, with concentration of Cr is 0.61 mg/kg. The concentration of Cr is decreasing with an increasing of blood cockle size. Malaysian Food Act 1983 and Regulation 1985 and WHO/FAO 2004 did not set any limit for Cr in bivalves. However, IAEA – 407 was reported that a permitted level for Cr in the marine organism is 0.73 mg/kg base on this permitted limit level all the samples were higher from the permissible level. Even though Cr level is slightly higher from limit set by IAEA-407, it still safe to consume.

Concentration found in this study is lower from other reported research [2,4 and 8]. The range of Cr in previous study is 0.18 to 9.80 mg/kg [2, 4, and 8]. The highest of Cr was found is 4.25 to 9.80 mg/kg. The highest concentration of Cr in Kuala Selangor might come from fertilizer from agriculture industry, emission from motor vehicle, steam generation power plant and from basic steel work foundries. All these industries are located near to Kuala Selangor region.

Copper

The concentration of Cu in cockles is 24.93, 12.52, 12.85 and 12.82 mg/kg for sample A, B, C and D respectively. The average concentrations of Cu in all blood cockle samples are 15.78 $\pm$ 6.10 mg/kg. The highest concentration of Cu in blood cockles in sample with length below 25 mm or sample A with concentration 24.93 mg/kg. While the lowest concentration of Cu in blood cockles is in sample size 25 to 30 mm or sample B with concentration 12.52 mg/kg. The entire sample is below the permitted level set by Malaysian Food Act 1983 and Regulation 1985 and WHO/FAO. The Cu concentration limit set by Malaysian Food Act 1983 and Regulation 1985 and WHO/FAO is 10 and 30 mg/kg respectively.

In this study the concentration of Cu is in the range of 8.48 - 24.93 mg/kg. The concentration of Cu in this study is higher compared to the others reported results [7, 8, 10-12]. Most of the researchers reported the range of Cu is 2.44 – 16.28 mg/kg [7, 8, 10-12]. The higher concentrations of Cu in Kuala Selangor samples might probably due to existing activities such as loading and offloading of fishes, cleaning and maintenance of boats, antifouling paint applications, and fuelling the crafts. Figure 1 shows distribution of Cu in cockle soft tissue.

Lead

The concentrations of Pb in cockles are 1.90, 0.80, 0.81 and 0.92 mg/kg for sample A, B, C and D respectively. The average concentrations of Pb in all cockles sample are 1.11 $\pm$ 0.53 mg/kg. The highest concentration of Pb is in sample A or shell length less than 25 mm, with concentration 1.90 mg/kg, while the lowest concentration of Pb in blood cockle is in sample B or shell length between 25 to 30 m, with concentration 0.80 mg/kg. The permitted concentration of Pb set in the Malaysian Food Act (1983) and Regulation (1985) is 2 mg/kg while WHO/FAO (2004) is 1.5 mg/kg. Only sample A exceed the permitted level set by WHO/FAO 2004, others sample is within the limit set by the WHO/FAO 2004. The results of this study show all sample have concentration of Pb below the concentration limit set by the Malaysian Food Act 1985. All samples are safely to consume because the range of Pb concentration in the cockles below the permitted limit set by Malaysian government.

The concentration of Pb in this study is in the range of 0.80 - 1.90 mg/kg. Most of the researchers found the concentration of Pb in cockles' soft tissue were ranged from 9 to 18.55 mg/kg [7, 8, 10-12]. Although blood cockle tissues have relatively low Pb contents, their Pb compositions reflect mixing of natural Pb with modern anthropogenic Pb emission sources (high Pb level in sediment). These emission sources include unleaded automotive gasoline, diesel fuel and leaded aviation gasoline [13]. Figure 3 shows the distribution of Pb in blood cockle soft tissue.

Ferum

Fe is the highest concentration that contain in cockles. The concentration of Fe in cockles' soft tissue in sample A, B, C and D are 563.52, 530.03, 1064.90 and 1343.70 mg/kg respectively. The average concentration of Fe in all samples is 875.55 $\pm$ 396.55 mg/kg. The highest concentration of Fe in blood cockles is 1343.70 mg/kg in sample D or sample size greater than 40 mm. The lowest concentration of Fe is 530.03 mg/kg in sample B or sample size 25 – 30 mm. Figure 2 shows the distribution of Fe concentration in cockles' samples vary with length shell size. The trends accumulation of Fe in blood cockles vary with shell length. From this graph, the trend of the Fe accumulation is higher at sample with length greater than 40 mm. the trend shows the increasing of Fe concentration with increasing of blood cockles sample length. The highest concentrations of Fe in cockles' were found at Kuala Selangor also may be related to human activities. Other factors that may contribute heavy metals into the Sungai Selangor including mining activities in the downstream rivers, oil palm and some residential areas located along the river [14].

Zinc

In this study the concentration of Zn in soft tissue of cockles' are 105.63, 96.43, 84.16 and 90.48 mg/kg for sample A, B, C and D respectively. The average concentrations of Zn in all cockles' samples are 94.17 + 9.13 mg/kg. The highest concentration of Zn is in sample size below than 25 mm or sample A with concentration 105.63 mg/kg. The lowest concentration of Zn in the sample of blood cockles is in sample size 30 to 40 mm or sample C is 84.16 mg/kg.

From this study, the concentration of Zn in all cockles' samples was below the permitted level set by Malaysian Food Act (1983) and Regulation (1985) and WHO/FAO2004. The allowable limit for Zn is 100 mg/kg for Malaysian Food Act1983 and Regulation 1985 and WHO/FAO 2004. All samples are safe to consume by consumer because the level of Zn is below the allowable limits. Figure 5 shows the distribution of Zn concentration in the blood cockle samples.

The concentration of Zn in blood cockles is only having slightly different from one to another researcher. Most of the researcher found that Zn concentration in blood cockles is over the limit set by the Malaysian Food Act (1985) and WHO/FAO, (2004) [10, 4, 8]. From this study shows that *Anadara granosa* was also well documented that organisms tend to accumulate light metals such as Zn, Cu and Fe in higher concentration in their tissue than the heavy metals such as Pb, Cd and Hg due to their significant role as a precursors in various enzymatic reactions. Similar results were reflected in this study where the bioaccumulation of Zn and Cu was multifold higher in the sample tissue than Pb accumulation [10].

Size-metal relationships

The highest concentrations of heavy metals were found in the cockles' with less shell length. Relationships between shell length of the two bivalve species and the concentration of heavy meals can be noticed that, all metals have negative correlations with shell-length. These inverse relationships can be attributed to different reasons: a) variation in the uptake and excretion rates of metals between small and large animals, b) small animals have ability to eat more than the large one which Pb accumulate pollutant in its body, c) dilution of the pollutant in the tissues of the large animals. Heavy metal levels considerably vary among individuals of the same species. The lower age of same species accumulated more heavy metal. Higher concentration of heavy metals were found in younger blood cockle and this reflects the short residence time of these metals within the blood cockle, combined with the higher rate of metabolism compared to older organism [14]. Accumulation of heavy metal levels in soft tissue of *Anadara granosa* from Kuala Selangor in this following order of abundance Fe> Zn> Cu> Cr>Pb> Cd. Figure 2 show the distribution of heavy metal in all samples of cockles.

Safe Rate Intake

The ingestion rate of cockle based on the mean value for Malay, Chinese and Indian ethnicities in Peninsular Malaysia are 5.36, 3.10 and 3.61 g/day, respectively [15]. Average Daily Intake (EDI) for an adult of 70kg (μg/kg body weight) of all metals in this studied is shown in Table 2. The entire sample in this study is safe to consume by all major races in Malaysia.

Table 2. The Estimated Daily Intake (EDI) for Cockles

Elements	PTDI[a]	Malay	Chinese	India
Cd	70	7.94	4.59	5.35
Cr	-	7.67	4.43	5.16
Cu	35 000	84.57	48.91	56.96
Pb	250	5.94	3.44	4.00
Fe	56 000	4692.3	2714.19	3160.72
Zn	70 000	339.97	291.94	339.97

PTDI[a] : Permissible tolerable daily intake (ug/daily/70 kg body weight)

Table 3. Concentration range of Heavy Metals in Cockles

Studies	Concentration Range						
	Locations	**Cd**	**Cr**	**Cu**	**Fe**	**Pb**	**Zn**
Present Study	Kuala Selangor	1.09-1.98	0.61-2.86	12.52 24.93	530.03-1343.70	0.80 - 1.90	84.16 - 105.63
Alina et al ., 2012	Straits of Malacca	0.25-0.47	-	-	-	0.19-0.28	-
Zahir et al., 2011	Kuah	-	-	9.75 - 14.95	-	1.23-2.23	99.75-121.75
	Kuala Triang	-	-	5.22 - 8.22	-	0.02-0.01	46.81-77.51
	Pantai Kok	-	-	7.42 - 9.70	-	0.03 - 0.05	71.88 - 88.12
Koh et al.,2008	Kuala Juru	3.60 -8.25	5.50 - 8.97	10.19 - 16.28	641.5 -1350	6.1 - 18.55	103.60 - 201.70
	Kuala Sepetang	1.25 -5.50	4.25 - 9.80	3.97 - 13.6	421.0 - 822.5	13.55 - 20.75	72.15 - 89.40
	Kuala Selangor	9.95 -12.20	6.74 - 9.08	2.44 - 6.59	686.50 - 878.50	4.1 -8.15	110.95 - 139.65
Yap et al.,2008	Jeram, Kuala Juru and Kuala Kurau	1.3 -9.44	-	5.41 – 7.39	455.91 - 1125.50	-	91.90 - 23.50
Mat & Maah, 2004	Kuala Selangor	4.66 -9.20		2.20 - 4.60		7.20 - 9.60	35.00 - 93.00
	Batu Kawan	1.40-2.80		3.7 0-5.30		2.10 - 3.70	50.20 - 61.80
Noordin Ibrahim, 1995	Kuala Juru	-	2.20 - 7.20	-	1426 -2075	-	185 -236
David & Kosol, 1985	Thailand	1.33 -6.47	0.18 - 0.56	4.89 - 8.75	-	0.37 - 1.41	65 -117.6

Conclusion

From this study, the results showed different sizes of soft tissues of *Anadara granosa* accumulated different levels of metals. The results of the shells showed the following order of abundance Fe> Zn> Cu> Cr > Pb > Cd. All the results were below the limits for blood cockle proposed by Malaysian Food Act 1983 and Regulation 1985. In this study shows that blood cockles with less shell length has more concentration of heavy metal compare from blood cockle has longer shell length. According from this results, blood cockle were within the limit for human consumption. Mean metal concentration were found to be higher in blood cockle have smaller shell length than those in blood cockle that have longer shell length. In this study also proved the limited ability of *Anadara granosa* in accumulating various heavy metals from its habitat in different rates. Nevertheless, high concentration of metals in surrounding sediment might partially from anthropogenic activities which would reflect in metal levels in aquatic organisms especially bivalves. Although level of heavy metal is not high, potential dangers emerge in future depending on the industrial wastewaters and domestic activities in this region.

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