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Bioscience Research

Print ISSN: 1811-9506 Online ISSN: 2218-3973

Journal by Innovative Scientific Information & Services Network



RESEARCH ARTICLE

BIOSCIENCE RESEARCH, 2019 16(SI): 288-295.

OPEN ACCESS

Levels of heavy metals in fishes from selected rivers at Kuantan, Pahang

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Reviewed by: Dr. Saiful Iskandar Khalit, Dr. Azman Azid

The metal contamination in aquatic ecosystem is considered to be unsafe not only for aquatic organisms but also for terrestrial organisms including the human. The long-term consumption of fish from the polluted waters may result in bioaccumulation of persistent pollutants in ultimate recipient perhaps human of the food web. This study aimed to determine the concentration of Aluminium (Al), Iron (Fe), Cadmium (Cd) and Lead (Pb) in the fish meat collected from four different rivers (Riau, Kuantan, Pandan and Pinang River) at Kuantan, Pahang, Malaysia. Fishes were collected using gill nets during wet and dry seasons. A total of 32 fishes were caught, comprising 7 families, 10 genera and 12 species. The meat or dorsal muscle of the fish was digested using acid digestion method and analyzed by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS). The highest mean concentration of Al and Fe was in *C. heteronema* which were 12.5894 ± 1.0681 mg/kg and 14.8630 ± 3.5736 mg/kg. *B. gonionatus* has the highest concentration of Cd and Pb which were 0.0068 ± 0.0101 mg/kg and 0.0788 ± 0.1684 mg/kg. The concentration of heavy metals were found to be increased in the wet season. The mean concentration of Al and Cd in fish meat were high at sampling station S3 (Pandan River) with the value of 8.872 ± 6.982 mg/kg and 0.013 ± 0.019 mg/kg. S4 (Pinang River) has the highest mean concentration of Fe in fish which was 12.201 ± 3.817 mg/kg and S2 (Kuantan River) has the highest concentration of Pb which was 0.060 ± 0.133 mg/kg. This study determined that the fish species caught in four different rivers in Kuantan were contaminated with heavy metals (Al, Fe, Cd and Pb). However, the heavy metals concentration in the fish meat still did not exceed the permissible limit stated by European Community (EC), Food and Agriculture Organization (FAO), Malaysian Food Act (MFA) and World and Health Organization (WHO) guidelines.

Keywords: Heavy Metal, Fish, Riau River, Kuantan River, Pandan River, Pinang River.

INTRODUCTION

Fish can give important sources of protein to people and consumption of fish has increased throughout the world because it provides a healthy, low cholesterol sources of protein and many nutrients (Agusa et al., 2004, Burger et al., 2005). Some heavy metals are essential for fish metabolism such as copper and zinc while some other has no role in biological systems such as

lead. The normal metabolism of fish, essential metals was taken up from water, food and sediment. Similar to route of essential metals, non-essential metals also were taken up by fish and accumulate in their tissues (Canli et al., 2003, Türkmen et al., 2005 and Dural et al., 2007). The impact of metals on aquatic ecosystems is still considered to be a major threat to organism health due to their potential bioaccumulation and

toxicity to many aquatic organisms (Shuhaimi-Othman et al., 2012).

Mining industry in Malaysia is expected to grow excellently because the ongoing demand for mineral supplies both nationally and globally (Majid et al., 2013). The only operated bauxite mining area in Malaysia is at Kuantan, Pahang. Bauxite in Kuantan area was formed from basalt. The main area for bauxite mining in Kuantan is Bukit Goh which heavily mined for bauxite (Paramanathan, 2002). Bauxite mining can cause great disruption because it has detrimental effect on water, air, land and aquatic life if the activities is not properly controlled (Abdullah et al., 2016, Saxena et al., 2000). Pollutants in the aquatic ecosystem will precipitate on the sediment surface form as deposited pollutants. Mining activities are known to generate environmental impacts such as pollution to the water quality in the nearby river (Lamare et al., 2014). Another factors of pollutant are anthropogenic activities within a watershed, such as agriculture and urbanization affected the sediment yield from the watershed (Toriman et al., 2012).

Human health can be affected by heavy metals contamination because heavy metals may accumulate in aquatic species and enter human food chain (Fernandes et al., 2007, Papagiannis et al., 2004, Türkmen et al., 2005). Heavy metals accumulation in fish is one of the biggest issues because many fish species were consumed by the population especially those who live near rivers (Yilmaz, 2003). The heavy metals can be neurotoxic, carcinogenic, mutagenic and teratogenic to human if the heavy metals were consumed above the recommended limit. General symptoms of metal poisoning in human are vomiting, convulsions, paralysis, ataxia, hemoglobinuria, gastrointestinal disorder, diarrhea, stomatitis, tremor, depression and pneumonia (McCluggage, 1997). The aim of this study was to determine the concentration of Al, Fe, Cd and Pb in different fish species at the selected rivers in Kuantan, Pahang, Malaysia.

MATERIALS AND METHODS

Study Area

Kuantan, Pahang is considered as social, economic and commercial hub for the East Coast Peninsular Malaysia. It is located at latitude 3° 45' 0" N, and longitude 102° 30' 0" E (Kusin et al., 2016). Kuantan also become one of the hot spot for the production of bauxite in Malaysia. Bukit Goh is one of the big scale bauxite mining are and

located in Kuantan, Pahang. Four sampling locations had been selected which are Kuantan, Riau, Pinang and Pandan River. Sampling was carried out during the wet season (February 2017) and dry season (May 2017).

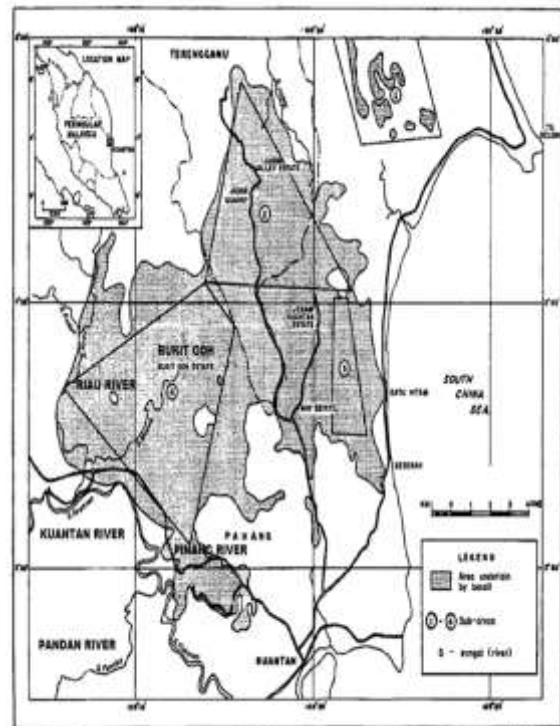


Figure 1: Map of Kuantan, Peninsular Malaysia

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 factor according to the sampling location.

Cyprinidae family included *Barbonymus gonionotus*, *Borbonymus schwanenfeldii*, *Cyclocheilichthys heteronema*, *Rasbora einthovenii* and *Rasbora torneiri* were identified from the samples obtained. Next is Channidae family which consist of *Channa lucius* and *Channa micropeltes*. We also managed to identify *Butis gymnopomus* from Eleotridae family, *Clarias gariepinus* from Clariidae family, *Hemibagrus wyckii* from the Bagridae family, *Ompok siluroides* from Siluridae family and *Pangasius micronemus* from Pangasiidae family.



Figure 2: Coordinate and image of the rivers.

Sample Analysis

Fish meat or muscle (dorsal muscle) was used in this experiment because it is the major target for metal storage and the most edible part of the fish (Tüzen, 2003). The fish meat was 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), 1984. 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 on at 100 °C for 2 hours before cooling it down for 1 hour. After that, 2 ml of 30 % hydrogen peroxide was added to each sample and heated for 1 hour until it form 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 volumetric flask until the volume reach 25 ml. The concentration of heavy metals were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

RESULTS

A total of 32 fishes were caught, comprising 7 families, 10 genera and 12 species. The captured fish species were listed in Table 1.

Table 1: Distribution of fishes caught in four sampling locations during both wet and dry seasons.

Species (n)	Local name	S1	S2	S3	S4
<i>Barbonymus gonionotus</i> (7)	Lampam Jawa	-	+	+	-
<i>Borbonymus schwanefeldii</i> (4)	Lampam Sungai	-	+	-	-
<i>Butis gymnopus</i> (3)	Ikan Ubi	-	-	-	+
<i>Channa lucius</i> (2)	Bujuk	+	-	-	-
<i>Channa micropeltes</i> (2)	Toman	+	-	-	-
<i>Clarias gariepinus</i> (2)	Keli	+	-	-	-
<i>Cyclocheilichthys heteronema</i> (2)	Temperas	-	-	+	+
<i>Hemibagrus wyckii</i> (5)	Baug	+	+	-	-
<i>Ompok siluroides</i> (1)	Tapah	-	-	+	-
<i>Pangasius micronemus</i> (2)	Bemban Patin	+	-	-	-
<i>Rasbora einthovenii</i> (1)	Susur Batang	-	-	+	-
<i>Rasbora torneiri</i> (1)	Seluang	-	-	+	-

All the fishes were collected at four sampling location which were Station 1 (Riau River), Station 2 (Kuantan River), Station 3 (Pandan River) and Station 4 (Pinang River) during wet and dry seasons. Dry weight was used in this study to determine the concentration of heavy metals because the value is more reliable and consistent compare to wet weight (Pérez-López et al., 2008).

During the sampling carried out in wet season, we managed to collect Bujuk, Toman, Baug, and Patin from Station 1 (Riau River). While at Station 2 (Kuantan River), Lampam Jawa, Lampam sungai and Baug were collected. At Station 3 (Pandan River), species selected were Tapah and Susur batang and at Station 4 (Pinang River), Ikan Ubi and Temperas were collected. During sampling in dry season, the species of fish that were collected at Station 1 (Riau River) were Keli and Baug. At Station 2

(Kuantan River), Lampam Jawa and Lampam Sungai were collected. At Station 3 (Pandan River), Susur batang was identified and at Station 4 (Pinang River), Ikan Ubi and Temperas were collected. The concentrations of heavy metals in meat for each species were measured. The concentration of Aluminium (Al), Iron (Fe).

Cadmium (Cd) and Lead (Pb) in fish meat collected at four sampling locations were determined and summarized in the Table 2

According to Table 3, the metal concentration was found to be higher during wet season. The

mean concentration of Al found in all fish species at sampling stations S3 was higher among the four sampling stations (Table 3) which was 8.872 ± 6.982 mg/kg. The result also the same with the concentration of Cd at station S3 which has higher concentration compared to other sampling stations. The S4 (Pinang River) accumulated the highest mean concentration of Fe (12.201 ± 3.817 mg/kg) in the fish muscle compared to other sampling station.

Table 2: Concentrations of heavy metals in fish species collected from Kuantan rivers during wet (February 2017) and dry seasons (May 2017) and the permissible limit in fish as stated by several guidelines.

Species	Mean heavy metal concentration (mg/kg)			
	Al	Fe	Cd	Pb
<i>Barbonymus gonionotus</i>	1.6758 ± 1.8388	6.0329 ± 5.8663	0.0068 ± 0.0101	0.0788 ± 0.1684
<i>Borbonymus schwanenfeldii</i>	6.3688 ± 7.3671	9.9469 ± 8.9419	0.0064 ± 0.0093	0.0234 ± 0.0176
<i>Butis gymnopomus</i>	3.8093 ± 2.2078	13.2147 ± 4.7490	0.0012 ± 0.0006	0.0169 ± 0.0052
<i>Channa lucius</i>	4.6768 ± 1.8499	10.3144 ± 1.5289	0.0022 ± 0.0003	0.0212 ± 0.0088
<i>Channa micropeltes</i>	1.8618 ± 0.4393	5.3714 ± 0.1666	0.0006 ± 0.0001	0.0110 ± 0.0013
<i>Clarias gariepinus</i>	1.1111 ± 0.8503	4.1685 ± 2.2601	0.0001 ± 0.0000	0.0088 ± 0.0022
<i>Cyclocheilichthys heteronema</i>	12.5894 ± 1.0681	14.8630 ± 3.5736	0.0024 ± 0.0029	0.0168 ± 0.0056
<i>Hemibagrus wyckii</i>	1.9810 ± 0.6285	5.3891 ± 2.1835	0.0016 ± 0.0011	0.0167 ± 0.0111
<i>Ompok siluroides</i>	5.8971 ± 0.0001	11.4210 ± 0.0001	0.0414 ± 0.0001	0.0193 ± 0.0001
<i>Pangasius micronemus</i>	4.3603 ± 1.6636	6.6841 ± 0.8902	0.0012 ± 0.0002	0.0306 ± 0.0175
<i>Rasbora einthovenii</i>	15.7473 ± 0.0001	13.0733 ± 0.0001	0.0062 ± 0.0001	0.00392 ± 0.0001
<i>Rasbora torneiri</i>	0.4892 ± 0.0001	6.4998 ± 0.0001	0.0006 ± 0.0001	0.0095 ± 0.0001
Permissible limit in fish				
EC (2001)	-	-	0.05 – 0.10	0.20 – 0.40
USFDA (1993)	-	-	-	0.5
WHO (1985)	-	-	2.0	2.0
FAO (2003)	-	-	0.05	0.20
MFA (1983)	-	-	1.0	2.0

Data showed as Mean ± SD.

Table 3: Comparison of heavy metals concentration among fish collected in different seasons and sampling station.

Parameter		Heavy metal concentration (mg/kg)			
		Mean (Standard Deviation)			
		Al	Fe	Cd	Pb
Season	Wet	4.584 (4.266)	9.429 (4.5561)	0.007 (0.011)	0.043 (0.096)
	Dry	2.825 (4.250)	5.755 (5.449)	0.001 (0.001)	0.009 (0.004)
Sampling station	S1	2.445 (1.525)	5.758 (2.312)	0.001 (0.001)	0.017 (0.012)
	S2	3.476 (4.875)	7.528 (6.988)	0.004 (0.006)	0.060 (0.133)
	S3	8.872 (6.982)	12.096 (4.500)	0.013 (0.019)	0.0133 (0.008)
	S4	5.084 (4.146)	12.201 (3.817)	0.006 (0.012)	0.013 (0.007)

C. heteronema has the highest concentration of Al and Fe which were 12.5894 mg/kg and 14.8630 mg/kg compared to other species. The lowest concentration for Al was in *R. torneiri* (0.4892 mg/kg) and the lowest concentration for Fe was in *C. gariepinus* (4.1685 mg/kg). *B. gonionatus* has the highest concentration of Cd (0.0068 mg/kg) but still below the permissible limit under standard guidelines. The lowest concentration of Cd was in *C. gariepinus* which was 0.0001 mg/kg. *B. gonionatus* has the highest concentration of Pb (0.0788 mg/kg) compared to other samples. The lowest concentration of Pb was in *R. einthovenii* (0.0039 mg/kg).

From Table 4, the highest content level of Al was at sampling station S4 (Pinang River) at 0.0268 ± 0.0144 ppm compared to other rivers.

The concentration of Fe and Pb were also found to be the highest at sampling station S3 (Pandan River) which are 0.7332 ± 0.0991 ppm and 0.0033 ± 0.0015 ppm.

Table 4: Concentration of heavy metal in water (Al, Fe, Cd, Pb) and Class of River based on National Water Quality Standard from Department of Environment (DOE) 2014.

Sampling Station	Heavy metal concentration (ppm)			
	Mean (Standard Deviation)			
	Al	Fe	Cd	Pb
S1	0.0101 (0.0045)	0.5035 (0.3632)	0.0005 (0.0006)	0.0006 (0.0005)
S2	0.0205 (0.0021)	0.3190 (0.0073)	0.0001 (0.0000)	0.0018 (0.0006)
S3	0.0251 (0.0239)	0.7332 (0.0991)	0.0002 (0.0000)	0.0033 (0.0015)
S4	0.0268 (0.0144)	0.1535 (0.1248)	0.0003 (0.0004)	0.0003 (0.0001)
Class of River (DOE, 2014)	All Natural Level			

In addition, S1 (Riau River) had the highest concentration of Cd with the value of 0.0005 ± 0.0006 ppm compared to all rivers. The values of heavy metals (Al, Fe, Cd and Pb) in the water samples were below than the permissible limit stated by National Water Quality Standard of Department of Environment (DOE, 2014). Thus, the water samples were not contained by heavy metals and safe to be consumed.

DISCUSSION

In general, there are many organizations which function to set the safeguard public health limits of heavy metal concentration in fish (Rohasliney et al, 2014). Permissible limits of

heavy metal contamination in Malaysia is determined by Malaysia Food Act (MFA 1983). In this study, the heavy metals were also compared with others international organization such as FAO (2003), EC (2001), USFDA (1993) and WHO (1995). Unfortunately, there are no information about permissible limit for Al and Fe in fish according to FAO (2003), EC (2001), USFDA (1993) and WHO (1995) standards. In fact, there was no description of Al and Fe toxicity in fish reported in literature especially at Kuantan rivers. But, this does not indicate that the presence of Al and Fe in fish is not harmful to the aquatic organism.

Al is not essential element in biological mechanism but can cause toxicity due to its peculiar chemical properties (Kawahara, 2007). Fe also can give adverse impact to the organism even though it is essential element that involve in biological systems (Cheney, 1995). Cadmium can be deadly and lethal to humans if the concentration is higher than standard limit. The effect of the Cd toxicity such as impairment of kidney function, hypertension, tumor and hepatic dysfunction (Waalkes, 2003). The concentration of Pb in all samples were below the permissible limits. Pb is defined as non-essential element and can cause toxic to human in high dose. The effect of Pb toxicity are renal failure and liver damage in human (Salem et al., 2000). Pb toxicity also can cause decreases in survival, growth, development, behaviour and metabolism in fish (Eisler, 1998). Bioaccumulation of metals in an animal tissue are contributed by several factors; biotic ones such as body size and mass, age, sex, diet, metabolism, and position in the food web and abiotic factors such as the salinity, distribution of metals in environment, temperature and interaction with other metals, however food is the factor that has the most influence on the accumulation of metals in animal tissues (Jakimska et al., 2011). Thus, different species may have different ability in metal accumulation into their tissue. Fish will accumulates metals in its tissue through absorption during respiration and breathing thus expose metals to human via food web.

Samples collected from wet season had higher concentration of Al, Fe, Cd and Pb compared to dry season. The increases of surface runoff during the wet season may cause the concentration of heavy metals become higher. Heavy rainfall also leads to draining of chemicals, heavy metals or pesticides around the mining area or agriculture farm nearest to the rivers.

However, there were also data reported from previous studies which indicates mean concentration of heavy metals found in fish were higher during dry season (Fufeyin, 1998, Idodo-Umeh, 2002, Obasohan et al., 2006, Obasohan et al., 2008, Oguzie, 2003). This is because during dry season, temperature become higher which lead to activity, ventilation, metabolic rate and feeding sessions increased (Obasohan, 2008). Concentration of heavy metals in wet season was low due to the dilution of heavy metals that associated with heavy rains (Fufeyin, 1998).

From the observation and survey carried out from the villagers, S3 (Pandan River) located near to agriculture activity site, thus, the use of fertilizers could contribute to the increase level of Cd in fish that caught at this location. These rivers also have the history on bauxite mining activity and until now the mining are is still exist. Al is one of the core metals that related to the bauxite (Abdullah et al., 2016). S4 (Pinang River) also had the history of bauxite pollution as stated by Department of Environment Pahang due to the mining area is nearer to the river. But, there is no information about the status of bauxite mining activity for the area. From the previous study, Fe also one of the main heavy metal that related to bauxite besides Al (Abdullah et al., 2016). The highest concentration of Pb was found at S2 (Kuantan River) which was 0.060 ± 0.133 mg/kg. Location of Kuantan river is known for its busy activities for agriculture and bauxite mining. This area is also busy with fisherman and other local activities. The oil spills from the boats during regular transportation could also contributed to the increased level of heavy metals. All of this factor can affect the concentration of heavy metals in rivers and fish.

The diversity in water usage and the limited resources has led to the effort in ensuring the quality and resource control, aside from enhancing a diversity of usage (Nussey, 2000).

CONCLUSION

The result from this study showed that the concentration of heavy metal in all fish species were in the order of $Fe > Al > Pb > Cd$. The fish species that caught in Kuantan rivers also contained by heavy metals. S3 (Pandan River) has the highest concentration of Al and Cd in fish compare to other sampling station which were 8.872 ± 6.982 mg/kg and 0.013 ± 0.019 mg/kg respectively. S4 (Pinang River) had the highest concentration of Fe which was 12.201 ± 3.817 mg/kg and S2 (Kuantan River) had the highest

concentration of Pb which was 0.060 ± 0.133 mg/kg. However, the heavy metal concentration in fish meat did not exceed the permissible limit stated by European Community (2001), Food and Agriculture Organization, 2003 (FAO), Malaysian Food Act, 1983 (MFA) and World and Health Organization, 1985 (WHO). The concentration of heavy metals in wet and dry season also different which were also stated in this study. Wet season has high concentration of heavy metal. Monitoring of the heavy metal concentration in fish need to be carried out regularly. Although the concentration of heavy metal in fish and water is at low permissible limit but in the future the potential for metal toxicity may became severe if the mining or agriculture activity near the river are not properly in control. To ensure a healthy freshwater fish and quality of water in the river, concentration of heavy metal in fish and water should be monitored regularly. This act also can prevent the effect of heavy metals to human health especially at Kuantan and its surrounding area.

CONFLICT OF INTEREST

The authors declared that present study was performed in absence of any conflict of interest.

ACKNOWLEDGEMENT

The authors would like to thank Universiti Sultan Zainal Abidin and Ministry of Higher Education of Malaysia for FRGS grant (FRGS/1/2016/Wab05/UNISZA/03/1).

AUTHOR CONTRIBUTIONS

Muhamad Najmi Bin Haris, Nadzifah Yaakub, Aishatul Amiera Abdul Halim, Wan Marlin Rohalin. Najmi designed and performed experiments, compiled the literature sources, interpreted data, wrote parts of the manuscript, analysed data and wrote the manuscript, Wan Marlin helped in data interpretation, reference checking, performed experiments and co-wrote the paper; NY checked the references, supervised the research and acted as corresponding author. All authors read and approved the final version.

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