Chapter 3 Determination of Nickel and Cadmium in Freshwater Fishes in Kuantan River and Riau River



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Abstract Nowadays, heavy metal pollution in Malaysia has become a major health concern in humans. Thus, this study was conducted to determine the level of cadmium (Cd) and nickel (Ni) in the muscle and gills of fishes collected from Kuantan river and Riau river. Field samplings were conducted between September and December 2017. Five different species of fishes: Barbonymus gonionotus, Barbonymus schwanenfeldii, Hampala macrolepidota, Chitala chitala, and Hemibagrus nemurus were digested by using acid digestion method and analyzed with Inductively Coupled Plasma-Mass Spectrometry (ICPMS). Concentration of Cd among species was in order of H.macrolepidota > B.gonionotus > B.schwanenfeldii > C.chitala > H.nemurus, whereas Ni level in fishes was: C.chitala > H. macrolepidota > B. gonionotus > H. nemurus > B. schwanenfeldii. Among all the species, H. macrolepidota from Kuantan river had the highest Cd in both muscle $(0.1761 \pm 0.0062 \text{ mg/kg})$ and gills $(0.2938 \pm 0.0066 \text{ mg/kg})$, whereas the highest Ni level in muscle was found in C. chi*tala* from Kuantan river with $(0.1473 \pm 0.0755 \text{ mg/kg})$ and in gills of *B.gonionotus* $(0.4544 \pm 0.0470 \text{ mg/kg})$ from the same river, respectively. It was observed that there was a significant difference (p < 0.05) in Cd in muscle between species. Ni concentration in fishes was lower than the permissible limit (WHO, 1985) while the concentration of Cd was recorded high but still below the limits of World Health Organizations (WHO) 1985 and the Malaysian Food Act (MFA) 1983.

Keywords Heavy metals · Kuantan River · Riau River · Nickel · Cadmium

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1 Introduction

Metal contamination in the aquatic ecosystem is considered to be unsafe not only for aquatic organisms but also for terrestrial organisms including humans. Heavy metals are well-known environmental pollutants that cause serious health hazards to human beings (Jarup 2003). Fish can accumulate heavy metals through uptake from different organs depending on the affinity of such organs to accumulate heavy metals. As a consequence, different organs have different heavy metal concentrations (Perera et al. 2015).

Nickel (Ni) and cadmium (Cd) are heavy metals that can cause toxicity to humans. The main threats of heavy metals to humans are associated with exposure of heavy metals from industrial waste, mining activities, and agricultural activities into rivers. Kuantan river and Riau river have potentially high concentrations of heavy metals since they are located nearer to the largest bauxite mining site, which is in Bukit Goh, Pahang. Bauxite ores contain heavy metals such as aluminum, cadmium, nickel, chromium, lead, and arsenic, which are neurotoxic or carcinogenic toxicologically (Hussain et al. 2016). The heavy metals runoff will contaminate the rivers with heavy metals and accumulate into the fish through respiration and breathing.

The consumption of freshwater fish by a large portion of the population remain urgent due to toxic heavy metals bioaccumulation in the fish. It is important to determine the concentration of heavy metals in fishes in order to evaluate the possible risk of consumption for human health. Moreover, it also results in bioaccumulation of heavy metals in man using water from this river since its tributaries pass through populated residential areas, towns, industrial and agricultural sites.

The risk associated with the exposure to heavy metals present in fresh fish or fish products had aroused widespread concern in human health. The risk of Ni and Cd contamination in muscle has received attention for both aspects of food safety and human health as it is a common edible part of fish.

Currently, the information about Pahang river water quality and safety of fish consumption is still not enough with the rapid industrialization activities. Even some organizations had stopped the mining operation, but still, lots of companies continue bauxite mining activities illegally without being responsible for clean-up works. Due to public awareness that metal enrichment in aquaculture may pose a potential health risk, this work investigated the levels of Cd and Ni in freshwater fishes and water samples collected from Kuantan river and Riau river. These sampling sites were selected on the basis of likely variation in metal levels due to anthropogenic activities, namely bauxite mining.

2 Methods and Materials

2.1 Study Area

Kuantan, Pahang is considered as the social, economic, and commercial hub for the East Coast Peninsular Malaysia. It is located at a latitude 30 45' 0" N and longitude of 102 30' 0" E (Kusin et al. 2016). Kuantan has also become one of the hot spots for the production of bauxite in Malaysia. Bukit Goh is one of the big scale bauxite mining, located in Kuantan, Pahang. Four sampling locations had been selected in Kuantan and Riau rivers. Sampling was carried out between February 2017 and May 2017.

2.2 Sample Collection

Several experimental gill nets were set up and left for 48 h at each sampling location. Every 24 h each net was inspected from morning until afternoon. The gill net was placed on the river based on several factors according to the sampling location.

2.3 Sample Analysis

The fish meat and gills were dissected and weighed for 10 grams per sample before being dried in the oven at 100 °C for 24 h. Samples were allowed to cool in a desiccator before the dry weights were taken. Acid digestion method was used to digest the meat samples based on the Association of Official Analytical Chemists (2016). Each sample was placed in the digestion tube and 10 ml of 69% of nitric acid was added before being left overnight at room temperature.

On the next day, the samples were digested at 100 °C for 2 h before cooling down for 1 h. After that, 2 ml of 30% hydrogen peroxide was added to each sample and heated for 1 h until a clear solution. Then, it was allowed to cool before solutions were filtered through filter paper into 25 ml of volumetric flask. Lastly, deionized water was added into the volumetric flask until the volume reach 25 ml. The concentration of heavy metals was determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

3 Results and Discussion

In this study, a total of 45 adult fishes were caught from Kuantan and Riau, comprising three families and five species. The distribution of captured fish species includes the Cyprinidae family, which were *Barbonymus gonionotus* (Lampam Jawa), *Barbonymus schwanenfeldii* (Lampam Sungai), and *Hampala macrolepidota* (Sebarau), while *Chitala chitala* (Belida) was from Notopteridae family and *Hemibagrus nemurus* (Baung) from Bagridae family. The findings regarding the levels of Cd and Ni found in the muscles and gills of the freshwater fishes collected from Kuantan and Riau rivers are presented in Tables 3.1 and 3.2.

As tabulated in Table 3.2, it was reported that the mean concentration of Cd in muscle and gills of freshwater species was in the following order: *H.macrolepidota* > *B.gonionotus* > *B.schwanenfeldii* > *C.chitala* > *H.nemurus*. The highest Cd level in muscle was observed in *H. macrolepidota* from Kuantan river (0.1761 \pm 0.0062 mg/kg) and the least value of Cd was found in muscle of *H.nemurus* from Riau river (0.0004 \pm 0.0002 mg/kg). *H.macrolepidota* had Cd level above established limits set by USFDA (1993), EC (2001), and FAO (2012); however, it was still below the WHO (1985) and MFA (1983) limits.

Therefore, *H.macrolepidota* collected for consumption from Kuantan river may pose adverse health risks of Cd intoxication in the human population. *H. macrolepidota* is a type of fish that inhabits the bottom layer of rivers and hunts for pellets, shrimp, bloodworms, or small insects. Mohsin and Ambak (1991) and Amundsen et al. (1997) had reported that carnivores could accumulate higher metal concentrations.

This statement is in agreement with the result that showed the highest concentration in this species. Whereas, *H.nemurus* from Riau river had the lowest Cd concentration with 0.0004 \pm 0.0002 mg/kg in muscle and 0.0044 \pm 0.0028 mg/kg in gills, respectively. Cd levels in *B.gonionotus*, *B.schwanenfeldii*, *C.chitala*, and *H.nemurus* were all below the established safe limits, and this species did not show a sign of danger since the concentration from all rivers was still far from the danger limit.

Species	Length (cm)	Weight (g)	No. of samples
Barbonymus gonionotus	24.0-26.0	600-800	9
Barbonymus schwanenfeldii	20.0-24.0	200-600	9
Hampala macrolepidota	18.0-20.0	150-200	9
Chitala chitala	30.0-45.0	500-800	9
Hemibagrus nemurus	24.0-32.0	400-600	9

Table 3.1 List of local fishes caught from Kuantan river and Riau river

Table 3.2 Mean concentration of cadmium $(mg/kg) \pm SD$ in muscle and gills of individual species collected from selected rivers

Location	Kuantan River		Riau River	
Species	Muscle	Gill	Muscle	Gill
Barbonymus gonionotus	0.0122 ± 0.0095	0.0422 ± 0.0078	0.0004 ± 0.0003	0.0134 ± 0.0147
Barbonymus schwanenfeldii	0.0056 ± 0.0024	0.0643 ± 0.0021	0.0005 ± 0.0001	0.0355 ± 0.0003
Hampala macrolepidota	0.1761 ± 0.0062	0.2938 ± 0.0066	0.0184 ± 0.0032	0.0749 ± 0.0052
Chitala chitala	0.0022 ± 0.0021	0.0510 ± 0.023	0.0006 ± 0.0029	0.0314 ± 0.0199
Hemibagrus nemurus	0.0005 ± 0.0223	0.0032 ± 0.0048	0.0004 ± 0.0002	0.0044 ± 0.0028

Location	Kuantan River		Riau River	
Species	Muscle	Gill	Muscle	Gill
Barbonymus gonionotus	0.0620 ± 0.0227	0.4544 ± 0.0470	0.0208 ± 0.0040	0.1139 ± 0.0511
Barbonymus schwanenfeldii	0.0216 ± 0.0019	0.3028 ± 0.0028	0.0124 ± 0.0041	0.2373 ± 0.0001
Hampala macrolepidota	0.0916 ± 0.0341	0.6805 ± 0.0241	0.0255 ± 0.0041	0.0747 ± 0.0143
Chitala chitala	0.0946 ± 0.0182	0.1831 ± 0.1921	0.0239 ± 0.0052	0.1360 ± 0.0022
Hemibagus nemurus	0.0291 ± 0.0056	0.0848 ± 0.0166	0.0180 ± 0.0008	0.0795 ± 0.0107

Table 3.3 Mean concentration of nicke $(mg/kg) \pm SD$ in muscle and gills of individual species collected from selected rivers

Cd is a nonessential heavy metal that can affect the kidneys and causes symptoms of chronic toxicity, such as the impairment of kidney function, poor reproductive capacity, hypertension, tumors, and hepatic dysfunction when ingested in high doses (Waalkes 2000). As Cd is the second product of mining activities, it could likely be discharged into the river in high concentrations, which would eventually accumulate in fishes (May et al. 2001). It also carries water from Lembing river, which is located near the Tin Ore Mining Industry.

According to Table 3.3, the levels of Ni were recorded in the range of 0.0216–0.0946 mg/kg in muscle and 0.0848–0.6845 mg/kg in gills. Mean concentration of Ni in muscle of freshwater species was in the following order: *C. chitala* > *H. macrolepidota* > *B. gonionotus* > *H. nemurus* > *B. schwanenfeldii*, meanwhile, in gills, it was in the following order: *B. schwanenfeldii*. > *H. macrolepidota* > *B. gonionotus* > *H. nemurus*. The highest Ni concentration in muscle was in *C. chitala* from Kuantan river with value of 0.0946 \pm 0.0182 mg/kg. Whereas, *B. schwanenfeldii* from Riau river showed the lowest Ni level in muscle (0.0124 \pm 0.0041 mg/kg) and *H. macrolepidota* had the lowest Ni in gills (0.0747 \pm 0.0143 mg/kg). This result proved that the accumulation of heavy metals is varying in different species. However, the Ni level in freshwater fishes in all rivers was still below the permissible limit set by the World Health Organization (1985) and the Food and Agriculture Organization (2003). Low concentration of Ni will not cause adverse effects on animals and human health since it is essential for growing (Bharagava 2017).

Differences of value between the current study and previous study determined the toxicity of the area and may give harmful to human society and community through ingestion and consumption. A previous report shows that there were three different fish species that have been studied along the Kelantan river (Hashim et al. 2014). The study reported that *B. gonionotus* from Kelantan river had maximum concentration of Cd 0.061 ± 0.076 mg/kg and *B. schwanenfeldii* with 0.100 ± 0.15 mg/kg. It also had reported maximum Ni concentration obtained from freshwater fishes in Kelantan River was 0.024 ± 0.037 , 0.262 ± 0.024 , and 0.056 ± 0.069 mg/kg, respectively, for *H. macrolepidota, C. chitala*, and *H. nemurus*. However, accumulation of Ni in *C. chitala* was reported lower than this present study.

	Cd	Ni
EC (2001)	0.05-0.10	_
WHO (1985)	2.00	0.50-0.60
FAO (2012)	0.05	0.40
MFA (1983)	1.00	-
USFDA (1993)	0.01-0.21	-

 Table 3.4
 The permissible limit of heavy metal cadmium (Cd) and nickel (Ni) in fish (mg/kg) by organizations

Fish are known to accumulate Ni in different tissues when exposed to elevated levels in their environment (Nussey et al. 2000; Obasohan and Oronsaye 2004). Lung inflammation and damage to the nasal cavity have been observed in fish exposed to Ni compounds. Ni is either proven to be or is strongly suspected to be essential in trace amounts, yet toxic in higher doses. Contact with Ni compounds (both soluble and insoluble) and ingestion of polluted fish as well as drinking water can cause a variety of adverse effects on human health (Table 3.4).

In this study, it is also reported that Ni level was higher compared to Cd in fishes from both the rivers. These observations may be due to the surrounding ecosystem status, as the sampling sites were nearby the bauxite mining area and nickel was present abundantly in the water environment, which may lead to a high probability to contribute high level of Ni in fish. High Ni concentration in fish might also be the result of effluent discharge received from households and the agriculture industry as Kuantan is the main river in Pahang. All these factors are the main contributors to the finding, which showed high Cd and Ni concentrations in freshwater fishes which originated from Kuantan river.

This study showed that both Cd and Ni levels in fish were higher in Kuantan river compared to Riau river. This might be due to the water flow of river was carried from upstream to downstream start from Kuantan to Riau river. By receiving industrial effluents generated by upstream, freshwater fish in Kuantan have a tendency to accumulate higher Cd and Ni in muscle tissue. A previous study shows that heavy metal content in aquatic organisms may be affected by their habitats and different ecosystems (Fidan et al. 2008).

In addition, it was found that the Cd and Ni concentration in gills was much higher than in muscle tissue. This statement is in agreement with Yeşilbudak and Erdem (2014), who mentioned that Cd was prone to be accumulated in gill compared to muscle tissue as gill is a metabolically active and readily available organ analyzed for biomonitoring. According to Mansor (2017), Cd concentration in muscle tissue of fish collected from Kelantan river was reported at 0.0181–0.0304 mg/ kg, while Baharom and Ishak (2015) reported the Ni concentration at 0.058–0.072 mg/ kg. Moreover, this study recorded that Cd found in gill showed the highest concentration compared to muscle tissue.

Gills have a tendency to accumulate high heavy metals as they had a large surface area for straightforward and persistent contact with contaminants in the water (Olgunoglu et al. 2015; Yilmaz 2003). Cd accumulation in gill of freshwater fish in Kelantan was ranged 0.0275–0.0335 mg/kg reported by Mansor (2017) which was lower than this study.

4 Conclusion

In conclusion, the accumulation of non-essential metal (Cd) and essential metal (Ni) had been varying in each species. Among species, *H. macrolepidota* was detected with the highest Cd concentration in muscle tissue $(0.1761 \pm 0.0062 \text{ mg/kg})$, and the least Cd concentration was detected in *H. nemurus* $(0.0013 \pm 0.0258 \text{ mg/kg})$. Ni concentration was detected the highest in *C. chitala* muscle $(0.1473 \pm 0.0755 \text{ mg/kg})$ and the least detected in *B. schwanenfeldii* (0.0562 ± 0.0066) . Cd and Ni concentration in gills was obtained higher compared to muscle.

Cd level in gill was detected highest in *H. macrolepidota* $(0.1250 \pm 0.0047 \text{ mg/} \text{kg})$, while Ni was highest in gills of *B. schwanenfeldii* $(0.2810 \pm 0.0044 \text{ mg/kg})$. In conclusion, Ni concentration in fishes was below the permissible limit stipulated by the World Health Organizations (WHO) (1985) and the Food and Agriculture Organizations (2012), and even though the concentration of Cd was recorded high, it was still below the limits of WHO (1985) and the Malaysian Food Act (MFA) 1983.

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