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Cadmium and Lead Concentrations in Water, Sediment, Fish and Prawn as Indicators of Ecological and Human Health Risk in Santubong Estuary, Malaysia

Adriana Christopher Lee[1], Farah Akmal Idrus[1,*], Fazimah Aziz[1]

[1]*Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia;*

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Abstract

Cadmium (Cd) and lead (Pb) are toxic heavy metals with a growing appeal for study due to their ability to bioaccumulate in fish which may pose threat to human health through fish consumption. This study reported the concentration of Cd and Pb in water, sediment, fish, and prawn in Santubong Estuary, Malaysia. Water, sediment, fish (*Arius maculatus*) and prawn (*Fenneropenaeus merguiensis*) samples were collected from three rivers namely Buntal, Penambir and Demak. These samples were digested and analyzed using Flame Atomic Absorption Spectrophotometer (FAAS) for the heavy metal contents. The potential ecological and human health risks were assessed by using the bioaccumulation factor (BAF), Geo-accumulation Index (Igeo), Enrichment Factor (EF), Provisional Tolerable Weekly Intake (PTWI), Health Risk Index (HRI) and Health Index (HI). Cd and Pb concentrations in water were within the permissible limits but were above the acceptable limits in sediment as recommended by WHO. The concentration of Cd in *A. maculatus* was (0.10 - 0.13 mg/kg) while the concentration of Cd in *F. merguiensis* was (0.11 - 0.15 mg/kg), and these values were below the safety limits set by FAO/WHO and MFA. The concentration of Pb in *A. maculatus* (0.19-1.46 mg/kg) was also below the safety limits; however, the concentration of Pb in *F. merguiensis* (1.35-2.97 mg/kg) surpassed these safety limits. The Igeo values were less than one, and EF values ranged between 5 and 20, suggesting that this area is polluted with heavy metals. The BAF values for Cd (0.001 - 0.002 mg/kg) and Pb (0.003 - 0.040 mg/kg) showed that there might be an appreciable chance of bioaccumulation of heavy metals in the fish and prawn. The PTWI of prawn was slightly above the acceptable PTWI of Pb recommended by FAO/WHO (2004). Comparison with the safety limits showed that the continuous consumption of these fish and prawn for a long period would impose bad impacts on health. HRI and HI in both organisms were greater than one, indicating that there were possible adverse effects. Therefore, close monitoring of this area is recommended to minimize the risks of aquatic organism consumption.

Keywords: cadmium, lead, fish, prawn, water, sediment

1. Introduction

Santubong Estuary is located at the Bako-Buntal Bay, bordered by Gunung Santubong and Bako National Park, Malaysia. It is an estuary with mangrove ecosystem. Mangroves are the most productive ecosystems due to their role as a nursery and breeding grounds for many fish species (Abu Hena *et al.,* 2017). Siddik *et al.* (2016) stated that turbid water of this ecosystem provides abundant food for juvenile fish. Surrounding areas of Santubong Estuary have been rapidly growing as an industrial area (i.e. Demak Laut Industrial Park) and the industrial activities in this area may have produced heavy metal wastes. Heavy metal pollution has been a serious global threat to the aquatic ecosystem due to its potential to cause an adverse effect on the different trophic levels through its persistence, the ability of bioaccumulation and biomagnification (Kumari *et al.,* 2018). Heavy metals are difficult to be degraded and eliminated (Lenart-Boron and Boron, 2014). Non-essential heavy metals like cadmium (Cd) and lead (Pb) have no role in biological processes, and are very harmful even in a low concentration (Mirnategh *et al.,* 2018). Heavy metals occur in the environment by natural processes such as formation of ores, weathering of rocks and leaching of rocks, airborne dust, forest fires and vegetation (Adebayo, 2017; Olawusi-Peters *et al.,* 2017) and human activities such as disposal of untreated industrial effluent and domestic sewage, atmospheric deposition of particulate matters, runoff from agricultural land and recreational activities (Adebayo, 2017; Olawusi-Peters *et al.,* 2017; Kumari *et al.,* 2018).

Heavy metals tend not only to be accumulated in water but also may be released under certain physicochemical conditions, moving up through the food chain (Tabari *et al.,* 2010). Moreover, mangroves serve as a natural sink for heavy metals accumulations from the freshwater river before entering the sea (Mitra, 2019). Hence, heavy metals have a high tendency to accumulate in the body of aquatic organisms such as fish and prawn. Fish may absorb heavy metals through several pathways like from food ingestion and surrounding water and sediment (Adebayo, 2017). Fish have the ability to accumulate heavy metals in their tissues (Rajeshkumar and Li, 2018) and this may transfer

[*] Corresponding author e-mail: aifarah@unimas.my.

into higher trophic level in the food chain (Kumari *et al.*, 2018) and accumulate in the human body, which will threaten human life if exceeding the recommended limit (Sihombing *et al.*, 2019).

Various standard measures were used to assess the human health risks associated with the measured levels of heavy metal contamination. The human health risk assessment of potentially toxic heavy metals such as Health Risk Index (HRI) and Hazard Index (HI) provides an estimation of the potential health risks associated with long term exposure to chemical pollutants (Ezemonye *et al.*, 2019). Monitoring contaminants in sediments were largely recognized, and it has been extensively used as environmental indicator to assess the metal contamination. Several indices were developed to assess the heavy metal risk to environment such as Geo-accumulation Index (Igeo) and Enrichment Factor (EF) used to examine the degree of contamination of the sediments and anthropogenic influence on the sediment quality (Enuneku *et al.*, 2018). Health risks to humans arising from the toxicity of heavy metals mainly include kidney and skeletal damages, neurological disorders, endocrine disruption, cardiovascular dysfunction, and carcinogenic effects (Maurya *et al.*, 2019).

A study conducted at the Estero Salado mangrove located in Ecuador has reported that the area has been contaminated by heavy metals such as copper (Cu), chromium (Cr), Cd and Pb from the industrial wastewater (Fernandez *et al.*, 2014). Tabari *et al.* (2010) stated that fish from estuaries associated with industrial and sewage discharges have been found to be contaminated with heavy metals. Unfortunately, studies on heavy metals pollution in Santubong Estuary have not been done; hence, the status of highly toxic heavy metal such as Cd and Pb in water, sediment, fish (*Arius maculatus*) and prawn (*Fenneropenaeus merguiensis)* in this estuary was still unknown. *A. maculatus* is known as the spotted catfish that comes from the family of Ariidae, and it is also called as Ikan Lundu by the locals (Froese and Pauly, 2020). *F. merguiensis* comes from the family of Penaeidae and is known as banana prawn (Palomares and Pauly, 2019). Both of *A. maculatus* and *F. merguiensis* are commercially important species. The polluting industries in this area are production of timber, food, furniture, electrical, paints, and the major industrial activities is steel production. Steel production generated a significant amount of air pollutants, solid by-products and residues, and waste-water sludge which contained various types of pollutants such as Cd and Pb (Musah *et al.*, 2021). This causes a major concern because large inputs of sewage from the nearby industrial area and villages may increase the concentrations of Cd and Pb, which may lead to both direct and indirect degradation of the aquatic ecosystem. Therefore, a clear understanding of their distribution pathways, fate and effect on aquatic ecosystem must be made in order to effectively control and manage heavy metal pollution (Ayotunde *et al.*, 2012). Thus, the aim of the present study was to investigate the concentration of Cd and Pb in water, sediment, fish *(A. maculatus)* and prawn *(F. merguiensis)* in Santubong Estuary. The information of this study would provide better understanding of Cd and Pb concentration in aquatic organisms in relation to the contamination level in water and sediment for better environmental monitoring, ecological risk assessment and water quality management.

2. Materials and Methods

2.1. Description of study area

This study was carried out at Santubong Estuary which is situated at the North East of Kuching, the capital city of Sarawak, Malaysia. It opens into the South China Sea through the Buntal Esplanade which is one of the openings for the entire basin. Three rivers were selected in this study namely: Buntal, Penambir and Demak. These rivers serve as important means of transportation, food source and aquaculture site for the locals and the primary occupation of the villagers in this area is fishing industry. Other than that, this area was nearby to Demak Industrial Park that is one of the biggest industrial areas in Kuching. The coordinates for the rivers were 01°41’49.38' N, 110°22’20.04” E (Buntal River), 01°39’44.28” N, 110°22’58.62” E (Penambir River) and 01°35’51.30” N, 110°23’34.08” E (Demak River) (Figure 1).

2.2. Sampling procedures

The sampling was conducted three times at three rivers (Buntal, Penambir and Demak) from April 2017 to July 2017 during the wet season. The coordinates of the river were recorded using Global Positioning Station (GPS) (Garmin, GPS 72H). Fish and prawn samples were caught by using three-layered gillnets (3.81-12.70 cm mesh sizes) that were set in the morning and then the caught samples were collected in the afternoon after approximately 6 hours. Sediment sample were collected using an Ekman grab sampler and stored in the resealable plastic bags. Water samples were collected using Van Dorn water sampler and were stored in the sample bottles. All the samples were transported back to the laboratory in cooler boxes with ice, and when they reached the laboratory they were kept in the freezer at -20˚C before further analysis. Selected water quality parameters such salinity, temperature, pH and dissolved oxygen were taken using YSI (Professional Plus, Pro 10102030) handheld multi-parameter while turbidity was taken using a turbidity meter (Extech, TB400).

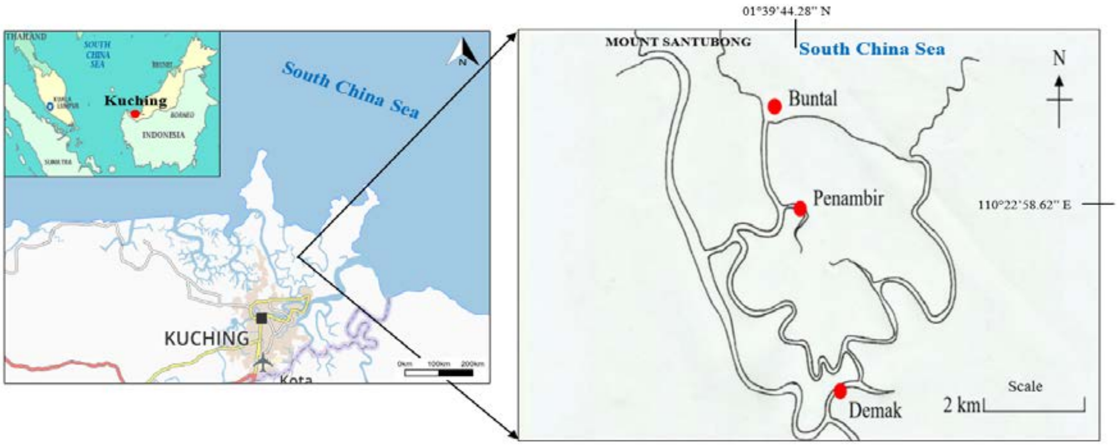

Figure 1. The map on the left shows the location of Santubong Estuary (located in between Santubong Peninsula and Bako) in Kuching, Malaysia while the map on the right shows the Santubong Estuary with the rivers (Buntal, Penambir and Demak).

2.3. Metals Analysis in Water and Sediment

Approximately 1 litre water samples from each river were filtered through a 0.45 µm filter paper and acidified using concentrated 65% HNO_3 for preservation at the time of collection (USEPA, 1992). Then, the water samples were analysed using FAAS (Thermo Scientific iCE 3000). The sediment samples were dried in an oven at 60°C until constant weight obtained. One gram of dried weight sample was weighed and put into 250 ml conical flask. The digestion process for sediment was done according to the standard method of USEPA (1996). After the digestion process, sample solutions were allowed to cool to room temperature, filtered through Whatman No. 41 filter paper, and the filtrate was collected in a 100 ml volumetric flask. Fifty ml of deionized water was added through filtration, and the sample was analysed using FAAS.

2.4. Metals Analysis in Fish and Prawn

The number of *A. maculatus* was collected; 22 samples at Buntal, 11 samples at Penambir and 27 samples at Demak while the number of *F. merguiensis* were collected; 42 at Buntal, 80 samples at Penambir and 31 samples at Demak. Then, the muscle samples of the *A. maculatus* and *F. merguiensis* were removed using ceramic knife. Muscle part was chosen because it is an edible part of the organisms. Then, they were dried in an oven at 60°C until constant weight was obtained. Dried sample was weighed for about 0.5 g. The acid digestion process for fish and prawn samples was done following the standard method by Alina *et al.*, (2012) and Mohammed *et al.* (2017). The concentrations of Cd and Pb then were determined by using FAAS.

2.5. Quality Control and Method Validation

The accuracy of the analytical methods for the analysis of heavy metal in water, sediment, fish and prawn samples were confirmed by using Certified Reference Material (CRM) MESS-4 and internal standard method. Every CRM and internal standard were analyzed three times and were compared to the certified values of metals concentration from National Research Council Canada (NRCC) and internal standard values. The recovery percentages attained for the CRM and internal standard of water, sediment, fish and prawn were between 80-120% meeting the acceptable recovery recommended by the Environment Agency (2013).

2.6. Bioaccumulation Factor (BAF)

The BAF are the ratio of heavy metals concentration in organism to that in sediment. BAF was determined using the formula (Equation 1) suggested by Olawusi-Peters *et al.* (2017).

$$\mathrm{BAF} = \frac{Cm}{Cs} \qquad \text{(Equation 1)}$$

Where:Cm = concentration of metal in organism (mg/kg). Cs = concentration of metal in sediment (mg/kg)

2.7. Assessment of Contamination Status in Sediment

The contamination status of sediment was evaluated using the Geo-accumulation Index (Igeo) and Enrichment Factor (EF). Igeo was used to determine and define metal contamination in sediments by comparing current concentration with pre-industrial levels, and the sediment is classified as unpolluted if value is less than zero (Nowrouzi and Pourkhabbaz, 2014). This index is expressed in Equation 2. Meanwhile, EF is used to estimate the anthropogenic impact on sediments by calculating differentiate between the metals originating from human activities and metals from natural source or the mixed source of the metals. The EF method normalizes the measured heavy metal content with respect to a sample reference metal such as aluminium (Al) (Zhu *et al.*, 2011). The sediment is in depletion to mineral if value is less than 2 and the EF values were calculated using Equation 3.

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \qquad \text{(Equation 2)}$$

Where: Cn = The concentration of the examined metal in sediment. Bn = The background value for the metal n: Al (8000 ppm), Cd (0.3 ppm) and Pb (20 ppm) (Turekian and Wedepohl, 1961).

$$\mathrm{EF} = \frac{(C_M/C_X)_{Sample}}{(C_M/C_X)_{Background}} \qquad \text{(Equation 3)}$$

Where: C_M = Concentration of examined metal in the sample of interest/ selected reference sample. C_X = Concentration of immobile metal in the sample of interest/ selected reference sample (Al was used in this study).

2.8. Human Health Risk Assessment Daily Intake Metal (DIM)

A survey to estimate the fish intake of villagers who lived at nearby the study region was conducted using a standard questionnaire. A total of 100 coastal villagers (male and female) with the age ranged from 17 to 87 years old were interviewed. The assessment of dietary intakes of Cd and Pb was conducted following the method of Ruaeny *et al.* (2015). The mean fish and prawn intake per week was 120 g per person and the average body weight of the villagers in this area was 60 kg. Then, the risks of dietary intakes of Cd and Pb were evaluated by comparing the weekly intake value with the provisional tolerable weekly intake (PTWI) according to FAO/WHO (2016): Cd (0.007 mg/kg) and Pb (0.025 mg/kg).

$$DIM = \frac{(Cm \times Mf)}{Mbw} \quad \text{(Equation 4)}$$

Where: DIM= Daily intake of metal (mg/kg/day).
Cm= Concentration of metal in fish (mg/kg)
Mf= Mean of fish intake (g/person/day)
Mbw = Average body weight (kg)

2.9. Health Risk Index (HRI)

The HRI referred to the ratio of the daily intake of metals in the food to the oral reference dose (RfD). The oral RfD is a numerical estimate of the daily oral exposure to humans that is not likely to cause harmful effects during the lifetime (USEPA IRIS, 2006). The USEPA (2001) has established the RfD for Cd in food at 0.00003 mg/kg day. The RfD for Pb was set at 0.0035 mg/kg day by the Joint FAO/WHO Expert Committee on Food Additives (JECFA, 1993). If HRI greater than one for any metal in food indicates that the consumer population faces a health risk (Yaradua *et al.*, 2018). The value of HRI depends on the DIM value of the food stuff and the RfD. The HRI for heavy metal exposure for fish and prawn consumption was calculated using the Equation 5 of Cui *et al.* (2004):

$$HRI = \frac{DIM}{RfD} \quad \text{(Equation 5)}$$

Where: RfD = Cd (0.00003 mg/kg day) and Pb (0.0035 mg/kg day)

2.10. Hazard Index (HI)

The HI is used to evaluate potential risk to human health upon exposure to more than one heavy metal (USEPA, 1989). It is assumed that the adverse effects will be proportional to the magnitude of the sum of multiple metal exposures, implying that higher metal exposure will cause a higher health risk. The HI is the sum of the HRI values as shown in Equation 6:

$$HI = \sum HRI = HRI_{Cd} + HRI_{Pb} \quad \text{(Equation 6)}$$

Where: HRI_{Cd} and HRI_{Pb} = HRI values for Cd and Pb

2.11. Statistical Analysis

The metal concentrations were reported as mean ± standard deviation (S.D). Analysis of Variance (ANOVA) with multiple comparisons using Tukey's test was performed to deduce the significant difference between the means at a significant level of 0.05. The relationship between the different variables was assessed using Pearson's correlation analysis. The statistical analysis was performed using Statistical Package for Social Sciences (SPSS) and Microsoft Excel (MS Excel).

3. Results

3.1. Physicochemical water parameters

The physicochemical parameters of water at these three rivers were shown in Table 1. The temperature of water ranged from 28.72 ± 1.28 °C at Buntal to 28.89 ± 0.46 °C at Demak. The highest turbidity was 92.37 ± 104.05 NTU in Penambir and the lowest turbidity was 59.76 ± 39.89 NTU at Buntal. The water was neutral with a pH range from 7.31 ± 0.72 to 7.64 ± 0.58. Dissolved Oxygen (DO) ranged from 3.48 ± 0.81 mg/L to 4.19 ± 0.91 mg/L. The value of salinity was found to be significantly among the three rivers ($p < 0.05$) and the salinity ranged from 11.49 ± 3.64 ppt to 22.16 ± 0.99 ppt.

Table 1. The physicochemical water parameters in Buntal, Penambir and Demak.

Parameters	Buntal	Penambir	Demak
Temperature (°C)	28.72 ± 1.28	28.78 ± 0.58	28.89 ± 0.46
Turbidity (NTU)	59.76 ± 39.89	92.37 ± 104.05	65.83 ± 46.65
pH	7.31 ± 0.72	7.59 ± 0.85	7.64 ± 0.58
DO(mg/L)	4.19 ± 0.91	3.56 ± 0.83	3.48 ± 0.81
Salinity (ppt)	22.16 ± 0.99	19.06 ± 5.47	11.49 ± 3.64

3.2. Analysis of metals in water

The concentrations of heavy metal in water were presented in Figure 2. Cd ranged from 0.02 ± 0.001 mg/L in Penambir to 0.03 ± 0.001 mg/L in Demak while the concentration of Pb ranged from 0.01 ± 0.002 mg/L in Buntal to 0.01 ± 0.005 mg/L in Penambir. WHO (2011) stated that the recommended standard of Cd in water is 0.003 mg/L and the Pb is 0.01 mg/L; hence, the concentration of Cd and Pb in water of these rivers was within the recommended standards.

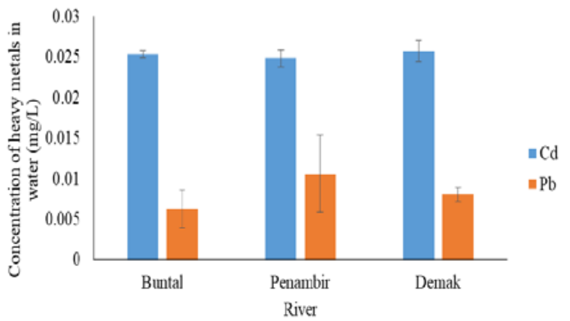

Figure 2. The mean concentration of Cd and Pb in water at Buntal, Penambir and Demak.

3.3. Analysis of heavy metals in sediment

The concentrations of heavy metal in the sediment samples were presented in Figure 3. The mean concentrations of Cd in Buntal were 0.33 ± 0.03 mg/kg, Penambir was 0.40 ± 0.02 mg/kg and Demak was 0.42 ± 0.03 mg/kg. Meanwhile, the mean concentration of Pb in Buntal was 22.86 ± 2.31 mg/kg, Penambir was 31.25 ± 2.41 mg/kg and Demak was 49.43 ± 8.31 mg/kg. WHO (2011) stated that the acceptable limits of Cd and Pb in sediments were 0.20 mg/kg and 0.30 mg/kg respectively; however, the concentrations of Cd and Pb in sediment in this study were generally higher than those limits.

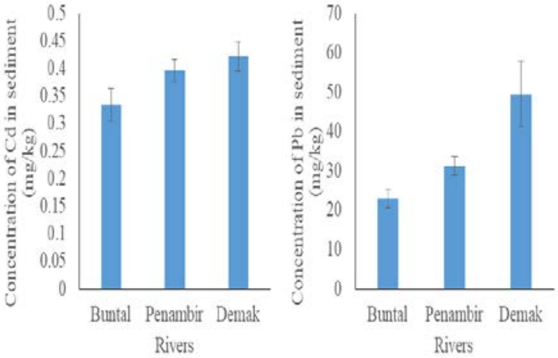

Figure 3. The mean concentration of Cd and Pb in sediment at Buntal, Penambir and Demak

3.4. Analysis of metals in fish and prawn

The heavy metal concentration in the muscle of *A. maculatus,* also called as spotted catfish, and *F. merguiensis* known as banana shrimp were presented in Figure 4. In *A. maculatus*, the concentrations of Cd were in the range of 0.1 ± 0.01 mg/kg in Buntal to 0.13 ± 0.04 mg/kg in Demak while the concentration of Pb were in the range of 0.19 ± 0.11 mg/kg in Buntal to 1.46 ± 0.47 mg/kg in Demak. In *F. merguiensis*, the range of Cd were in the range of 0.11 ± 0.04 mg/kg in Buntal to 0.15 ± 0.01 mg/kg in Penambir while the concentration of Pb were in the range of 1.35 ± 0.51 mg/kg in Penambir to 2.97 ± 1.13 mg/kg in Buntal.

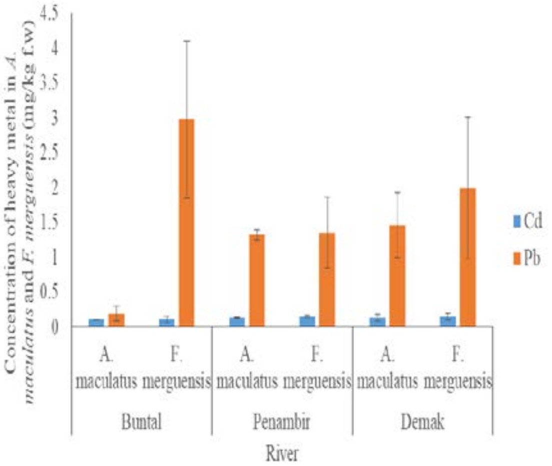

Figure 4. The mean concentration of Cd and Pb in *Arius maculatus* and *Fenneropenaeus merguiensis* caught from Buntal, Penambir and Demak.

3.5. Bioaccumulation Factor (BAF)

In this study, *F. mergeunsis* showed a higher BAF values than *A. maculatus* in all the three rivers and Cd was accumulated at higher level compared to Pb (Table 2).

Table 2. The BAF of Cd and Pb in *Arius maculatus* and *Fenneropenaeus merguiensis* in Buntal, Penambir and Demak.

River	Species	BAF (mg/kg)	
		Cd	Pb
Buntal	*Arius maculatus*	0.26	0.01
	Fenneropenaeus merguiensis	0.28	0.09
Penambir	*Arius maculatus*	0.34	0.04
	Fenneropenaeus merguiensis	0.38	0.04
Demak	*Arius maculatus*	0.34	0.04
	Fenneropenaeus merguiensis	0.37	0.06

3.6. Assessment of Contamination Geo-accumulation index (Igeo) and Enrichment Factor (EF)

The Igeo and EF values were shown in Table 3. The Igeo values for Cd and Pb were found to be greater than one, suggesting that the area is moderately polluted. Meanwhile, the EF values for Cd and Pb were in the range of 5 to less than 20, which indicated that the area is significant contaminated. Thus, both of these indices confirmed that the sediment in this area was contaminated.

Table 3. The Igeo and EF values in Buntal, Penambir and Demak.

River	Igeo		EF	
	Cd	Pb	Cd	Pb
Buntal	0.003	0.003	6.39	6.57
Penambir	0.004	0.004	7.59	8.98
Demak	0.004	0.007	8.08	14.20

3.7. Human Health Risk Assessment Weekly Intake of Metal (WIM), Health Risk Index (HRI) and Hazard Index (HI)

The WIM of Cd in *A. maculatus* in all rivers were found to be below the PTWI of Cd recommended by the FAO/WHO (2016). However, the WIM of *F. merguiensis* at Buntal and Demak were slightly above the PTWI for Pb (Table 4).

Additional comparisons with the permitted limits of heavy metal in fish and prawn set by the FAO/WHO (2011) and MFA (1983) were also shown in Table 4. In *A. maculatus*, the concentrations of Cd were below the permitted limit set by both FAO/WHO (2011) and MFA (1983) while the concentration of Pb were above the FAO/WHO (2011) but still under the MFA (1983) permitted limit. In *F. merguiensis*, the concentrations of Cd were also below the permitted limit set by both FAO/WHO (2011) and MFA (1983), but the concentrations of Pb were above the permitted limit set by the FAO/WHO (2011). The concentration of Pb in *F. merguiensis* was also above the permitted limit set by the MFA (1983) except at Penambir and Demak.

The HRI values of Cd in both organisms were greater than one. Meanwhile for Pb, only the HRI values of *F. merguiensis* at Buntal and Demak was greater than one. The HI values in both organisms were also greater than one in every river (Table 4).

Table 4. Comparison of WIM, HRI and HI values in *Arius maculatus* and *Fenneropenaeus merguiensis* with PTWI and safety limits.

River	Species	WIM		HRI		HI
		Cd	Pb	Cd	Pb	
Buntal	*Arius maculatus*	0.001	0.003	6.64	0.11	6.75
	Fenneropenaeus merguiensis	0.002	0.04	7.19	1.69	8.88
Penambir	*Arius maculatus*	0.002	0.02	8.63	0.75	9.38
	Fenneropenaeus merguiensis	0.002	0.02	9.79	0.77	10.56
Demak	*Arius maculatus*	0.002	0.02	8.63	0.83	9.46
	Fenneropenaeus merguiensis	0.002	0.03	9.51	1.13	10.64
PTWI	FAO/WHO (2016)	0.007	0.025			
Safety limits	FAO/WHO (2011)	0.2	0.3			
	MFA (1983)	1	2			

Table 5. Pearson correlations analysis between physicochemical water parameters and heavy metals in the water.

	Cd	Pb	Salinity	Turbidity	pH	DO	Temperature
Cd	1						
Pb	0.076	1					
Salinity	0.193	0.216	1				
Turbidity	-0.547*	0.131	-0.309	1			
pH	0.491*	-0.001	0.135	-0.584*	1		
DO	0.497*	-0.307	0.465	-0.527*	0.622*	1	
Temperature	0.535*	0.356	0.13	-0.308	0.021	-0.228	1

* Correlation is significant at the 0.05 level.

3.8. Correlation between heavy metals in water and sediment

The result shows no correlation between Cds-Cdw with the value of r = 0.076, while Pbs-Pbw also showed no correlation with the value of r = 0.107 (Table 6). However, the Cdw-Pbs and Cds-Pbs shows positive correlations with the values of r = 0.485 and r = 0.703, respectively.

Table 6. The Pearson correlation analysis between heavy metals in water and sediments.

	Cdw	Pbw	Cds	Pbs
Cdw	1			
Pbw	0.076	1		
Cds	-0.061	0.37	1	
Pbs	0.485*	0.107	0.703*	1

* Cds is Cd in sediment, Pbs is Pb in sediment, Cdw is Cd in water and Pbw is Pb in water.
* Correlation is significant at the 0.05 level.

4. Discussion

Aquatic ecosystems are experiencing great pressure from the increasing industrial activities due to the accidental spill of waste and dumping of waste. Hence, the monitoring of the levels of pollutants is becoming increasingly urgent as a critical measure to ensure good quality of food and water. The results obtained in the current study reveal the physicochemical water parameters of water measured in the three rivers of the Santubong Estuary. The temperature falls within the acceptable value (28- 30 °C) for a survival of aquatic organism (Olawusi-Peters *et al.,* 2017; Lawson, 2011). There were no variations in water temperatures across the rivers; and this may be due to the constant flow of water, so the temperature was not changing. The increase of temperature may affect metals uptake by organism since influx and efflux rates of metals changes (Pourang *et al.,* 2004). Turbidity is an index of water clarity, and it was higher in all the rivers. The turbidity increases constantly from the river mouth to the mangrove. The recorded salinity indicates a brackish environment with a range from 0.5 to 30 ppt (Karleskint *et al.,* 2009; Olawusi-Peters *et al.,* 2017). The salinity decreases from Buntal to Demak. The decreasing salinity values from the river mouth to the middle were similar to those of Kazemi *et al.* (2013). Arshad *et al.* (2011) also reported that salinity range increases where the river water meets the ocean. The water samples were neutral, and the pH values in this study matched with other researchers' proven view, mangrove which is near to the sea has pH of sea water of approximately 6.5-8.5 (WHO, 2011). The acidification of the aquatic environment will lower pH and reduce bioavailability of physiologically important free metals (Henry *et al.,* 2012). DO is an important aquatic parameter, whose presence is vital to aquatic fauna. It plays crucial role in the growth, distribution and behaviour of aquatic organisms. The DO level in this study was within the favourable condition (4-6 mg/L) for aquatic life to survive (Olawusi-Peters *et al.,* 2017). Thus, low DO content is potentially to cause by the presence of pollutants such as heavy metals in that area, while higher DO level indicates an adequate supply and availability of oxygen to support marine species growth and activity.

The concentration of Cd and Pb in water in this study was higher than the level in the study of Sany *et al.* (2012), but they were still within the recommended standard range set by WHO (2011). The concentrations of both heavy metals in water were not significantly different among the three rivers ($p > 0.05$). For sediment, the concentrations of Cd and Pb were generally high and were above the acceptable limits described by WHO (2011) and the concentration of Cd and Pb in the sediments showed significant difference ($p < 0.05$) between rivers. Demak River located at the Demak Industrial Park showed the highest concentration of both metals, and this indicated that the industrial activities in this area were polluting the aquatic ecosystem. The concentrations of Cd and Pb in sediment in this study were lower compared to the study done by Sany *et al.* (2013) in Selangor, Malaysia; however, the concentration of Pb in sediment in this study was found to be higher than Langat Estuary that received high metals pollution from the industrial and shipping activity (Mokhtar *et al.,* 2015). Sediment recorded the highest metal concentrations, and this may be due to the fact that when metal pollutants are released into aquatic environment, they do not remain in aqueous phase but are adsorbed on to the sediments. Thus, the sediment acts as a sink for pollutants, hence the reason for its higher concentrations of these metals. Meanwhile, the Igeo values for Cd and Pb were found to be less than one, suggesting the area to be moderately polluted. The EF values for Cd and Pb in all rivers were between 5 and 20, which indicated that the area is significantly contaminated. The high level of metals in sediments influences the level of metals in water, which would contribute widely to the bioaccumulation in aquatic organisms.

The heavy metal concentration in the muscle of *A. maculatus* and *F. merguiensis* were presented in Figure 4. The concentrations of Cd in both organisms were below the safety limits by FAO/WHO (2011) and MFA (1983); however; the concentration of Pb in *F. merguiensis* surpassed these safety limits. The result observed in this study is similar to the findings in the reports of Ahmed *et al.* (2019). This showed that consuming these fish and prawn in large quantities and on a regular basis for a long period of time might also impose a bad effect on human health. Other than that, the constant and consistent exposure of fish and prawn to these metals would thereby decrease their fitness in the ecosystem. Ahmed *et al.* (2019) stated that that metal concentrations in fish muscles varied widely depending on the location and species. In this study, the *F. merguiensis* had comparatively higher concentration of metals than *A. maculatus* as they live close to the bottom of sediment. The metal accumulation in fishes could be highly influenced by sampling locations and habitats. However, only the concentration of Pb in *A. maculatus* was significantly different among the three rivers ($p < 0.05$), and the concentration of Cd and Pb in *F. merguiensis* was not significantly different among the three rivers ($p > 0.05$). Generally, strong correlations between specific heavy metals in the environment may reflect similar levels of contamination or release from the same sources of pollution. In this study, strong positive correlations were found between Cd in sediment and Pb in sediment (Table 5), indicating that they had the same source either natural or anthropogenic. Cd and Pb are non-essential elements; Cd and Pb originated from nearby industrial activities might end up in the aquatic ecosystem which will greatly affect the aquatic organisms that live in this area.

The level of concentration in the waters, sediments, and organisms at Santubong Estuary amongst the three rivers follows the order Pb > Cd, while the sequence of the concentration of heavy metal in the rivers was Demak > Penambir > Buntal. This showed that the industrial activities and human settlement directly influence the metals concentration in water, sediment and aquatic organism in this estuary. This is alarming for authorities and dangerous to the local people who feed on the organisms since Cd and Pb are very toxic and harmful to human body. The correlation analysis shows that concentration of Cd in water was positively correlated with pH, DO and temperature. There were also no correlations between the heavy metal concentrations in the water with the heavy metals in sediment.

The BAF was generally high, indicating that the bioaccumulation of heavy metals occurred in these organisms. The accumulation of the metal in aquatic organism depends upon the classification of species, entry pathways, metabolic characters of the sampled tissues and the surrounding environmental condition in which the species live (Ahmed *et al.,* 2019). *F. merguiensis* has the highest BAF compared to *A. maculatus* due to the fact that it is a benthic organism; thus metals in sediments may greatly contribute to high metals accumulation in *F. merguiensis*. The occurrence of appreciable high BAF values in Santubong Estuary was an indication of the high human activities going on in the area. Generally, the calculated level of PTWI for Cd lies in the normal ranges, and the fishes were assumed as safe to be consumed; however, the continuous exposure of Pb to the fish and prawn may cause toxicity in future. The calculated PTWI of Cd and Pb at Kuala Terengganu by Chuan *et al.* (2018) were found to be higher than the present study, indicating the continuous consumption of the species would impose some health problem. The acceptable guideline value for HRI and HI is 1. However, the HRI and HI values in this study were exceeding 1. These high values of HRI and HI indicated that the aquatic organisms may pose serious human health risk after consumption.

5. Conclusion

The physicochemical water parameters and heavy metals concentration in water of Santubong Estuary revealed a brackish environment with low chemical pollutants burden. However, the concentration of Cd and Pb in sediment were generally higher when compared with recommended values and based on the pollution indices (Igeo and EF), the sediment was polluted. The accumulation of heavy metals is predominant in sediments compared to water and organisms because sediments act as an important sink for all contaminants. The concentration of Cd in *A. maculatus* and *F. merguiensis* was within the recommended limits; however, the concentration of Pb in these organisms was considerably high and thus causing worry. The prolonged consumption of both organisms in this area will pose some serious health problem to the consumer based on the human health risk assessments since heavy metals accumulate. Thus, great attention should be given to this estuary to control the anthropogenic inputs and proper regular monitoring of heavy metal concentrations in this estuary should be conducted. The industrial activities that operate nearby this estuary also should adopt more sustainable and ecoinnovative management options to reduce potential ecological and human health risk of heavy metal pollution.

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References

Abu Hena MK, Idris MH, Rajaee A and Siddique, MAM. 2017. Length–weight relationships of three fish species from a tropical mangrove estuary of Sarawak, Malaysia. *J Appl Ichthyol.,* **33(4):** 858-860.

Adebayo, I. 2017. Determination of Heavy Metals in Water, Fish and Sediment from Ureje Water Reservoir. *J Environ Anal Toxicol.,* **7(4):** 1-4.

Ahmed ASS, Sultana S, Habib A, Ullah H, Musa N, Hossain MB, Rahman MM and Sarker MSI. 2019. Bioaccumulation of heavy metals in some commercially important fishes from a tropical river estuary suggests higher potential health risk in children than adults. *PLOS ONE,* **14(10):** 1-21.

Alina M, Azrina A, Mohd Yunus AS, Mohd Zakiuddin S, Mohd Izuan Effendi H and Muhammad Rizal R. 2012. Heavy metals (mercury, arsenic, cadmium, plumbum) in selected marine fish and shellfish along the Straits of Malacca. *Int Food Res J.,* **19(1):** 135-140.

Arshad AB, Ara R, Amin SMN and Effendi M. 2011. Influence of environmental parameters on shrimp post- larvae in the Sungai Pulai seagrass beds of Johor Strait, Peninsular Malaysia. *Sci Res Essays,* **6(26):** 5501-5506.

Ayotunde E, Offem B and Ada F. 2012. Heavy Metal Profile of Water, Sediment and Freshwater Cat Fish, Chrysichthys nigrodigitatus (Siluriformes: Bagridae), of Cross River, Nigeria. *Rev Biol Trop,* **60:** 1289-1301.

Chuan O, Aziz NM, Shazili NA and Yunus K. 2018. Selected heavy metals content in commercial fishes at different season landed at Fisheries Development Authority of Malaysia Complex (LKIM) Complex, Kuala Terengganu, Malaysia. *J Sustain Sci Manag.,* **13:** 29-38.

Cui YJ, Zhu YG, Zhai RH, Chen DY, Huang YZ, Qui Y, Liang JZ. 2004. Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. *Environ Int.,* **30:** 785-791.

Environment Agency. 2013. "Method implementation document for EN14385." http://www.sa.org/Files%20Public%20Area/Documents/MID%2014385%20V3.1%20draft.pdf (June 26, 2020).

Enuneku A, Omoruyi O, Tongo I, Ogbomida E, Ogbeide O and Lawrence Ikechukwu E. 2018. Evaluating the potential health risks of heavy metal pollution in sediment and selected benthic fauna of Benin River, Southern Nigeria. *Appl Water Sci.,* **8 (224):** 1-13.

Ezemonye LI, Adebayo PO, Enuneku AA, Tongo I and Ogbomida E. 2019. Potential health risk consequences of heavy metal concentrations in surface water, shrimp (*Macrobrachium macrobrachion*) and fish (*Brycinus longipinnis*) from Benin River, Nigeria. *Toxicol. Rep.,***6,** 1-9.

FAO/WHO. 2016. "Joint FAO/WHO standards programme CODEX committee on contaminats in foods." http://www.fao.org/fao-who-codexalimentarius/sh-proxy/en/%3Flnk%3D1%26url%3Dhttps%25253A%25252F%25252Fworkspace.fao.org%25252Fsites%25252Fcodex%25252FMeetings%25252FCX-735-10%25252FWD%25252Fcf10_INF1e.pdf (June 26, 2020).

FAO/WHO. 2011. "Joint FAO/WHO food standards programme codex committee on contaminants in foods fifth session." http://www.fao.org/input/download/report/758/REP11_CFe.pdf (June 26, 2020).

Fashchuk DY. 2011. **Geographic and ecological information model of marine basin, In: Marine Ecological Geography. Environmental Science and Engineering.** Berlin, Heidelberg: Springer.

Fernandez J, Andrade S, Silva-Coello CL and De la Iglesia R. 2014. Heavy metal concentration in mangrove surface sediments from the north-west coast of South America. *Mar Pollut Bull., **82*** **(1-2):** 221-226.

Froese R and Pauly D. 2020. "Species of *Arius maculatus* in FishBase." https://www.fishbase.se/summary/Arius-maculatus (August 28, 2020).

Henry R, Lucu C, Onken H and Weihrauch D. 2012. Multiple Functions of the Crustacean Gill: Osmotic/ionic Regulation, Acid-Base Balance, Ammonia Excretion, and Bioaccumulation of Toxic Metals. *Front Physiol.,* **3 (431**): 1-33.

JECFA. 1993. "Joint FAO/WHO Expert Committee on Food Additives. Evaluation of Certain Food Additives and Contaminants: Forty-first Report of the Joint FAO/ WHO Expert Committee on Food Additives. WHO Technical Report Series, No.837. Geneva." https://apps.who.int/iris/handle/10665/36981 (August 25, 2020).

Karleskint G, Turner RK and Small J. 2009. **Intertidal communities. Introduction to Marine Biology (3rd edition).** Belmont, CA: Cengage Learning.

Kazemi Z, Hashim NB and Ismail, M. 2013. Estimating the Mean Salinity, Dissolved Oxygen and Temperature of the West of Johor Strait, Malaysia. Proceedings of the Land and Water Conference. Universiti Teknologi Malaysia, Skudai, Malaysia.

Kumari P, Chowdhury A and Maiti S. 2018. Assessment of heavy metal in the water, sediment, and two edible fish species of Jamshedpur Urban Agglomeration, India with special emphasis on human health risk. *Hum Ecol Risk Assess.,* **24 (6):** 1477-1500.

Lawson EO. 2011. Physico-Chemical Parameters and Heavy Metal Contents of Water from the Mangrove Swamps of Lagos Lagoon, Lagos, Nigeria. *Adv Biol Res.,* **5(1):** 08-21.

Lenart-Boron A and Boron P. 2014. The Effect of Industrial Heavy Metal Pollution on Microbial Abundance and Diversity in Soils - A Review. In: Hernandez-Soriano MC (Ed.), **Environmental Risk Assessment of Soil Contamination**. IntechOpen, United Kingdom, pp. 10.5772/57406.

MFA. 1983. **Malaysian Food Act:Malaysian food and drug.** Kuala Lumpur: MDC Publishers Printer Sdn. Bhd.

Maurya P, Malik DS, Yadav KK, Kumar A, Kumar S and Kamyab H. 2019. Bioaccumulation and potential sources of heavy metal contamination in fish species in River Ganga basin: Possible human health risks evaluation. *Toxicol Rep.,* **6:** 472-481.

Mirnategh SB, Shabanipour N and Sattari M. 2018. Seawater, Sediment and Fish Tissue Heavy Metal Assessment in Southern Coast of Caspian Sea. *Int J Pharmac Res Allied Sci.,* **7(3):**116-125.

Mitra, A. 2019. **Mangrove Forests in India**. Springer, Cham.

Mohammed E, Mohammed T and Mohammed A. 2017. Optimization of an acid digestion procedure for the determination of Hg, As, Sb, Pb and Cd in fish muscle tissue. *MethodsX* , **4:** 513–523.

Mokhtar F, Aris AZ and Praveena S. 2015. Preliminary Study of Heavy Metal (Zn, Pb, Cr, Ni) Contaminations in Langat River Estuary, Selangor. *Procedia Environ Sci.,* **30:** 285-290.

Musah BI, Peng L and Xu Y. 2021. Evaluation of chromium application in the steel industry in China: Implications on environmental quality. Proceedings of the International Conference on Environmental Science and Technology. Beijing, China.

Nowrouzi M and Pourkhabbaz A. 2014. Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Hara Biosphere Reserve, Iran. *Chem Speciat Bioavailab.,* **26(2):** 99-105.

Olawusi-Peters O, Akinola JO and Jelili AO. 2017. Assessment of Heavy Metal Pollution in Water, Shrimps and Sediments of Some Selected Water Bodies in Ondo State. *Int J Res Agric Sci.,* **5 (2):** 55-66.

Palomares MLD and Pauly D. 2019. On the creeping increase of vessels' fishing power. *Ecol Soc.,* **24 (3):** 31-37.

Pourang N, Dennis J and Ghourchian H. 2004. Tissue Distribution and Redistribution ofTrace Elements in Shrimp Species with the Emphasis on the Roles of Metallothionein. *Ecotoxicol.,* **13:** 519-533.

Rajeshkumar S and Li X. 2018. Bioaccumulation of heavy metals in fish species from the Meiliang Bay, Taihu Lake, China. *Toxicol Rep.,* **5:** 288-295.

Ruaeny TA, Hariyanto S and Soegianto A. 2015. Contamination of copper, zinc, cadmium and lead in fish species captured from Bali Strait, Indonesia, and potential risks to human health. *Cah Biol Mar,* **56:** 89–95.

Sany SBT, Salleh A, Sulaiman AH, Sasekumar A, Rezayi M and Tehrani GM. 2012. Heavy metal contamination in water and sediment of the Port Klang coastal area, Selangor, Malaysia. *Environ Earth Sci,* **69:** 2013-2025.

Siddik MAB, Chaklader MR, Hanif MA, Islam MA and Fotedar R. 2016. Length–weight relationships of four fish species from a coastal artisanal fishery, southern Bangladesh. *J Appl Ichthyol.,* **32:** 1300–1302.

Sihombing V, Gunawan H and Sawitri R. 2019. Heavy metal residues in water and fishes at Karangsong Mangrove Conservation Area, Indramayu. Proceedings of the International Conference on Biology and Applied Science. UIN Maulana Malik Ibrahim Malang, Indonesia.

Tabari S, Saeedi Saravi SS, Bandany G, Dehghan A and Shokrzade M. 2010. Heavy metals (Zn, Pb, Cd and Cr) in fish, water and sediments sampled form Southern Caspian Sea, Iran. *Toxicol Ind Health.,* **26:** 649-656.

Turekian KK and Wedepohl KH. 1961. Distribution of the Elements in some major units of the Earth's crust. *Geol Soc Am Bull.,* **72:** 175-192.

USEPA. 1992. "SW-846 test method 3005A: Acid digestion of waters for total recoverable or dissolved metals for analysis by Flame Atomic Absorption (FLAA) or Inductively Coupled Plasma (ICP) spectroscopy." https://www.epa.gov/hw-sw846/sw-846-test-method-3005a-acid-digestion-waters-total-recoverable-or dissolved-metals (June 26, 2020).

USEPA. 1996. "Method 3050B: Acid digestion of sediments, sludges, and soils." https://www.epa.gov/homeland-security-research/epa-method-3050b-acid-digestion-sediments-sludges-and-soils (June 26, 2020).

USEPA. 2001. "Integrated Risk Information System Methylmercury (MeHg) (CASRN 22967-92-6)." https://cfpub.epa.gov/ncea/iris/iris_documents/documents/subst/0073.htm (June 26, 2020).

USEPA IRIS. 2006. "United States Environmental Protection Agency. Integrated Risk Information System." Washington, DC USA, http://www.epa.gov/iris/substS (June 26, 2020).

USEPA. 1989. "Risk Assessment Guidance for Superfund volume 1: Human Health Evaluation Manual (Part A): Interim Final." Washington, DC, USA, https://www.epa.gov/sites/production/files/2015-09/documents/rags_a.pdf (June 26, 2020).

WHO. 2011. "Guidelines for drinking water quality 4th ed. Geneva." https://apps.who.int/iris/bitstream/handle/10665/44584/9789241548151_eng.pdf;jsessionid=CD184970088EC72CCAC9B13667259C73?sequence=1 (June 26, 2020).

Yaradua I, Alhassan A, Kurfi A, Nasir A, Idi A, Ibrahim M and Kanadi A. 2018. Heavy Metals Health Risk Index (HRI) in Human Consumption of Whole Fish and Water from Some Selected Dams in Katsina State Nigeria. *Asian J Fish Aquat Res.,* **1(1):**1-11.

Zhu L, Xu J, Wang F and Lee B. 2011. An assessment of selected heavy metal contamination in the surface sediments from the South China Sea before 1998. *J Geochem Explor.,* **108(1):** 1-14.