



ANALYSIS OF BIOACCUMULATION OF BIOMERCURY (Hg) IN HAIR AND ITS IMPACT ON THE HEALTH OF MINING WORKERS IN MALOMBA VILLAGE, DONDO SUB-DISTRICT, TOLITOLI DISTRICT

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ABSTRACT

Mercury is a dangerous and toxic material, persistent, bioaccumulates, and harmful to human health. Mercury is used in the gold processing process using the amalgamation method carried out by people in gold mining without permits. Exposure to mercury in gold processing can occur through direct contact with the skin and inhalation of mercury vapor. Mercury exposure in the body can be analyzed using hair, So this study aims to determine the levels of mercury that accumulate in the hair of mine workers and the impact of mercury content in hair on the health problems of gold mine workers in Malomba Village. The hair samples used were destroyed using H₂SO₄ and HNO₃: HCl (1:3) and analyzed using a cold vapor type Atomic Absorption Spectrophotometer (CV-AAS) at a wavelength of 253,7 nm. The results obtained are, the highest mercury level was 9,82 µg/g, the lowest mercury level was -0,10 µg/g and the control sample was 3,91 µg/g. The limit of mercury levels in hair according to the WHO is 1 µg/g, so the mercury level in respondents KL does not exceed the threshold, while the other 9 respondents exceed the provisions of the mercury threshold in hair, and there are 2 respondents who have symptoms of mercury exposure, namely respondent YP showing symptoms of mercury exposure in the form of tremors, frequent tingling, itching, weakness of taste buds, difficulty swallowing, diarrhea, and headaches, while respondents OP showed symptoms of mercury exposure in the form of frequent tingling, itching, easy fatigue, headaches and eye irritation.

Keywords: Mercury (Hg), Hair, Gold mining, Tolitoli.

1. INTRODUCTION

Mercury or quicksilver is a dangerous and toxic material, in the form of a heavy metal that is liquid, silver white, odorless and easily evaporates at normal/room temperature where it usually takes the form of organic and inorganic compounds that are persistent, bioaccumulate and dangerous to health. humans such as disorders of fetal development, nervous system, digestive and immune systems, lungs, kidneys, skin and eyes and the environment (Permenkes RI, 2016). Currently, mercury (Hg) is still widely used in gold mining without permits, in the amalgamation process which uses mercury as amalgam. The amalgamation process is a mixing process between gold and mercury.

The amalgamation technique is carried out by mixing rocks containing gold and mercury using a drum (Komalig, 2011). The amalgamation process carried out in the gold processing process can cause toxicity for miners and residents around mining. The effects of mercury pollutants on human health in general can include illness (acute and chronic), disruption of physiological functions (nerves, lungs, sensory abilities), sensory irritation and accumulation of dangerous substances in the body (Mukono in Erdanang, 2016). The high risk of mercury exposure in traditional gold processing is during the filtering and annealing processes. In the filtration process, mercury which is still in inorganic form will be absorbed and enter the body through the skin because in the filtration process mercury is mixed, while in the incandescence process the processor will be exposed to mercury vapor through inhalation because the gold ore that has been bound with mercury will be heated to a temperature very high and mercury evaporation will occur (Ministry of Health in Erdanang, 2016). Continuous direct contact with heavy metals can cause an increase in chemical elements in the body caused by the bioaccumulation system (Masruddin & Mulasari, 2021).

Bioaccumulation is a progressive increase in the concentration of a type of compound in an organism caused by the rate of uptake of the compound being greater than its release (Anderson & Fisher, 2002).



Determining mercury exposure in the body can be done by measuring levels in body tissues, such as blood, urine, hair and nails, which are known as biomarkers (Grandjean et al., 2005).

Hair is one of the indicators used to assess the extent of mercury contamination, because the concentration of mercury in hair is persistent enough that it does not disappear even when washing with shampoo or dyeing the hair, but can decrease by 30-50% when the hair is straightened or curled. This is because hair straighteners contain thyoglycolic acid which has the effect of reducing MeHg in hair (Chamid et al., 2010). Hair is mainly composed of a protein called keratin. This protein includes large amounts of the sulfur-containing amino acid cysteine. Many of these cysteines are involved in disulfide bonds, which bind each keratin and provide strength to the hair. Mercury has a great affinity for sulfur and bonds strongly with it. When hair is actively growing in the hair follicle, mercury in the blood can diffuse into the tissue and bind to the growing hair strands (Faial et al., 2014).

One of the gold mines that uses mercury in the processing process is in Malomba Village, Dondo District, Tolitoli Regency. This gold mining activity started in 2010. The location of the mining activity is only 500 meters from the residential area of Malomba village. In the gold processing process, miners use mercury to bind the gold (Rosita, 2022). This allows mining workers in Malomba Village to be contaminated with mercury as a result of mining activities. Thus, it is necessary to carry out research to determine the levels of mercury that accumulate in miners' hair and its impact on health problems for mine workers in Malomba Village, Dondo Sub-District, Tolitoli District.

2. METHODS

This study is a type of experimental research conducted in the laboratory to determine the level of mercury accumulated in the hair of mine workers and using a questionnaire to determine the impact of mercury content in hair on health problems of gold mine workers in Malomba Village, Dondo Sub-District, Tolitoli District. The sample used in this study is the hair of mine workers who are still actively processing gold. The samples used totaled 10, with 9 samples taken from three points of the miner's location. and 1 control sample taken from respondents who are not mine workers and have never been to the mining site. The sampling technique used is accidental sampling, where sampling is carried out on respondents who happen to be at the research location (Ariawan, 1998).

2.1 *Tools and Materials*

The tools used in this research were scissors, hot plate, analytical balance, 50 mL measuring flask, dropper pipette, measuring cup, beaker, stir bar, 100 mL Erlenmeyer, watch glass, funnel, plastic sample, filter paper and a set of absorption spectrophotometer tools. atom. The materials used were hair samples, standard Hg 1000 ppb solution, nitric acid (HNO₃), hydrochloric acid (HCl), sulfuric acid (H₂SO₄), acetone, liquid soap and distilled water.

2.2 *Hair Sampling*

Gold miners' hair samples were taken by cutting the hair in areas near the scalp randomly, with a size of around 3 cm in the amount of 0.2 - 1 gram and putting it in a labeled plastic clip (Rosmiati & Silvia, 2021). Each respondent who provided a hair sample filled out a questionnaire to determine the impact of mercury on miners' health problems. This procedure was carried out for all samples.

2.3 *Sample Preparation*

The hair samples obtained were washed with liquid soap and clean water, then dried. After that, continue with washing using 10 mL of acetone solution for 15 minutes and stirring using a glass stirrer. Next, the hair samples were rinsed 3 times using distilled water, then dried at room temperature and stored in a vacuum desiccator. After that, the hair is cut finely with scissors (Faial, et al. 2014). Hair samples that had been dried and finely cut were weighed and put into a 100 mL Erlenmeyer flask. In an Erlenmeyer flask, 5 mL of H₂SO₄ and 10 mL of HNO₃ : HCl (1:3) are added for 1 gram of hair sample. The Erlenmeyer is heated on a hotplate until the



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yellow solution is clear and white smoke comes out. After that, the sample was cooled, then filtered and the filtered solution was adjusted using distilled water in a 50 mL volumetric flask to the limit mark (Rosmiati & Silvia, 2021). Next, the mercury (Hg) concentration in the sample was measured using a cold vapor atomic absorption spectrophotometer at the Analytical Chemistry Laboratory, FMIPA ITB.

2.4 Preparation of Standard Solutions

The 1000 ppb standard solution for mercury metal is made into a series of standard solutions of 10 ppb, 50 ppb, 100 ppb, 150 ppb, 200 ppb and 250 ppb. Then, the absorption of the solution was measured at a wavelength of 253.7 nm. The standard solution absorption data obtained was used to create a calibration curve.

2.5 Sample Measurement

Determination of mercury metal in hair samples was determined by measuring its absorption using an Atomic Absorption Spectrophotometer (SSA) instrument with a wavelength of 253.7 nm (Rosmiati & Silvia, 2021). The sample absorption data obtained was analyzed to obtain the concentration of mercury metal in the mine workers' hair using a calibration curve.

2.6 Data Analysis Technique

Data obtained from the Atomic Absorption Spectrophotometer (SSA) test were then analyzed using a calibration curve. In addition, health data on mining workers obtained using questionnaires was tabulated, then described to determine the impact of mercury content in respondents' hair on health problems.

3. RESULTS & DISCUSSION

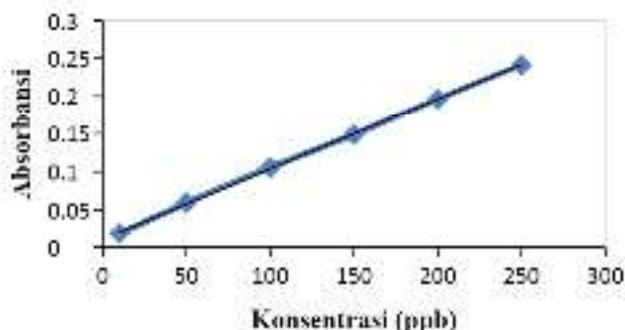
3.1 Preparation of Standard Solutions and Calibration Curves

Hg analysis in miners' hair samples was carried out using a standard calibration method. In this method, standard Hg solutions with various concentrations are prepared. Data from absorbance measurements of standard solutions with varying concentrations can be seen in Table 1.

Table 1. Results of Absorbance Measurements of Standard Hg Solutions.

Name	Concentration (ppb)	Absorbance
Standard 1	10	0,0182
Standard 2	50	0,0591
Standard 3	100	0,1053
Standard 4	150	0,1486
Standard 5	200	0,1964
Standard 6	250	0,2414

Data on the absorbance results of the standard Hg solution in Table 1 were then analyzed and a calibration curve was created, where the increase in concentration was directly proportional to the increase in absorbance. The calibration curve between concentration and absorbance can be seen in Figure 1.



**Figure 1. A Linear Relationship between Concentration and Absorbance.**

Based on the calibration curve of the Hg standard solution in Figure 1, it shows that there is a linear relationship between concentration and absorbance. The greater the concentration of the standard solution, the greater the absorbance obtained. The linear relationship between concentration and absorbance has a regression equation $y = 0.0009x + 0.0112$ and $r = 0.9996$.

3.2 Mercury Levels in Mine Workers' Hair

Mercury levels in the hair of mine workers and control samples were obtained from calculations using a calibration curve. Data on mercury levels in hair samples obtained from the analysis results can be seen in Table 2.

Table 2. Mercury Metal Levels in the Hair of Mine Workers and Control Samples.

No	Location	Code Sample	Absorbance	Mercury levels (Hg) ($\mu\text{g/g}$)	Average level mercury (Hg)
1.	Location 1	SAK	0,0474	9,82	6,91
		HW	0,0568	8,24	
		AR	0,0604	2,67	
2.	Location 2	RK	0,0496	3,20	2,95
		OP	0,0346	2,88	
		RM	0,0388	2,77	
3.	Location 3	SJ	0,0486	2,57	1,27
		YP	0,0267	1,33	
		KL	0,0103	-0,10	
4.	-	AM	0,0632	3,91	-

The results of research conducted using an atomic absorption spectrophotometer with standard calibration methods showed that mercury levels in mine workers' hair ranged from -0.10-9.82 $\mu\text{g/g}$ and control samples were 3.91 $\mu\text{g/g}$. Limits for mercury levels in hair according to World Health Organization (WHO), namely 1 $\mu\text{g/g}$, so that the mercury level in the KL sample code does not exceed the threshold limit, while the other 9 samples exceed the threshold limit for mercury in hair. The results of this research are in line with research by Nasir et al (2021), regarding the analysis of mercury levels in the hair of gold miners in Alue Baro Village, Meukek District using atomic absorption spectrophotometry, with the results of their research showing that the Hg levels in miners' hair were 1.01 – 2.08 mg /kg and the sample used as a comparison was 0.64 ppm. The results of this study indicate that the concentration of Hg in gold miners' hair has exceeded the tolerance limit set by WHO, namely 1 mg/kg.

The comparison of mercury levels between location 1, location 2 and location 3 can be seen in Figure 2, where location 1 has a higher average mercury level compared to the average mercury level at location 2 and location 3.

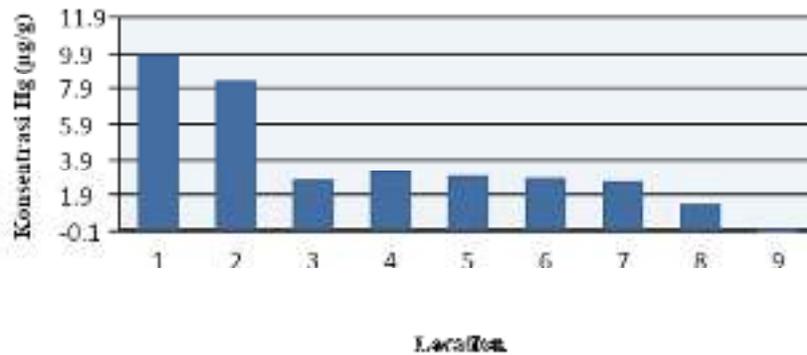


Figure 2. Mercury Levels by Location.

Based on the location of the miners, the average level of mercury in the hair of respondents who work at location 1 is higher than that of respondents who work at location 2 and location 3. This is because miners who work at location 1 use quite a lot of mercury to form gold metal grains. Location 2 has moderate mercury levels because when processing gold, miners use less mercury metal than at location 1, where when forming gold grains, miners sometimes get gold grains that have fused with mercury metal. Location 3 has low mercury levels because when processing gold the miners do not use mercury metal due to seepage of mercury metal from location 2 so that the gold obtained has formed grains that have been mixed with mercury metal.

Mercury contamination in gold miners is probably caused because in general, miners carry out the gold processing process without using personal protective equipment such as gloves and masks, so they can come into direct contact with mercury when mixing mercury with gold. Mixing mercury with gold will form an amalgam which is then burned to obtain pure gold and the mercury will evaporate into the air. In the gold processing process, mercury metal will enter the human body in several ways, namely through inhalation which can occur if the metal is in the form of vapor, so it will enter the body through the lungs. Metals in the skin will be absorbed through the pores, then passed to the bloodstream and distributed throughout the body (Mahmud et al., 2018).

Control samples with mercury concentrations exceeding the threshold indicate that both mining workers and people living around mining sites can be contaminated by mercury. The high levels of mercury in the control sample were probably caused by, based on the results of interviews conducted with respondents who said that, there had been a gold buyer who lived in the respondent's house for approximately 1 year, and at that time there were still lots of miners so that the respondent's house was the place where this was done. amalgam burning. This is because in the process of annealing or burning amalgam, gold ore that has been bound with mercury will be heated at a very high temperature and the mercury will evaporate, resulting in an inhalation process or the process of mercury entering the body, especially through the lungs in the form of vapor (Sonata et al., 2021).

3.3 Mining Workers' Health Conditions

The health condition of mine workers is known from the results of direct interviews using a questionnaire, with 10 questions using the Guttman scale. The questionnaire consists of 2 answer choices, namely Yes and No. Score 1 for a Yes answer and 0 for a No answer. The total results of mining workers' answer choices can be seen in Table 3.

Table 3. Total Results of Mine Workers' Answer Choices.

Respondent	Results of Answer Choices	
	Yes	No
SAK	4	SAK
HW	0	HW
AR	4	AR
RK	1	RK



OP	5	OP
RM	3	RM
SJ	4	SJ
YP	7	YP
KL	1	KL
-AM	0	-AM

The total data resulting from the mine workers' answer choices in Table 3 was then analyzed using the Guttman scale. From the Guttman scale analysis, there are 2 categories, namely mercury impact if the score is $\geq 50\%$ and no mercury impact if $< 50\%$. The percentage results using the Guttman scale can be seen in Table 4.

Table 4. The Percentage Results Use the Guttman Scale.

Respondent	Results Percentage Answer Yes (%)	Category
SAK	40	No impact
HW	0	No impact
AR	40	No impact
RK	10	No impact
OP	50	Impactful
RM	30	No impact
SJ	40	No impact
YP	70	Impactful
KL	10	No impact
-AM	0	No impact

Waste from gold processing which is carried out using the dangerous chemical mercury (Hg) has the potential to cause a decrease in environmental quality and risk health problems for miners and miners. people living around mining sites. Based on the results of interviews using a questionnaire regarding the health conditions of mine workers, it shows that 2 respondents with sample codes YP and OP are included in the mercury impact category, while the other 8 respondents are included in the no mercury impact category. Based on direct interviews using a questionnaire, several symptoms were identified that could indicate the toxic effects of mercury. Respondents with sample code YP showed symptoms of mercury exposure in the form of tremors, frequent tingling, itching, weakness of the sense of taste, difficulty swallowing, diarrhea and headaches, while respondents with sample code OP showed symptoms of mercury exposure in the form of frequent tingling, itching, easy fatigue, headaches and eye irritation. This is in line with the statement of Priyambodo et al (2020), stating that if someone is poisoned with mercury, they will experience symptoms in the form of tremors, headaches, difficulty swallowing, decreased hearing, blurred vision, thick legs and arms, diarrhea, a blocked mouth, and swollen gums. Apart from that, some research stated that one of the early symptoms of chronic poisoning is a tingling sensation.

Respondents with sample codes YP and OP are included in the category above productive age, namely > 40 years, making it possible for respondents to easily experience symptoms of mercury exposure. This is in line with the statement of Bagia et al. (2023), which states that age can affect endurance or physical ability to respond to exposure to mercury entering the body. Age is one of the factors that can influence the emergence of symptoms due to exposure to mercury if miners are over the age of productive age (>40 years) because there has been physical decline, so physical abilities have been limited, and the body's endurance has decreased. Age affects a person's health, body mass fraction, decreased liver and kidney function, increased fat tissue, and decreased blood flow velocity, thus prolonging the presence of toxins in the body. In addition, Prihantini & Hutagalung (2018), also stated that the factors that determine whether health effects occur and their severity include the type of mercury in question, dose, age, duration of exposure, and route of exposure (inhalation, swallowing or skin contact).



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Mercury is one of the most toxic metal elements in the environment and is very dangerous for human health and the ecosystem. Organic mercury compounds are generally more toxic than inorganic compounds. Methylmercury (MeHg) is the species that has received the most attention because of its bioaccumulation ability, affinity for macromolecules, and slow metabolism. Methylmercury (MeHg) is the most toxic mercury compound and is formed when inorganic mercury in the environment is methylated by microorganisms in soil, sediment, air or water (Hong et al., 2012). Complex biogeochemical processes that occur in an environment can change the element mercury into Methylmercury (CH_3Hg^+). This change process requires at least two chemical reaction steps, namely the oxidation process of Hg^0 becomes Hg^{2+} , then a chemical reaction occurs which changes the form of Hg^{2+} become CH_3Hg^+ . Chemical reactions that can change the form of Hg^{2+} become CH_3Hg^+ is called methylation. The chemical reactions that occur in the methylation process are controlled by sulfate reducing bacteria and microbes (Alpers & Hunerlach In Sumarjono, 2020). In severe cases, MeHg can cause neurological damage, memory loss, vision and hearing problems, and motor coordination problems. Long-term exposure to methylmercury can increase the risk of cancer and heart disease (Hong et al. 2012).

The emergence of health problems among illegal gold miners is due to the pollution that occurs during the mining process. In the gold processing process, miners use mercury (Hg) to bind the gold. The use of mercury when processing gold should be done with the correct procedures and knowledge, however in this illegal gold mining the miners process gold using mercury without using personal protective equipment so that the miners come into direct contact with the mercury used. Gold processing using mercury is carried out repeatedly by miners, allowing the accumulation of mercury metal in the miners' bodies which results in health problems (Masruddin & Mulasari, 2021).

4. CONCLUSION

Based on the results of the research that has been carried out, the following conclusions can be drawn. First, mercury levels accumulated in the hair of gold mining workers in Malomba Village, Dondo District, Tolitoli Regency with the highest level being $9.82 \mu\text{g/g}$, the lowest level being $-0.10 \mu\text{g/g}$ and the control sample being $3.91 \mu\text{g/g}$. The limit for mercury levels in hair according to the World Health Organization (WHO) is $1 \mu\text{g/g}$, so the mercury level in the KL sample code does not exceed the threshold limit, while the other 9 samples exceed the threshold limit for mercury in hair.

Second, of the nine miners who were used as research samples, 2 respondents with sample codes YP and OP were included in the mercury impact category, while the other 7 respondents were included in the no mercury impact category, with the symptoms felt by respondent YP indicating symptoms of exposure mercury in the form of tremors, frequent tingling, itching, weakness of the sense of taste, difficulty swallowing, diarrhea and headaches, while respondents with sample code OP showed symptoms of mercury exposure in the form of frequent tingling, itching, fatigue, headaches and eye irritation.

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