IOP Conference Series: Materials Science and Engineering

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Mercury (Hg) Contents Analysis in Sediments at Some River Estuaries in Kayeli Bay Buru Island

To cite this article: Abraham Mariwy *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **546** 022012

Mercury (Hg) Contents Analysis in Sediments at Some River Estuaries in Kayeli Bay Buru Island

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Abstract. Since 2011, a considerable gold deposit was found at several locations on Buru islands, such as Botak Mountain, Gogorea, and Nona Mountain. These attracted thousands of illegal miners who used amalgamation techniques in traditional gold processing. In practicing, the mercury-containing tailings were then stored in a container or directly discharged into the river, potentially polluting the waters of Kayeli Bay as well as all fishery resources in it. This was of course worrisome because mercury (Hg) was a very toxic heavy metal and could poison humans through the food chain. This study was conducted to analyze mercury levels in sediments some river estuaries in the bay Kayeli. The mercury contented the sample was performed using a mercury analyzer. The results showed that mercury in Suket river was 1.62 mg/kg, Wailata river was 8.27 mg/kg, Anahoni river 4.99 mg/kg while Waiapu river was 0.53 mg/kg. These results indicated that sediment at the mouth of several rivers in the Kayeli Bay has been contaminated with mercury, even far beyond the standard set by the US EPA of 0.2 mg/kg.

Keywords: Amalgamation, mercury, bioaccumulation, sediment

1. Introduction

Poverty and the absence of jobs had encouraged the growth of the people's gold mine, which has now become a phenomenon in approximately 70 countries in the world with an estimated number of miners about 15-20 million people, while 80-100 million people either directly or indirectly rely on This sector [1, 2]. The mining of the people was legal or illegal, organized in groups or individuals, and operates in small and medium scale. In practiing everyone could be involved in the people's mining business regardless of gender and age [3].

In Indonesia, they spread in various regions and one of the areas that became focusing on public attention in the last few years was a Mount Botak gold mine located in Wamsait Village Waelata Sub-district, Buru Island, Moluccas Province. The gold mining of the people, which began operations in 2011, had attracted thousands of miners from other regions in Indonesia. Although, the gold mine in Mount Botak had been officially closed at the end of 2015 based on Presidential instructions, but the large number of miners who had operated at the mine all using amalgamation techniques in the process was potentially damaging to the environment because the amalgamation process used mercury (Hg).

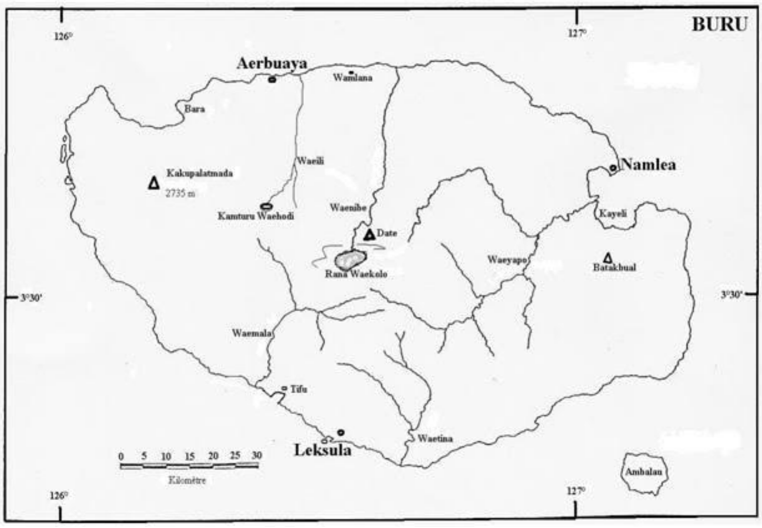

Figure 1. Buru Island

In the process of amalgamation by miners traditionally, soil and rock material containing gold was mixed with mercury (Hg) aqueous media and stirred using a trammel (amalgamator). This technique utilized the rotation given by the trammel to destroy the soil and rocks that were still mixed with gold so that the mercury would bind the gold. Next it was washing and repeating to separate the amalgam (Au-Hg mixture) and the tailings [4]. This process of amalgamation had taken place since Roman times and it was still used today [5]. In practicing, the tailings that were still containing mercury then collected in a container or directly discharged into the river, potentially polluting the water body or agricultural areas were around the watershed.

One of the rivers was around the Mount Botak mine that had been contaminated with mercury was the Wamsait River. The river had been the center of amalgam using thousands of trammels so that mercury contamination caused by the waste disposal (*tailing*) of the amalgamation process was highly. A study was conducted by Male et al in 2013 showed that mercury levels in tailings ponds around the river were at 680 mg/kg while mercury levels in sediments at some points of the Wamsait estuary reached more than 3.00 and 7.66 mg/kg [6]. In addition to the Wamsait River or the other name Wailata, some river that empties into the bay Kayeli was the river Suket, Anahoni, and Waiapu. Two rivers in Like Anahoni and Waiapu utilized as a means of mercury waste disposal in the process of amalgamation using mercury on a small scale, while the Suket river free from amalgamation process.
This study was conducted to determine the concentration of mercury (Hg) in the sediments at the mouth of the river Suket, Anahoni, Wailata and Waiapu. This research was very important because the sediment that had been contaminated with mercury on helping of SBR (sulfate bacteria reduction) bacteria would move into the food chain through biomagnification process so it could poison the human being at the top of the food chain [7]. The bay was rich in fishery resources such as crabs and various types of fish that were the top predators in aquatic ecosystems and had a central position in the food network. As a source of fish and crab protein, many were consumed by human and thus become the main source of exposure to mercury in humans [8].

2. Methods

The equipment used in this research were mercury analyzer, glass beaker, analytical scales, oven, hot plate, glassware, knife, cold box, GPS, thermometer, pH meter and salinometer. Materials research: sediment, samples, 10 mL HNO3 65%, 10 mL $HClO_4$ 70-72%, 25 mL H_2SO_4 95-97%, $SnCl_2$ 10%

w/v, filter paper, 1 mL Na_2S 10% w/v, HNO_3 10% v/v, 20 mL $KMnO_4$ 5% w/v, (NH_2OH) 2 NaCl 10% and mercury standard solution.

2.1. Sampling

Field research stage that included measurement of temperature, pH and salinity knew the condition of the waters at the location and sampling of goldband goatfih and giant mud crab was done on Augustus. The sample was then loaded into the cooler and under the laboratory to prepare and analysis process.

2.2. Sediment Sample Preparation

Prepared samples were weighted by Sediment 1 (1.0459), sediment 2 (1.0025), sediment 3 (1.0355), sediment 4 (1.0107), sediment 5 (1.1866) grams and included in Erlenmeyer 100 mL. A 5 mL of H_2SO_4 and 5 mL HNO_3: $HClO_4$ (1:1) were mixed. The mixture was heated over a hotplate until clear and white smoke comes out. The result obtained was filtered and the filtrate solution was adjusted with water on a 50 mL flask until the marker boundary. After making the blank, 10 mL of sample was transferred into a test tube, 0.1% of $KMnO_4$ was added, and mixed with 0.1 mL hydroxylamine hydrochloride; the mixture was shaken out, 0.5 mL of $SnCl_2.2H_2O$, and finally the mixture was analysed using mercury analyser.

2.3. Standard Solutions Preparation

From 100 ml of Hg 100 ppm solution was piped 1 mL. Then put into a 100 mL pumpkin flask and added aquadest to the limit. This solution contained 1000 ppb mercury solution. Then from this mother liquor, piped as much as 1 mL and put into a 10 mL flask. The solution was aquadest to the limit. This solution contained 100 ppb mercury solution. Furthermore, standard solutions of mercury with concentration range (ppb) were made: 0.5; 1.00; 2.50; 7.50; 10.00; 15.00 and 20.00 by means of each moult (mL) 0.05; 0.10; 0.25; 0.75; 1.00; 1.50 and 2.00 of 100 ppb mercury solution. Then put each into a 10 mL measuring flask and fixed up to the boundary with aquadest. This solution was further poured in a test tube and added 0.1 mL of $KMnO_4$, shaken, added 0.1 mL again of hydroxylamine hydrochloride, shaken, and added 0.5 ml of $SnCl_2.2H_2O$. Each of these solutions was analyzed using a mercury analyser.

3. Results and Discussion

3.1. Physical and Chemical Water Parameters at Kayeli Bay

Water parameters observed in this study including temperature, salinity and (pH). The results of observations for the physical and chemical conditions of waters conducted during the study provided an overview of the conditions of the Waters at Some River Estuaries of Buru Island as shown in Table 1.

Table 1. Physical and Chemical Parameters at Some River Estuaries in Kayeli Bay

Samples Code	Coordinate	Temperature (°C)	pH	Salinity (‰)
S.R	S=03°22.349 E=127-05.588	29	6.6	30
A.R	S=03°22.349 E=127-05.588	29	4.8	31
W.R	S=03°22.349 E=127-05.588	30	5.2	31
Wai. R	S=03°22.349 E=127-05.588	31	5.0	31

From Table 1, it could show in the sampling area was still on the threshold based on the criteria of water quality standard in accordance with the decree of the Minister of Environment of the Republic of Indonesia No. 51 of 2004, for marine biota ranged from 28-30 °C [9]. Environmental temperature greatly affected the growth of aquatic organisms. Almost all organisms were very sensitive to drastically changing environmental temperatures, sudden changing in ambient temperature of 5 °C that could cause stress or even death in some organisms. While salinity at the sampling point in the waters of Kayeli Bay was recorded at 30-31‰. Salinity was an environmental parameter that updates biological processes and it will directly update the growth rate, the amount of food consumed, the value of food conservation, and the survival of water biota. The changes that occur in water salinity can affect the functional and structural properties of aquatic organisms by changing in the osmosis of total concentration, density, body fluid balance and viscosity [10].

At the location of the sampling, it was also done the measurement of (pH). Increasing the concentration of CO_2 in the water would result in decreasing the pH of the water. Increasing the pH could cause the toxicity of ammonia to increase, whereas with the increase of free CO_2 content the pH of the water will decrease so that its effect on the ammonia toxicity will decrease [11]. Based on the results of measurements (pH) in the waters of Kayeli Bay, could be concluded that, the condition of these waters is not good according to the quality standard accordance with the decree of the Minister of Environment of the Republic of Indonesia No. 51 of 2004 which ranged between pH 7.0-8.5 [12]. The pH value based on the measurement result of 5.0 indicates that the waters are in acidic condition. This is certainly very worrying because the production of methyl mercury (CH_3Hg^+) in the sediment takes place at a pH less than 6 [13].

3.2. Mercury Concentrations in Sediment Samples

This research used calibration curve analysis technique. In this study the Hg standard solubility was prepared from 100 mg Hg solution, in which the standard solution was diluted from 100 ppb to 0.5; 1.00; 2.50; 7.50; 10.00; 15.00; and 20.00 ppb. The result of absorbance of standard mercury (Hg) solution by using mercury analyzer can be seen in Table 2.

Table 2. Concentration and absorbance Mercury standard solution (Hg)

Concentration (μg/L)	Absorbance
0.50	0.0128
1.00	0.0225
2.50	0.0608
7.50	0.1687
10.00	0.2312
15.00	0.3231
20.00	0.3231

From the absorbance obtained then made the calibration curve between the concentration with the absorbance. The calibration curve represented the relationship between the absorbed beam of radiation (A) with the concentration (C) of the known substance of the concentration. Under Lambert-Beer law the absorbance would be directly proportional to concentration. Concentration was higher than the resulting absorbance was Higher. The following calibration curve of mercury standard solution (Hg) Figure 2.

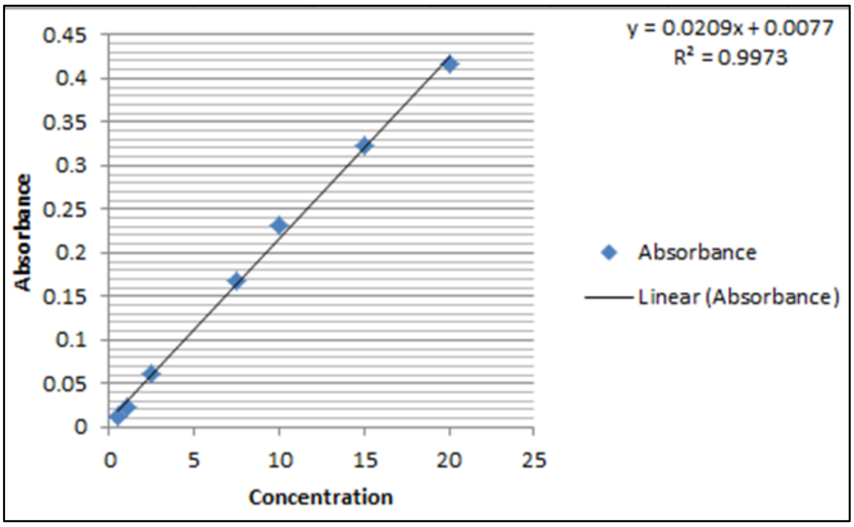

Figure 2. Mercury Standard Curve

Based on the measurement of standard solution, linear equation was obtained y =0,02091x + 0,00768 and correlation coefficient value R^2=0.99867. Figure 2 showed that the standard calibration curve has a linear tangent. The shape of the curve follows Lambert Beer's law with increasing concentration resulting in higher absorbance. From the curve value R^2=0.99867 obtained had met the requirements set, with the provisions of R^2>0.99. The absorbance of the sample solution was then measured, the concentration and absorbance of the sample were used to calculate the mercury (Hg) content found in goldband goatfish samples and giant mud crab by substituting the linear equations of the standard curve and the coefficient value R^2. The mercury concentrations in the samples of sediments were shown in Table 3

Table 3. Mercury Concentration in Samples

Samples Name	Weigth (gr)	Volume (mL)	Mercury Concentration (ppm)
S.R	1.08219	50	0.53
A.R	1.0259	50	1.62
W.R	1.0195	50	8.27
Wai. R	1.0194	50	4.99

Based on Table 3 above showed that the highest mercury (Hg) level was at Wailata river estuaries/ Wamsait which was 8.27 mg/kg, second order was Waiapo river that east 4.99 mg/kg, third order was Anahoni river equal to 1.62 mg/kg, while the Suket river wass 0.53 mg/kg. The amount of mercury in the mouth of the Wailata/Wamsait river was caused by the river being the center of gold amalgamation using mercury. While on the Waiapu river, considerable mercury content was caused by the largest river in Buru district as a means of disposal of mercury by residents around the river body which also uses amlgamation techniques, although on a small scale. The same was true of the Anahoni River. The smallest level was in the Suket river was 0.53 mg/kg. Although there was no amalgamation activity in the river, but the current pattern in Kayeli bay was strong enough to spread mercury still in the body of water toward the river Suket and settle in the river mouth. Mercury concentrations in the samples could be seen in Figure 3.

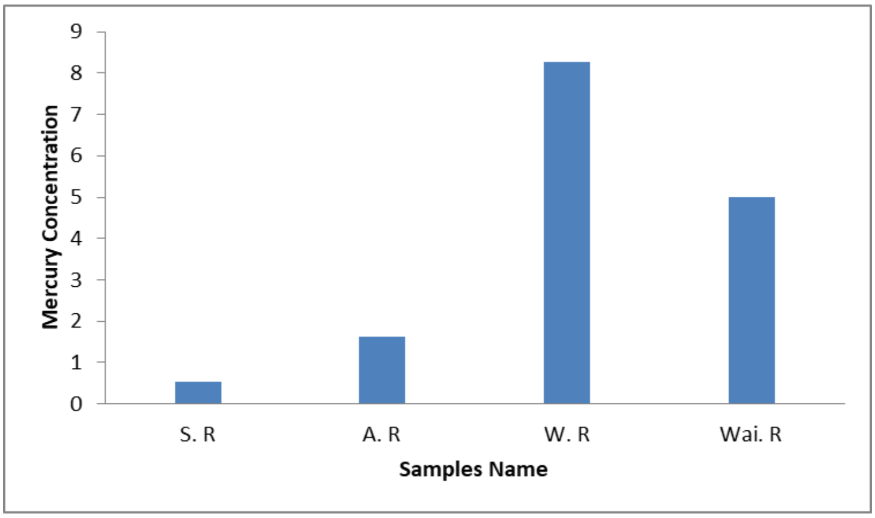

Figure 3. Mercury concentrations in the samples diagram

These results indicated that sediment at the mouth of several rivers in the Kayeli bay had been contaminated with mercury, even far beyond the standard set by the US EPA of 0.2 mg/kg. These results were in line with the mercury content that began to be detected in the body of Jackfruit seeds and Mangrove crab. As it is known that mercury in sediment with the help of SBR bacteria (sulfate bacteria reduction) will move to the marine biota body through biomagnification process through the food chain thus potentially poisoning humans [14].

4. Conclusion

Mecury content analysis in sediment at some river estuaries in Kayeli bay showed that the highest mercury (Hg) concentration. Mercury concentration in estuary of Wailata was 8.27 mg/kg, Waiapu was 4.99 mg/kg, Anahoni was 1.62 mg/kg, while estuary of Suket of 0.53 mg/kg. These results indicated that sediment at at some river estuaries the Kayeli bay had been contaminated with mercury, even far beyond the standard set by the US EPA of 0.2 mg.

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