Mercury in sediment and freshwater organisms from Kr. Sikulat River around the artisanal gold mining plants in Sawang, Aceh Province, Indonesia

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Abstract. Artisanal gold miners in Sawang use mercury in gold separation process. The workers put gold ore and mercury into the tumblers to extract gold and silver by amalgamation method. After gold and silver are isolated from the ore as amalgam, mercury is vaporized by burning with an oil burner. Furthermore, wastewater containing mercury is discharged at landfills and Kr. Sikulat River stream. With the purpose of knowing the impact of small-scale gold mining plant in Sawang, the concentrations of mercury in Kr. Sikulat River sediment and the accumulation of mercury in tissues of freshwater organisms from Kr. Sikulat River were investigated. Sediments were taken from locations near the gold mining plant and freshwater organisms were caught in the estuary from Kr. Sikulat River. Samples were transported live to the laboratory and sampled dissected after death. Tissue from each organism were removed and grained after dried. Total mercury analyzed using an Atomic Absorption Spectrometry (AAS), AA-6300 Shimadzu. The results showed that the concentration of mercury in sediment found 0.0339 mg-Hg/kg, while the concentration of mercury in the water phase were found 0.005 – 0.047 mg-Hg/L. Mercury was also found in the concentration of 0.1903 mg-Hg/kg accumulated in the shellfish, but it was not found accumulated in other freshwater organisms such as fish and shrimp. Based on these results, a regular monitoring program in Kr. Sikulat River is necessary conducted in order to better elucidate the rate of bioaccumulation and biomagnification by organisms.
Keywords: mercury; artisanal gold mining; bioaccumulation; and Kr. Sikulat River.

Introduction

Artisanal gold mining is one of the major sources of mercury (Hg) contamination in many developing countries (United Nations Environment Programme, 2002). These activities relies mainly on manual labor and makes use of simple methods. It offers poor people an important means of livelihood and has served as a safety net in times of economic distress (Limbonga, *et al*., 2003). In artisanal gold mining practiced in many developing countries, especially in Indonesia, gold is separated from ore by the use of mercury, which forms an amalgam with gold. All related processes are undertaken with a low level of technical knowledge and skills, no regulation, and with disregard for the safety of human and environment health. The amalgamation method of artisanal gold mining causes mercury emissions to leak into the environment in several different ways. For example, when Mercury is unintentionally spilled onto the ground. Atmospheric transport and deposition at normal temperature is the pathway delivering mercury to rivers, lakes, and oceans. Moreover, mercury is often discharged together with other wastes into inadequate tailings ponds, or is disposed of directly into rivers and waterways. Another means of introducing mercury into the environment take place when purifying the amalgam by burning and vaporized mercury is released into the atmosphere.

Many researchers have been reported contamination of mercury in environment from gold mining activities. Bose-O'Reilly, *et a*l. (2010) reported clinical examinations and mercury levels in people living and working in the Indonesian gold mining areas. The primary result is that mercury is a serious health hazard in the small-scale gold mining areas of Tatelu (North) and Kerang Pangi (Central Kalimantan). Working for many years in the amalgamation or burning process, especially amalgam-burning has resulted in severe symptoms of mercury intoxication. Limbong *et al.*, 2003 observed the emissions of mercury from artisanal gold mining in North Sulawesi and indicated that an increase took place along the three main rivers in the watershed. Natural process also causes the entering of mercury in aquatic ecosystem such as mineral deposits, volcanoes, forest fires, oceanic emission, and crust degassing. It also could be released by human activities such as smelters processing sulfide ores (i.e., in the production of metals such as gold, copper, iron, lead and zinc) and cement kilns, roasting of sulfide ores for production of sulfuric acid (Hylander and Meili, 2003). Mercury contamination in some rivers in Indonesia mosly caused by the gold mining activities, such as Ciliunggunung River in Sukabumi Regency (Widodo, 2008), Tawalaan, Bailang, and Kima River in North Sulawesi (Limbong *et al.*, 2003), and Barito, Kahayangan, Rungan River in Central Kalimantan (Gumiri *et al.*, 2009), and Kr. Meureubo River in West Aceh (Suhendrayatna *et al.*, 2010). The gold ore from the mining is processed with a direct amalgamation method and produces low gold concentrate, but the concentrate of mercury discarded to the river is high enough. Furthermore, low levels of technical knowledge and skills and no regulation are also applied in all related gold mining processes in Indonesia (Limbong *et al.*, 2003).

In the last three years, our peer group focussed study on the emissions and environmental implications of mercury from artisanal gold mining in Aceh. In 2010, we reported that high concentration of mercury was detected in main tissues of freshwater fish and shellfish from Kr. Meurebo River, West Aceh and the accumulated mercury in organisms were significantly greater in shellfish than in fish which mean concentrations were 2.882$\pm$148 and 0.321$\pm$18.7 mg/kg-dry weight, respectively. High mercury levels in organism samples provided strong indication of a high bioaccumulation from the Kr. Meurebo River (Suhendrayatna, *et al.*, 2010) and also Kr. Sabe River area in Aceh Jaya (Suhendrayatna, *et al.*, 2011). Bioaccumulation of mercury by fish from Kr. Sabe River was found minimum in head (0.046$\pm$10.0 mg/kg-dry weight), whereas maximum bioaccumulation founded in the gill (0.399$\pm$1.5 mg/kg-dry weight). Mercury concentrations varied in the order: Gill > Muscle > Bone > Eye > Head (Suhendrayatna, *et al.*, 2011). Solutions to these problems must be formulated as soon as possible in order to avoid a major health, economic, and ecological disaster arising from the continuing discharge of mercury in Aceh.

With the purpose of knowing distribution of mercury in sediment and freshwater organisms from river around the artisanal gold mining plants, this study investigated in the watershed of Kr. Sikulat River. Kr. Sikulat River is located in Sawang Sub-district, the south part of Aceh, Indonesia and only 2 – 4 m deep on average. The major source of pollution is predicted by the waste effluents from the artisanal gold plant lies in the upstream of the river as parts of Sikulat Mountain. The gold separation processes are undertaken with a low level of technical knowledge and skills, no regulation, and with disregard for the safety of human and environment health. The situation is generating serious potential health and environmental risks in that area. As part of an ongoing monitoring program, total mercury concentrations were examined in the organism's samples from the Kr. Sikulat River, which receives drainage from gold plant practices. This study assessed the levels of mercury concentration in biological samples from organisms such as fishes and shellfishes in a watershed of Kr. Sikulat River.

Materials and Methods

Study area

Study area focused on the Kr. Sikulat River watershed near to gold processing activities centered on the Panton Luas village, Sawang Sub-District, South Aceh District which selected sampling locations are as follow.

(1) A. 1 Kr. Sikulet watershed near housing area (N : 03°23'28,2" E : 097°07'14,9")
(2) A. 2 Watershed near artisanal gold mining effluent (N:03°23'41,5" E:097°07'53,7")
(3) A. 3 Watershed near artisanal gold mining effluent (N:03°23'38,2" E:097°07'54,1"). The sampling site illustrated in Figure 1.

Reagents

Hg^{2+} standard solution (1000 mg/L, $HgCl_2$ in 0.02 M HCl), methylmercury (II) chloride, and hydrochloric acid were purchased from Wako Pure Chemical Industries, Ltd. All chemicals used were analytical grade quality. All solutions were prepared in ultrapure water prepared by a Purelab Ultra Ionic (Organo Co., Ltd.).

Experimental Procedure

Fish and shellfish were caught in the estuary from Kr. Sikulat River and sampling sites were selected in the downstream of river that correlated to the contaminant sources as illustrated in Figure 1. All organisms were transported live to the laboratory and sampled dissected after death. Organs from each organism were removed and grained after constant dried at 35°C.

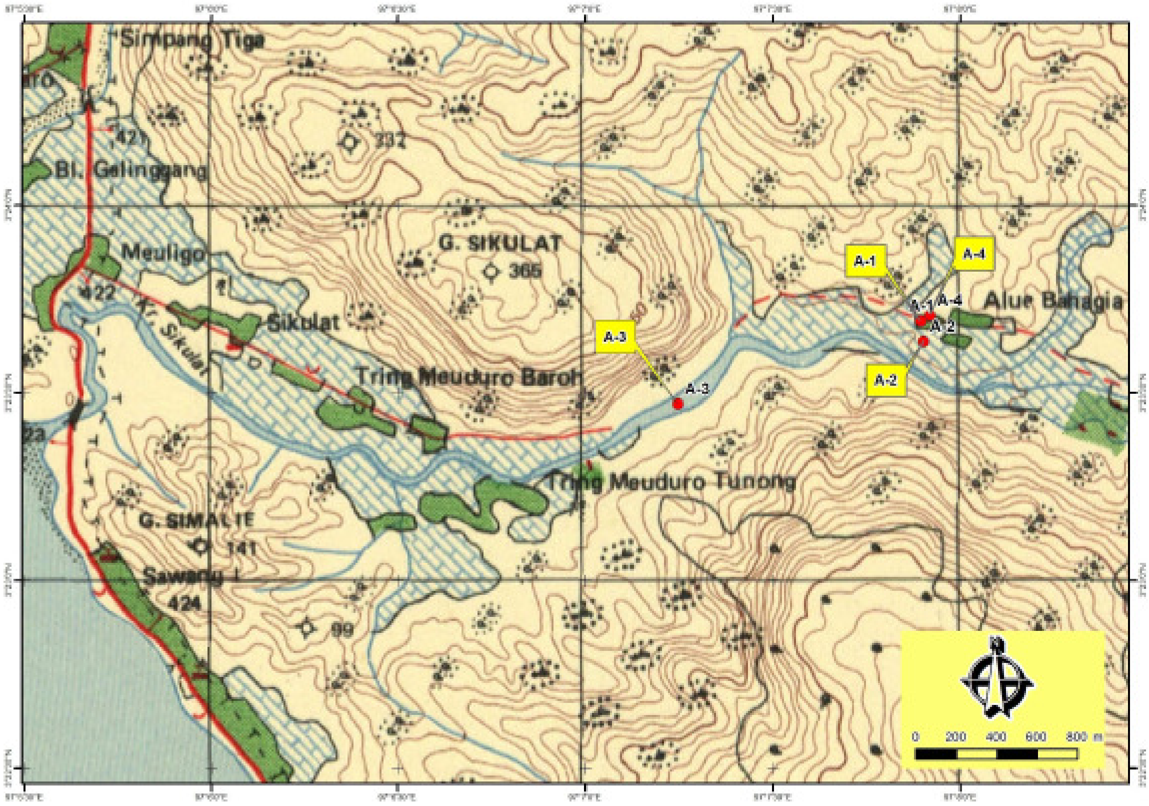

Figure 1. Sampling site area

Analysis procedure

Dried fish tissue samples were digested using nitric acid and hydrogen peroxide along with hotplate heating, and the Mercury concentrations of fish tissues were examined. Total Mercury for all samples were determined by the cold vapor technique using an Atomic Absorption Spectrometry (AAS), AA-6300 Shimadzu, according to the method suggested by Akagi and Nishimura (1991). Quality control was monitored for all chemical analyses. Instrument calibration was verified by analyzing certified calibration solutions during each instrumental run.

Results and Discussion

Mercury levels among the three sampling phases were variable at sampling sites A1, A2, and A3 as shown in Table 1. The mercury concentration in water phase was found in the ranged between 0.001 and 0.047 mg-Hg/L. Watershed near artisanal gold mining effluent zones had a significant effect on the concentration of mercury (0.005-0.047 mg-Hg/L). Observations in the watershed near artisanal gold mining effluent zones were upper the acceptable limit, weather in the watershed near housing area is well below the acceptable limit. The mercury concentrations found in watershed near artisanal gold mining effluent were almost higher than both the Indonesian Government Regulation and the US EPA acceptable limit. The US EPA mercury water quality criterion for protection of freshwater in 0.0012 mg-Hg/L (USEPA 1985). The water quality criterion for mercury based on the Indonesian Government Regulation No. 82 year 2001 is 0.001 mg/L. Compared to the concentrations of mercury in sediments, those in water were very low. This finding suggests that mercury rapidly attaches to suspended solid particles and organic matter, and that mercury thus can rapidly slump to the river bottom.

Mercury concentrations found in Kr. Sikulat River sediment in the range 0.0339 to 0.1980 mg-Hg/kg-dry weight as shown in Table 2. Mercury in sediment near the artisanal gold mining effluent zones found higher than in sediment near housing area. This finding suggests that the sediments near the artisanal gold mining effluent zones have been exposed by mercury from the processing. This fact is supported from the analysis results of mercury accumulated in aquatic organisms.

The analysis results of accumulation of mercury in the river organisms are tabulated in Table 3. All observations were well not detected, except for shellfish in the watershed near artisanal gold mining effluent (Site A.3). The accumulation of mercury in shellfish found in the concentration of 0.1903 mg-Hg/kg-dry weight. All observations of mercury accumulated in organisms were well below the acceptable limit in the United States 1.0 mg/kg and in Canada 0.5 mg/kg, respectively (FDA, 2009 a; FDA, 2009b).

Table 1. The Distribution of mercury in river system around the artisanal gold mining

Sampling site	Coordinate	Hg in water phase (mg/L)
A. 1 Watershed near housing area	N : 03°23’28,2” E : 097°07’14,9”	0.001
A. 2 Watershed near gold mining	N : 03°23’41,5” E : 097°07’53,7”	0.005
A. 3 Watershed near gold mining	N : 03°23’38,2” E : 097°07’54,1”	0.047

Note : Acceptable limit Hg in water phase based on the Indonesian Government Regulation No. 82 year 2001 is 0.001 mg/L.

Table 2. Distribution of mercury in sediment around the artisanal gold mining

Sampling site	Coordinate	Hg in sediment (mg-Hg/kg-dry weight)
A. 1 Watershed near housing area	N : 03°23’28,2” E : 097°07’14,9”	0,0339
A. 2 Watershed near gold mining	N : 03°23’41,5” E : 097°07’53,7”	0,1307
A. 3 Watershed near gold mining	N : 03°23’38,2” E : 097°07’54,1”	0,1980

Note : Acceptable limit for total mercury content in sediment based on Canada Government Regulation is 0.5 mg-Hg/kg-dry weight.

Table 3. Mercury accumulated in freshwater organisms around the artisanal gold mining

Sampling site	Coordinate	Hg (mg-Hg/kg-dry weight)		
		Fish	Shrimp	Shellfish
ST. 1	N : 03°23’28,2” E : 097°07’14,9”	tr	Tr	tr
ST. 2	N : 03°23’41,5” E : 097°07’53,7”	tr	Tr	tr
ST. 3	N : 03°23’38,2” E : 097°07’54,1”	tr	Tr	0.1903

Note: Limit Hg in organisms based on the Canada and US Government Regulations are 0.5 mg-Hg/kg-dry weight and 1 mg-Hg/kg-dry weight, respectively; tt = tracer

Compared to results of studies in different locations, the content of mercury in aquatic organisms at this location was well below. A comparison with literature data (Table 4) showed that the specimens here analyzed had mercury level higher in freshwater shellfish than those reported for freshwater fishes in other parts of the world (FDA, 2009a; FDA, 2009b), except for freshwater fish from mercury contaminated area in Sulawesi, Mexico, and North Mississippi (Limbong *et al.*, 2003; Ache, B.W. *et al.*, 2000; Huggett, *et al.*, 2001), which showed comparable levels. Nearly all fish and shellfish contain traces of methyl mercury. However, larger fish that have lived longer have the highest levels of methyl mercury because they've had more time to accumulate it. These large fish (swordfish, shark, king mackerel, and tilefish) pose the greatest risk. Small fish absorb methyl mercury from water as they feed on aquatic organisms. The longer fish lives causes more methyl mercury accumulated in its body. Large, long-lived, larger fish that feed on other fish (high in the food chain) accumulate the highest levels of methyl mercury.

Table 4. Mercury concentration in tissues of freshwater organisms from different locations

Species	Location	Hg Concentration (mg/kg-dw)	Refferences
Shellfish	Kr. Sikulat River (near artisanal gold mining effluent)	0.1903	This study
Fish, *C. canos*	Kr. Sabe River (upstream)	0.362 $\pm$ 23.9*)	Suhendrayatna, *et al.*, 2011
Fish, *C. canos*	Kr. Sabe River (downstream)	0.335 $\pm$ 23.2*)	Suhendrayatna, *et al.*, 2011
Shellfish, *P. exilis*	Krueng Sabe River (upstream)	1.305 $\pm$ 87.5*)	Suhendrayatna, *et al.*, 2011
Shellfish, *P. exilis*	Krueng Sabe River (downstream)	1.285 $\pm$ 23.5*)	Suhendrayatna, *et al.*, 2011
Trout	FDA 2002-04, USA	0.072	FDA, 2009b
T. mossambica	FDA 1990-02, USA	0.010	FDA, 2009b
Catfish	FDA 1990-04, USA	0.049	FDA, 2009b
Perch	FDA Survey 1990-02, USA	0.140	FDA, 2009b
Shrimp	FDA 1990-02, USA	tt	FDA, 2009b
Fish, *C. canos*	Kr. Meurebo River, Meulaboh	0.321	Suhendrayatna, *et al.*, 2010
Shellfish, *P. exilis*	Kr. Meurebo River, Meulaboh	2.882	Suhendrayatna, *et al.*, 2010
Small fish	Talawaan River, Sulawesi	3.140	Limbong *et al.*, 2003
Small fish	Bailang River Sulawesi	0.510	Limbong *et al.*, 2003
Small fish	Kima River, Sulawesi	0.453	Limbong *et al.*, 2003
M. Salmoides	Gulf coast, Mexico	0.430	Ache, B.W. *et al.*, 2000
Carp	Enid Lake, North Mississippi	0.352	Huggett, *et al.*, 2001

Note: tt = tracer; *) Average of data from two replicated series of measurements

Conclusions

This present study has shown the concentration of mercury in sediment found 0.0339 mg-Hg/kg-dry weight, while the concentration of mercury in the water phase were found 0.005 – 0.047 mg-Hg/L. Mercury was also found in the concentration of 0.1903 mg-Hg/kg-dry weight accumulated in the shellfish, but it was not found accumulated in other freshwater organisms such as fish and shrimp. Based on these results, a regular monitoring program in Kr. Sikulat River is necessary conducted in order to better elucidate the rate of bioaccumulation and biomagnification by organisms.

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