The heavy metals lead (Pb), chromium (Cr), copper (Cu) and cadmium (Cd) contents in the white shell *Meretrix meretrix* Linnaeus, 1758

M Litaay*, R V Jehadum, R Mardaranti and E Soekendarsi

Dept Biology, FMIPA Hasanuddin University, Makassar, Indonesia

*E-mail: mlitaay@fmipa.unhas.ac.id

Abstract. The research about the contain of heavy metals lead (Pb), chromium (Cr), copper (Cu) and cadmium (Cd) in the soft body of the white shells *Meretrix meretrix* Linnaeus, 1758 from local market Makassar has been conducted. This research was aimed to determine heavy metal contain in white shells *M. meretrix* Linnaeus from local markets of Makassar. Heavy metal contain in white shells, sea water and sediment were analysed using Atomic Absorption Spectrophotometer (AAS). The result of the analysis shows that the content of Pb in *M. meretrix* L. from the central market and the Tanjung market are 8.322 and 5.627 ppm. Cr content in shell from Sentral market and Tanjung market was 0.102 and 0.052 ppm. Moreover, copper (Cu) and cadmium (Cd) content in white shells was not detected. The sea water from Metro Tanjung Bunga contain Cd 0.33 ppm and Cu was not detected. While the heavy metal content of Cd and Cu in sea water from Pangkep was not detected. The sediment from Metro Tanjung Bunga, contain Cd was 1.38 ppm and Cu was 1.84 ppm. While the heavy metal contain of Cd in sediment from Pangkep was not detected and Cu was 15.96 ppm. The content of metal Pb and Cr in *M. meretrix* L. exceeds the environmental quality standard.

1. Introduction

The sea has various kind of biodiversity which one of them is bivalvia, a shellfish organism whose economic value is considerably high as it is utilizable by people for consuming and its shell for craft materials. Besides that, it is also commonly used for heavy metal pollution indicator in consideration of its habitation, where it dwells in substrate or its bio-cumulative nature is high to heavy metal. Since bivalvia is widely consumed, this biocumulator creature should be come into account especially in constant consumption [1]. The existence of heavy metal in environment, particularly the aquatic ecosystem, might cause health problem if it is ingested by eatable organism like shellfish in long term period. The metal in aquatic biota, like shellfish, is in constant interaction with ones in surface water; such as suspended materials and sediment [2].

Heavy metal as one of industrial waste component could inflict the problem itself for its undegraded propensity in environment and can become potential toxic for living things [3]. Cadmium (Cd) and Copper (Cu) are kind of the heavy metals used in various industrial activity. Cadmium is found in textiles industrial waste, electroplating, and chemical factory. While, copper is used in metal coating, in paint, plastic, batteries, insecticides, pesticides, glasses, and ceramics. The increasing
contribution of waste containing Cadmium, Copper and other heavy metals into water bodies would badly endanger aquatic ecosystem.

Among the shellfish species, M. meretrix is one that often found in Makassar public market, with flat triangle shape, smooth, and shiny. Not only in Makassar, M. meretrix, or locally known as Kerang Kepah by Tarakan people, is popular there and has a high economic value, and being consumed in many areas. M. meretrix is known by several local names like kerang tahu, kerang susu, kerang putih, kerang lamis, contains 15 amino acids consisting of 9 essential amino acids and 6 non essential ones. The essential amino acids are namely histidine, arginine, threonine, valine, methionine, isoleucine, leucine, phenylalanine, and lysine. While, non-essential amino acids are such as aspartic acid, glutamic acid, serine, glycine, alanine, and tyrosine [4]. This author also added that this shellfish also a good source for karbohidrate, fat and minerals. Its great benefit for human body and its state as common property in marine resources make many people harvest it. M. meretrix categorized as filter feeder species for its low mobility which makes it easily accumulates heavy metal inside its body [5]. Filter feeder species also naturally feed themselves with small entities under water including heavy metals, which consequently would be accumulated inside their body [6]. This research aimed to identify heavy metal content of Lead (Pb), Chromium (Cr), Copper (Cu) and Cadmium (Cd) accumulated in white shellfish M. meretrix collected from Makassar local markets of Indonesia.

2. Materials and Methods

2.1. Equipments and Materials
The tools used for this research were plastic, freezer, laboratory chemical analysis equipment, Atomic Absorption Spectrophotometer (AAS), oven, mortal, desiccators. The materials used for this research were white shellfish M. meretrix, Distilled water, HNO₃ concentrated, H₂SO₄ concentrated, standard liquid of Pb 1000 ppm, Cr 1000 ppm, Cu 1000 ppm and Cd 1000 ppm, and Whatman filter paper.

2.2. Sample Source
The sample of the white shellfish M. meretrix was taken from Public Market of Metro Tanjung Bunga Street and Makassar Central Market. Sampling was done by buying white shellfish M. meretrix directly in market, using random system without considering the size. Sea water and sediment from sample’s origin were Pangkep and Metro Tanjung Bunga Makassar.

2.3. Procedure
The sample was cleaned up by separating the flesh from its shell. The flesh was dried out in the oven with temperature 60⁰ – 70⁰ C for 24 hours. The dried sample was chilled inside the desiccators. After that, it was grinded by using mortal until fine, weighed as much as 30 g, put into closed container which was added with 1.5 ml H₂SO₄ concentrated and 3.5 ml nitrate acid (HNO₃) concentrated, then left for 24 hours. Next, sample was heated up on the water heater in temperature 60⁰ – 70⁰ C for 2-3 hours until the sample powder was soluble (the liquid turned clear). The sample was chilled again in room temperature, added by 1 ml HNO₃ concentrated, slowly stirred then added by 9 ml distilled water, finally, the sample was analyzed by using Atomic Absorption Spectrophotometer (AAS).

3. Result and Discussion

3.1. Heavy Metal Content in soft body of M. meretrix Linnaeus
The result analysis of heavy metal content of lead (Pb), chromium (Cr), copper (Cu) and cadmium (Cd) in the soft body of the white shellfish M. meretrix sample taken from different markets is shown in Table 1.
Table 1. Heavy metal content in the soft body of *M. meretrix*

| No | Location (Market)       | Heavy Metal Content (ppm) | Pb  | Cr  | Cu  | Cd  |
|----|-------------------------|----------------------------|-----|-----|-----|-----|
| 1  | Metro Tanjung Bunga     |                            | 8.32| 0.10| nd  | nd  |
| 2  | Makassar Central Market |                            | 5.62| 0.05| nd  | nd  |

Note: nd (Not detected)

It is obvious from Table 1 that Pb and Cr content were detected from samples while Cu and Cd were not detected in samples from two markets. Soft body of *M. meretrix* from Metro Tanjung Bunga market contained more Pb (8.32 ppm) and Cr (0.10 ppm) compared to sample from Makasar central market that of 5.62 ppm Pb and 0.05 ppm Cr, respectively.

3.2. Heavy Metal Content in the Sea water, and Sediment Samples.

The result analysis of heavy metal content of lead (Pb), chromium (Cr), copper (Cu) and cadmium (Cd) in water and sediment samples taken from two different locations is shown in Table 2. As indicated in the Table 2, the analysis of heavy metal content of Pb, Cr, Cu and Cd in water and sediment samples, taken from the two locations, shows different result. The water from Metro Tanjung Bunga has 0.33 ppm of Cd and the Cu content is not detected. While, in the water from Pangkep, both Cu and Cd contents were not detected. As for the sediment, from Metro Tanjung Bunga, Cd content is detected in amount of 1.38 ppm and 1.84 ppm for Cu content. While, the sediment form Pangkep has no Cd content whereas its Cu content is 15.96 ppm. Both locations are source of shellfish. Metro Tanjung Bunga is for ones that sold in Metro Tanjung Bunga market and Pangkep is for ones that sold in Makassar Central Market.

Table 2. Heavy metal content in water and sediment samples

| No  | Location                  | Pb   | Cr  | Cu  | Cd  | Pb  | Cr  | Cu  | Cd  |
|-----|----------------------------|------|-----|-----|-----|-----|-----|-----|-----|
| 1   | Metro Tanjung Bunga       | 4.65 | 1.31| nd  | 0.33| 39.35| 33.54| 1.84| 1.38|
| 2   | Pangkep                   | 6.63 | 0.16| nd  | nd  | 14.70| 40.35| 15.96| nd  |

Note: nd (Not detected)

White shellfish *M. meretrix* is a dwelling organism in the bottom of water that prefers smooth-sand habitation. It has low mobility (slow movement) and does not immerse itself into substrate deeply as it has short siphon. *M. meretrix* is categorized as filter feeder which has nature to eat small entities in the bottom of water including heavy metal that would be accumulated inside the body. The pollutants (heavy metal) which enter the organism body would take part in food chain, diffuse through shell and gill, and then being absorbed by digestive tract. Metals in biota body would be stored up in the tissue, especially liver and kidney [6].

Heavy metals turn as pollutant mainly as it is un-degradable by living organism in environment, then accumulated there, especially in the bottom of water, forming complex compound with organic and anorganic materials by adsorption and combination. Pollutant contamination in environment could decrease the potency of biological resources. The pollution of industrial materials, containing dangerous part of heavy metal like Mercury (Hg), Cadmium (Cd), Plumbum (Pb), tends to increase toxication and public health problem case, and to some stage can act as carcinogenic. Cu is one of the essential heavy metal that is necessary for organism however it would be toxic in excessive amount.

Sea water is a component linking to mainland environment, where waste disposal would be disembogued. It is also a direct landfill of various human activities in a cheap and easy way.
Therefore, many kinds of waste and pollutant, especially metals, could be found there. Heavy metals, which enter marine environment, would be soluble in the water then accumulated in sediment. This might increase along with time depending on water environment condition. If sediment carrying capacity is considerably high, the sediment in the bottom of water would be lifted and moved. Based on gravitation theory, when a particulate has bigger density than water, it would settle in the bottom of water or the sedimentation process would occur. Mostly as a result, the heavy metal content in sediment is higher than the sea water. Heavy metal concentration dissolved in sea water depends highly on water condition where more human activities, both in mainland and water, would influence it [7]. According to [8], Cd source in body water which contributed by industrial waste water is very few in amount while the biggest contribution is come from solid waste.

In the present study, heavy metal Cu and Cd content in the flesh of white shellfish *M. meretrix* sample, taken from Metro Tanjung Bunga market and Makassar Central market, is not or found (undetected). It indicates that there is no heavy metal accumulation in white shellfish *M. Meretrix* body. However, this research fact does not imply that the flesh contains no heavy metal. It is possible that the shellfish contains heavy metal but in small amount so that it is undetected by the equipment. Heavy metal will always be toxic for living things even of the fact that some of them are necessary in small amount. It would be accumulated inside the body and in continual long term periodic would endanger human health.

According to National Standardization Agency of Indonesia Sentence in 2009, Cadmium content in ready-consumed bivalvia product must not exceed 1.00 ppm while for Cu, there is still no limitation on the list. It is probably caused by the less poisoning case of Cu in food or specific study on it has not been done yet. Water and sediment samples examined in this research are taken from Metro Tanjung Bunga and Maccini Baji Port of Pangkep as the locations of shellfish sources that sold in Metro Tanjung Bunga market and Makassar Central Market. These samples are used as supporting data of Cu and Cd existence. The analysis shows that Metro Tanjung Bunga seawater sample contain 0.33 ppm Cd and undetected Cu while for sediment sample, Cu is found in amount of 1.84 ppm and Cd 1.38 ppm. As for the seawater sample taken from Maccini Baji Port of Labakkang, Pangkep, Cu and Cd are undetected while the sediment sample contain 15.96 ppm Cu and undetected Cd.

In Environmental and Forestry Ministry Decree Kep.No.51/MENLH/2004 about water quality standard, the limit for Cu content is 0.008 ppm and 0.001 ppm for Cd. Here, the result shows that Cu and Cd in seawater sample taken from Metro Tanjung Bunga has exceeded the threshold set by The Ministry of Environment and Forestry or in other words, that location has been contaminated. In addition, despite of the research fact that there is no Cu and Cd detected in sea water sample taken from Pangkep, its sediment contains 15.96 ppm of Cu which is considerably high too then it can be said that the location is also contaminated.

The case of undetected heavy metal in water is somehow supposed to the seawater dynamic movement, which is caused by several physical factors such as wind, stream, wave, and tide, so that the dilution is constantly occurred, making the heavy metal content low [9]. In this study, heavy metal content in sediment is higher than in the seawater. It is because heavy metal has easy binding and settling nature in sediment [10]. Heavy metal characteristic is binding easily with the organic material and settling in the bottom of water then interflowing with the sediment so that its content in sediment is higher than in the water [11].

The sediment taken from Metro Tanjung Bunga is sandy type while ones from Pangkep is sandy mud type. According to [12] stated that sediment type could affect its heavy metal content. In addition, [13] also argued that particle size has significant role in heavy metal distribution into sediment. Organic material content is related to sediment particle size. In smooth sediment, organic material presentation is higher than the rough one. It is related to the calm environment condition therefore sediment deposition is enabled in the form of mud which is following by higher material organic accumulation.

The analysis of White shellfish *M. meretrix* flesh gives the result of undetected heavy metal content. Furthermore in seawater sample analysis, the heavy metal content is low and undetected.
While in sediment sample analysis, the heavy metal content is considerably high. Besides habituation factor, metal absorption rate from water can be influenced by life cycle phase condition, biota size, sex, and adaptability [14][15][16]. Public interest in consuming shellfish makes the sellers want to provide it in large amount without considering its size, in which this might affect the biota life cycle phase in nature.

The high frequency of shellfish is also presumed affecting heavy metal absorption quantity. Heavy metal absorption of biota takes relatively long time period. As the white shellfish *Meretrix meretrix* has the quality of filter feeder, it is assumed that the heavy metal accumulated in sample body is undetected since heavy metal content in seawater sample is also undetected. Another assumption of this low metal accumulation is physiologic disorder of the shellfish itself which cause the balance function between input with level of output is not maximal then influence the accumulation process of heavy metal and its deployment in shellfish body tissue [12]. High concentration of metal in sediment does not necessarily cause symptoms of toxicity also in the matter of accumulation into organism [10]. Different studies on snails found that the magnitude of heavy metal accumulation in snail tissues depends upon the type of heavy metal and snail species. [17]. The result from several studies metals contents (Cd, Co, Cr, Mo, Ni, Pb, V, and Zn) on *Meretrix meretrix* in the Arabian Gulf during 1985 and 1991, as reported in review by [18], indicated that metals concentration were various. However, there was a magnitude of increase in metal concentration in clams collected from are close to mining area. This may suggest that oil spill probably affected metal accumulation.

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4. Conclusion
This research leads into a conclusion that amongst four heavy metal observed, the only lead (Pb) content in the White shellfish *Meretrix meretrix* exceeds the environmental quality standard.

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