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Analysis of Heavy Metals Concentration in Fish and Crustaceans from Muar River

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Abstract: Contaminations of the aquatic environment may enter the food chain and pose health risks to the population. This study aims to determine the heavy metals concentrations in the Muar River and assess the population's health risk. The analysis of heavy metals concentration was analyzed using the Atomic Absorption Spectroscopy (AAS) using the microwave digestion technique. The hierarchy of the heavy metals in seabass *(Lates Calcarifer*) is Zn > Cd > Cu > Pb > Cr > Fe while in prawn (*Penaeus* sp.) is Zn > Cu > Cd > Pb > Cr > Fe and in oyster (*Crassostrea* sp.) is Cd > Zn > Cu > Cr > Fe > Pb. These metals concentrations were below the maximum permissible limits set by the Malaysian Food Act (1983) and Regulations (1985). Target Health Quotient (THQ) value based on the studied metals shows that seabass, prawn, and oyster were below 1, which indicates that the consumptions of the fish and crustaceans from Muar River are safe for human consumption and health.

Keywords: Heavy Metals, Atomic Absorption Spectroscopy, Microwave Digestion, Target Health Quotient

1. Introduction

Malaysia is one of the countries that has the largest continental shelf areas within the tropical world [1]. The total coastline for Malaysia is 4800 km. If it is being compared with other areas, this region is very rich in biodiversity. It is considered to contain a tremendous species diversity of marine life in the world [2]. Rapid urbanization, development, agricultural and industrial activities have spread along the seas and rivers, leading to more pollution. Fish and crustaceans have become a threat to human health because of the accumulation of high heavy metals concentration resulting from these activities. Heavy metals such as Cadmium (Cd), Mercury (Hg), Chromium (Cr), and many more have not only been known for their high density but also their adverse effects on the ecosystem and living organisms.

Accumulation of heavy metals in fish can affect fish early growth and development because they are more sensitive than during the mature stage. Heavy metals can be neurotoxic, carcinogenic, mutagenic, or teratogenic. Several symptoms related to metal poisoning to humans include vomiting, paralysis, ataxia, gastrointestinal disorder, diarrhoea, and pneumonia [3]. The human's liver-kidney,

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central nervous system, mucus tissue, intestinal tract, and reproductive system may be damaged if humans consume fish and crustaceans contaminated with heavy metals [4]. Crustaceans help measure contamination levels in surface sediment because crustaceans may act like a typical common organism and are considered discrepant aquatic species [5]. Waste such as industrial wastes, municipal wastes, and pesticides that came from rapid urbanization are being discharged, resulting in heavy metals accumulation in tissues of crustaceans such as oysters, prawn, and fish. As consumption of seafood is increasing daily, with the current rapid urbanization, seafood safety must be ensured so that it does not compromise with heavy metal pollution.

Therefore, this study determines the bioaccumulation of heavy metals concentrations (Cu, Cd, Cr, Fe, Pb and Zn) in seabass, prawn and oysters from the Muar River, Johor. These samples were determined by atomic absorption spectrometer (AAS) using microwave digestion techniques and comparing them with the Target Health Quotient (THQ) equation. THQ and total THQ for each metals must be lower than 1 and if it is greater than 1, there are potential health risk exposed to the society [6].

2. Materials and Methods

2.1 Reagents and Apparatus

All reagents were of analytical reagent grade. Deionized water was used for all dilutions. Nitric acid, HNO_3 (HmbG Chemicals, 70%) and hydrogen peroxide, H_2O_2 (R&M Chemicals, Essex, United Kingdom, 35%) were used in this experiment. All glassware and apparatus used during heavy metals analysis were washed with deionized water and soak in 5% nitric acid for 24 hours. They were rinsed with deionized water and allowed to air-dry at room temperature before used [6]. The standard element solutions used for calibration were produced by diluting a stock solution of 1000 ppm of the prepared standard solution. The samples were digested by microwave digestion (CoolPex, Preekem) and using an atomic absorption spectrometer (AAS) (Agilent Technologies 200 Series 240AA) for heavy metals detection.

2.2 Collection of seabass, prawn and oyster

Sample collection was carried out along the Muar River (Figure 1). Seabass and prawn sample was collected from a local fisherman that captured them from Muar River. Oysters were collected from Oyster Bay, a place for oyster breeding. The sample was collected 3 times with a time interval of 1 month between each sample collection in September, October, and November. The collected samples were kept at 4-5^{o}C and delivered to the food analysis laboratory in 4-5 hours. The sample was washed thoroughly with deionized water until all the dirt and unwanted things were removed entirely and dried using filter paper. Samples were kept in clean polythene bags and stored in the refrigerator at -20^{o}C until further use.

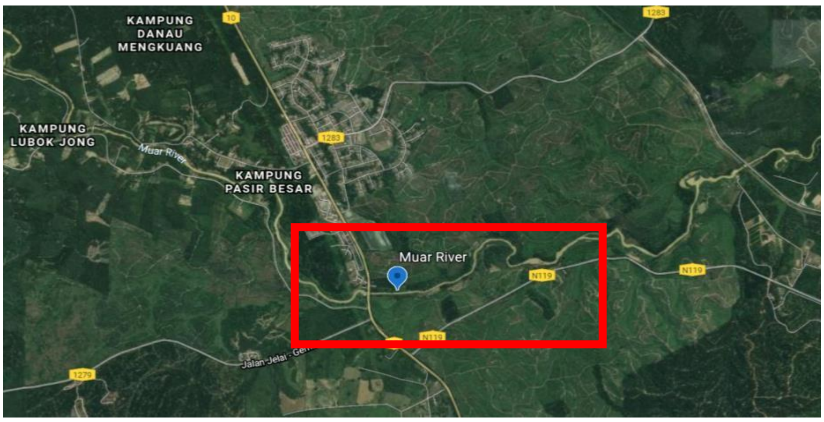

Figure 1: Location of the Muar River

2.3 Microwave digestion method

1 g of edible tissues from each sample was weighed by analytical balance (Smith Analytical Balance) and placed in the digestion vessel. The samples then being digested using 6 ml of concentrated HNO_3 (65%) and 2 ml of H_2O_2 (30%) [5]. Digestion conditions for the microwave system were applied at a pressure of 30 bars, ramp to 130ºC for 5 minutes, to 160ºC for 10 minutes, and elevated to 180ºC for 15 minutes [6]. Different time and temperature is set for certain stage because this will increase the reaction rate of digestion [8]. The digested sample was triplicate for each heavy metals analysis: Cd, Cr, Cu, Zn, Fe, and Pb.

2.4 Atomic Absorption Spectrometer (AAS) measurement

The digested solution is transferred into 50 ml boiling tubes and diluted with deionized water to make up the final volume to 25 ml. AAS analyzed heavy metals of the samples with the following wavelength, Cd (228.8 nm), Cr (357.9 nm), Cu (324.8 nm), Fe (248.3 nm), and Zn (213.9 nm)[6].

2.5 Estimation of human health risk assessment

Target Health Quotient (THQ) [8] were calculated from the findings to estimate the non-carcinogenic health risks from the consumptions of crustaceans/fish. It is useful to estimate the probability of the hazard (e.g., heavy metals) exposure that may affect health. THQ is calculated by using the formula below [7][8];

$$\mathrm{THQ} = \frac{\mathrm{EF} \times \mathrm{ED} \times \mathrm{FIR} \times \mathrm{CM}}{\mathrm{BW} \times \mathrm{AT} \times \mathrm{RfD}} \times 10^{-3} \quad Eq.\ 1$$

where, EF is exposure frequency (365 days/year); ED is exposure duration 70 years (average lifetime); FIR is food intake rate (fish: 36 g/person/day; crustaceans 5.42 g/person/day); CM is heavy metals concentration in fish/crustaceans (mg/kg); BW is the average body weight (60 kg); AT is average exposure time for non-carcinogenics (365 years x number of years exposure); RfD is oral reference dose (mg/kg/day). RfD for Cu, Cd, Pb, Zn, and Fe was 0.04, 0.001, 0.0035, 0.3, and 0.7 mg/kg/day respectively [6].

3. Results and Discussion

3.1 Heavy metals concentrations in fish and crustaceans.

AAS was used to analyze the heavy metals concentration (Table 2) in seabass, prawn, and oyster after the microwave digestion technique.

Table 2: Mean concentrations of heavy metals in seabass, prawn, and oyster.

Samples	Mean concentration of heavy metals (mg/kg)					
	Cu	Cr	Cd	Pb	Zn	Fe
Seabass	0.51 ± 0.16	0.32 ± 0.05	0.58 ± 0.10	0.40 ± 0.06	0.67 ± 0.16	BDL
Prawn	0.50 ± 0.23	0.38 ± 0.24	0.48 ± 0.22	0.47 ± 0.02	0.70 ± 0.03	BDL
Oyster	0.97 ± 0.35	0.81 ± 0.21	1.29 ± 0.62	0.52 ± 0.14	1.02 ± 0.59	0.56 ± 0.46

Cu is widely used in industrial processes such as the production of Cu pipes, cable and wires. High intakes of Cu may lead to liver and kidney damage [10]. The highest concentration of Cu is in oyster with a value of 0.97 ± 0.35 mg/kg, while seabass and prawn were reported 0.51 ± 0.16 mg/kg and 0.50 ± 0.23 mg/kg, respectively. Cu concentration in seabass, prawn, and oyster are still below the permissible level set by Malaysia Food Act 1983 and WHO/FAO, which is 10 and 30 mg/kg, respectively.

Cr is an essential mineral that can bring many benefits to the human body. The recommended daily intake of Cr is 50-200 µg [11]. Oyster recorded the highest amount of Cr with the value of 0.81 ± 0.21 mg/kg followed with prawn, 0.38 ± 0.24 mg/kg and seabass 0.32 ± 0.05 mg/kg. There is no permissible limit for Cr according to the Malaysian Food Act 1983. However, according to WHO/FAO, the permitted level of Cr is 1.0 mg/kg, and IAEA-407 reported that the permissible limit of Cr in aquatic life is 0.73 mg/kg. Based on this permitted limit, the Cr level in the oyster is slightly higher than the permissible limit by IAEA407. However, it is still safe to consume.

Cd contamination in aquaculture sites is common due to industrial and agricultural activities such as applying fertilizers to crops [12]. Long-term exposure of Cd may result in kidney damage and increase the probability of getting prostate cancer [13]. Water pollution in Muar River came from numerous sources of pollution from agricultural wastewater and minor sourced pollutions derived from domestic and industrial wastewater. Hence, Muar River is categorized in Malaysia Environmental Quality Report 2009 by Department of environment as slightly polluted river [14].

Malaysian Food Act 1983 and Regulation 1985 stated that the permitted level of Cd in fish and crustaceans is 1.00 mg/kg, while WHO/FAO stated that the permitted level of Cd is 0.05 mg/kg. In the current study, oyster recorded the highest concentration of Cd among the other two samples, which is seabass and prawn. Mean concentration of Cd metals in the oyster is 1.29 ± 0.62 mg/kg while seabass and prawn recorded 0.58 ± 0.10 mg/kg and 0.48 ± 0.22 mg/kg respectively. Oyster has exceeded the permitted Cd concentration from the law above.

The concentration of Pb among those three samples is not too significant. Pb concentration for oyster is 0.52 ± 0.14 mg/kg which is the highest, seabass 0.40 ± 0.06 mg/kg and prawn recorded 0.47 ± 0.02 mg/kg. Pb is a non-essential metal that can be toxic to humans when ingested or inhaled at a high level [14]. Pb concentration in all the samples is still below the permissible limit set by the Malaysian Food Act 1983 and WHO/FAO. However, according to the Turkish Food Codex, the maximum permitted limit of Pb for fishes is 0.4 mg/kg, indicating that all of the samples have exceeded the permissible limit. Nevertheless, it is still considered safe.

Zn is an essential element that is only needed in a small amount by the human body. Zn is believed to help boost the immune system and enhance the growth of children and infants. , Zn concentration in the oyster is 1.02 ± 0.56 mg/kg which is the highest followed by prawn, 0.70 ± 0.03 mg/kg and seabass 0.67 ± 0.16 mg/kg. However, the concentration of Zn in all the samples are below the allowable limit. The allowable limit for zinc is 100 mg/kg by Malaysian Food Act 1983, Regulation 1985 and WHO/FAO 2004.

Fe is needed by the body to reduce the risk of Fe deficiency diseases which is anaemia. Fe deficiency may also cause respiratory system problem such as having trouble breathing [15]. The only sample that shows Fe content is oyster, a concentration of 0.56 ± 0.46 mg/kg. In contrast, seabass and prawn give negative values that indicate the Fe content below detection limits of AAS. The detection limit of Fe by AAS is 0.018 µg/mL. Therefore, Fe content in seabass and prawn is below the detection limit. However, there is no allowable limit of Fe in any laws and regulations due to the unlikeliness of Fe contamination.

The order of heavy metals concentration in seabass is Zn > Cd > Cu > Pb > Cr > Fe, for prawn is Zn > Cu > Cd > Pb > Cr > Fe and for oyster is Cd > Zn > Cu > Cr > Fe > Pb. In this study, oyster shows the highest mean of all heavy metals concentrations than seabass and prawn. Reinecke *et al.* (2003) and Wang *et al.* (2001) reported that crustaceans that live at the bottom of the aquatic site could accumulate more metals, and it is one of the most important organisms that play important roles in metal detoxification [16], [17]. Crustaceans are the most suitable bio-indicator to monitor the heavy metal concentrations in aquatic life [18]. Oyster, *Crassostrea* sp., seems to be a perfect bio-indicator of heavy metals in the river since it has high filtration rates and accumulates heavy metals [19].

3.2 Health risk assessment of heavy metals in fish and crustaceans

Health risk assessment can determine human exposure to environmental hazards that can cause potential adverse health hazards. THQ is used to estimate the non-carcinogenic health risks from the consumption of fish and crustaceans. THQ was calculated by using *Equation* 1.

Table 2: THQ values of fish and crustaceans

	Samples	Target Hazard Quotient Total THQ				
	Cu	Cd	Pb	Zn	Fe	
Seabass	0.00765	0.34800	0.06857	0.00134		0.42556
Prawn	0.00129	0.04336	0.01213	0.000211		0.05699
Oyster	0.00219	0.11653	0.01342	0.000307	0.00007	0.13252

THQ values for seabass, prawn, and oyster shows no greater value than 1. Therefore, the health risks associated with studied heavy metals through the consumption of fish and crustaceans is insignificant. Total THQ also shows no greater value than 1. If the total THQ exceed 1, it means that the population is facing a carcinogenic health risk from the accumulative heavy metals through the consumption of fish and crustaceans [20]. THQ values for all samples were below harmful levels, which indicated the consumption of both fish and crustaceans from the Muar River would not result in health risks from the six studied metals.

4. Conclusion

This study was developed to provide data on heavy metals concentration on fish and crustaceans from the Muar River. In conclusion, heavy metals concentration in all samples using Target Health Quotient (THQ) shows seabass, prawn, and oyster was below the acceptable limit by comparing with Malaysian Food Act 1983, Regulation 1985 and WHO/FAO. It is recommended for human consumption, but a long-term monitoring system of metal bioaccumulation in fishes needs to be done to provide useful information for assessing the potential health risks of metals in Malaysia.

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