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Research Article

Heavy Metals (Cu, Pb and Cd) in Water and Angel Fish (*Chelmon rostractus*) from Batam Coastal, Indonesia

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ABSTRACT

Fish play an important role in human nutrition and therefore need to be carefully and routinely monitored to ensure that there are no high levels of heavy metals being transferred to human through their consumption. This study has been carried out to determine level of heavy metals (Cu, Pb, and Cd) in water and angel fish, *Chelmon rostractus* collected from coast of Batam. We report levels of Cu, Cd and Pb in water and angel fish from Coast Batam using Atomic Absorption Spectroscopy (AAS). Level of heavy metals obtained in water and fishes were fluctuative. Cu was obtained in both, water and fish muscles. Level of Cu in fishes muscle still under the permissible limit, but it was exceeded permissible limit for water. Cd not detected in water, but it was obtained in fish muscles. Level of Cd in fishes from Tanjung Pinggir site was exceeded permissible limit. High level of Pb was found in water and fish muscles. Level of Pb in water and fish muscles were exceed permissible limit. It is indicated that the coast Batam has contaminated with Cu, Pb and Cd.

Keywords: *heavy metals, angel fish, marine pollution, Batam coastal*

1. Introduction

Nowdays, there have been an increasing of water pollution. The aquatic environment was contaminated by such heavy metals. Heavy metal pollution is a major threat to the environment. Some heavy metals often contaminating water are mercury, Cu, Pb, Zn, Sn, As (Ashraf et al., 2012), and Cd (Sarong et al., 2013)

Industrial activities, transportation, agriculture and domestic caused heavy metal contamination in open waters (Sarong et al., 2013). Fishes accumulate heavy metals in their body through absorption and humans can be exposed to heavy metals through their meal (Ashraf et al., 2012). Heavy metals that have already been consumed will be bound in the sulfihidril with irreversible bond, so that the metal is fixed and cannot be secreted and in certain concentration, they can have negative effects, depending on the type of metal (Simbolon et al., 2014).

Metal accumulation is a tool to identify the impact of heavy metals in aquatic ecosystems because it shows the adverse of effects on the organism (Baharom and Ishak, 2015). Fishes have been used as bio-indicators for heavy metals in water (Supriyanto, 2007; Riani, 2010; Nirmala, et al., 2012; Damiano, et al., 2011; Ashraf, et al., 2012; Ibemenuga, 2013; Setiawan et al., 2013 and El- Moselhy, et al., 2014). The use of fishes as bio-indicators can determine the actual state of the levels of pollutants before and after the observation (Ashraf et al., 2012). According to Supriyanto et al. (2007), the level of heavy metals in fish closely related to the disposal of industrial waste near the fish live. The accumulation rate of heavy metals in fishes depends on the characteristics of chemical compounds, concentration and species of fish (Sarong et al., 2013; Supriyanto et al., 2013).

Angelfish, Chelmon rostractus, is classified as family of *Chaetodontidae* with colorful characteristic body consisting of orange from a dorsal fin, anal fin, and in parts of the

body including color dappled consisting of orange and white, while the tail of them is white. According to Setiawan (2006) *C. rostractus* which live at depths of 1-25 m is found at rocky shores, reefs, estuaries, and deploy in the Western Pacific (Andaman sea-Japan, Indonesia, and Australia). *Chaetodontidae* is classified as reef fish and spread of just around reefs (Suryanti et al., 2011). Experts agree on classifying the fish as an indicator species of healthy condition or absence of coral reefs, because this fish is truely coral reef dweller (Laikun et al., 2014; Suryanti, et al., 2011). These fish are omnivorous and feed on soft coral polyps as a primary food source (Frimanozi et al., 2014).

This study aimed to evaluate the levels of metals Cu contaminant, Pb and Cd in seawater and *Chelmon rostractus* of aquatic environment of *Batam. Chelmon rostractus* was chosen because it is the species of fish mostly caught in the trap of sampling sites (**Table 1**).

2. Material and Methods

Sampling location

Fish sampling was conducted in the western side of Batam Island from April to May 2016 by using traps that were planted in the sea bottom. Sampling sites covered an area of Tanjung Pinggir (Station 1), Tanjung Riau (Station 2), Marina Beach (Station 3) and Tanjung Uncang (Station 4). Coordinates of sampling site can be seen on the map (Figure 1).

Table 1. Data of *C. rostractus* at sampling sites

Sampling Sites	Sample Number	Weight (gram)	Size (cm)
Tj. Pinggir	19	41.32 ± 7.77	12.23 ± 0.71
Tj. Riau	12	28.67 ± 10.60	10.75 ± 1.54
Marina	4	31.25 ± 10.50	11.03 ± 1.25
Tj. Uncang	9	27.89 ± 7.20	10.91 ± 0.83

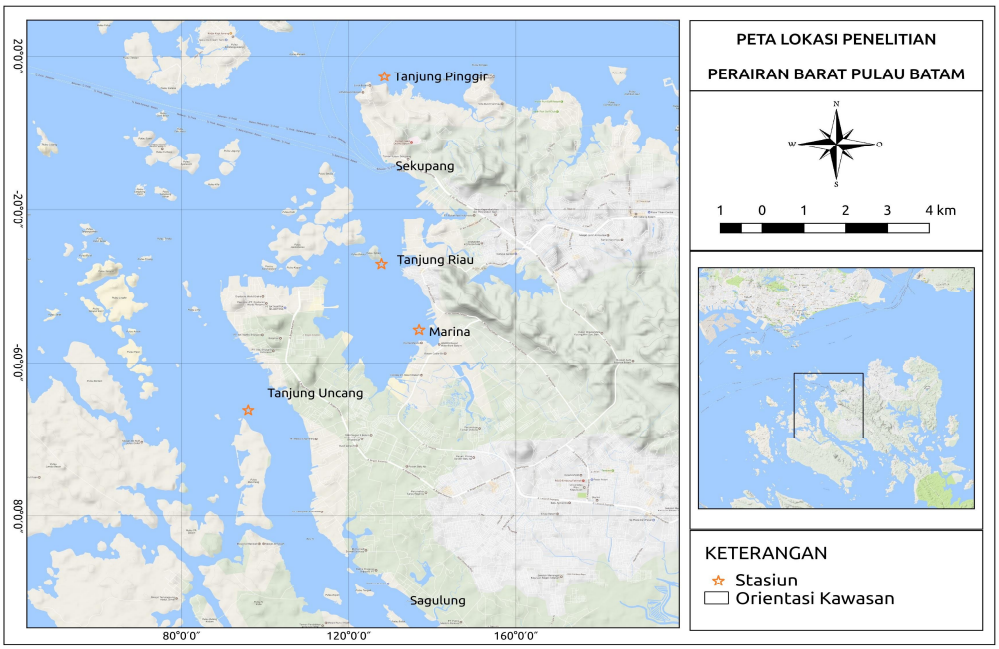

Figure 1. Research site

Sample preparation

Separating the fish meat using Dolphin surgical equipment was the first preparation to do. Then it dried by using an oven Kirrin Model KBO-250RA at a temperature of 105 ° C for 3 until homogeneous. Then the mixture was added 5 ml of HNO_3 and heated using *heat mantle* for 30 minutes or until a clear liquid was obtained with a volume of ± 10 ml. Samples which were destructed were filtered using Whatman filter paper No. 41. The filtrate obtained was accommodated in a 50 ml of volumetric flask, and diluted to mark the boundary.

The determination of heavy metals

The determination of heavy metals Cu, Cd and Pb were performed using AAS of Shimadzu AA-7000. Metal analysis method refers to ISO 6989.16: 2009 for metal Cd, ISO 6989.6: 2009 for Cu and ISO 6989.8: 2009 for metallic Pb. The accuration of testing methods of metal Cd were tested using Certified Reference Materials (CRM) IM-12 artificial LIPI standards traceable to the National Institute of USA and PTB Germany, with a value of 98.7 ± 3.2% accuracy, precision 2.94 %, LOD = 0.007 mg/L and LOQ = 0,023 mg/L. The accuracy of testing methods of metallic Pb was tested by using Certified Reference Materials (BAT) IM-12 artificial LIPI standards which is traceable to the National Institute of USA and PTB Germany, with a value of accuration 98.7 ± 3.2%, precision 2.16 %, LOD = 0.028 mg / L and LOQ = 0.092 mg / L. Meanwhile, the accuracy of testing methods of metallic Cu to hours. Determination of heavy metals was done in Integrated Testing Laboratory, Faculty of Math, University of Sriwijaya, Palembang. Acid destruction was performed at ± 5 gram of sampling, which was put into a round bottom flask, added 50 ml of demin water, and shaken the *recovery* test, with a value of 88.66% accuracy, precision 1.181%, LOD = 0.033 mg / L and LOQ = 0,109mg / L.

Data analysis

The data were analyzed descriptively to see the results of measurement of parameters and to see the results of the samples test in the laboratory by comparing the quality standards based on Minister of the Environment Decree No. 51 of 2004 on Quality Standard of Sea Water; for biota. Furthermore, the content of Cd and Pb of fish refers to the ISO 7387: 2009 and FAO, while for metal Cu refers to the FAO standard 2003 (Baharom and Ishak, 2015).

3. Results and Discussion

Physical-chemical parameters of seawater

Heavy metals dissolved naturally in water were free ionic form, the pair of inorganic ions, organic or inorganic complexes. The physical and chemical establishment of heavy metals in the aquatic environment was affected by salinity, temperature, pH, redox potential, organic matter and suspended solids, biological activity and properties of the metal (Mamboya, 2007). Table 2 presented the physical-chemical parameters of seawater from the sampling site.

Table 2. Physical-chemical parameters of seawater

Parameter	Research Sites (Station)			
	TP	TR	MR	TU
Flows velocity (m/s)	0,099	0,108	0,135	0,161
pH	8,0	8,0	8,1	8,1
Salinity (‰)	30,3	34,3	34,3	34,7
DO (mg/l)	7	6,9	6,7	7,7
Brightness (m)	2,5	1,8	1,54	3,66
Temperature (°C)	29,4	31,9	31,9	31,7

Station: TP=Tanjung Pinggir, TR= Tanjung Riau, MR=Marina, TU= Tanjung Uncang

Physical-chemical parameters of the water environment relates each other (Sa' and Mahmoud, 2014) The Flow has a very important role in the water, because the flows effected on the distribution of organisms, dissolved gases and minerals contained in the water. The flow velocity is in the range from 0.099 to 0.161 m/s and the largest flow velocity encountered in the area of Tanjung Uncang. This is possible because this location is the open sea, while the other location Tanjung Pinggir, Tanjung Riau and Marina, is a semi-open waters. The open sea can easily carry dissolved metals into other areas, so it could contaminate other locations. Batam Island covers from Sekupang to Port of Sagulung is a center of industry and shipbuilding. In addition, there are at least seven ports that serve routes between islands, national and international routes. Flow velocity has an impact on the distribution of heavy metals in the water, so it also affects the levels of heavy metals in organisms in these waters.

The pH value in all stations is in common relatively, that is in the range of 8-8.1. The pH value of sea water tends to be encourage the deposition of metals in seawater. At high pH, Cu, Cd and Pb tends to precipitate as insoluble hydroxides, oxides, carbonates or phosphates, thereby decreasing the toxicity of these metals (Mamboya, 2007; Rochyatun and Rozak, 2007).

Salinity value is in the range of 30.3 to 34.7‰, with the highest salinity values at station 4, Tanjung Uncang. Sea water with high salinity and has a higher ionic strength, so it can affect the destabilization of suspended solid particles, forming aggregations which is followed by the deposition due to gravity (Maslukah, 2013). Salinity can also affect the presence of heavy metals in the water, if there is a decrease in salinity due to the desalination process will lead to the improvement of the level of toxic heavy metals and heavy metal bioaccumulation greater (Yudiati, Sedjati, Enggar, & Metoda, 2009).

Dissolved oxygen levels, brightness and temperature are factors that influence each other. The low of DO and the high of BOD and COD of waters is an indicator of biological and chemical contaminants highly (Dwiyitno et al., 2008). The value of DO in sea water sampling ranged from 6.9 to 7.7 mg/l, the highest value of DO was in station 4, and the lowest in the station 3. The level of DO in water affected the levels of heavy metals in fish. According to Muiruri, Nyambaka, and Nawiri (2013), the fish has to extract oxygen from water by passing the water through its gills. Thus, the gills potentially absorbed heavy metals that can be considered as a significant indicator to estimate the level of heavy metal contamination in the water.

The brightness is affected by suspended solids. If the brightness or light was low penetration, it will affect the decrease in photosynthetic activity that will affect the rise in water temperature (Sa' and Mahmoud, 2014). In this study, the highest seawater transparency repeatedly was in Uncang Tanjung, Tanjung Pinggir, Tanjung Riau and Marina. In this study, there is a correspondence between the value of the brightness levels and the dissolved oxygen in each sampling location.

The temperature of seawater at the research site was between 29.4 ° C - 31.9 ^{0} C. Based on Authman (2015), the high temperatures can cause high activity and the rate of heavy metals circulation in fish, the lower affinity of oxygen in the blood can increase the rate of accumulation of pollutants and the rate of metabolism which lead to increase the feeding behavior, so it will increase the concentration of metals in fish, if the metal is taken through the food chain.

Levels of heavy metals Cu, Cd and Pb in seawater and angelfish

The results of the analysis of the content of Cu, Cd and Pb in seawater and angelfish are shown in Table 3. Cu was detected in seawater sampling at all locations, except in the area of Tanjung Uncang. However, the Cu was detected in fish at all sampling sites. Cd was not detected in seawater samples, but it was detected in samples of fish at all sampling sites. Further, the metal Pb was detected in samples of seawater and fish at all sampling sites.

Levels of heavy metals were observed in each of the sampling sites followed the pattern Pb> Cu> Cd. The result of the analysis of heavy metals in seawater samples was obtained Cu and Pb levels reached 0,04 mg/l. The high potential of Pb and Cu in this location was predicted to have related to the sources of pollutants in the region. Based on Distribution of Shipping Industry Map in Batam, it is known that the west area of Batam Island from Sekupang to Port Sagulung is a center of industry and shipbuilding. In addition, there are at least seven ports that serve routes between islands, national and international in this area.

The level of Cu in seawater at all locations have exceeded environmental quality standards for biota set by the Ministry of Environment No. 51 of 2004 indicating that the water was contaminated by Cu. Cu was not detected in water samples from the Tanjung Uncang which is the industrial estate and shipbuilding was allegedly associated with the high-speed flow at that location, so that the movement of contaminants dissolved was faster. The content of Cu in fish samples ranged from 0.07 to 0.88 mg/kg. This value still meets the standards of FAO for Cu in fish that is 30 mg/kg. The highest Cu levels was found in fish sample from the Tanjung Uncang. This area is a crowded area with electronics and shipbuilding industries. According to Ashraf et al. (2013), *the intake* of heavy metals by fish living in waters contaminated depends on ecological characteristics, metabolism and other factors such as salinity, the level of contamination of water, food and sediment.

Cu is an essential metal and serves as micronutrients for cellular metabolism. In the process of enzyme metabolism, Cu is a decisive factor. However, Cu can be toxic very much to aquatic organisms intracellular mechanism if its concentration of water exceeds normal limits (Authman, 2015).

Pb levels in seawater sampling are in the range of 0.03-0,04 mg/l. This value has exceeded the value of the environmental quality standards set by the Ministry of Environment for the biota is 0.008 mg/l. Similarly, Pb was observed in fish samples that have exceeded the maximum limit specified in SNI 7378: 2009 and the standard of FAO in 2003. Thus, there is a trend of high risk to health if people eat fish caught in the region.

According to Authman (2015), the concentration and bioavailability of lead is mainly dependent on the absorption of sediment and organic compounds in the water, in addition to the pH, alkalinity and hardness. Aquatic organisms accumulate Pb from water and food. However, it is more reliable for Pb to accumulate in fish in aquatic contamination. Pb can contaminate waters through *ballast* water discharges of ship and emissions of oil-fueled engine used as *an anti-knock* on the machine. Premium is generally used as a fuel in transportation. Tetraethyl lead is usually added to the low-quality fuel to increase the fuel octane rating to spare from the noisy of machines. Besides that Pb also serves as a lubricant for inter valves to prevent an explosion during the combustion in the engine. Pb is also used as an ingredient in paints that are useful to accelerate the drying process layer through oxidation and polymerization in the ship repair business (Ismarti et al., 2015).

Table 3. Heavy metal concentration levels of Cu, Cd and Pb in the seawater samples and angelfish

Heavy Metal	Sampling Sites (Station)				Standards
	TP	TR	MR	TU	
Cu					
Water (mg/l)	0.04±0.02	0.04±0.01	0.04±0.01	bdl	Kepmen LH No. 51 Th. 2004 (0.008 mg/l); FAO (30mg/kg) (Baharom and Ishak, 2015)
Fish (mg/kg)	0.07 ± 0.00	0.79 ± 0.06	0.26 ± 0.03	0.88 ± 0.04	
Cd					
Water (mg/l)	bdl	bdl	bdl	bdl	Kepmen LH No. 51 Th. 2004 (0.001mg/l) SNI 7378: 2009 (0.1 mg/kg); FAO (0.5 mg/kg) (Baharom and Ishak, 2015)
Fish (mg/kg)	0.16 ± 0.01	0.09 ± 0.00	0.03 ± 0.03	0.09 ± 0.03	
Pb					
Water (mg/l)	0.03±0.00	0.04±0.00	0.04±0.00	0.04±0.00	Kepmen LH No. 51 Th. 2004 (0.008 mg/l); SNI 7378: 2009 (0.3 mg/kg) FAO (0.5 mg/kg) (Baharom and Ishak, 2015)
Fish (mg/kg)	0.71 ± 0.01	2.09 ± 0.16	0.88 ± 0.04	2.57 ± 0.00	

bdl = below limit detection, n= 3

Cd level on *C.* rostractus was in the range from 0.09 to 0.3 ppm. Although not detected in seawater but Cd was detected in fish at all sampling sites. The highest cadmium level in fish was observed in fish from Tanjung Pinggir site, which is equal to 0,16 mg/kg. This value is even longer than allowed by SNI 7378: 2009, although still within the range allowed by FAO. Cd contamination was predicted from the local activity of people who throw waste into the sea. Cd is a minor metal compound that is widely used in various products, such as electronic products, coloring/paint, batteries, photography, plastic, agricultural pesticides, and fuel (Dwiyitno, 2008).

4. CONCLUSION

Cu was detected in seawater samples at all research sites, except in the area of Tanjung Uncang. However, Cu was detected in fish at all sampling sites. Cu levels in seawater samples have exceeded environmental quality standards, but Cu level in the fish still meet the standards of the FAO. Cd was not detected in samples of seawater, but it was detected in samples of fish at all sampling sites. Cd levels of fish in three sampling sites still meet the standards of SNI 7378: 2009, except for the fish of the Tanjung Pinggir site. Pb levels in water and fish in all locations has exceeded the permitted levels. This indicates that Batam waters have been contaminated by metals i.e. Cu, Cd and Pb.

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