

Accumulation of Heavy Metals (Cu and Pb) In Two Consumed Fishes from Musi River Estuary, South Sumatera

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Abstract

Fish is one of the protein sources for humans which its existence is susceptible to the contamination, one of which is the heavy metal. The lack of information regarding the content of heavy metal in the edible fish in South Sumatera makes this study important to be done. This study was aimed to analyze the concentration of heavy metal in two species of edible fishes at Musi River Estuary site. The study was conducted in the estuary section of Musi River from September to November 2014. The heavy metals of Cu and Pb in the water and in the fish organs were analyzed using AAS with a type of Spektra A-20 Variant Plus using a mixture of Air-Acetylene flame. The result showed the variation of Cu and Pb concentrations in each of species and three organs observed. The concentration of Cu and Pb in the liver was higher than in the gills and the muscle (liver>gills>muscle). The concentration of Cu and Pb in the muscle of all fish species were not exceed the safe limit for consumption.

Keywords: Cu and Pb, consumed fish, Musi River estuary

Introduction

Fish is a source of protein needed by humans in the fulfillment of their daily needs. Similarly, for the people in South Sumatera, a variety of foods made from fish are often found in this area. Musi River as one of the largest rivers is a key area to the production of fish in South Sumatera. The data from BRPPU (2010), the Research Institute for Inland Water Fisheries, Research and Development Agency, Fisheries and Marine Affairs, showed that the fishery activities in Musi River is one of the six sectors contribute to the regional income of South Sumatera Province, including one of the capture fishery centers.

In addition, many activities such as agriculture, plantation, coal stockpile, harbor and water transportation, as well as the industry are found along the Musi River that could probably contribute to the waste inputs containing some chemical components such as heavy metals. Aryawati and Agustriani (2004) reported that blood clams (*Anadara granosa* Linnaeus) collected eastern coast of South Sumatera contained Cu and Zn ranging from 0.387-28.62 mg.kg⁻¹ although the concentrations were still below the limit allowed for the seafood. The result of a study carried out by Purwiyanto and Lestari (2012) also showed the presence of Pb and Cu contents in crab *Scylla*

serrata muscle sold and consumed by people around Palembang city. Birmansyah (2008) showed that the content of Pb in the fraction of Musi River estuary sediment ranged from 0.0196–1.747 µg.g⁻¹ and concentrated higher in the industrial areas, transportation and harbor, that were around the Ampera Bridge and Pusri. Moreover, Setiawan *et al.*, (2013) found that the level of mercury in the muscle of *Pangasius polyuranodons* was 16,750 µg.kg⁻¹.

As a top of food chain pyramid in the water, the fishes are potential to accumulate a large amount of metal from the water (Mansour and Sidky 2002). The information about the concentration of heavy metal in fish is important in relationship to the environmental management and human health since the heavy metal toxicity can cause the brain and kidney damages, even the arsenic can cause a cancer (Dural *et al.*, 2007). This study is to reveal the information about the accumulation of Cu and Pb in two species of consumed fishes live in estuary of Musi River, as well as its eligibilities for human consumption. The result of this study is expected to be used as a reference for the local people and government.

Materials and Methods

The sampling was carried out at two research stations with there were three substations. Station 1

(02°59'44,44"S-104°50'13,8"E) is the river section located in the center of the Palembang city, South Sumatera which is an urban area, industrial (PT. Pusri, Pertamina and coal stockpile) as well as a boat transportation line. Station 2 (02°16'56,4"S-104°55'25,0"E) is the estuary area that located around the mouth of Musi River (Sungsang), is a residential area, boat transportation line and dock of local fishermen's fishing vessels (Figure 1).

The sampling referred to the technique developed by Bahnasawy (2010). Water samples 1 L were collected from the surface water (a range of depth was about 0-50 cm) using Vandorn water sampler, then it was filtered using the filter paper of Whatman 7184-004 with cellulose membrane (membran Cicles, Cellulose nitrat, white plain 0,45 µm, diameter 47 mm).

The dissolved phase was stored in a polyethylene bottle and preserved with concentrated HNO₃ to pH < 2 (Batley and Garner, 1977; APHA/AWWA/WEF Standard Methods Centennial ed, 2005; Taftazani et al., 2005). The water sample (250 ml) was put into the teflon separating funnel, then extracted with APDC/NaDDC/MIBK. The organic phase was reextracted with HNO₃ (back extraction) (Bruland et al., 1979; Arifin, 2011). The

sample was allowed to stand for 20 minutes, added by 9.75 ml of distilled water and stirred. The result of the extraction in the water phase was taken and kept in a polyethylene bottle, then measured using atomic absorption spectrophotometer (AAS) type of Spektra A-20 Varian plus using a mixture of Air-Acetylene flame.

The target fishes in this study were the common fishes caught and consumed by the local people. The fish species that represented Station 1 was Seluang (*Rasbora* sp.) whereas the species represented the estuary area was Belanak (*Mugil chepalus*). The fish samples were obtained from local fishermen and identified for its species and kept in a coolbox. In the laboratory, the samples of biota organs were placed in the evaporator dish and heated in the oven at the temperature of 105°C for 12 hours. After cooling, those samples were crushed to be homogeneous. 4 gram biota organ sample was digested in a beaker glass with 10 ml concentrated HNO₃ on a hotplate at a temperature of 85°C for 8 hours. Before the digestion process ended, 3 ml H₂O₂ was added to the biota tissue sample. The liquid phase was transferred into the volumetric flask and the volume was matched up to 20 ml by adding the deionized distilled water and allowed to stand overnight for then analyzed with

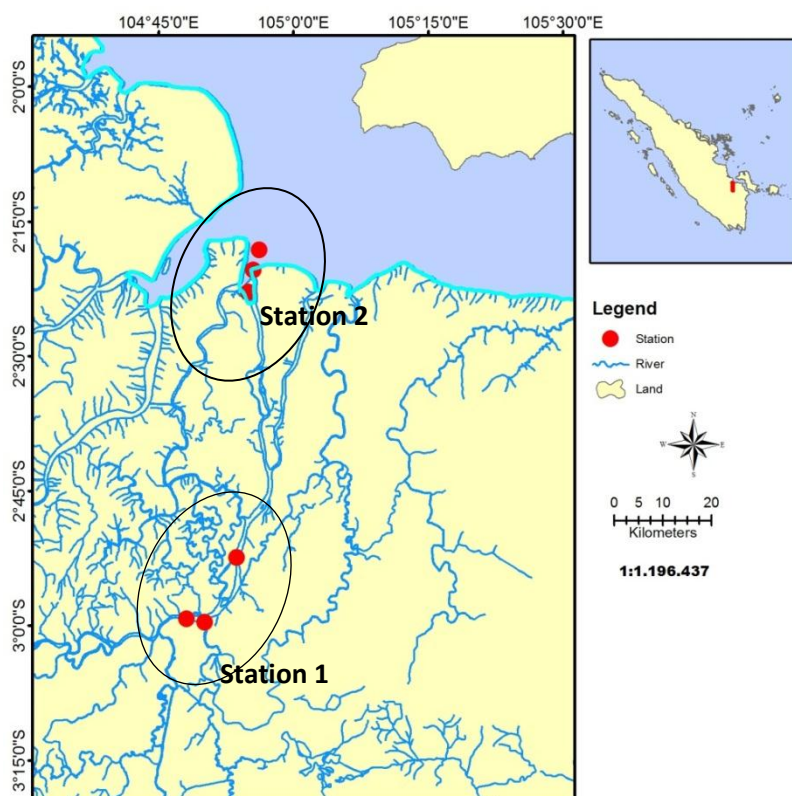


Figure 1. Location of Research Stations

atomic absorption spectrophotometer (AAS) type of Spektra A-20 Varian plus using a mixture of Air-Acetylene flame (Arifin, 2011). The limit detection of AAS SpectraA-20 Plus Varian for Cu was 0.003 $\mu\text{g.kg}^{-1}$ and for Pb was 0.01 $\mu\text{g.kg}^{-1}$. To guarantee the quality of the measurement, a measurement to the certified materials was also done (*Certified Reference Material*) using DORM-3 from *Institute for National Measurement Standards, National Research Council of Canada*. The concentration unit of Cu and Pb used was $\mu\text{g/kg}$ wet weight.

Result and Discussion

Heavy Metal in the Water

The average concentrations of dissolved heavy metals in water column ranged from 1.8-4.7 $\mu\text{g.L}^{-1}$ for Cu and 1.7-3.1 $\mu\text{g.L}^{-1}$ for Pb (Table 1). It was widely perceived that the concentration of Cu was higher than Pb. According to Waldichuk (1974), the normal concentrations of Cu and Pb in marine waters are 2 $\mu\text{g.L}^{-1}$ and 0.03 $\mu\text{g.L}^{-1}$, respectively. Referring to this condition, there is an indication that there have been increased of Cu and Pb concentrations in estuary of Musi River. It could be due to the large number of industry, transportation, agriculture and plantation along the Musi River. BAPEDALDA (2006), the Environmental Impact Control Agency of South Sumatera, reported that there were approximately 20 industries in the downstream of Musi River, i.e. industries of wood processing, rubber (crumber), fertilizer, ceramic, boat dock, detergent, oil, gas, cold storage, electroplating as well as soft drink, and most industries known had not had the optimal Waste Water Treatment Plants. In addition, Musi River is also an area of shipping line for many types of vessels such as coal or wood carrier barges, ferries and other passenger ships as well as cargo ships. These various activities have the potential to contribute the pollutants such as heavy metals.

Cu is one of the essential metal and at the low level required by the organisms as a co-enzyme in the metabolism process (Riani 2012). According to Perales-Vela *et al.*, (2007), Cu can serve as an electron carrier both in the process of photosynthesis and respiration. The toxicity of Cu will occur when this metal gets into the body of organism in a large amount or exceeds the tolerance value of this organism (Palar, 2004). In contrast, Pb is not needed at all in the metabolism process of organisms, even classified into the group of heavy metal with high toxicity to organisms. Therefore, the presence of Pb harms the aquatic organisms, even can result in a disability of aquatic biota, as

happened to chironomous larvae (Riani *et al.*, 2014).

Heavy Metal in Each Organ

The average concentrations of heavy metal varied in fish species and organ type (Figure 2). The average concentrations of Cu and Pb in the muscle of *Rasbora* sp. were 282.5 $\mu\text{g.kg}^{-1}$ and 157.5 $\mu\text{g.kg}^{-1}$, respectively, 1157.8 $\mu\text{g.kg}^{-1}$ Cu and 222.5 $\mu\text{g.kg}^{-1}$ Pb in the gills and 2384.2 $\mu\text{g.kg}^{-1}$ Cu and 996.1 $\mu\text{g.kg}^{-1}$ Pb in the liver. The accumulations of Pb found in all organs during the research were higher than the result of the study done by Harteman and Aunurrafik (2013) in the estuaries of Kahayan River and Katingan River, South Kalimantan. They found that Pb concentration in the gills of *Rasbora* sp ranged from 7-23 $\mu\text{g.kg}^{-1}$, in the liver from 12-22 $\mu\text{g.kg}^{-1}$ and in the muscle from 1-17 $\mu\text{g.kg}^{-1}$.

Furthermore, in the muscle of *M. chepalus*, Cu and Pb concentration found were 271.3 $\mu\text{g/kg}$ and 201.5 $\mu\text{g.kg}^{-1}$, respectively, while in the gills were 1261.4 $\mu\text{g.kg}^{-1}$ Cu and 236.6 $\mu\text{g.kg}^{-1}$ Pb, and in the liver 8424.3 $\mu\text{g.kg}^{-1}$ Cu and 849.6 $\mu\text{g.kg}^{-1}$ Pb (Figure 2). These numbers were higher than the result of the study done by Dural *et al.*, (2007) in Laguna Tuzla Turkey. The ranges of Cu and Pb concentrations in the muscle of *M. cephalus* were 0.47-0.62 $\mu\text{g.g}^{-1}$ and 0.49-1.07 $\mu\text{g.g}^{-1}$, respectively, 4.77-12.03 $\mu\text{g.g}^{-1}$ Cu and 1.85-3.12 $\mu\text{g/g}$ Pb in the liver and 3.43-7.82 $\mu\text{g.g}^{-1}$ Cu and 2.67-6.75 $\mu\text{g.g}^{-1}$ Pb in the gills.

Cu and Pb concentrations varied among the three organs. Figure 2 shows that the liver accumulated Cu and Pb higher than the muscle and the gills. The order of the accumulation of metal in the fish organs were liver>gills>muscle. El-Moselhi *et al.*, (2014) stated that most of the researchs found that liver was a target organ for the accumulation of heavy metals such as Cu, Zn and Fe. Likewise, the studies conducted by Yilmaz *et al.*, (2007); Yilmaz (2009) and Riani (2015) found that generally heavy metals concentrated higher in the liver and gills tissues, but its concentrations in the muscle were smaller. Dural *et al.*, (2007) stated that liver tissue is highly active in uptake and storage of heavy metals. It is well known that large amount of metallothionein induction occurs in the liver tissue of fishes. According to Zhao *et al.*, (2012) the accumulation of essential heavy metal in the liver is associated with its role in metabolism. In addition, Cu in the liver tissue binds with the binding protein such as metallothionein which acts as essential metal store to meet the enzymatic and other metabolic needs (Dural *et al.*, 2007; Gorur *et al.*, 2012). Increased metal concentrations in liver may

Table 1. Average Concentration and Standard Deviation of Cu and Pb in Waters ($\mu\text{g.L}^{-1}$)

Station	Sub Station	Concentration of Metal (Average \pm SD)					
		Cu			Pb		
1	1	4,73	\pm	1,03	2,09	\pm	0,86
	2	3,49	\pm	0,51	1,73	\pm	0,94
	3	3,30	\pm	0,89	2,59	\pm	1,12
	4	3,16	\pm	0,97	2,5	\pm	0,60
2	5	1,83	\pm	1,16	3,14	\pm	1,22
	6	2,07	\pm	0,71	1,94	\pm	0,71

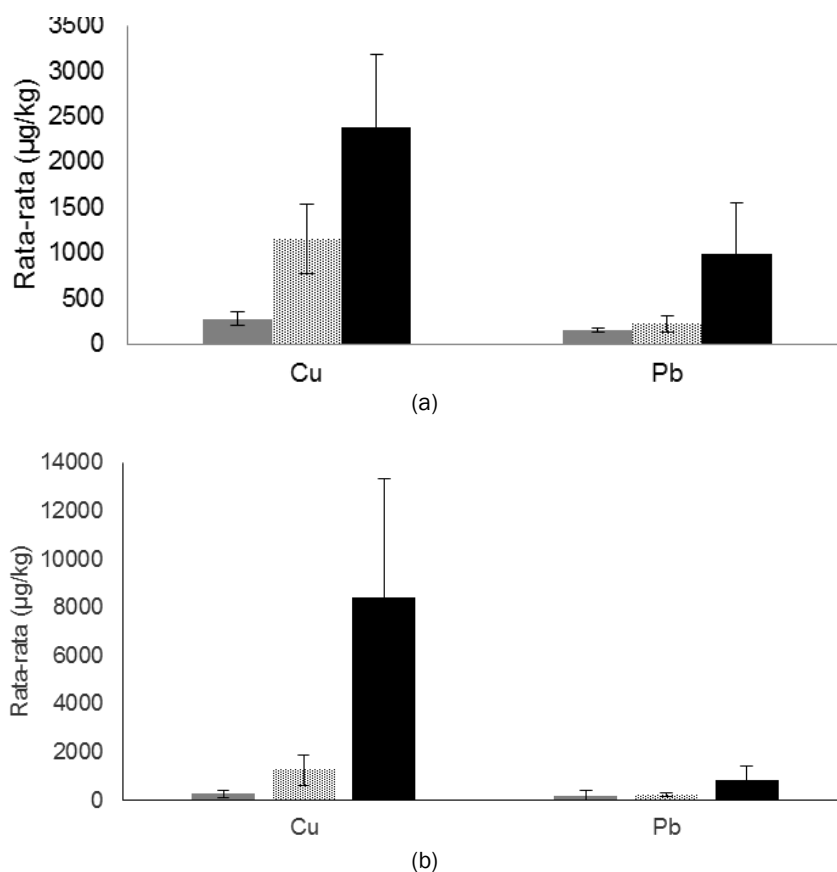


Figure 2. Concentrations and standard deviation of Cu and Pb ($\mu\text{g.kg}^{-1}$) in muscle, gills and liver of species (a) *Rasbora* sp; (b) *Mugil chepalus*.

Note. ■ = muscle, ▨ = gills, ■ = livers,

represent storage of sequestered products in this organ (Tepe *et al.*, 2008). Furthermore, Dinata (2004) confirmed that the high accumulation of metal in the liver makes this organ to be the one that most frequently experiences the damage. This is because the liver is the entrance for all substances that enter the body, and hence very potential to suffer toxication first before the other organs. Yilmaz (2009) said that the liver is the target organ in the accumulation of metal because its ability

in storage and excretion. Some pilot research and case studies discovered that the target organs such as liver, gonad, kidney and gills are the active metabolic tissues and can accumulate the metal to a higher level.

After the liver, gill is the organ that is able to accumulate heavy metals in larger amount than the muscle. This is because the gill is the organ that plays a role as the first entrance for the metal to get

into the body. As reported by Jeziarska and Witeska (2001), the gill is a part that binds and absorbs the metals in ionic forms from the water. The high metal content in the gills tissues can be associated with the fact that gills are playing the different role in the absorption of metals from the environment. Because of the respiratory function, the gills always have a direct contact with the water, and it also has the most delicate epithelium of all organs (Coetzee et al., 2002). Some other researchs also reported that the gills have a high tendency to accumulate heavy metals (Wong et al., 2001; Coetzee et al., 2002; Yigit and Altindag, 2006). This is because there is a metal complexing with mucus that does not allow these to be cleaned completely from the lamellae until the analysis is carried out (Heath, 1987).

Cu is potential to give a negative effect if it enters the organism in a large amount or exceeds the limit value. The decrease in the growth rate occurs in line with the increase of Cu concentration that creates an interference in gills performance, especially in the process of osmoregulation (Sihono et al., 2014). The fish suffering the difficulty in respiration and cause stress and further effects on a decrease of appetite and consequently can affect the growth rate. This is deteriorated by the toxic effect of Cu that damaged the olfactory sensory system of the fish (McIntyre et al., 2008), so it will have a difficulty in responding the food. Besides, the physiological effect of Cu exposure is low of growth due to increases of metabolic activity for the process of detoxification and homeostasis maintenance.

The gills, liver and kidney are the organs that most sensitive to the toxicity of heavy metals because can interfere the function of gill lamellae, liver hepatocyte figures cells, as well as functions of glomerulus and tubules of kidney. Kalisińska and Salicki (2010) said that the accumulation of Pb in the muscle < liver < kidney. Riani (2012; 2015) explained that the concentration of Pb in the gills were positively correlated with the level of organ damage even may threaten organism. The concentration of heavy metal in the gills reflects its

concentration in the water as a medium in which the fish live, whereas the concentration of heavy metal in the liver indicates the occurrence of metal accumulation in this organ (Rao and Padmaja, 2000). It is further mentioned that the liver and gills are recommended as organs indicators of the environmental pollution compared to the other fish organs (Karadede, 2004).

The muscle is the slightest in accumulating the heavy metals of Cu and Pb compared to the liver and gills, but it is important to be studied considering that this part was consumed by the humans. Miller et al., (1992) stated that the muscle is the weakest indicator in detecting the contamination of Cu and Zn at the low level. Allen-Gil and Martynov (1995) explained that the low concentrations of Cu and Zn in the muscle can caused by the low ability of the muscle in binding the protein (*metallothionein*).

The result of this study also found the variation of concentrations Cu and Pb in two species that had been observed. Figure 2 shows that each species accumulated Cu and Pb in different amounts in each its organ. The gills and liver of *M. chepalus* accumulated Cu greater than other with the values of 1261 µg.g⁻¹ and 8424 µg.g⁻¹, respectively. This may be caused by the foraging habit of *M. chepalus* in muddy substrate. These values are higher than the result of study done by Dural et al., (2007) in Laguna Tuzla Turkey, the highest concentration of Cu was detected in the liver of *M. cephalus* (12.03 µg.g⁻¹ dw). Likewise, the concentration of Cu in the liver organ of *M. cephalus* (71.9 µg.g⁻¹) in the Kaveri River, South India (Bhuvaneshwari et al., 2012).

El-Moselhy et al. (2014) reported that the difference in feeding habit, habitat and living environment affects to the heavy metal accumulation. According to Zhao et al. (2012) metal accumulation and distribution in the organ are interspecific. Many factors can influence heavy metals uptake such as the sex, size, age,

Table 2. Maximum limits for heavy metals in food in several countries (mg.kg⁻¹ ww)

No	Heavy metal	UK	Australia	Hongkong	European Regulation	Indonesia*)
1	Cadmium	-	0,2	2,4	0,2	-
2	Lead	-	1,8	7,2	0,5	2,4
3	Chromium	-	-	1,2	-	-
4	Copper	24	-	-	-	24
5	Zinc	60	-	-	-	121
6	Arsenic	-	-	-	-	1,2
7	Nikel	-	-	-	-	-

Note : *) Degree of Genera Director of Food and Drug Supervision No. 03725/B/SK/VII/89 concerning minimum limit of metals in food (Soegianto, 2008)

reproductive cycle, movement pattern, eating habit and environment. Yilmaz *et al.* (2007) stated that the difference concentration of heavy metals in muscle, liver and gills shows the capacity of each organ in accumulating the heavy metals.

Safety of consumption

According to FAO (1983), the maximum residual concentrations of Pb and Cu allowed in the marine products for human health purpose are 1,5 mg.kg⁻¹ ww and 10 mg.kg⁻¹ ww, respectively. If it compared with the values given by some countries (Soegianto, 2008) that apply the heavy metal limit for the seafood (Table 2) and FAO (1983), it can be concluded that the concentration of heavy metals in muscles of all fish species observed are still within the safe limit for consumption. However, this condition can be used as a "warning" for the people and the local government to be more aware in the future to manage the environment. If the concentrations of Cu and Pb continue to increase and cause the accumulation in muscles, it may be harmful to human health.

The quality standards of maximum permissible concentration of metal allowed contained in the muscle of marine biota applied by several countries and organizations are presented in the unit of dry weight. Table 1 represents the result of conversion into the unit of wet weight in assuming the marine fishery products contained the average water content of 70 % (Uthe and Chou, 1988).

Conclusion

Cu and Pb were accumulated in two species and all organs that observed. The highest accumulations occurred in the liver organs of all species. The liver of *M. chepalus* accumulated the highest Cu and Pb than other. Based on the maximum limits of heavy metals that are allowed in food established by several countries as well as by FAO, the concentrations of Cu and Pb in the muscles of four species of consumption fishes live in the estuary of Musi River are still safe and possible to be consumed.

Acknowledgements

We thank to Azrina Ulfa, Harry Prastio and Meriansyah for assistance in the field and laboratory. We also thank to Mrs. Lestari, Mr. Abdul Rozak and Mr. Taufik Kaisupy for giving helpful advice for technical assistance in metal analyses. To Mr. M. Muhaimin for helping manuscript correction.

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