Analysis of Mercury in Water and Sediment Distribution and Its Bioaccumulation Potential in Fish in the Small Scale Gold Mining Area (Case Study: Ciberang River, Lebak, Banten)

Desiana Prilia*, Katharina Oginawati, Herto Dwi Ariesyady

Environmental Engineering, Institut Teknologi Bandung, Bandung 40132, Indonesia

ABSTRACT

The existence of small scale gold minings which located in Kecamatan Lebakgedong, Lebak, Banten Province are potentially contaminate the aquatic environment since the tailing from amalgamation process are directly discharged into water body. Sampling was done for 15 points spread from the upstream in Cisoka River to the downstream in Ciberang River. The extract of water, sediment, and fish samples were examined to get Hg content using Atomic Absorption Spectrophotometry (AAS). The results showed that 14 water samples were under the quality standards based on Indonesia Government Regulation 82/2001 amounted 2 mg/m^3, while there were one sample had very high Hg concentration amounted 66.6 mg/m^3. For sediment, all samples were above quality standards based on US EPA 2012 amounted 180 mg/m^3, with the highest Hg concentration of 43,508.3 mg/m^3. The BCF calculation of Channa striata and Barbonymus gonionotus provided value above 1,000, which is in the range of 1,561.11 to 4,354.17. The mercury distribution maps were shown by ArcGIS 9.3. The maps are covering mercury pollution in water and sediment, pollutant source location, river water discharge, pH, conductivity, and overlay of each map.

Keywords: Fish bioaccumulation; mapping; mercury; sediment; small scale gold mining

1. INTRODUCTION

Gold is one of minerals with high economic value that is well abundant and well distributed in Indonesia. Gold is traded in almost of the mineral trading markets around the world. Due to its benefits and high economic value, gold mining became one of the well known livelihood of Indonesian people. One type of gold mining in Indonesia is small scale gold mining or better known as Artisanal Small scale Gold Mining (ASGM).

Based on the results of the investigation conducted by Sutisna in Gunradi (2011), found that metal mineralization was found in a few prospects, one in Cisoka and in Cihinis-Muara,

Lebak, Banten. Herman (2005) was collecting data of mercury distribution in Ciberang mining area. The results showed that mercury content in river sediments have significant value especially at the river points in the central location of mining activities in Ciupih River and Cisoka River.

The small scale gold mining activities in Indonesia are characterized by the use of exploration and exploitation techniques in simple and inexpensive way. Rocks and quartz which contain gold or ore are milled by using mercury processor. The gold processing usually uses the amalgamation technique by mixing the ore with mercury to form amalgam with water. As

many as 10-30% of mercury are being used for activities, then will be released or lost to the environment. In the process of amalgamation, mercury could be released into the environment at the washing and combustion step. Heavy metals could not be degraded biologically (Kaoud and El-Dahshan, 2010). Heavy metals that dissolved in water will be carried by river flows, therefore it will accumulate in estuaries and beaches of a marine fishery resource.

In sediments, inorganic mercury is ready to be transformed by bacteria into methyl mercury (MeHg). Sediment is a major repository of mercury in the aquatic environment, about 80% of mercury in the moving aquatic systems appears in the sediments (Shao et al., 2010). Mercury in sediments surface can be transferred into the water column via diffusion, re-suspension, produced by human activities, as well as the entry into the aquatic food web through the absorption of mercury by the benthos that obtained food from the sediments near the water surface (Oh et al., 2009).

Mercury has been recognized as a very toxic metal in the environment and poses a serious threat of wild mammals, birds, and human due to the fact that it could be biomagnified along food chain (Zhang et al., 2009). Like in Minamata case, human got physical disability caused by the consumption of fish that accumulate methyl mercury due to mercury pollution in water bodies. The accumulation of MeHg in aquatic systems will constantly pose a threat to fish and other biota, including human (Liang et al., 2010).

Monitoring and evaluating of mercury pollution in Ciberang River need to be done to determine the potential of mercury pollution, so the Minamata cases will not happen again considering there are lots of ASGM around. Therefore, this is a necessity to do a research to determine mercury distribution in water and sediments of the river, so that it could provide an overview of pollution through mapping. Besides, the determination of bioaccumulation in the river fish is needed also in order to be able to observe the concentration of mercury inside. This study is possible to determine the quality of aquatic environment in water, sediment, and fish in Ciberang River, and also to learn more about the distribution of mercury.

## 2. MATERIALS AND METHODS

2.1 Research sites

Study site is located in Kecamatan Lebakgedong, Kabupaten Lebak, Banten Province. The selection of research areas is based on the small scale gold mining activities that have pollution source from mercury processor wastewater which discharged directly into the river. Study site is shown in Figure 1. The river was used as the object is Ciberang River and several tributaries, including Ciupih River, Cisoka River, Ciladaeun River, and Cihinis River which part of the Ciujung Watershed.

2.2 Determination of sampling points

The numbers of sampling points are 15. The point locations are spread from the upstream in Cisoka River to the downstream in Ciberang River. Distribution points were selected based on the existence of mercury processor around the point, tributaries, and also Ciberang River as the major water body. Sampling point is a point where the water and sediment were taken. For fish, it was not determine the points in advance, but directly when the fish samples obtained. The coordinate for each sampling point were taken by Global Positioning System (GPS). Figure 2 shows map of sampling points' distribution.
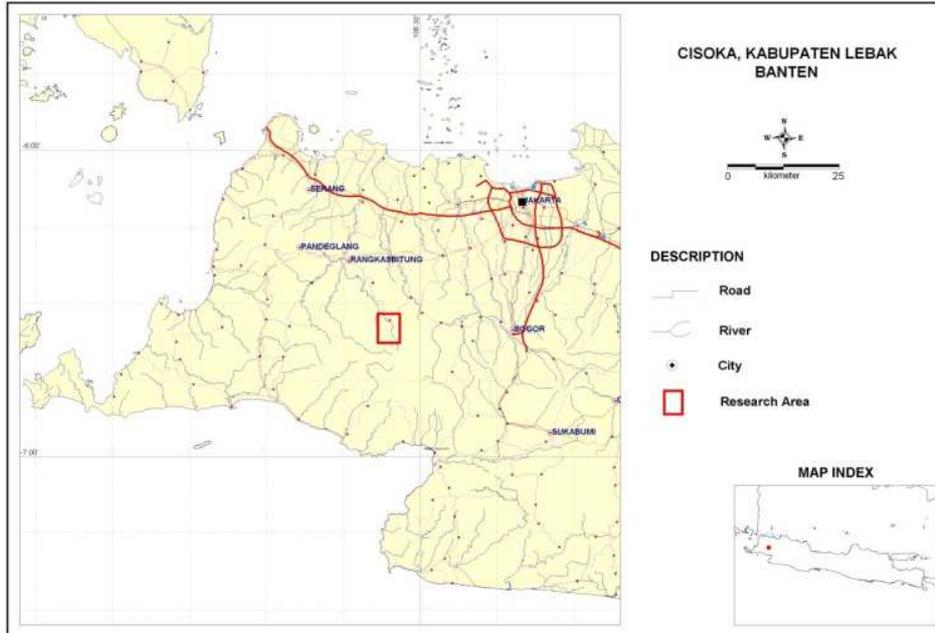
Figure 1 Location of study (Gunradi, 2011)
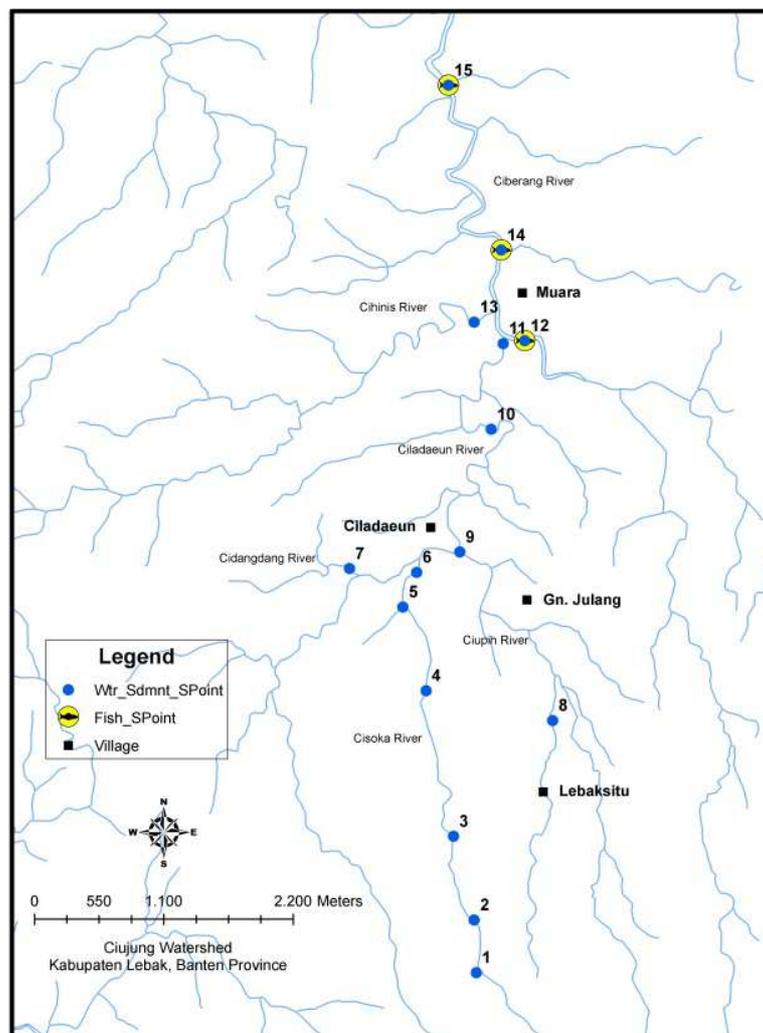
Figure 2 Map of sampling points

2.3 Primary data collection

Primary data that were collected include mercury concentration in the river water, sediment, and fish. The river water and sediment sampling were carried in 3 places for each sampling point location, which is located on the edges of the river and in the middle of the river, and based on grab sampling method. River water sampling was done by using a water sampler, bottles, HNO_3 as preservatives, and cooler box. Sediment sampling was done by using a judge sampler and then the samples were refrigerated in the cooler box. As for the fish samples, it was taken by using a fishing pole. Species of fish that was taken was any species obtained at the time when sampling activity done. Then, the fish were refrigerated in the freezer.

Hg content in water extraction process was determined according to HNO_3 extraction based on Standard Methods for the Examination of Water and Wastewater (2001). Hg analysis in sediment was conducted based on US EPA Method 200.2. For fish, Hg content was determined according to the extraction process based on SNI 01-2354.6-2006 concerning extraction of mercury in fishery products. Fish samples which would be extracted and analyzed were a mix of whole body of the fish. Before extraction, the whole body was being blended. In the mercury extraction process, there was no heating process due to the volatile nature of mercury. The extraction result from water, sediment, and fish samples were examined by Atomic Absorption Spectrophotometry (AAS) to obtain the mercury content.

2.4 Secondary data collection

Secondary data that were needed are Banten map, Ciujung Watershed map, river discharge of Ciberang River, and also data of mercury concentrations in water and sediment monitoring activities that have been conducted.

Secondary data collections were done by literature study which had derived from previous research and also data collection from related instance.

2.5 Mapping the contaminants distribution

The distribution mapping of mercury is displayed by using the ArcGIS 9.3 software. The maps which were created include mercury pollution in water and sediment maps, pollutant source location map, river water discharge map, and overlaid of each map.

2.6 Data analysis

The data is covering analysis of conditions along the river segment. Based on the results from AAS, several things will be conducted:

-Analysis of mercury pollution in water, sediment, and fish distribution.

-Making profile of mercury pollution in water and sediment in the river segment by comparing the distance with concentration.

-Determining the bioconcentration factors of mercury in fish.

-Analysis of the results of the mercury mapping in river ecosystems.

Samples by AAS measurement results obtained units in mg/m^3. For water samples, conversion unit was done into ppm (mg/l). For the sediment and fish samples, the unit must be converted in advance by using equation (1) as follows.

Metal concentrations in sediment and fish in ppm (mg/kg)

$$= \frac{\text{Concentration measured (ppm)}}{\text{Wet Weight (gr)}} \times \text{Dilution (mL)} \quad (1)$$

The bioconcentration factor of mercury calculation in fish was done using the following equation (2).

$$\text{BCF} = \frac{\text{Concentration of mercury in fish (mg/kg)}}{\text{Concentration of mercury in water (mg/L)}} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Mercury pollution profile

Pollution profile created to determine the correlation between concentration of pollutants and river flow path. The graph shows mercury concentrations graph in water in the river segment where the research was done. The river segment has a main river and four tributaries. The mercury concentration was obtained is the average value of three sampling sites, there were the edges and middle of the river. Mercury pollution profile in the river water is shown in Figure 3.

Based on the analysis, it is obtained the mercury content in water is in the range of 0.09 up to 66.6 mg/m^3. The results in Figure 3 show that almost all points from upstream to downstream contain very small mercury compared to the water quality standard based on Indonesia Government Regulation 82/2001 (2001) for class II and III which are allocated for fisheries, amounted 2 mg/m^3. Variations in distance do not provide significant difference value. Although the concentration of Hg is very small, but it has to consider its existence because of the nature Hg that is difficult to be eliminated (Darmono, 1995).

Exceptions for point 8, which has the highest mercury content amounted 66.6 mg/m^3. The presence of cyanide processor around point 8 is estimated to be responsible for the high mercury content. Cyanide processor is a tool that is used in the cyanidation process. Gold cyanidation process uses cyanide (CN-) instead of mercury. At this process, tailings from the amalgamation process are used as the raw material. The little efficiency of the amalgamation process makes the tailings have to be taken back to the gold cyanidation process. High content of mercury at point 8 is possible because of the cyanidation process waste contain high mercury that derive from the tailings. Several tailing samples taken and the analysis results obtained variation of mercury content, which is between the range of 0.63 to 77.91 mg/m^3. The waste is directly discharged into river and cause a very high content of mercury.

Mercury pollution profile is also done for the sediment river. Figure 4 shows the profile of mercury pollution in sediment river.
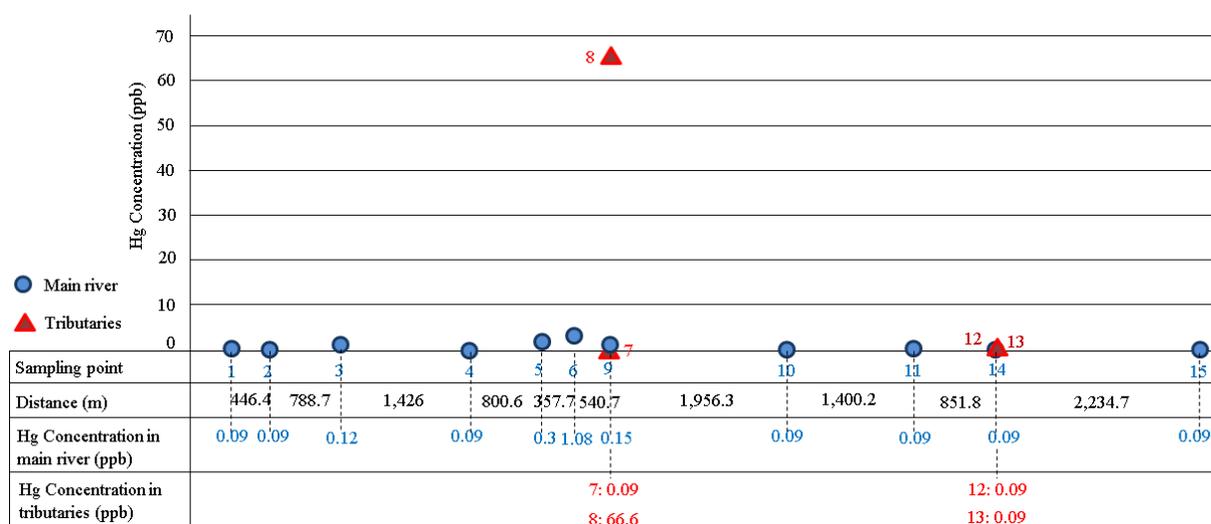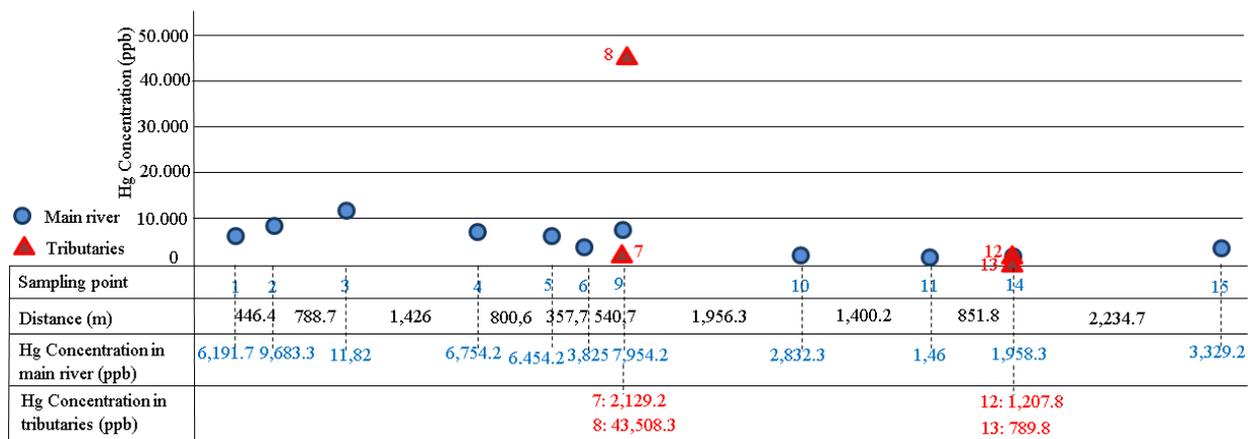

Figure 3 Profile mercury pollution in river water

Figure 4   Profile mercury pollution in river sediment

It will show big difference value when comparing mercury content in sediment with mercury content in water. Mercury pollution in river sediment could happen due to natural processes (weathering of mineralized rocks), the traditional gold processing (amalgamation), or industrial processes that use raw materials containing mercury (Rohmana et al., 2006). In addition, the mercury could settle down, so mercury which contained in water will move into sediment.

Based on the results, obtained the mercury content in sediment have variation in the range of 789.75 up to 43,508.33 mg/m^3. It shows that all the sampling points have very large mercury compared to the sediment quality standard for mercury based on US EPA, amounted 180 mg/m^3. Distance variations cause difference significant value. Based on Figure 4, there are some points that have increased mercury content. At the point 1, 2, and 3 which lies on the Cisoka River, the mercury content is increase, this is because of so many mercury processors around point 2 and 3. In the aquatic environment, most artificial chemicals and waste materials will eventually accumulate in sediments. The mercury processor produces pollutants to the river and cause mercury accumulation in sediment.

In addition, the increasing mercury content can be seen also at the point 8. Equal to the mercury content in water, the point 8 has the highest value of mercury concentration in sediment compared to the other points, amounted 43,508.3 mg/m^3. This is influenced by the presence of cyanide processors waste disposal around point 8.

In general, Figure 4 shows that increasingly in the direction of the river downstream, then the mercury concentration in sediment is declining. It accordance to the monitoring conducted by Gunradi (2011), which states that there are decreasing value of mercury content at downstream points in Cisoka area.

3.2   Bioaccumulation mercury in fish

Based on the results from fish sampling, the fish species obtained are gabus fish (Channa striata) and tawes fish (Barbonymus gonionotus) in Ciberang River. The mercury content in fish samples were analyzed and calculated for the Bioconcentration factor (BCF) value. BCF is a factor that shows the relationship between the concentration of a compound in the environment and the concentration of the same compound in living tissue (Sutarto, 2007). Table 1 shows the value of BCF in fish samples.

Table 1 BCF in fish samples

Sampling Point	Fish Code	BCF
12	*Barbonymus gonionotus* 1	3,227.778
	Barbonymus gonionotus 2	3,529.67
	Barbonymus gonionotus 3	3,152.778
	Barbonymus gonionotus 4	2,327.778
	Barbonymus gonionotus 5	4,354.167
14	*Barbonymus gonionotus* 6	3,243.056
	Barbonymus gonionotus 7	3,077.778
	Barbonymus gonionotus 8	3,611.111
	Barbonymus gonionotus 9	3,333.333
	Barbonymus gonionotus 10	3,829.167
15	*Channa striata* 1	1,561.111
	Channa striata 2	1,951.389
	Channa striata 3	1,876.389

Bioaccumulation could be dangerous if the ratio between mercury in organic matter and mercury in environment has a value of 100-1,000 (Soemirat, 2003). Based on Table 1, it can be seen that the BCF derived from all samples have very large value, which above 1,000.

Based on Screening Level Ecological Risk Assessment Protocol US EPA Region 6, methyl mercury BCF value of water to fish that recommended is 11,168. Another source, the Technical Support Document for Exposure Assessment and Stochastic Analysis California EPA, states that BCF value of inorganic mercury is 5,000. BCF values from analytical results obtained under these two values. Differences in the results of BCF with the two values can be influenced by several factors, such as species, age and metabolic rates of organisms, and also the characteristics and concentration of the metal (Tucker, 2000).

3.3 Mercury pollution mapping in river ecosystem

Pollution maps created include map of mercury pollution in water (Figure 5), map of mercury pollution in sediment (Figure 6), and map of mercury pollution in fish (Figure 7). Those maps are overlaid with mercury processor inventory map and river water discharge map.

Based on Figure 5 and Figure 6, can be seen that increasingly in the direction of the river downstream, then the discharge value is also increasing. Inversely to the mercury concentration in water and sediment, that increasingly in the direction of the river downstream, then the concentration is declining. Similarity is shown in Figure 7, that the farther to downstream, the average mercury concentration in fish are getting smaller. It is clear that there is a correlation between the discharge with metal concentration. The smaller river water discharge, causing the metal ion is easier to settle and in fish is easier to accumulate, causing high concentrations of mercury. Inversely, if the mercury concentration is low, because of the river water discharge is large enough, so that metal ions tend to be carried by water flow and only few that settle down.
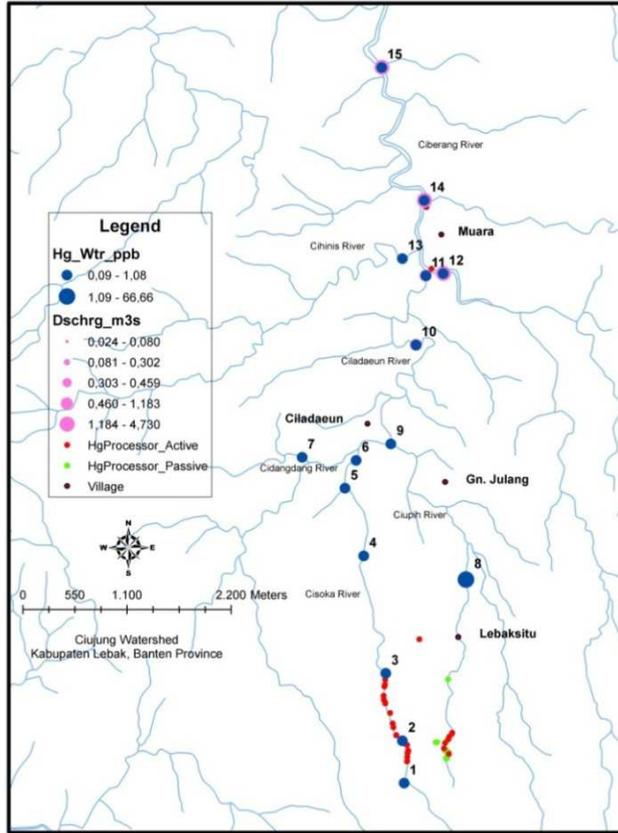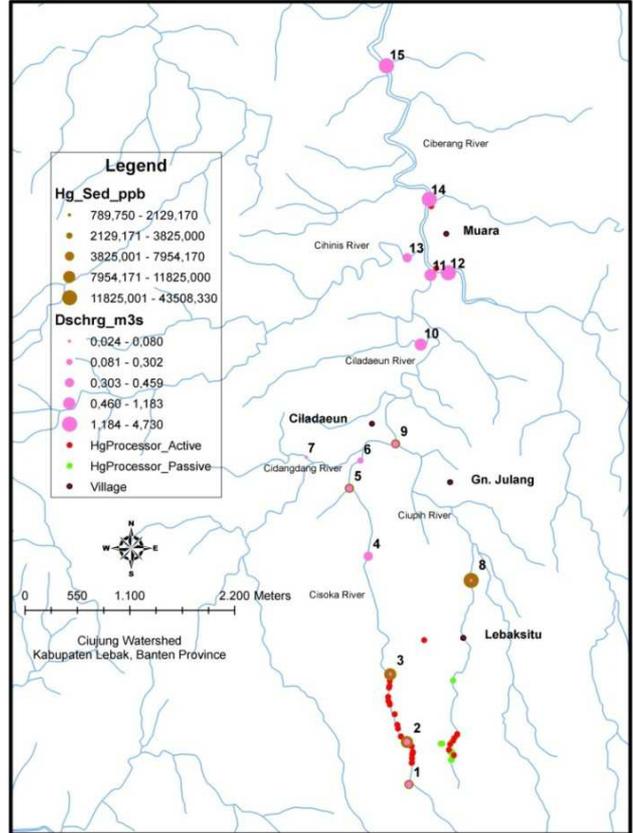
Figure 5   Map of Hg pollution in water

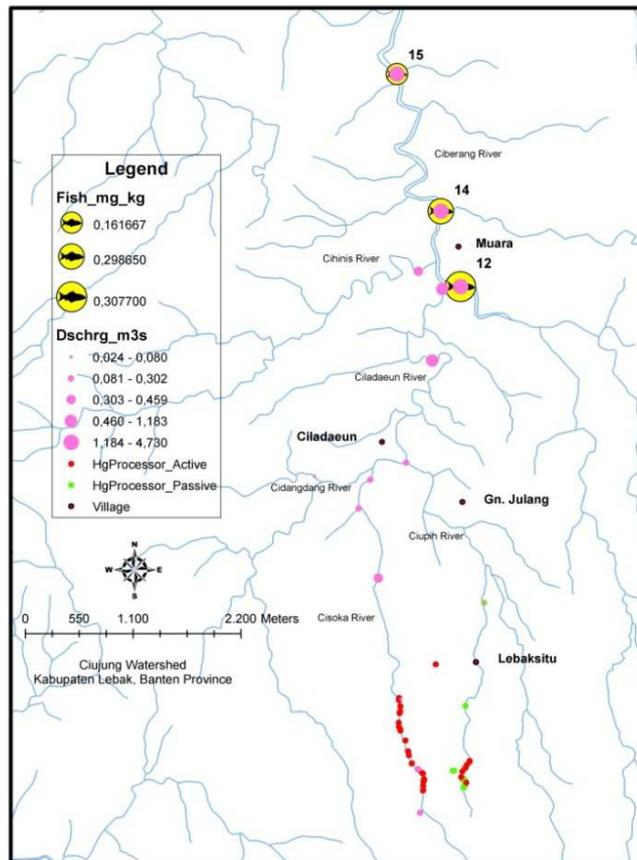**Figure 6**   Map of Hg pollution in sediment

Figure 7   Map of Hg Pollution in fish

CONCLUSIONS

From the samples analysis at 15 points, it is known that 14 water samples had mercury concentrations below the standard quality and whole sediment samples had mercury concentrations above the standard quality. Mercury characters are easy to settle and accumulate, causing the mercury content in water very small and the mercury content in sediments very large. The existence of gold mining and processing activities are also very close related to the increasing of mercury in stream sediment element. Calculation BCF of Channa striata and Barbonymus gonionotus have value above 1,000, which include in dangerous category if consumed. River water discharge greatly affects the amount of mercury present in aquatic systems. River water discharge which has large value will make the metal ions flown in water, causing only a few that settled and accumulated.

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