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The Occurrences of Heavy Metals in Water, Sediment and Wild Shrimps Caught from Barito Estuary, South Kalimantan, Indonesia

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ABSTRACT

The research investigated the occurrences of heavy metal (Pb, Cu, and Cd) in waters, sediments, and wild shrimps collected from the Barito River estuary. Water and sediment samples were collected from 11 study sites by purposive sampling. At the same time, shrimps samples were captured around the sites. The study showed low levels of heavy metals in water samples; those were: Cd<0.0019 mg/L, Cu<0.001 mg/L, and Pb<0.0019 mg/L. Low levels of heavy metals were also detected in sediment samples, those were Cd <0.24 mg/kg, Cu <0.013-0.69 mg/kg, and Pb<0.024 mg/kg. Heavy metals contaminations were detected in *Parapenaeopsis sculptilis*, those were Cd = 2.802 mg/kg; Cu = 3.399 mg/kg, and Pb = 1.294 mg/kg. In *Acetes japonicus*, the heavy metals concentration were Cd = 2.127 mg./kg, Cu = 5.518 mg/ kg, and Pb = 2.723 mg/kg. In *Penaeus merguiensi*, the heavy metals concentrations were Cd = 8.598 mg/kg, Cu = 6.403 mg/kg, and Pb = 5.433 mg/kg. This study indicated the increases of heavy metals concentrations from water to sediment and finally into the shrimps. The presence of heavy metals in shrimps indicated the bioaccumulation of toxic metals, especially for Pb and Cd concentrations which exceeded the tolerable limit according to JECFA.

1. Introduction

Barito River is one of the major rivers in the South Kalimantan and Central Kalimantan Provinces. This main river of Barito flows from Muller Mountain into the Java Sea, and it has a length of about 900 km, a wide average of about 800 m, and a depth average of about 8 m (Arisanty and Saputra 2017). The role of the Barito River for human life is increasing in line with the population increase. An increase in population and various activities can cause an increase in the amount of waste, including those containing heavy metals (Khan *et al.* 2018).

As environmental pollutants and potentially toxic materials, many heavy metals have drawn great attention worldwide (Liu *et al.* 2009; Montuori *et al.* 2013; Zhang *et al.* 2012). Water containing heavy metals is very harmful to human health. Heavy metals that enter the water will undergo various processes, including transport by tidal currents, dilution, associated with suspended material, coagulation and sedimentation to the bottom, associated with organic sediment material, absorbed by plankton, and in turn, will enter the food chain (Eisler 1986; Pandey *et al.* 2003). Human activity has a major impact on the acceleration of heavy metals accumulation in the food chain. World Health Organization estimated 60-80% of 60 to 80% of the body burden of toxic metals in people living in industrialized or urbanized areas is mainly caused by the intake of metals via food consumption (Pullina *et al.* 2014).

The concentrations of heavy metals will increase if urban, agricultural, and industrial wastes which contain these pollutants enter the sea through rivers and settle to the bottom of the waters, which eventually become toxic to marine organisms (Hawker and Connell 1992). According to Yu *et al.* (2011), metals in sediments can be in various forms and bonds, among others, as free ions and bonded to carbonates, which are very unstable; thus, they are easily released into the water then absorbed by organisms.

The occurrences of heavy metals in river mouth ecology are a threat to aquatic organisms and human health. Some heavy metals, such as Cd and Pb, induce inflammation and increase free radicals and oxidants that damage various organs, including the liver and kidneys (Suhartono *et al.* 2015). This study aims to investigate the concentrations of heavy metals (Pb, Cu,

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and Cd) in water and sediments and the occurrence of these heavy metals in the shrimps captured around the Barito estuary. Wild shrimps were chosen as samples of aquatic organisms in this present study because shrimp is part of net food connected with water and sediment as its habitat.

2. Materials and Methods

2.1. Study Area and Sampling Site

This research was conducted at the Barito estuary, a traffic lane for coal cargo ships and other cargo vessels. Samplings of heavy metals in water, biota, and sediments were carried out in the waters of the Barito estuary. The number of water sampling points is set up at 11 points spreading in the river mouth. Whereas for sediment, samplings were conducted at 5 points. Water and sediment samples were taken directly at the research location, while shrimps samples were obtained from fishers who captured shrimp around the Barito estuary. The location of the study is illustrated in Figure 1.

2.2. Sample Preparation and Analysis

Five hundred milliliters of water samples from each sampling site were filtered through Whatman filter paper no. 42. Detailed preparation of water samples and determination of Pb, Cu, and Cd using atomic absorption spectrophotometry (Perkin Palmer 3110) were conducted according to the protocol of Indonesian Standard of Industry (SNI) no. 6989.16:2009 for Pb, no. 6989-6:2009 for Cd, and no. 6989-8:2009 for Cu.

In the laboratory, sediment samples were dried at 80°C to constant weight and then ground and filtered through a 63 um sieve. Detailed preparation of sediment samples and determination of Pb, Cu, and Cd using atomic absorption spectrophotometry (Perkin Palmer 3110) were conducted according to the protocol of BBTKL no. IKM.FR.14.BBTKL.

Shrimps samples were dried at 105°C to constant weight, and then the samples were ground and sieved. Detailed preparation of shrimps samples and determination of Pb, Cu, and Cd using atomic

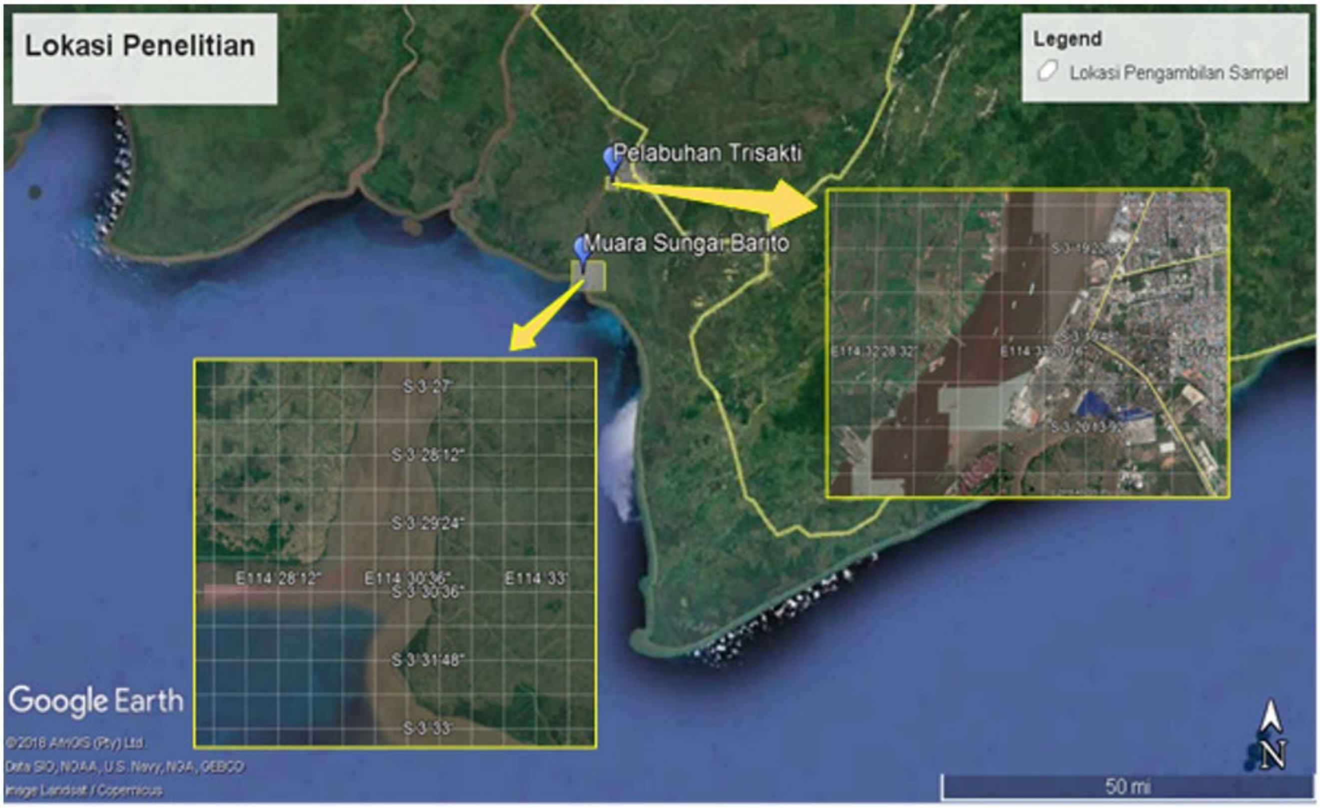

Figure 1. Site sampling for water and sediment in the Barito river estuary

absorption spectrophotometry (Perkin Palmer 3110) were conducted according to the protocol of Indonesian Standard of Industry (SNI) no. 6989-82:2018.

2.3. Data Analysis

Data were analyzed statistically to determine the mean and standard deviation. Safety of shrimp consumption (crustaceans) in the Barito estuary waters is based on the calculation of PTWI (Provisional Torelable Weekly Intake), which is the maximum temporary amount of a substance in milligrams per kilogram of body weight that can be consumed in a week without causing adverse effects on health. Determination of pollution status of heavy metal content to the level of heavy metal pollution is done by Metal Pollution Index (MPI) based on the formulas of Usero *et al.* (1997) and Giusti *et al.* (1999).

3. Results

3.1. The Concentration of Heavy Metals in Water

Results showed water samples collected from 11 sites of Barito river estuary containing a low concentration of heavy metals, namely Cd <0.0019 mg/L, Cu <0.001 mg/L, and Pb <0.0019 mg/L (Table 1).

Table 1. Heavy metals concentration in water samples (mg/L)

Sampling site	Heavy metal (mg/L)		
	Cd	Cu	Pb
03°27'00,1" S-114°30'56,1"	<0.0019	<0.001	<0.0019
03°28'24,1" S-114°30'23,7"	<0.0019	<0.001	<0.0019
03°30'22,7" S-114°28'27,3"	<0.0019	<0.001	<0.0019
03°33'57,2" S-114°31'12,2"	<0.0019	<0.001	<0.0019
03°31'02,0" S-114°22'29,1"	<0.0019	<0.001	<0.0019
03°32'01,0" S-114°24'56,9"	<0.0019	<0.001	<0.0019
03°34'50,2" S-114°29'15,9"	<0.0019	<0.001	<0.0019
03°39'58,6" S-114°28'25,4"	<0.0019	<0.001	<0.0019
03°39'58,6" S-114°28'35,9"	<0.0019	<0.001	<0.0019
03°34'46,1" S-114°31'26,7"	<0.0019	<0.001	<0.0019
03°33'16,7" S-114°31'27,7"	<0.0019	<0.001	<0.0019

3.2. The Concentration of Heavy Metals in Sediment

Analysis of sediment samples showed that Cadmium, Copper, and lead were not detected in three of five sampling sites. Those heavy metals were only found in one site, whereas Cadmium was found in two sites (Table 2).

3.3. The Concentration of Heavy Metals in Shrimps

Determination of heavy metals in the biota (shrimps) showed increases in Cadmium, Copper, and lead concentrations than in water and sediment. As shown in the Table 3, the average levels for each heavy metal in the shrimps were Pb = 3.150 mg/kg, Cu = 5.107 mg/kg, and Cd = 4.509 mg/kg.

Determination of heavy metals in shrimps species captured around sampling sites indicated an increase in the levels of heavy metals from water to the sediments and finally in the biota of sediment (shrimp). The presence of heavy metals in shrimps suggested the occurrence of bioaccumulation of this toxic substance, as shown in Figure 2.

Table 2. Heavy metals concentration in sediment samples (mg/L)

Sampling site	Heavy metal (mg/L)		
	Cd	Cu	Pb
03°27'00,1" S-114°30'56,1"	0.00	0.00	0.00
03°28'24,1" S-114°30'23,7"	0.61	0.26	0.69
03°30'22,7" S-114°28'27,3"	0.00	0.00	0.00
03°33'57,2" S-114°31'12,2"	0.35	0.00	0.00
03°31'02,0" S-114°22'29,1"	0.00	0.00	0.00

Table 3. The concentration of heavy metals in shrimps samples (mg/kg)

Shrimp species	Heavy metal (mg/L)		
	Cd	Cu	Pb
Penaeus merguiensi	8.598±0.749	6.403±1.079	5.433±0.685
Parapenaeopsis sculptilis	2.802±0.084	3.399±0.118	1.294±0.086
Acetes japonicus	2.127±0.041	5.518±0.083	2.723±0.027

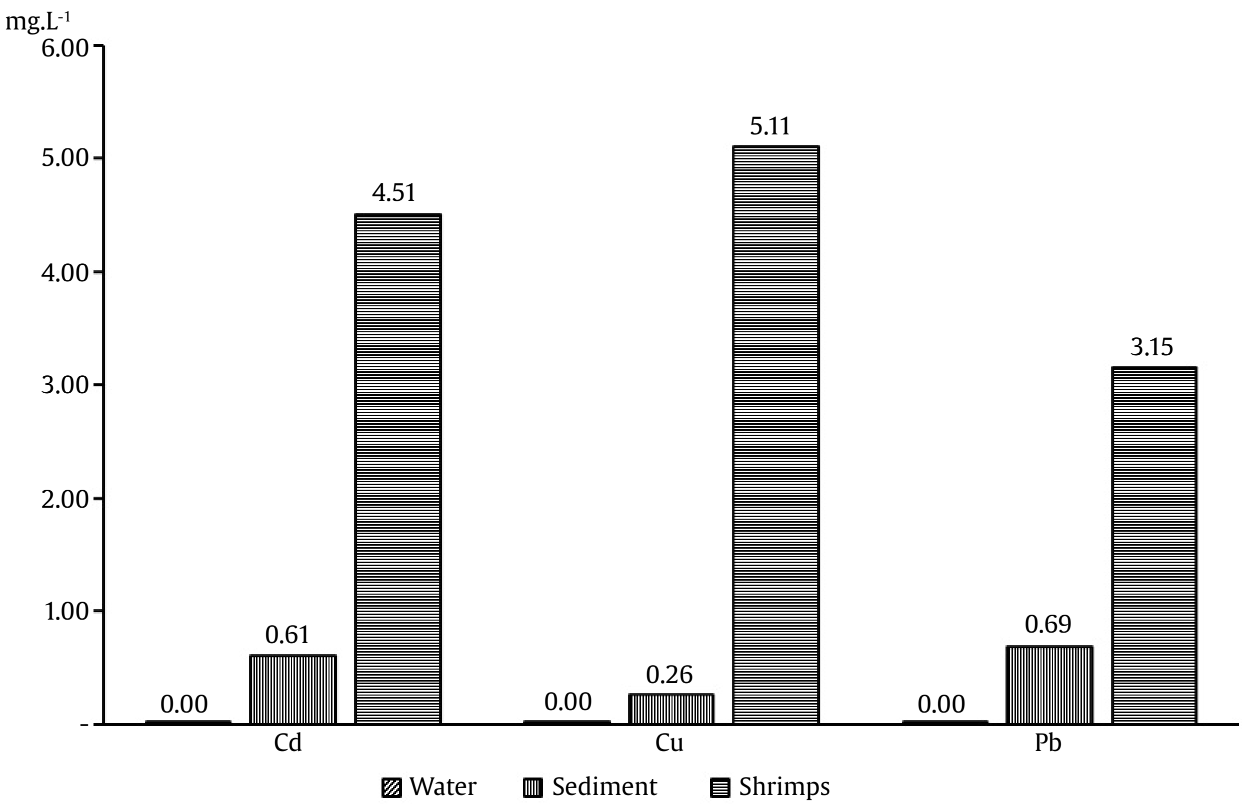

Figure 2. Heavy metals concentrations in water (mg/L), sediment (mg/kg), and shrimps (mg/kg) of Barito river

4. Discussion

Various human activities result in heavy metals accumulation in the water, such as industrial, agricultural, and domestic sewage (Liu *et al.* 2016). This study found low Cadmium, Copper, and lead concentrations in water samples of the Barito river mouth. This finding was in agreement with the statement of Gaur *et al.* (2005) that only a small portion of free heavy metal ions can remain in the dissolved phase in aquatic systems, as most parts settle in the sediment by adsorption, hydrolysis, co-precipitation, and other physical and chemical processes. Sofarini *et al.* (2010) found heavy metals in water samples of Barito River are low, except for containing Hg (0.28 mg/L) and Pb (0.18 mg/L). Sediments samples analysis indicated the locality and low levels of heavy metals occurrences in the Barito river's sediments. Only from a site sampling was containing all of the studied heavy metals. Previous studies by Sofarini *et al.* (2010) notified accumulation of heavy metals, especially Cd levels, in the sediment of Barito River. The occurrence of heavy metals in the sediment was worrying considering the possible bioaccumulation of heavy metals in the river bed biota. Further analysis showed the concentrations of heavy metals in the biota (shrimps) were higher than the concentrations found in the water and sediment. The average levels for each heavy metal in the shrimp were Pb = 3.150 mg/kg, Cu = 5.107 mg/kg, and Cd = 4.509 mg/kg. This result is in agreement with the study of Rahman (2006) that found high contamination of Pb (42-105 ml/kg) and Cd (8-17 mg/kg) in crustacean samples collected from the coastal area connected to the Barito River mouth. However, the levels of these three heavy metals were still low compared to Ahmad *et al.* (2010) in the waters of the Buriganga River, Bangladesh.

Several aquatic biotas have been used for biomonitoring purposes. These organisms accumulate heavy metals in their bodies and are sensitive to chemical pollutions as they directly contact the polluted part of the habitat (Khan *et al.* 2018). Determination of heavy metals in shrimps species captured around sampling sites indicated accumulation of heavy metals from water to the sediments and finally in the biota of sediment (shrimp). The occurrences and levels of Cadmium, Copper, and Lead in shrimps of this study were in harmful levels for human consumption because they have exceeded the tolerance threshold (Provisional Torelable Weekly Intake) according to JECFA (2010) in CCCF (2011), namely 0.025-0.050 mg Pb per kg body weight and 25 µg Cd per kg body weight per month.

The anthropogenic release has been considered the main source of heavy metals accumulation in water, sediment, and aquatic organisms (Savorelli *et al.* 2017; Aliko *et al.* 2018). The consumption of these metals at high levels could adversely impact human health. High exposure to Cadmium through ingestion causes immediate poisoning and damage to the liver and kidneys. In addition, compounds containing Cadmium are also carcinogenic (El-Moselhy *et al.* 2000). Excessive intake of Copper might cause vomiting, hematemesis (vomiting blood), and gastrointestinal distress (Arvind 2002). Children are the most vulnerable group to the toxic effects of Lead and can suffer permanent adverse health effects, particularly the brain and nervous system development. In adults, lead causes long-term harm, including increased risks of high blood pressure, kidney damage, and neurological effects (Voegborlo *et al.* 2012).

In conclusion, this study indicated that the occurrences in the low levels of heavy metals, particularly Cadmium, Copper, and Lead in the water and sediment of the Barito river, might result in bioaccumulation of these toxic substances into the wild shrimps to reach the harmful levels for human consumption. Therefore any efforts have to be initiated to reduce these heavy metals levels in the human food chain.

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