Analysis Of Lead (PB) And Mercury (HG) Heavy Metal Content In Octopus (Octopus Spp.) At Some Traditional Markets In Medan City, North Sumatra

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Abstract: Octopus is an economically important fishery commodity. All types of octopus including octopus become fishery products that can be consumed. The export value of world octopus in 2014 can reach 350,710 tons with a value of $ 133 trillion. The objective of the present study was to examine the heavy metal content of Lead and Mercury In Octopus obtained from several traditional markets in the City of Medan. The sampling time is carried out three times, namely in June, July, and August 2018. The results showed octopus in the results of laboratory tests of Lead (Pb) heavy metals with the AAS tool furnace graph method on Lead (Pb) and the Hydrid method on Mercury (Hg). It is known that the highest Pb content is in the sample of 6 which is 0.017 mg / kg and the lowest is in the sample 2 which is 0.007 mg/kg. Pb and Hg in each sample of octopus is low according to the World Health Organization (WHO), EU and BPOM.

Keywords: Octopus, Lead, Mercury, Furnace Graph Method, Hydrid Method.

1. Introduction

Heavy metal pollution to the environment is a process that is closely related to the use of these metals by humans. At the beginning of its use, the effect of pollution on the environment is unknown. The process of oxidation in metals that causes a bond is actually signs of pollution. Recently, heavy metal poisoning from foodstuffs has increased in number. Environmental pollution by heavy metals can occur if industries that use these metals do not pay attention to environmental safety, especially when disposing of their waste. Certain metals in high concentrations will be very dangerous if found in the environment (water, soil and air) [1]. The North Sumatra provincial government in its program also seeks to improve the welfare of fish farmers and fishermen communities through increasing production and development of fisheries businesses. North Sumatra is one of the provinces in Indonesia which in its Regional Revenue (PAD) relies on the fisheries sector including aquaculture and capture fisheries. As an area that is included in the Minapolitan program which is currently being proclaimed by the North Sumatra Ministry of Maritime Affairs and Fisheries, it is moving to carry out the program by building various facilities, facilities and infrastructure that support increased fisheries production. Octopus is an economically important fishery commodity. All types of octopus including octopus become fishery products that can be consumed. All types of octopus including octopus become fishery products that can be consumed. The export value of world octopus in 2014 can reach 350,710 tons with a value of $ 133 trillion. In general, the body of the octopus is distinguished according to the head, neck and body. In the head area there are eight arms which function to catch prey and move. The octopus mouth is in the arm ring. In the inside of the mouth there is a pair of overlapping jaws that are shaped like the beak of an inverted cockatoo and also a scarred tooth or radula. Octopus has two large eyes and protrudes around the edges of the head. Octopuses have nearly 3600 vision fields so they can detect prey and enemies [6]. Heavy metals that can directly or indirectly harm humans such as Lead (Pb) can result in a system of hemoglobin formation (Hb) causing anemia, disruption of the central and peripheral nervous system, renal system, reproductive system, idiots in children, epilepsy (epilepsy), skeletal defects and damage to somatic cells. The effect of Hg on human health, such as being able to inhibit the path of blood to the brain, damaging kidney and liver function, disrupting the metabolic processes of the nervous system, and if it is acute it can cause dysfunctional in other organs. One of the most dangerous pollutants for human health is heavy metals. The World Health Organization (WHO) and the Food Agriculture Organization (FAO) recommend not eating sea food contaminated with heavy metals. Heavy metals have long been known as an element that has a very high toxicity and has the ability to accumulate in human organs [3]. Anticipating the negative influence of the influence of heavy metals on octopus generated on the surrounding community, it is necessary to supervise the quality of Pb and Hg in the octopus found in the waters. Analysis of metal levels of Pb and Hg was carried out by Atomic Absorption Spectrophotometer (AAS) with dry destruction preparation techniques on lead metal and wet destruction on mercury metal. The choice of atomic absorption spectrophotometer method because it has highsensitivity, is easy, inexpensive, simple, fast, and the required samples are few and do not require preliminary separation.

2. Materials And Method

2.1 Study area

Samples of octopus were collected from 8 traditional markets. sample 1 (Padang Bulan Market), Sample 2 (BelawanInpres Market), Sample 3 (Red Market), Sample 4 (Cemara Market), Sample 5 (PetisahMarket), Sample 6 (SeiKambing Market), Sample 7 (Belawan Gabion Market),

and Sample 8 (Marelan Induk market) from June to September 2018. Take samples from each market.The collected samples stored in ice boxes are then transported to Integrated Laboratories, Aquatic Resource Management, University of North Sumatra, Medan and Quarantine Agency Fish, Medan Fisheries Product Quality and Safety Control (BKIPM) 1 for further analysis.

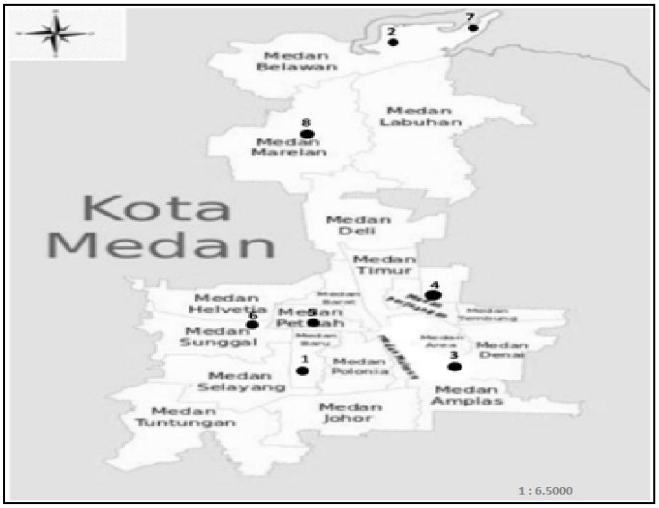

Figure 1. *Research Location on 1)Maket Padang, 2)Market Inpres Belawan, 3)Market Merah, 4)Market Cemara, 5)Market Petisah, 6)Market Sei Kambing, 7)Market Gabion Belawan,and 8) Market Induk Marelan*

2.2 Material

The tools used in this study were 25 ml, 100 ml and 250 ml beakers, blender / homogenizer, polypropylene bottles, porcelain cup, 25 ml and 50 ml measuring cups, hot plate, 50 ml and 1000 ml measuring flask, micropipette, Drop Pipette, 10 ml 5 ml and 1 ml Volumetric Pipette, Knife, Spatula, Glass Stirrer, Atomic Absorption Spectrophotometer Analytik Jena ZeeNit p700, Analytical Scales with Accuracy of 0,0001 g, Furnace Furnace , Polypropylene Container, and Fume Hood. The material that will be used in this study is meat from Octopus (Octopus spp.), Fish Flour Standard Material References (SRM), Nitric Acid (HNO_3) 65%, HNO_3 0.1 M; Dilute 7 ml of 65% HNO_3, Cloride Acid (HCl) 37%, Aquadest, Nitric Acid (HNO_3) 65%, Sulfuric Acid (H_2SO_4) 95% -97%, Boiling.

2.3 Procedures

Sub-procedures-1 (**Furnace Graph Method**)

Preparation techniques for Method of Graph Lead Furnace (Pb) with Dry Ashing these samples in accordance with SNI 2354.5: 2011 where Pulverize / puree the sample with a blender / homogeneous place the sample in a polystyrene container. Then, weigh the product as much as 0.5 g in a porcelain dish and record the weight (W). After that, put the sample into a furnace. Then, increase the temperature of the ignition furnace in stages 100^{o}C every 30 minutes until it reaches 450oc for 18 hours. After 18 hours remove the sample from the ignition furnace and cool it at room temperature. After cold add a few drops of H_2O and 1 ml of HNO_3 as much as 65%. Then steam over the hot plate at 100 ° C until dry. Next Reinsert the sample and into the 450 ° C ignition furnace and maintain for 3 hours. After the ash is completely formed add 5 ml HCl of 5 ml Steam on a hot plate at 100^{o}C until dry. Add 10 ml of 0.1 M HNO_3 and refrigerate at room temperature for 1 hour, 50 ml polypropylene flask and add a modification matrix solution. Ready samples are measured by AAS using air-acetylene.

Sub-procedures-2 (**Hydrid Method**)

Hydrid Method in Testing Mercury (Hg) in accordance with SNI 2354.6: 2016 namely pulverize / puree the sample with a blender / homogenizer. Then weigh 5 g of wet product or 0.5 g of dry product with analytical scales and record the weight (W). After that Enter into elmeyer. Next Add 3 pieces - 5 pieces of boiling stone. Then add 10 mg - 20 mg V_2O_5. Add tururts of 10 ml of 65% HNO_3 and 10 ml of H_2SO_4 95% - 97%. Warm up with low heat until boiling. Next rinse the coolant with 15 ml of deionized water. Add 2 drops of H_2O_2 30% through the top end of the cooler. Then add the distilled water with 100 ml to Elmeyer. Ready samples are measured by AAS using air-acetylene.

2.4 Data Analysis

The reading curve for calibration of heavy metal lead and mercury in the AAS tool uses the following formula: Cd or Hg concentration (µg/g) = **((D-E) x Fp x V)/ W**, where: D is sample concentration (mg/L) from the AAS reading, E is concentration of blank sample (mg/L) from the AAS reading, Fp is the dilution factor, V is the final volume of the prepared sample solution (ml), it was converted into liters prior calculated, W is sample weight (g).

3. Study Findings

The results of testing of Lead (Pb) heavy metals can be seen in table1 and Merkury (Hg) in table 2. Analysis of lead levels (Pb) in octopus obtained from the spectrophotometric method can be seen in Table 1. obtained from eight market in Medan, North Sumatra which shows that eight samples are very volatile. In Table 1.shows that the highest lead content in octopus in several traditional markets in the city of Medan, North Sumatra which were in sample 6 of 0.017 mg / kg and the lowest lead content in sample 3 is 0.007 mg / kg. In examining heavy metal content of lead (Pb) in octopus meat using a standard test called CRM with a value of 0.411 mg / kg.

Tabel 1. *Heavy metal concentration of Lead (Pb) in octopus (Octopus spp.)*

Sample Code	Market	Cons (mg/Kg)	CRM	Certificate
Sample 1	Maket Padang	0.009	0.411	0.404± 0.062
Sample 2	Market Inpres Belawan	0.007	-	-
Sample 3	Market Merah	0.012	-	-
Sample 4	Market Cemara	0.015	-	-
Sample 5	Market Petisah	0.016	-	-
Sample 6	Market Sei Kambing	0.017	-	-
Sample 7	Maket Gabion Belawan	0.008	-	-
Sample 8	Market Induk Marelan	0.008	-	-

Note: - = similar

In Table 2. shows that the highest mercury content in octopus in several traditional markets in the city of Medan, North Sumatra in sample 7 of 0.28 mg / kg and the lowest

lead content in sample 5 is 0.0016 mg / kg. In examining heavy metal content of mercury (Hg) in octopus meat using a standard test called CRM with a value of 0.411 mg / kg.

Tabel 2. *Heavy metal concentration of Mercury (Hg) in octopuses (Octopus spp.)*

Sample Code	Market	Cons Hg (mg/Kg)	CRM	Certificate
Sample 1	Maket Padang	0.005	0.378	0,412± 0.036
Sample 2	Market Inpres Belawan	0.003	-	-
Sample 3	Market Merah	0.28	-	-
Sample 4	Market Cemara	0.15	-	-
Sample 5	Market Petisah	0.0016	-	-
Sample 6	Market Sei Kambing	0.0017	-	-
Sample 7	Maket Gabion Belawan	0.28	-	-
Sample 8	Market induk Marelan	0.11	-	-

Note: - = similar

The results of analyses of Pb metal content in the meat showed the highest value of Pb in 3, 4, 5 and 6 which were 0.012 mg/kg, 0.015 mg/kg, 0.016 mg/kg and 0,017 mg/kg (market 3 (market Merah), 4 (market Cemara), 5 (market Petisah) and 6 (market Sei Kambing) and the lowest were in 2, 7, 8 and 1 which is 0.007 mg/kg, 0.008 mg/kg, 0.008 mg/kg and 0,009 mg/kg for market 2 (market Inpres Belawan), 7 (market Gabion Belawan), 8 (market Induk Marelan) and 1 (market Sei Kambing) Analysis of the safe threshold of lead levels in octopus compared to the safe limits of BPOM, the European Union and BPOM Based on graph 1, the highest Pb content is found in the sample of 6, which is 0.017 mg / kg and the lowest is in the sample 2, which is 0.007 mg / kg. according to BPOM, the maximum limit of Pb is 2.0 World Health Organization (WHO) which is the maximum Pb limit is 2.0 while according to the European Union the maximum limit of Pb is 0.5 Therefore, the sample of octopus is still safe for consumption and can be an export commodity.

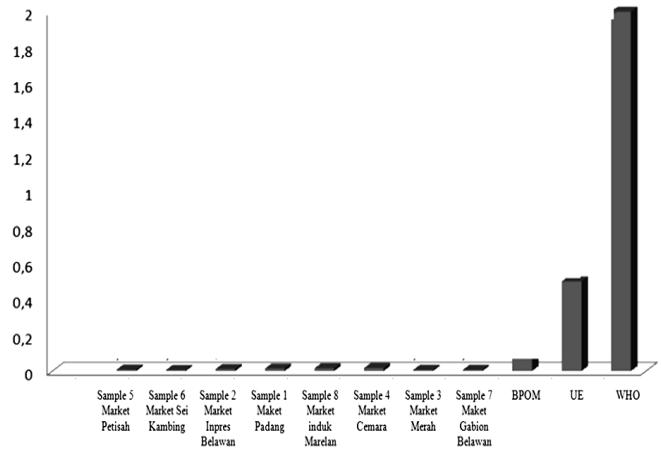

Figure 1. *Graph of Lead (Pb) heavy metal threshold for octopus*

Analysis of the safe threshold of mercury levels in octopuses compared to the safe limits of BPOM, the European Union and BPOM. It shows that the highest Mercury (Hg) content were in 8, 4, 3 and 7 which is 0.11 mg/kg, 0.15 mg/kg, 0.28 mg/kg and 0,28 mg/kg (market 8 (market Induk Marelan), 4 (market Cemara), 3 (market Merah) and 7 (market Gabion Belawan) and the lowest Were 0.0016 mg/kg, 0.0017 mg/kg, 0.003 mg/kg and 0,005 mg/kg (market 5 (market Petisah), 6 (market Sei Kambing), 2 (market IndukBelawan) and 1 (market Padang Bulan). Based on graph 2. the highest value of Hg content is found in sample 7 of 0.28 mg / kg and the lowest lead content in sample 5 is 0.0016 mg / kg. So that from the test results it can be concluded that the content of heavy metals Hg in each octopus sample is low according to BPOM, with the maximum limit of Pb is 0.2 mg / kg, the World Health Organization (WHO) which is the maximum limit of Hg is 0.5 mg / kg whereas according to the EU, the maximum limit of Pb is 2 mg / kg. Therefore, the sample of the octopus is still safe for consumption and can be an export commodity.

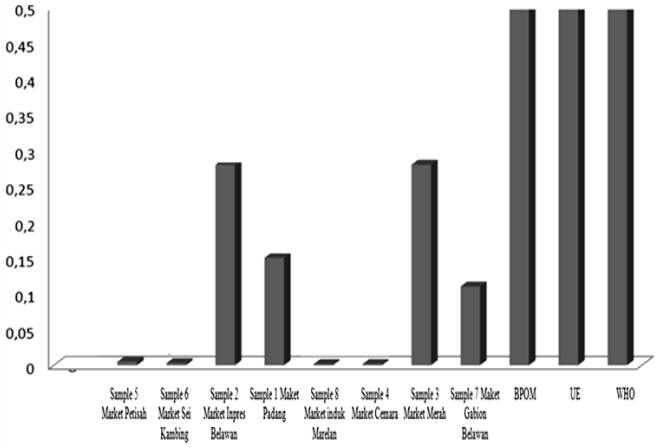

Figure 2. *Graph of threshold of heavy metal Mercury (Hg) in octopus*

4. Discussion

The metal content of Pb, and Hg in Octopus meat obtained is very volatile. Most of the average heavy metal content of Pb and Hg octopus respectively ranged from 0.007mg / kg, 0.008 mg / kg, 0.008 mg / kg, 0.009 mg / kg, 0.012, 0.015 mg / kg, 0.016 mg / kg and 0.017 mg / kg in lead and 0.005 mg / kg, 0.003 mg / kg, 0.28 mg / kg, 0.15 mg / kg, 0.0016 mg / kg, 0.0017 mg / kg, 0, 28 mg / kg, and 0.11 mg / kg on mercury metal testing. The results of analyses of Pb metal content in the meat showed the highest value of Pb in 3, 4, 5 and 6 which were 0.012 mg/kg, 0.015 mg/kg, 0.016 mg/kg and 0,017 mg/kg market 3 (market Merah), 4 (market Cemara), 5 (market Petisah) and 6 (market SeiKambing) and the lowest were in 2, 7, 8 and 1 which is 0.007 mg/kg, 0.008 mg/kg, 0.008 mg/kg and 0,009 mg/kg (market 2 (market Inpres Belawan), 7 (market Gabion Belawan), 8 (market IndukMarelan) and 1 (market SeiKambing), shown in (table 1). Based on table2. It shows that the highest Mercury (Hg) content were in 8, 4, 3 and 7 which is 0.11 mg/kg, 0.15 mg/kg, 0.28 mg/kg and 0,28 mg/kg (market 8 (market IndukMarelan), 4 (market Cemara), 3 (market Merah) and 7 (market Gabion Belawan) and the lowest Were 0.0016 mg/kg, 0.0017 mg/kg, 0.003 mg/kg and 0,005 mg/kg (market 5 (market Petisah), 6 (market Sei Kambing), 2

(market IndukBelawan) and 1 (market Padang Bulan). Laboratory test results of Heavy Metal Lead (Pb) and Cadmium (Cd) with AAS method furnace graph method on Lead (Pb) and Hydrid method on Mercury (Hg).Based on Table 1. It is known that the highest Pb content is in the sample of 660 which is 0.017 mg / kg and the lowest is in the sample 417 which is 0.007 mg / kg. Based on table 2. It is known that the highest value of Mercury (Hg) content is in the sample 451, which is 0.28mg / kg and the lowest is 659 which is 0.0016 mg / kg. So that from the test results it can be concluded that the weight of Pb and Hg in each octopus sample is low according to the World Health Organization (WHO), namely the maximum Pb limit is 2.0 and the maximum limit of Hg is 0.5 while according to the EU the maximum limit of Pb is 0.5 and the maximum limit of Hg is 0.5. Therefore, the sample of the octopus is still safe for consumption and can be an export commodity. In facilitating accurate testing of the entire testing system during the development or application of a test material using the AAS furnace graph method on Lead (Pb) and the Hydrid method on Mercury (Hg) Certified reference material is used. Certified reference material is a material or substance that has certain properties that are quite homogeneous, stable, and has been certified with a standard technical procedure established to be used in measurement or testing which is an important role in validating data accuracy. In testing Lead (Pb), CRM has a value of 0.411 mg / kg and CRM Mercury (Hg), which is used as a comparison of test materials in measurement or testing so that the results can be validated accurately. The high content of heavy metals in octopus meat is suspected because of the accumulation of heavy metals due to the high contamination of heavy metals in the water. The level of octopus accumulation on heavy metals can be calculated by comparing the heavy metal content in octopus meat. When associated with bioconcentration factors, the level of octopus accumulation of heavy metals in water is greater than that found in sediments. Heavy metal lead and mercury enter through the food chain system so that it enters the body of the octopus through plankton then zooplankton and is subsequently consumed by fish where heavy metals accumulate will have a long residence time and levels will continue to grow if the waters continue to be polluted. Methylmercury bioaccumulates and biomagnifies in aquatic food webs at higher rates and to a greater extent than any other form of mercury. "Bioaccumulation" refers to the net uptake of a contaminant from the environment into biological tissue via all pathways. It includes the accumulation that may occur by direct contact of skin or gills with mercury-contaminated water as well as ingestion of mercury-contaminated food. "Biomagnification" refers to the increase in chemical concentration in organisms at successively higher trophic levels in a food chain as a result of the ingestion of contaminated organisms at lower trophic levels. Methylmercury can comprise from 10 percent to over 90 percent of the total mercury in phytoplankton and zooplankton (trophic levels 1 and 2), but generally comprises over 90 percent of the total mercury in fish (trophic levels 3 and 4). Fish absorb methylmercury efficiently from dietary sources and store this material in organs and tissues. The biological half-life of methylmercury in fish is difficult to determine but is generally thought to range from months to years [4]. Octopus as an indicator of water pollution shows that waters in northern Sumatra are still safe in the contamination of heavy metal lead and mercury because it is seen from the test results obtained still below the safe limit of SNI and WHO. That Fish is a water organism that can move quickly. Fish generally have the ability to avoid the influence of water pollution. If the body of the fish has contained high levels of heavy metals that have exceeded the normal limits that have been determined indicates environmental pollution has occurred. Related to this, in general heavy metals enter the body's tissues through several pathways, namely the digestive tract, respiratory tract, and penetration through the skin. The average value of lead levels in fish determined by SNI and WHO is 0.3 ppm [9]. Accumulation of heavy metals that occur in fish is caused by contact between octopus and aquatic medium containing toxic compounds. Contact takes place with the transfer of chemicals from the water environment into the fish's body surface or. Heavy metals can accumulate in the body of the fish through several paths, including respiration, food channels (biomagnification) and through the skin (diffusion). The metal is absorbed in fish meat by blood which then binds to blood proteins and then is distributed throughout the body's tissues. The highest metal accumulation is usually found in the liver and kidneys. Accumulation of heavy metals in fish body tissues from the largest to the smallest, namely, gills, liver, and muscle (meat)[10]. There is this research. The researchers tested the gill section of octopus because this part is a part that always interacts with the physical chemical parameters in the aquatic environment so that in this part the accumulation rate of metal weighs greater than the other content. The level of lead content in different organs shows that the highest value is in the order of 0.07561mg / kg obtained in the octopus gills studied in the summer. While the lowest content is in the range of 0,00056 mg / kg obtained in meat. According to this level, we can determine the sequence of lead accumulation in various octopus organs as follows: Gills> digestive glands> meat. The concentration of heavy metals is generally higher in gills because of their physiological role in fish metabolism [2]. The high content of heavy metals in octopus meat is due, octopus is classified as demersal fish, likes sandy beaches and slow swimming. Octopus also belongs to a group of carnivorous fish that are foraging by digging holes in sand using their cone-shaped snouts. Aquatic organisms that are demersal, meaning that many lives are found in the bottom of the waters and take materials that are in the bottom of the water as a source of food. The occurrence of accumulation of heavy metals in the bottom of the water is possible to enter the body of the biota through a chain of food chains [4]. Octopus is a bioindicator of environmental pollution, including chemical contamination. This is because fish show a reaction to the presence of contamination in waters within certain concentration limits, such as changes in activity, effects on abnormal growth to death. Contamination of heavy metals in the waters is thought to originate from domestic waste, industry along the watershed (DAS) and the sea. The results of the analysis of heavy metal content in various octopuses are presented in Tables 1 and 2 [7]. Heavy metals that enter the octopus body will continue to grow and will continue to accumulate without even the slightest escape through metabolic activity until the octopus is no longer able to tolerate the heavy metal content of lead in its body. That heavy metal lead is very toxic, has bioaccumulative properties in the body of aquatic organisms, and will continue to be accumulated until the organism is no longer able to tolerate the heavy metal content of lead in its body.

Lead can be accumulated directly from water and from sediments by marine organisms. Due to the bioaccumulative nature of lead metal, the concentration of metal in the form of dissolved water is low, in the sediment increasing due to the processes of physical, chemical and biological biology, and in the body of animals the water increases several times [5]. Although the amount of Pb and Hg absorbed by the body is only small, the Pb and Hg metals are very dangerous. This is because lead and mercury compounds can have toxic effects on various types of organs. The impact of the negative impact of lead metal is very harmful to human health, especially for children. Among them are affecting cognitive function, learning ability, inhibiting growth, decreasing the function of organs (kidneys, nervous system and reproduction), increasing blood pressure and affecting brain development. In adults, lead can cause increased blood pressure, digestive disorders, kidney damage, nerve damage and reproductive disorders. The pathology found in cases of Lead poisoning in digestion is inflammation of the digestive tract, liver and kidney damage [8].

5. Conclusion

Conclusion of laboratory test results for Heavy Metal Lead (Pb) with AAS tool furnace graph method on Lead (Pb) and Hydrid method on Mercury (Hg). Based on Table 1. It is known that the highest Pb content is in the sample of 6 which is 0.017 mg / kg and the lowest is in the sample 2 which is 0.007 mg / kg. Based on table 2. It is known that the highest value of Mercury (Hg) content is in the sample 3, which is 0.28mg / kg and the lowest is 5 which is 0.0016 mg / kg. So that from the test results it can be concluded that the weight of Pb and Hg in each octopus sample is low according to the World Health Organization (WHO), namely the maximum Pb limit is 2.0 and the maximum limit of Hg is 0.5 while according to the EU the maximum limit of Pb is 0.5 and the maximum limit of Hg is 0.5. Therefore, the sample of the octopus is still safe for consumption and can be an export commodity.

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