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Analysis of mercury and nickel content in fish and shrimp a result aquaculture of ponds in Pomalaa, Kolaka Regency

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Abstract. The Nickel Mining Industry in Pomalaa, Kolaka Regency, Southeast Sulawesi has been operated since 1909. In its development, mining activities have begun to cause problems, namely pollution and environmental damage. Research on metals around the nickel mining waters has been done by taking samples of milkfish and shrimp which are cultivated by the community in ponds. The metal analysis was carried out using AAS (*Atomic Absorption Spectrophotometer*) variance AA50. The presence of mercury metal in fish samples (B₆) and shrimp (U₄₀ and U₅₀) was not detected, but was found in fish samples (B₂ and B₄), and shrimp (U₃₀) with the contents of B₂ each at 7.0510±0.77 mg/kg, B₄ of 2.0700±0.12 mg/kg, and U₃₀ of 4.6560±1.04 mg/kg. Based on SNI7387:2009 (The maximum limit of mercury contamination in food) is known to fish and shrimp as a result of the cultivation of these ponds has undergone mercury metal pollution. Nickel is found in all types of samples, both in fish and shrimp. The value of nickel metal content in fish (B₂ is 0.5000±0.11 mg/kg; B₄ is 0.5000±0.11 mg/kg; and B₆ is 0.5000±0.17 mg/kg). While the nickel content in shrimp (U₃₀ is 1.1550±0.51 mg/kg; U₄₀ is 0.7650±0.17 mg/kg; and U₅₀ is 0.6650±0.17 mg/kg). For nickel content, the values referred to as standards are WHO Regional Office for Europe, Copenhagen, Denmark, 2000 Air Quality Guidelines, Chapter 6.10 Nickel - Second Edition. Concerning these standards, it was found that fish and shrimp from aquaculture ponds in these locations had suffered nickel metal pollution.

1. Introduction

Kolaka Regency has experienced rapid economic growth and development due to the presence of industrial estates, especially the mining industry and other economic zones. This development certainly has a positive influence on the regional economy and community income, but no less important will hurt the territorial waters. One of the mining industries operating in this region is the nickel mine. The Nickel Mine, which is based in Pomalaa, a nickel-producing sub-district in Kolaka Regency, Southeast Sulawesi, has been going on for a long time starting around 1909. In its development, mining activities have begun to face problems, namely pollution and environmental damage [1]. The damaged area is not only in the hills and land but also to the coast and the surrounding sea.

Economic and industrial developments allow food insecurity to occur because of the occurrence of pollution, which is an excess of the industrialization process towards food sources. Food sources,

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especially in the sea and coastal areas, are likely to be contaminated with various pollutants, both physically, biologically and chemically. These adverse effects can be in the form of pollution in marine waters that can disrupt the safety of food sources from the sea, such as macroalgae, fish, shrimp, mollusks and others [2] [3].

Republic of Indonesia Government Regulation number 28 of 2004 emphasizes the need for efforts to prevent food from possible biological, chemical and other objects that can interfere with, harm, and endanger human health [4]. In international trade, there have also been stipulated new food security requirements formulated through the Sanitary and Phytosanitary (SPS) Agreement and Technical Barriers to Trade (TBT) Agreement in the Uruguay round on Negotiating Multilateral Trade. Food safety not only affects human health but also determines the economic value of the food itself.

The results of Hamzah's research in 2009 at the study site found that the water quality in the location was in a moderate polluted state to be heavily polluted [5]. Likewise, the results of Syahrir's study in 2018 that marine sediments in the waters of Hakatutobu and Dawi-Dawi have experienced nickel metal pollution [1]. The results of this study corroborate the allegation that marine biota that is of economic importance as food sources from the sea and coast are also polluted. Therefore, research efforts to monitor pollutants, especially metals contained by food sources at sea and coastal areas are important to do.

Death due to heavy metal pollution is indeed less than disability. Due to the negative impact of heavy metal pollution mingles with other diseases or the causality of other diseases. However, the effects of heavy metal pollution are known, among others, blood pressure, headache, low cardiac variability, memory, spatial visual defects, deficits in fine motor function, and mental retardation. The victim has lost consciousness and insanity.

2. Methods

2.1. Location and research station

This research was conducted from July to November 2018 in the coastal area of Pomala Sub-District, Kolaka Regency. Determination of the observation station was done by purposive random sampling. Considerations in determining the station represent the area of shrimp and fish farms belonging to the local community located on the coast and close to the nickel mining area. A total of three sampling points were determined in this study. Point 1 is located at coordinates 04°8'55.96"LS and 121°37'6.39"BT, point 2 is located at 04°9'42.87"LS and 121°36'43.62"BT, and point 3 is located at 04°9'45.41"LS and 121°37'11.02"BT. The station's position is determined by using the Garmin GPS 60 Geographic Positioning System (GPS). The sampling station is shown in the following picture 1.

2.2. Data collection

2.2.1. Sampling

The samples collected in this study were Milkfish (*Chanos chanos* Forsskal) and Vaname Shrimp (*Litopenaeus vannamei*). Milkfish is collected in 3 levels, size 2 ($B_2 = 2$ tails per kg), size 4 ($B_4 = 4$ tails per kg), and size 6 ($B_6 = 6$ tails per kg). Vaname shrimps are also collected in 3 levels, size 30 ($U_{30} = 30$ tails per kg), size 40 ($U_{40} = 40$ tails per kg), and size 50 ($U_{50} = 50$ tails per kg). All size of the biota is a measure of the level of harvest and is generally consumed by the community. The samples that have been collected are 6 kg each of each type and level of size taken from the map of community-owned aquaculture ponds. Furthermore, the sample was taken using a coolbox to do metal analysis in the Laboratory of Aquatic Productivity and Quality, Faculty of Marine and Fisheries Sciences, Hasanuddin University, Makassar.

2.2.2. Metal and Data Analysis

Metal pollutants which are analyzed are Mercury (Hg) and Nickel (Ni). The weighted sample was put into the erlemeyer flask and stored in a fume hood, then reconstructed with 65% nitric acid (HNO_3)

solution as much as 10 mL and 70-72% perchloric acid (HClO₄) solution of 0.5 mL until all the meat was immersed in the reagent solution and destroyed or the foam is gone. Then heated on a hot plate equipped with temperature control until it reaches a temperature of 500°C. This heating is done until all samples are destroyed or dissolved. Then the sample is left until it is completely cold, then diluted by spraying distilled water on the erlemeyer flask wall while filtered using Whatman paint No.1 in the measuring cup until the volume reaches 50 mL. The results of this destruction are then analyzed to determine the concentration of metals contained in the sample.

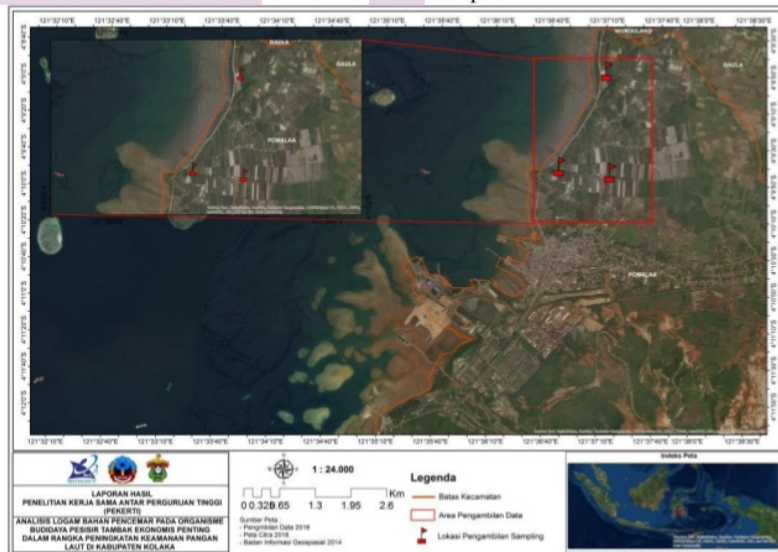


Figure 1. Location of the research station.

Metal analysis was carried out using AAS (Atomic Absorption Spectrophotometer) variance AA50. To get the actual metal content the formula uses:

$$K_{actually} = \frac{K \text{ AAS} \times V}{BK}$$

Where: K_{actually} = Real metal content (mg/kg), K AAS = Metal content read by AAS (mg/L), V = Volume of reading determination (mL), BK = Dry sample weight (g).

The heavy metal content of mercury found in biota is compared to the quality standard set by SNI 7387: 2009 (Maximum limit of mercury contamination in food). For nickel heavy metal content the values referred to as standards are WHO Regional Office for Europe, Copenhagen, Denmark, 2000. Water Quality Guidelines, Chapter 6.10 Nickel - Second Edition [6] [7].

The data obtained were analyzed by descriptive and inferencing statistics. Data on the concentration of heavy metals Hg and Ni and environmental factors are presented in the form of graphs/tables which are equipped with average values and standard deviations. Software used in data analysis in this study includes Microsoft Excel 2010 and Graphad Prism5.

3. Results and Discussions

From a series of researches and analyzes that have been conducted, the results obtained as shown in the following table 1:

Table 1. The average concentration of heavy metals from food biota cultivated in ponds in Pomala District.

Number	Types of Biota	Heavy metal concentration (Average ± SD)	
		Hg (mg/kg)	Ni (mg/kg)

1.	Milkfish :		
	B ₂	7,0510 ± 0,77	0,5000 ± 0,12
	B ₄	2,0700 ± 0,12	0,5000 ± 0,12
	B ₆	Tt	0,5000 ± 0,18
2.	Vaname Shrimp:		
	U ₃₀	4,6560 ± 1,04	1,1550 ± 0,56
	U ₄₀	Tt	0,7650 ± 0,18
	U ₅₀	Tt	0,6650 ± 0,13
	Quality standards	0,5 * (fish)	< 0,5 **
		1,0 * (shrimp)	

* SNI 7387:2009
 ** WHO, 2000
 Tt : *Not detected*

3.1. Heavy Metal Content of Mercury (Hg) in Fish and Shrimp

The concentration of heavy metal Hg in milkfish and Vaname shrimp is presented in Figure 2. Based on the results of measurements, the presence of heavy metals Hg was not detected by the tool in fish samples (B₆) and shrimp (U₄₀ and U₅₀). Such conditions can be caused because the biota has not reached the age or size in accumulating heavy metals Hg. This can be seen by the discovery of Hg content in larger samples of fish and shrimp. Heavy metals are more likely to accumulate to the fish body. Accumulation of heavy metals can occur due to the continuous bioaccumulation process and the biomagnification process through the food chain in aquatic animals [8].

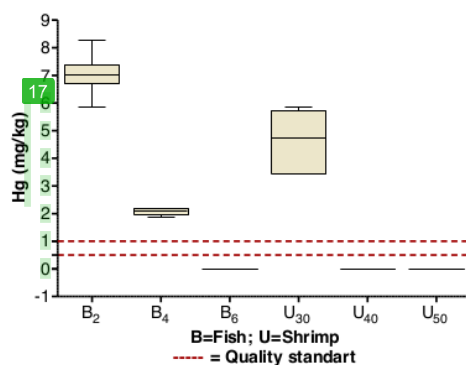


Figure 2. Heavy Hg metal content in biota of vaname milkfish and shrimp.

The heavy metal content of Hg in fish was found to be highest in fish B₂ at 5.8650-8.2821 mg/kg with an average value of 7.0510±0.77(SD) mg/kg, then fish B₄ of 1.8840-2.1687 mg/kg with an average value of 2.0700±0.12(SD) mg/kg. In the shrimp, the highest content of heavy metal Hg in U₃₀ shrimp was 3.4520-5.8680 mg/kg with an average value of 4.6560±1.04(SD) mg. The concentration is high and crosses the threshold according to the quality standard set by SNI 7387:2009 (Maximum limit of mercury contamination in food), which is a maximum of 0.5 mg/kg for fish and processed products, while for other shrimp and crustacean biota maximum 1.0 mg/kg. The *t-test* results at the 0.05 level showed that fish and shrimp from the ponds had mercury metal contamination. The results of the observations also showed a tendency that the higher the weight or size of the organism, the higher the content of Hg contained in the body of the organism.

The high concentration of Hg found in fish and shrimp from pond culture in Pomala is suspected because the location of the study is located around the mining and processing area of nickel. Toxic metals such as Hg found around nickel mines. The high concentration of Hg is caused by the processing of the ore requiring a stream of water to separate fine rocks with a mixture of mercury and

nickel using drum [9]. The presence of heavy metal content of mercury (Hg) in the soil around the nickel mine is due to the use of mercury in the process of separating large amounts of metal ore so that it can produce higher mercury waste and have an impact on the surrounding environment. These contaminants are thought to also spread to the atmosphere through intermediaries with the removal rate of metals from the soil depending on factors such as mineralogy of mining waste, total metal concentration, speciation and the presence or absence of competing ions [10] [11] [12].

Hg is included in the group of non-essential heavy metals and is the most toxic heavy metal to organisms [13]. The concentration of mercury exposure of 0.5 mg/m^3 to 1.2 mg/m^3 will cause acute poisoning. For HgCl_2 compounds with a concentration of 29 mg/kg , organic mercury such as $\text{Hg}(\text{CN})_2$ with a concentration of 10 mg/kg will cause death [14]. Chronic poisoning by mercury will cause interference with the digestive system and the nervous system. Symptoms of chronic poisoning by mercury can be: inflammation of the gums (gingivitis), teeth easily released, tremors at the fingertips or feet will continue to spread to the face, tongue, larynx and Parkinson's. Unlike Pb toxicity, the diagnosis of Hg toxicity cannot be done by biochemical tests. Indicators of Hg toxicity can only be diagnosed by analysis of Hg levels in blood or urine and hair [15].

The results of the study can be taken into consideration in managing fish and shrimp farming especially those located around the mining site, considering the results of this study revealed that fish and shrimp from the pond culture are not suitable for consumption by the community. People who consume food contaminated with heavy metals Hg in large quantities can affect the body because it inhibits the work of enzymes and causes cell damage. The properties of the membrane from the cell wall will be damaged due to binding to mercury so that that cell activity can be disrupted. Acute conditions can cause damage to the stomach and intestines, cardiovascular failure (heart and its origin), and acute kidney failure that can cause death [16].

3.2. Heavy Metal Content of Nickel (Ni) in Fish and Shrimp

The toxicity sequence of some metals from very low to very high is $\text{Sn} < \text{Ni} < \text{Pb} < \text{Cr} < \text{Co} < \text{Cd} < \text{Zn} < \text{Cu} < \text{Ag} < \text{Hg}$. Nickel is an element that has low toxicity. Nickel LC50 values for several types of freshwater fish and sea water fish range from 1-100 mg/liter [13]. Nickel content in natural freshwater is 0.001-0.003 mg/liter [17]; whereas in marine waters it ranges from 0.005-0.007 mg/liter [18]. To protect the life of organisms in the aquatic, nickel content should not exceed more than 0.025 mg/liter [17].

The concentration of heavy metals Ni in milkfish and Vaname shrimp is shown in Figure 3. Based on the results of measurements, heavy metals Ni are found in all types of samples, both in fish and shrimp. The value of heavy metal content of Ni in fish was obtained for each fish B_2 by $0.3140\text{-}0.6045 \text{ mg/kg}$ with an average value of $0.5000 \pm 0.12(\text{SD}) \text{ mg/kg}$, fish B_4 of $0.4035\text{-}0.6860 \text{ mg/kg}$ with an average value of $0.5000 \pm 0.12(\text{SD}) \text{ mg/kg}$, fish B_6 of $0.2245\text{-}0.7775 \text{ mg/kg}$ with an average value of $0.5000 \pm 0.18(\text{SD}) \text{ mg/kg}$. While the value of Ni heavy metal content in shrimp is obtained by each U_{30} shrimp of $0.49\text{-}1.8160 \text{ mg/kg}$ with an average value of $1.1550 \pm 0.56(\text{SD}) \text{ mg/kg}$, shrimp U_{40} of $0.5550\text{-}0.9750 \text{ mg/kg}$ with an average value of $0.7650 \pm 0.18(\text{SD}) \text{ mg/kg}$, shrimp U_{50} of $0.4790\text{-}0.7950 \text{ mg/kg}$ with an average value of $0.6650 \pm 0.13(\text{SD}) \text{ mg/kg}$.

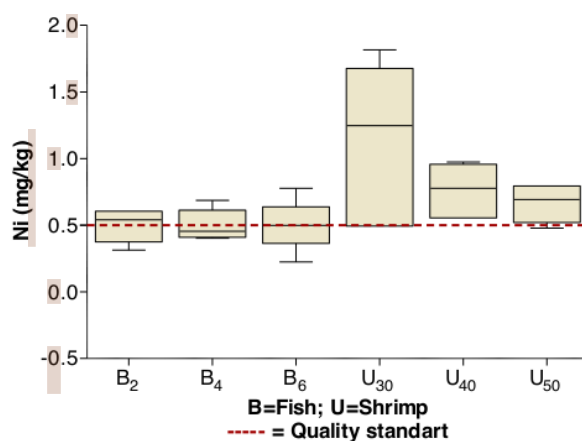


Figure 3. Ni Heavy metal content in vaname milkfish and shrimp biota

The maximum standard [6] standard of Ni content in fish and shrimp for nickel content values referred to as standard are WHO Regional Office for Europe, Copenhagen, Denmark, 2000 Water Quality Guidelines, Chapter 6.10 Nickel - Second Edition. Ni content, according to this quality standard is less than 0.5 mg/kg for most food products. The results of the *t-test* at the real level of 0.05 concerning these standards, it was found that fish and shrimp from aquaculture ponds in these locations had experienced nickel metal pollution. The results also showed that the greater the size and weight of shrimp and fish, the greater the value of Ni content contained in the body of the organism.

The high concentration of Ni found in fish and shrimp from pond culture in Pomala is suspected because the location of the study is located around the mining [15] area and nickel processing industry. Waste produced by industrial activities generally contains toxic heavy metals such as Hg, Cd, Pb, Cu, Zn, and Ni [19]. In addition to having high pollutant power, it is also often dangerous and toxic. Therefore many of the waste produced by industry is classified as hazardous and toxic (B3) [20].

Mining activities carried out by these companies are geographically located in hilly areas around the coast of Pomalaa Subdistrict and side by side with community service activities in the coastal areas, namely the development of floating net cages, ponds, sea cucumber cultivation, and seaweed cultivation. In addition to producing nickel ore, the nickel mining companies also produce several types of liquid waste, and solid waste from exploration activities, land exploitation, nickel smelting processes in factories and other activities carried out by communities around the mine. Besides this mining activity will influence the social and economic life of the surrounding community [21].

Nickel is released into the atmosphere by industries that mine or use nickel, nickel alloys or nickel compounds. This is also released into the atmosphere by coal-burning power plants and garbage incinerators. In the air, it attaches to tiny particles of dust that settle on the ground or are taken out of the air in rain or snow; this usually takes several days. Nickel released in industrial waste [24] later ends in soil or sediment, it is very attached to particles containing iron or manganese [22]. Many harmful effects of nickel are caused by disturbances with important metal metabolism, such as Fe (II), Mn (II), Ca (II), Zn (II), Cu (II) or Mg (II), which can suppress or modify the effects toxic and carcinogenic nickel. The toxic function of nickel is mainly due to its ability to replace other metal ions in enzymes and proteins or to bind cellular compounds containing O-, S-, and N-atoms, such as enzymes and nucleic acids, which are then inhibited. Nickel has been shown to have immunotoxic by altering the activity of all certain types involved in the immune response, resulting in asthma [23].

4. Conclusion

The results showed that both fish and shrimp cultivated in community-owned ponds in Pomala Subdistrict had been contaminated with mercury and nickel metals, so they were not suitable for consumption or seafood. Therefore, it is recommended to policy makers and all stakeholders to stop the sources of mercury and nickel pollutants, refining, trading and use in all sectors so as not to pollute the environment and increase health risks to the community.

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