Determination of Nickel and Cadmium in Freshwater Fishes at Sungai Kuantan, Sungai Riau And Sungai Pinang

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ABSTRACT

Heavy metal exhibit toxic and persistent characteristics, can enter into the food chains and the ecosystem where they cause adverse impact on the biotic and abiotic components of ecosystem. Heavy metal pollution in Malaysia has become a major health concern for humans. Thus, this study was conducted to determine the level of cadmium (Cd) and nickel (Ni) in the muscle and gill of fishes collected from the Sungai Kuantan and Sungai Riau. Field sampling was conducted between September and December 2017. Five different species of fishes: Barbonymus gonionotus (Lampam Jawa), B. schwanenfeldii (Lampam Sungai), Hampala macrolepidota (Sebarau), Chitala chitala (Belida), and Hemibagrus nemurus (Baung) were digested by using acid digestion method and analysed with Inductively Coupled Plasma-Mass Spectrometry (ICPMS). Concentration of Cd among species were in order of: H. macrolepidota > B. gonionotus > B. schwanenfeldii > C. chitala > H. nemurus, whereas Ni level in fishes were: C. chitala > H. macrolepidota > B. gonionotus > H. nemurus > B. schwanenfeldii. Among all the species, H. macrolepidota from Sungai Kuantan had the highest Cd in both muscle (0.1761±0.0062 mg/kg) and gills (0.2938±0.0066 mg/kg) whereas the highest Ni level in muscle was noted in C. chitala from Sungai Kuantan with (0.1473±0.0755 mg/kg) and in gills of B. gonionotus (0.4544±0.0470 mg/kg) from the same river respectively. It was obtained that there was a significant difference (p<0.05) of Cd in muscle between species. Ni concentration in fishes was below the permissible limit stipulated by World Health Organizations WHO (1985) and Food and Agriculture Organizations (2012) but the concentration of Cd was recorded high. However, it was still below the World Health Organization (WHO) 1985 and Malaysian Food Act (MFA) 1983.

Keywords: Heavy metals, nickel, cadmium, freshwater fishes, Sungai Kuantan

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 consequences different organs have a different heavy metal concentration (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 a river. Sungai Kuantan, Sungai Pinang and Sungai Riau have potential with a high concentration 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 neurotoxin 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 remains urgent due to toxic heavy metals bioaccumulation in the fish. It is important to determine the concentration of heavy metals in fish to evaluate the possible risk of consumption for human health. Moreover, it also results in bio-accumulation 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 the common edible part of fish.

In many contaminated situations with heavy metals, Cd had become an important element of concern because of its bio accumulative nature in food webs. Therefore, fish living in polluted waters prone to accumulate heavy metals in their tissues (Perera et al., 2015). Moreover, mining, smelting, refining, casting of alloys and electroplating industries are major contributors of nickel contaminations. Both of elements were commonly found in bauxite ores. Even some organizations had stopped the mining operation, but still, lots of companies continue bauxite mining activities illegally without responsible for cleanup 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 the Sungai Kuantan and Sungai Riau. These sampling sites were selected based on likely variation in metal levels due to anthropogenic activities, namely bauxite mining.

**MATERIALS AND METHODS**

**Study area**

Global Positioning System (GPS) (GARMIN GPSMAP 62sc) was used to determined coordinate of three sampling location. These rivers are surrounded by palm oil plantation, bauxite mining, quarry activities and other anthropogenic activities that could cause pollution to the rivers. The problem exists without a clearly defined bauxite mining operation zone. It is because the bauxite mining at Kuantan is occurring near to resident area but scattered. The schools and residential areas are very close to the bauxite mining sector and are the most vulnerable time for children and individuals doing an operation. The extensive land clearing is mainly related to sources of water pollution. (Amin, 2017). Kuantan, Pahang is considered a social, economic, and commercial hub for the East Coast Peninsular Malaysia. It is located at latitude 30 45’ 0” N, and longitude 102 30’ 0” E (Kusin et al., 2016). Kuantan also becomes one of the hot spots for the production of bauxite in Malaysia. Bukit Goh is one of the big scale bauxite mining is and located in Kuantan, Pahang. Four sampling locations had been selected which are Kuantan, and Riau. Sampling was carried out between September 2017 to December 2017.

**Sample collection**

Several experimental gill nets were set up and left for 48 hours at each sampling location. Every 24 hours 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. The gill net with dimension of (120’x10’x 4’) and (120’x10’x 3’) was used
to trap the fish. The gill nets were set between 4 to 8 hours before pulling the net for fish inspection. Commonly the net was set in late of evening and pulled in the next morning. The net was set up along the river that covers the most river pools. Collected fishes were immediately preserved in an ice box and kept frozen at 0°C to 20°C until further analysis.

**Lab analysis**

The fish meat and gills were dissected and weighed for 10 grams per sample before dried in the oven at 100 °C for 24 hours. Samples were allowed to cool in 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 (AOAC, 2016). Each sample was placed in the digestion tube and 10 ml of 69 % of nitric acid was added before left overnight at room temperature. On the next day, the samples were digested at 100 °C for 2 hours before cooling them down for 1 hour. After that, 2 ml of 30 % hydrogen peroxide was added to each sample and heated for 1 hour until it forms 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 reaches 25 ml. The concentration of heavy metals were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Analytical quality was assessed using Quality Control Standard 21 (Perkin Elmer Pure) was used as Standard Reference Material (SRM1646a) for instrument recovery. Recoveries of all the elements ranged from 96 to 105% of the certified value. Triplicate readings were obtained for every sample.

**RESULTS AND DISCUSSION**

In this study, a total of 45 adult fishes were caught from Kuantan, Riau, comprising three families and five species. The distribution of captured fish species includes Cyprinidae family which were *Barbonymus gonionotus* (Lampam Jawa), *Barbonymus schwanenfeldii* (Lampam Sungai) and *Hampala macrolepidota* (Sebarau) while *Chitala chitala* (Belida) from Notopteridae family and *Hemibagrus nemurus* (Baung) from Bagridae family. The findings regarding levels of Cd and Ni found in the muscle and gill of the freshwater fishes collected from Kuantan and Sungai Riau are presented Table 2 and 3.

<table>
<thead>
<tr>
<th>Species</th>
<th>Length (cm)</th>
<th>Weight (g)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Barbonymus gonionotus</em></td>
<td>24.0-26.0</td>
<td>600-800</td>
<td>9</td>
</tr>
<tr>
<td><em>B. schwanenfeldii</em></td>
<td>20.0-24.0</td>
<td>200-600</td>
<td>9</td>
</tr>
<tr>
<td><em>Hampala macrolepidota</em></td>
<td>18.0-20.0</td>
<td>150-200</td>
<td>9</td>
</tr>
<tr>
<td><em>Chitala chitala</em></td>
<td>30.0-45.0</td>
<td>500-800</td>
<td>9</td>
</tr>
<tr>
<td><em>Hemibagrus nemurus</em></td>
<td>24.0-32.0</td>
<td>400-600</td>
<td>9</td>
</tr>
</tbody>
</table>

As tabulated in Table 2, it was reported that the mean concentration of Cd in muscle and gills, based on the freshwater species were *H. macrolepidota* > *B. gonionotus* > *B. schwanenfeldii* > *C. chitala* > *H. nemurus*. The highest Cd level in muscle was observed in *H. macrolepidota* from Sungai Kuantan (0.1761± 0.0062mg/kg) and the least value of Cd was found in muscle of *H. nemurus* from Sungai Riau (0.0004±0.0002mg/kg). *H. macrolepidota* had Cd level above established limits set by USFDA (1993), EC (2001), and FAO (2012) however still below WHO (1985) and MFA (1983) limits. Therefore, *H. macrolepidota* collected for consumption from Sungai Kuantan may possessed adverse health risk of Cd intoxication in the human population. *H. macrolepidota* is a type of fish that inhabits the bottom layer of the rivers and is hunted for pellets, shrimp, bloodworms, or small insects. Mohsin & Ambak (1991); 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 Sungai Riau had the lowest Cd concentration with 0.0004±0.0002 mg/kg in muscle and 0.0044±0.0028mg/kg in gills respectively. Cd levels in *B. gonionotus*, *B. schwanenfeldii*, *C. chitala*, and *H. nemurus*. 

**Table1: list of local fishes caught from Sungai Kuantan and Sungai Riau**

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were all below than established safe limits this species did not show a sign of danger since the concentration from all rivers still far from the danger limit.

Cd is a non-essential 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 be likely discharge into a river with high concentration and eventually accumulate in fish (May et al., 2001). It also carries the water from Lembing River which is located near the Tin Ore Mining Industry.

Table 2: Mean concentration of cadmium (mg/kg) ±SD in muscle and gills of individual species collected from selected rivers.

<table>
<thead>
<tr>
<th>Location</th>
<th>Species</th>
<th>Sungai Kuantan</th>
<th>Sungai Riau</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Muscle</td>
<td>Gill</td>
<td>Muscle</td>
</tr>
<tr>
<td></td>
<td>0.0122±0.0095</td>
<td>0.0422±0.0078</td>
<td>0.0004±0.0003</td>
</tr>
<tr>
<td></td>
<td>0.0056±0.0024</td>
<td>0.0643±0.0021</td>
<td>0.0005±0.0001</td>
</tr>
<tr>
<td></td>
<td>0.1761±0.0062</td>
<td>0.2938±0.0066</td>
<td>0.0184±0.0032</td>
</tr>
<tr>
<td></td>
<td>0.0022±0.0021</td>
<td>0.0510±0.023</td>
<td>0.0006±0.0029</td>
</tr>
<tr>
<td></td>
<td>0.0005±0.0223</td>
<td>0.0032±0.0048</td>
<td>0.0004±0.0002</td>
</tr>
</tbody>
</table>

According to table 3, the levels of Ni were recorded in the range of 0.0216-0.0946mg/kg in muscle and 0.0848-0.6845mg/kg in gills. Mean concentration of Ni in the muscle of freshwater species were C. chitala > H. macrolepidota > B. gonionotus > H. nemurus > B. schwanenfeldii. Meanwhile in gills were B. schwanenfeldii > H. macrolepidota > B. gonionotus > C. chitala > H. nemurus. The highest Ni concentration in muscle was in C.chitala from Sungai Kuantan with value of 0.0946±0.0182 mg/kg. Whereas, B. schwanenfeldii from Sungai Riau showed the lowest Ni level in muscle (0.0124±0.0041mg/kg) and H. macrolepidota had the lowest Ni in gills (0.0747±0.0143mg/kg). This result proved that the accumulation of heavy metals are varying in different species. However, the Ni level in freshwater fishes at all river were still below the permissible limit set by World Health Organization (1985) and Food and Agriculture Organization (2003). Low concentration of Ni will not cause adverse effect 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. Previous report shows 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±0.15mg/kg. It also had reported maximum Ni concentration obtained from freshwater fishes in Kelantan River was 0.024±0.037, 0.262±0.024, 0.056±0.069 mg/kg respectively for H. macrolepidota, C. chitala, and H. nemurus. However, the accumulation of Ni in C. chitala was reported lower than in this present study.

Fish are known to accumulate Ni in different tissues when exposed to elevated levels in their environment (Nussey et al., 2000; Obasohan & 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 are strongly suspected to be essential in trace amounts, yet are 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: Mean concentration of nickel (mg/kg) ±SD in muscle and gills of individual species collected from selected rivers.

<table>
<thead>
<tr>
<th>Location</th>
<th>Species</th>
<th>Muscle</th>
<th>Gill</th>
<th>Muscle</th>
<th>Gill</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sungai Kuantan</td>
<td>Barbonymus gonionotus</td>
<td>0.0620±0.0227</td>
<td>0.4544±0.0470</td>
<td>0.0208±0.0040</td>
<td>0.1139±0.0511</td>
</tr>
<tr>
<td>Sungai Riau</td>
<td>B. schwazenfeldii</td>
<td>0.0216±0.0019</td>
<td>0.3028±0.0228</td>
<td>0.0124±0.0041</td>
<td>0.2373±0.0001</td>
</tr>
<tr>
<td>Sungai Kuantan</td>
<td>Hampala macrolepidota</td>
<td>0.0916±0.0341</td>
<td>0.6805±0.0241</td>
<td>0.0255±0.0041</td>
<td>0.0747±0.0143</td>
</tr>
<tr>
<td>Sungai Riau</td>
<td>Chitala chitala</td>
<td>0.0946±0.0182</td>
<td>0.1831±0.1921</td>
<td>0.0239±0.0052</td>
<td>0.1360±0.0022</td>
</tr>
<tr>
<td>Sungai Kuantan</td>
<td>Hemibagrus nemurus</td>
<td>0.0291±0.0056</td>
<td>0.0848±0.0166</td>
<td>0.0180±0.0008</td>
<td>0.0795±0.0107</td>
</tr>
</tbody>
</table>

Table 4: Established Permissible Limit of Cd and Ni in Fish (mg/kg) by organizations

<table>
<thead>
<tr>
<th>Cd</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC (2001)</td>
<td>0.05-0.10</td>
</tr>
<tr>
<td>WHO (1985)</td>
<td>2.00</td>
</tr>
<tr>
<td>FAO (2012)</td>
<td>0.05</td>
</tr>
<tr>
<td>MFA (1983)</td>
<td>1.00</td>
</tr>
<tr>
<td>USFDA (1993)</td>
<td>0.01-0.21</td>
</tr>
</tbody>
</table>

This study, also reported that Ni levels were higher compared to Cd in fishes from both rivers. These observations may be due to the surrounding ecosystem status, as the sampling sites were nearby bauxite mining areas and nickel was present abundantly in the water environment which may lead to a high probability to contribute a high level of Ni in fish. High Ni concentration in fish might also be the result of effluent discharge received from domestics 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 concentration in freshwater fishes which originated from the Sungai Kuantan.

This study showed both Cd and Ni level in fish was higher at Sungai Kuantan compared to Sungai Riau. The river's water flow was transferred from Kuantan to Sungai Riau, starting from upstream and ending downstream. Freshwater fish in Kuantan accumulate more Cd and Ni in muscle tissue as a result of consuming industrial effluents from the upstream. The concentration of heavy metals in aquatic organisms may be influenced by their habitats and ecosystems, according to a prior study (Fidan et al., 2008).

In addition, it was obtained that the metals Cd and Ni concentration in gills were much higher than metals in muscle tissue. This statement is in agreement with Yeşilbudak & Erdem (2014), which mentioned that Cd was prone to be accumulated in the gill compared to muscle tissue as gill is a metabolically active and readily available organ which are analyzed for biomonitoring. Previous study by Kamaruzzaman et al, 2010, the bioaccumulation in fish stomach collected in Sungai Pahang was observed in most metals since, it is the major organ involved in xenobiotic metabolism in fish (Rashed, 2001; Fernandes et al., 2007). Zn accumulated the most in all the fishes followed by Cu and Pb, Cu and Zn. According to Mansor (2017), Cd concentration in muscle tissue of fish collected from Kelantan river was reported 0.0181 to 0.0304 mg/kg, while Baharom & Ishak (2015) reported the Ni concentration 0.058 to 0.072 mg/kg. Moreover, this study recorded Cd found in gill showed the highest concentration compared to muscle tissue. Gill tend to accumulate high heavy metal as it had a large surface area for straightforward and persistent contact with contaminants in the water (Olgunoglu et al., 2015; Yilmaz, 2003). As compared to different rivers by Mansor (2017), the Cd accumulation in the gill of freshwater fish in Kelantan was ranged 0.0275 to 0.0335 mg/kg. It is quite lower than the result obtained from this study. Kuantan's uncontrolled bauxite mining business has caused damage on the ecosystem. If there is no effective rehabilitation plan in place for the exploited area, the impact may continue. Even if chronic physical illness is not visible right now due to its gradual etiology, the diseases may manifest many years later if the current risk is not adequately addressed and controlled (Abdullah et al., 2016).
CONCLUSION

As a conclusion, the outcomes of this study was the accumulation of non-essential metal (Cd) and essential metal (Ni) had been varies in each species. Among species, *H. macrolepidota* was detected with highest Cd concentration in muscle tissue (0.1761± 0.0062mg/kg) and the least Cd concentration was detected in *H. nemurus* (0.0013±0.0258 mg/kg). Ni concentration was detected the highest in *C. chitala* muscle (0.1473±0.0755 mg/kg) and the least detected in *B. schwanenfeldii* (0.0562±0.0066). Cd and Ni concentration in gills was obtained higher compared in muscle. Cd level in gill was detected highest in *H. macrolepidota* (0.1250± 0.0047 mg/kg) while Ni highest in gills of *B. schwanenfeldii* (0.2810± 0.0044 mg/kg). As a conclusion, Ni concentration in fishes were below than the permissible limit stipulated by World Health Organizations WHO (1985) and Food and Agriculture Organizations (2012) but the concentration of Cd were recorded high. However, it was still below than the World Health Organization (WHO) 1985 and Malaysian Food Act (MFA) 1983.

ACKNOWLEDGMENTS

The authors would like to thank Universiti Sultan Zainal Abidin and KPT FRGS Fund (RR212) for giving the opportunity to carry out this research.

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How to cite this paper: