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308 Lasani Town, Sargodha Road, Faisalabad - Pakistan
Mob: +92 300 3008585, Fax: +92 41 8815544
E-mail: editorpjn@gmail.com

Mercury Distribution and its Potential Environmental and Health Risks in Aquatic Habitat at Artisanal Buladu Gold Mine in Gorontalo Province, Indonesia

Anwar Mallongi¹, Preeda Parkpian², Poranee Pataranawat³ and Sopa Chinwetkitvanich³

¹Department of Environmental Health, Faculty of Public Health, Hasanuddin University, Jl. Perintis Kemerdekaan KM. 10, Tamalanrea Makassar, 90245, Indonesia

²School of Environment, Resources and Development, Asian Institute of Technology (AIT), Pathumthani, Thailand

³Department of Sanitary Engineering, Faculty of Public Health, Mahidol University, Rajvithi Road, Bangkok, 10400, Thailand

Abstract: Total mercury (THg) in water column, sediment and aquatic biota as well as environmental and health risks at artisanal Buladu gold mine and vicinity areas of Gorontalo Province, Indonesia were investigated both in summer and rainy seasons. THg was determined by CV-AAS (Cold Vapor Atomic Absorption Spectrophotometer; Spectr. AA6200) after NaBH_4 (Sodium Borohydride) reduction, with detection limit was of 0.001 $\mu\text{g/L}$. Site-specific exposure parameters such as body weight (bw) and consumption rate of fish and shellfish were determined and calculated using target hazard quotient (THQ) formulation for health risk assessment. This study showed that the assessment of average balance of Hg: Au ratio forecasted that approximately 1.3 g of Hg in open burning process was released to atmosphere to produce 1 g of gold. Likewise, 15.88 g of Hg is lost to produce 1 g of gold during amalgamation process in particular equipment, the tromols. Moreover, the highest levels of THg concentrations in water column, sediment and shells in uncontaminated track were 41 $\mu\text{g/L}$, 5238 $\mu\text{g/kg dw}$, 215 $\mu\text{g/kg dw}$ for *Bellamnya javanica* and 397 $\mu\text{g/kg dw}$ for *Mya arenaria* in summer season, respectively, whereas in rainy season the lower THg concentration were 24 $\mu\text{g/L}$, 5077 $\mu\text{g/kg dw}$, 141 $\mu\text{g/kg dw}$ for *Bellamnya javanica* and 180 $\mu\text{g/kg dw}$ for *Mya arenaria*, respectively. However, in contaminated track, the significant elevated THg were found about 123 $\mu\text{g/L}$, 5612 $\mu\text{g/kg dw}$, 1455 $\mu\text{g/kg dw}$ for *Bellamnya javanica* and 1745 $\mu\text{g/kg dw}$ for *Mya arenaria* in summer season, respectively, whereas in rainy season the highest concentration were 165 $\mu\text{g/L}$, 6950 $\mu\text{g/kg dw}$, 1250 $\mu\text{g/kg dw}$ for *Bellamnya javanica* and 1745 $\mu\text{g/kg dw}$ for *Mya arenaria*, respectively. THg elevated in *Thunnus sp.* was also found at station one in big tuna with the value of 762 $\mu\text{g/kg dw}$. Those elevated THGs were consistent and significantly different between those two seasons in term of bioaccumulation level. In addition, the estimated weekly intake (EWI) of Hg for *B. javanica*, *M. arenaria* and *Thunnus sp.* exceeded the accepted maximum tolerable weekly intake of 0.005 $\mu\text{g/kg bw}$. Nevertheless, THQ values were still less than 1 with the maximum levels of 0.06, 0.11 and 0.69 in summer season, respectively. These results suggested that Hg containing wastewater discharged into the Buladu River and the atmospheric fallout from Hg emission were the major sources of Hg in the areas of interest. Consequently, Hg, resulting from Hg released from the gold mine that has been operated for 30 years more, has gradually accumulated in the aquatic ecosystems of the Buladu River and the Sulawesi Sea.

Key words: Gold mining, mercury distribution, amalgamation, aquatic ecosystem, estimated weekly intake, hazard quotient

INTRODUCTION

Elemental Hg-Au amalgamation mining practices are used widely in many developing countries resulting in significant Hg contamination of surrounding sediment, water and biota as well as adverse effects on human health (Gray, 2002). During ore amalgamation, Hg is used to recover gold followed by open burning. Some Hg escapes and releases directly into the air and deposit onto the soil which run down to water bodies by runoff as elemental Hg droplets or as coatings of Hg adsorbed on

to sediment grains (Telmer, 2006; Castilhos, 2006). During the amalgamation process, Hg is transported in the environment either by water and air, as well as by biological organisms through the food-web. Hg can enter the air as a vapor, then drop both as dry and wet deposition, it settles to sediment at the bottom and will be absorbed by phytoplankton or ingested by zooplankton and microorganisms, or fish as higher trophic levels in food chain as transformation process life (Benoit *et al.*, 1998).

While Hg^{2+} is the dominant form of mercury deposited into aquatic environments, health risks to both humans and wildlife are primarily associated with the consumption of fish containing elevated levels of MeHg (EPA, 2002). MeHg, on average, composes less than 1-2% of the total concentration of mercury in aquatic sediments (Benoit *et al.*, 2001). MeHg, organic mercury compound is one of the most toxic, others are the inorganic mercury compound that is fairly soluble in water. In addition, inorganic mercury can be methylated by indigenous microorganisms in the environment such as; soils, sediments, fresh water and salt water, to form organic mercury. Almost all of the Hg found in animal tissues is in the form of MeHg which is toxic for alive (WHO, 1989).

Currently, Indonesia produces around four percent of global gold production, half of which originates from the giant Grasberg mine, the world largest gold mine, on the western half of Papua. This mine, which is believed to contain the world's largest gold reserves (67.4 million ounces) and makes it the largest taxpayer to the Indonesian government. Other gold industries are in Sumbawa, East and Central Kalimantan and Sulawesi. As gold industry production in Indonesia by far outpaces domestic gold demand, most of its domestic production is exported to other countries. There are two method of gold processing i.e., Cyanide process; the technique using dissolution with alkaline cyanide has been highly developed over recent years. It is particularly appropriate for low grade gold and silver ore processing (e.g., less than 5 ppm gold) but its use is not restricted to such ores and small artisan operations, in some cases illegally. In order to maximize gold extraction, mercury is often used to amalgamate with the metal. The gold is produced by boiling away the mercury from the amalgam, a hazardous process due to toxicity of mercury vapour.

Gold exploration and exploitation activities in Buladu initiated by the Dutch government began in the Dutch East Indies Era in 18th century. During the 1970s, exploitation activities continued and mining was created again by the local community. At that time, the gold mine activities were conducted traditionally by panning of sand and rock deposits along the Buladu River. Starting from the 1990s, this area became a traditional gold mining area. Originally, mining systems were operated using simple mechanization (Hunta, 2008; Department of Mining and Forestry, 2008). At present, the mining developed rapidly with large number of miners as many as about 450 people and become one of the most active gold mining in Gorontalo Province.

The accumulation of mercury from gold ore processing in the Buladu gold mine may occur in the aquatic systems such as the river and the sea. At present, no informative data were available in this area, thus this study emerges to investigate distribution and

accumulation of mercury to evaluate the environmental status as well as the environmental health risks in the artisanal Buladu gold mine and vicinity areas in Sumalata District of Gorontalo Province, Indonesia.

MATERIALS AND METHODS

Study area and sampling protocol: This study was conducted in the Buladu artisanal gold mine, Gorontalo Province, Indonesia. It has a tropical climate influenced by summer season that usually runs from June through October and rainy season from November through April. The North Wind blows in from January to March (summer season), followed by the West Wind from April to May. The South Wind blows from July to August. In addition, the East Wind (November-December), is quite strong in the sea with high sea waves ranging from 1 to 2 meters. In Gorontalo, there are two yearly seasons of monsoon winds; the Southeast Monsoon for summer and the Northwest Monsoon for rainy season (Department of Meteorological and Geophysical, 2001). Buladu District, the main and the major gold mining area in Gorontalo Province is surrounded by the Celebes Sea in the North, Deme I Village in the East, the Boalemo District in the South and Wubudu Village in the West. Its topography consists of plains at the coastal area and becomes hilly several hundred meters ahead from the shorelines. The artisanal gold mining area itself is located at about 3500 m from the sea and on hill side whereas the tromols (amalgamation processing equipment) and panning area are located at only about 700 m and 100 m from the sea, respectively.

There are three aquatic tracks of the Buladu Rivers that run from the hill down to the sea. The east and the middle ones are regarded as uncontaminated tracks and kept by the community as water resources for household use and the west one is the contaminated track resulting from the Hg containing wastewater discharged from tromol processing centre as the point source. In this study, two upstream stations (A1-A2) and three downstream stations (A3-A5) of main aquatic track (the middle one) were selected for uncontaminated track for water column, sediment and shellfish. In the Sulawesi Sea, there are four sampling stations (A6-A9) for sea water and fish (Fig. 1).

Mercury mass balance: Informal interviews with miners and gold industry owner were obtained as well as the data of mercury losses during amalgamation process. The mercury recovered after squeezing and burning the amalgams were also measured (Table 1).

Buladu river

Water column: Fresh water samples were collected using non metallic convertible water sampler (Kemmerer water sampler) in both summer and rainy seasons at the mid depth of mid stream from upstream

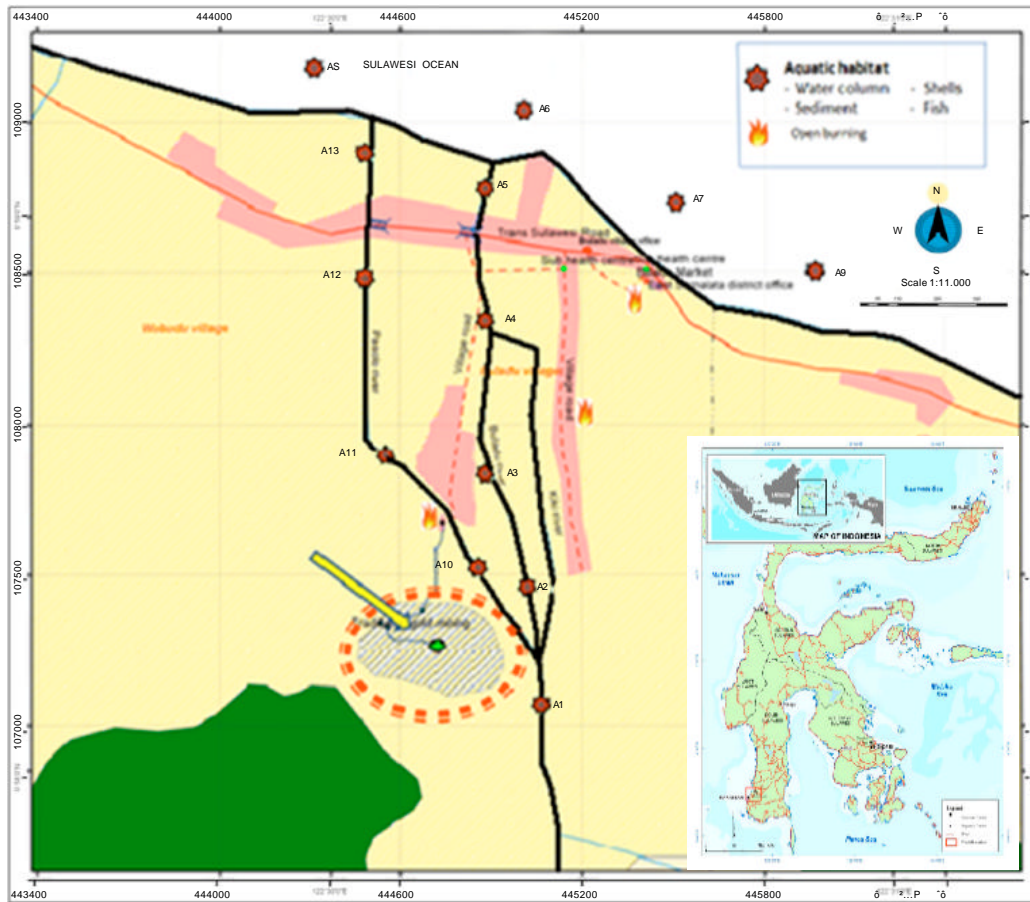


Fig. 1: Sampling locations in aquatic tracks of the Buladu River and the Sulawesi Sea in study area. A1-A5 = uncontaminated track, A6-A9 = the Sulawesi Sea, A10-A13 = contaminated track

to downstream. There were 5 stations in the uncontaminated aquatic track (A1-A5) and 4 stations at the contaminated sites (A10-A13). Selected parameters for water quality were measured both in field and laboratory (Table 2).

Sample collections were conducted in both summer and rain seasons. Duplicate set of water samples was collected and kept at 4°C using polyethylene high density bottles. Laboratory analyses were done immediately within ten days following collection. All water samples were preserved with HNO₃ and determined against the reference standard materials by CV-AAS (cold vapor absorption atomic spectrophotometer) for THg analysis.

Sediment and shellfish: Sediment samples were collected using modified PVC core sampler (40 cm long and 10 cm in diameter) whereas shellfish (*Bellamya Javanicus* and *Mya arenaria*) were handily collected from 5 stations of non contaminated aquatic track. The sediment was collected at the depth of 0-5 cm and 6-10

cm, then, sieved through a 2-mm mesh sieve to prepare a sediment sample (Dennis and Zupko, 1995). After homogenization, mix on an equal weight of each sample to obtain a final composite sample for the mercury analysis. After collected, samples were kept at 4°C in dark place.

The sediment characteristics were investigated (Table 3) and the THg were determined by CV-AAS using a standard reference material (SRM 1646a estuarine sediment) to obtain QA/QC. Likewise, shellfish samples were collected at the same stations where sediment and water samples collected. Approximately 20-25 shellfish with the size in the range of 6-8 cm in length for *B. Javanicus van den bush* and in the range of 4-6 cm in length for *M. arenaria* were collected. Shellfish tissues were immediately cut off and placed into polyethylene sample bags and kept at 4°C in an ice box before being transported to laboratory and kept in a freezer (-20°C). Soft tissue of shellfish were removed and cut in section of small pieces and lastly, the homogenized representing samples were frozen until being analyzed.

Table 1: Hg used in amalgamation process in the Buladu gold mine

Evaluation processes	Procedures
Mercury entering the system	Mercury was weighed before being introduced into the amalgamation process
Mercury recovered from amalgamation process (excess Hg)	Mercury was weighed after squeezing to obtain the amalgam
Mercury emission from open burning	Amalgam was weighed before burning to recover gold following by the remaining gold ore
Mercury lost in tailings	Estimated by the weight difference in each step of process; mercury recovering and emission

Source: Patricio *et al.* (2009)

Table 2: Water characteristics and analyses

Parameters	Method of analyses	References
Field Measurement		
a. Temperature	S-C-T Meter	Water Quality Control, Aquarius Tech (2002)
b. pH	pH Meter	Standard method 4500-H+
c. Dissolve oxygen	Dissolved oxygen meter	US EPA (1986), EPA (2005)
d. Conductivity	S-C-T Meter	US EPA (1986), EPA (2005)
Laboratory Measurement		
a. Dissolved organic carbon (DOC)	Total organic carbon analyzer	APHA <i>et al.</i> (1998), 5310B
b. Suspended particulate matter (SPM)	Pre-weighed polycarbonate membranes (nucleopore 0.45 nm pore in size)	APHA <i>et al.</i> (1998), 5310B
c. THg	CVAAS, CVAAS, (SHIMADZU, Spectr. AA 6200), (Lousiana State University)	Gambrell (1991)

Table 3: Sediment characteristics and THg analyses

Parameters	Method of analyses	References
pH	(1:1 Using DI water)	Standard method 4500-H+
Cation exchange capacity (CEC) (meg/100 g)	Ammonium acetate saturation	Chapman (1965)
Organic Matter (OM)	Acid-dichromate oxidation	US EPA (1986); EPA (2005)
Organic Carbon (OC)	Multiplying the organic carbon by 1.742	US EPA (1986); EPA (2005)
Particle size distribution	Hydrometer method	Sheldrick and Wang (1993)
Sediment texture	Soil/sediment Texture Triangle	Berry <i>et al.</i> (2007)
THg	CVAAS, (SHIMADZU, Spectr. AA 6200), (Lousiana State University)	Gambrell (1991)

Sulawesi sea

Water column: Water samples in the Sulawesi Sea were collected at 4 stations (A6-A9) at mid depth about 100 m from the shore in both summer and rainy seasons. Selected parameters for water quality were measured (Table 3).

Fish: Tuna fish (*Thunnus* sp.) was collected with hook-and-line to complement dock sampling efforts. Five to ten of tuna fish (*Thunnus* sp.) were collected within the specified length range of 35-75 cm as they are widely distributed and available in all seasons and consumed daily by local people. Water and fish samples were analyzed using the same methods as did for those in the aquatic tracks.

THg analysis for water, sediment and biota: All samples were digested for THg analysis by the method used at the Wetland Biochemistry Institute, Louisiana State University (Gambrell, 1991). THg concentrations were determined by Atomic Absorption using CV-AAS (Atomic Absorption Spectrophotometer; SHIMADZU, Spectr. AA 6200) after NaBH_4 (Sodium Borohydride) reduction for total Hg Analysis. The detection limit was 0.001 $\mu\text{g/L}$.

Laboratory quality control: All samples were analyzed at the certified Laboratory of Health in Makassar, Indonesia. In order to have an accuracy in procedures of

analyses, calibrations were done using three replicate samples of standard reference material (SRM 1646a estuarine sediment) from the U.S. Department of Commerce, National Institute of Standard and Technology (NIST), Gaithersburg, MD 20899 and 3 samples of blank. All analyses of parameters were done by three replicates. The method detection limit (MDL) with seven reagent blanks was calculated and used as a tool for verification as well. The calculated MDL in this experiment was of 0.57 $\mu\text{g Hg/L}$. The certified SRM 1646a value is 0.04 $\mu\text{g/g}$ and measured values were 0.0389 ± 0.0078 ($\mu\text{g/g ww}$) with the recovery percentage of 97.25.

Potential environmental risks: The potential environmental risks were determined using a quantitative screening hazard quotient (HQ). Here the estimates of ecotoxicity (dose) to exposure respond is compared to estimate the potential environmental risks. The Hg concentrations in background areas about 15 km upstream and downstream from the area of concern were determined. The ratio of the exposure estimated to the effect concentration considered to represent a safe environmental concentration or screening benchmark is shown in the following formulation (US EPA, 1997):

$$\text{HQ} = \frac{\text{EEC}}{\text{Screening Benchmark}} \quad (1)$$

where, EEC: Estimated (maximum) environmental contaminant concentration at the site; how much contaminant in the soil, sediment, or water (e.g., mg contaminant/kg soil). Screening benchmark = Generally a No-Adverse Effects Level concentration (NOAEL); if the contaminant concentration is below this level, the contaminant is not likely to cause adverse effect. However, If the HQ value is >1 then it indicates the state of risks to the environment (US EPA, 1997).

If: HQ<0.1, no hazard exists HQ 0.1-1.0, hazard is low. HQ 1.1-10, hazard is moderate HQ>10, hazard is high (Lemly, 1996).

Potential health risks:

Provisional tolerable weekly intake (PTWI): The provisional tolerable weekly intake (PTWI) is used to evaluate health concerns of shellfish and fish consumer in study area. The observed levels of contamination need to be assessed in relation to relevant guidelines. The PTWI guideline recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) shows appropriate safe exposure levels to estimate the amount of contaminants ingested over a lifetime without appreciable risks. In the case of Hg, PTWI guidelines for THg recommended at a level of 5 µg/kg bw is used (FAO, 1996). The estimated weekly intakes were calculated using the equation below:

$$EWI = \frac{(C_{Hg} \times Cons_R)}{BW} \quad (2)$$

where, EWI: Estimated weekly intakes, C_{Hg} : Hg concentration in contaminated biota (fish and shellfish), $Cons_R$: weekly consumption of aquatic biota in local community; gram/week and BW: The human body weight (base on 70 kg).

Target hazard quotient (THQ): Consumption of food containing mercury has been identified as a health risk. The U.S. Environmental Protection Agency (US EPA) and the National Academy of Sciences recommend keeping this corresponds to a reference dose (RfD) of THg do not greater than 5.0×10^{-4} µg g/day. Non-cancer risk assessments were typically conducted to estimate the potential health risks of pollutants using the target hazard quotient (THQ). It is a ratio of the estimated dose of a contaminant to the dose level below which there will not be any appreciable risk. If the value of THQ is less than unity, it is assumed to be safe for risk of non-carcinogenic effects. The method is available in US EPA Region III Risk based Concentration as described by the following equation:

$$THQ = \frac{EF \times ED \times FIR \times C}{RFD \times BW \times 10^{-3}} \quad (3)$$

where, THQ: Target hazard quotient, EF: Exposure frequency (365 days/year), ED: The exposure duration (70 years), FIR: The food biota ingestion rate (100 grams/person/day), C: The metal concentration (Mercury), RFD: The oral reference dose ($Hg = 5.0 \times 10^{-4}$ µg/g/day), BW: Average body weight (70 kg), AT: Averaging exposure time for non-carcinogens (365 days/year x ED).

RESULTS AND DISCUSSION

Mercury mass balance: In one process of amalgamation using 20-30 tromols, approximately 50 kg or one sack of mineral ores and 7-10 L of water were filled into each tromol with some strong stones for crushing. Then some leaves of *Mercurialis annua* Hexaploid were added to keep the temperature stable during processing and had been grounded and crushed with circular movements for 3-4 h. Then Hg, exactly of 600 g, was added in each tromol and had been grounded and crushed for another half an hour. Re-milling the concentrate had been operating until the miner noticed that all gold were well extracted. The amounts of mercury used, recovered and released during the process of amalgamation were shown in Fig. 2.

The amalgamation process had been operated about 8-10 h per day using a shifting system (4-5 h in the morning and the afternoon). When it was operated in a set of 20 tromols, unpurified gold of 36 g totally or 1.8 g of gold in each tromol was produced. After squeezing the Hg lost into the atmosphere via open burning process about 2.5 g/tromol, or 2.5 g of Hg lost to produce 1.8 g of gold or 1.25 g of Hg lost to produce 0.9 g of gold (rounded up to 1.3 g of Hg to produce 1 g of gold). If 1.3 g of Hg released per 1 g of gold then the Hg lost could be calculated from the equation of 36 g gold x 1.3 Hg x 4 sets of tromols = 187.2 g of Hg released per the whole group of tromols sets. If all 4 sets of tromols do amalgamation together twice a day it means Hg will be released about 374.4 g/day (in September, 2011). Cumulatively, the anthropogenic due to the Hg used in amalgamation process released annually into the atmosphere in Buladu gold mine and vicinity area approximately about 134.784 g or 135 kg/year. Those mercury releases may run to the environmental compartments both in aquatic systems such as the river, the sea and the living biota and also terrestrial habitats for ground water, agricultural plants, soil and mostly remaining in the atmosphere. However, it was included the Hg discharged into the wastewater and soil prior to open burning process. In addition, in the case of Luwuk Gold Mine area, the Hg used for amalgamation about 8 hour / day using a two system for one group of tromol consist of 15-120 tromols each group. Thus generated a 1.5 g of gold in each tromol was produced due to the limited mineral gold ore available, (Mallongi and Herawaty, 2015).

Table 4: Water characteristics in summer and rainy seasons (September, 2011 and February, 2012)

Stations	Station description	-- Depth (m) --		----- pH -----		Temp. (°C)		Conductivity (µS/cm)		DOC (mg/L)		-- TDS (mg/L) --	
		SS**	RS	SS	RS	SS	RS	SS	RS	SS	RS	SS	RS**
Buladu river													
A1	Upstream, 200 m from A3	1.0	1.0	8.6	7.6	27	22	84	45	7.12	6.12	59	130
A2	Upstream, 100 m from A3	0.9	1.2	8.0	7.0	26	21	71	39	7.48	6.55	36	60
A3	Buladu community centre	0.9	1.1	7.3	7.5	28	23	72	30	6.76	6.12	36	50
A4	Downstream, 100 m from A3	0.9	1.1	7.6	7.5	29	23	71	38	6.76	5.68	36	60
A5	Downstream, 200 m from A3	1.1	1.2	7.4	7.3	30	24	71	31	7.12	5.24	36	60
Sulawesi sea													
A6	About 100 m from A5 in the Sea	40	60	7.7	7.2	33	25	417	56	7.12	6.90	2083	3553
A7	About 500 m from A6 to the East	40	70	7.3	7.0	32	24	595	53	7.48	6.55	2976	4447
A8	About 500 m from A6 to the West	35	75	7.3	7.1	31	22	583	51	7.12	6.90	2916	6316
A9	About 1000 m from A6 to the East	35	75	7.3	7.0	30	21	429	52	6.76	6.55	2143	4290

A1-A5 = Uncontaminated aquatic tracks in Buladu River, A6-A9 = The Sulawesi Sea (100 m from Shoreline), **SS: Summer season = RS: Rainy season

Table 5: Sediment characteristics in summer seasons (September, 2011)

Station	Locations	pH	----- Particle size analyses -----						Sediment texture
			OMI (%)	CEC (meg/100 g)	Sand (%)	Silt (%)	Clay (%)		
A1	Upstream 200 m from A3	6.5-6.9	0.7-0.8	11-12	56-57	21-22	23-24	Sandy clay loam	
A2	Upstream 100 m from A3	6.9-7.2	1.1-4.3	10-16	56-58	22-23	21-23	Sandy clay loam	
A3	Buladu community center	6.9-7.1	1.0-2.8	13-16	66-68	21-22	11-13	Sandy loam	
A4	Downstream 100 m from A3	6.0-6.2	1.2-2.3	11-13	65-66	21-22	13-14	Sandy loam	
A5	Downstream 200 m from A3	7.3-7.4	3.1-3.2	8-9	50-52	37-38	13-15	Loam	

A1-A5 = Uncontaminated aquatic tracks in Buladu River, OMI: Organic matter, CEC: Cation exchange capacity, SS: Summer season

Table 6: THg in water, sediment and shellfish in uncontaminated and contaminated aquatic tracks at Buladu River

Station	Location	Water column (µg/L) n = 3			Sediment (0-10 cm) (µg/kg dw) n = 6			Shellfish (µg/kg ww) n = 15		
		SS	RS	Thg	SS	RS	Thg	SS	RS	Thg
Uncontaminated track										
A1	Upstream, 200 m from A3	41	24	5225	4826	198	141	397	180	
A2	Upstream, 100 m from A3	32	20	5238	5077	215	77	132	119	
A3	Central of Buladu community	35	23	3673	2936	146	60	133	151	
A4	Downstream, 100 m from A3	13	12	1155	1105	184	81	204	153	
A5	Downstream, 200 m from A3	11	8.7	2774	1192	182	36	221	169	
Contaminated track										
A10	Upstream, 50 m from gold factory	123	117	5612	5373	1355	1250	1775	1656	
A11	Central community, gold factory	181	165	7124	6950	1455	1132	1954	1745	
A12	Downstream, 200 m from A11	124	112	4332	4175	1213	1152	1654	1430	
A13	River mouth, 400 m from A11	85	71	4258	3034	1221	1141	1670	1358	
Permitted concentration		2.0	2.0	174	174	100	100	100	100	

*A1-A5 = Uncontaminated track : A10-A13 = Contaminated track. **SS: Summer Season (September, 2011), RS: Rainy Season (February, 2012)

Table 7: Potential environmental risks (HQ) of Hg in the Buladu River (2 tracks) and the Sulawesi Sea in summer and rainy seasons (September, 2011 and February 2012)

Stations	Locations	--- Water column (µg/L) ----		Sediment 0-10 cm depth (µg/kg dw)	
		SS	RS	SS	RS
Buladu river					
Uncontaminated track					
A1	Upstream 200 m from station 3	21	12	30	28
A2	Upstream 100 m from station 3	16	10	30	29
A3	Central Community	18	12	21	17
A4	Downstream 100 m from station 3	6.5	6	6	6.4
A5	Downstream 200 m from station 3	5.5	4.4	16	6.9
Contaminated track					
A10	Upstream, 50 m from gold factory	62	59	32	31
A11	Central community, near factory	91	83	41	40
A12	Downstream, 200 m from A11	62	56	25	24
A13	River mouth, 400 m from A11	43	36	24	17
Sulawesi sea					
A6	100 m from A5 in the sea	1.7	0.4	-	-
A7	500 m from A6 to the East	10	0.6	-	-
A8	500 m from A6 to the West	4.5	0.9	-	-
A9	1000 m from A6 to the East	2.6	0.9	-	-

Screening Benchmark HQ>1 = at risk. A1-A5 = Uncontaminated track, A10-A13 = Contaminated track, A6-A9 = Contaminated track, SS: Summer season, RS: Rainy season

In cases where only a gravity concentrate is amalgamated, losses are normally about 1 to 2 units of Hg for each unit of gold produced, (Telmer, 2006; Patricio, 2009; Mason and Sullivan, 1997; Teran-Mita, 2013) but it can be significantly lower if a Hg capturing system is used when the amalgam is burnt in retorts or fume hoods. For example, in Central Kalimantan, commonly 1.3 g of Hg is consumed to amalgamate 1 g of gold from a gravity concentrate produced by sluicing alluvial ore (Telmer, 2006). In this case 0.3 g of Hg is discharged to water with the tailings and 1 g of Hg is emitted to the atmosphere when the amalgam is burnt and consistent with the consumption of Hg in Brazil as recorded by Sousa and Veiga (Sousa and Veiga, 2007). The ratio of $Hg_{lost} / Au_{produced}$ varies from one operation to another and is very dependent on the type of ore brought by miners and also the amount of gold produced (Patricio, 2009).

Water characteristics: The water characteristics of sea and fresh water in both summer and rainy seasons varied insignificantly at those stations studied and were in the normal range with little variations (Table 4). Two major parameters of pH and DOC that could affect the Hg concentration in water were ranged between 7.3 to 8.6 and 6.76 to 7.48 mg/L, respectively. The highest temperature was found in the sea about 33°C and the lowest one found in the river at 26.2°C. Generally, conductivity and TDS of sea water were significantly higher than those in the river. However, water quality parameters in summer were slightly higher than those in rainy season except the higher values of TDS which resulting from runoff.

In fact, it is the distance from the point source which has contributed a major effect to the elevated THg in each

station. The THg measured in water was merely contributed from wastewater discharge from the centre of amalgamation process as well as dry deposit fall out of emitted source. It may consistent with the transformation process of Hg^0 (g-gas) to Hg (II) and Hg (II) (p-particulate) in turbid water by which anthropogenic sources of Hg^0 to air can generate in Hg deposition to both land and water (USGS, 2007). Hg^0 is produced in freshwater by the process of humic acid reduction of Hg (II) or demethylation of MeHg mediated by sunlight. Hg^0 can be found either in liquid or dissolved forms in aquatic systems (Amyot *et al.*, 2005).

In addition, in rainy season, pH (ranged from 7.0 to 7.6) were a little bit lower than those in summer season. DOC (ranged from 5.24 mg/L to 6.90 mg/L) as well as temperature of 20°C at all stations where the highest one was found at station A6 with temperature of 25.2°C in the sea and the lowest one was found at station A9 (21°C). Similarly, conductivity and TDS were significantly different between river and sea water samples (Table 4).

Sediment characteristics: Sediment characteristics were investigated only in the river, in summer. pH, was in the normal range from 6.0-6.2 to 6.9-7.2. Organic matter, the major characteristic concern in Hg concentration in sediment, was found higher than 3% at stations A2 and A5 with the values of 4.3 and 3.2%, respectively. Less of organic matter at the other stations mainly due to runoff with high flow rate from the ore separating site.

Likewise, cation exchange capacity (CEC) was found in the range of 8-9 to 13-16 (meg/100 g), respectively. The results were slightly different from each stations

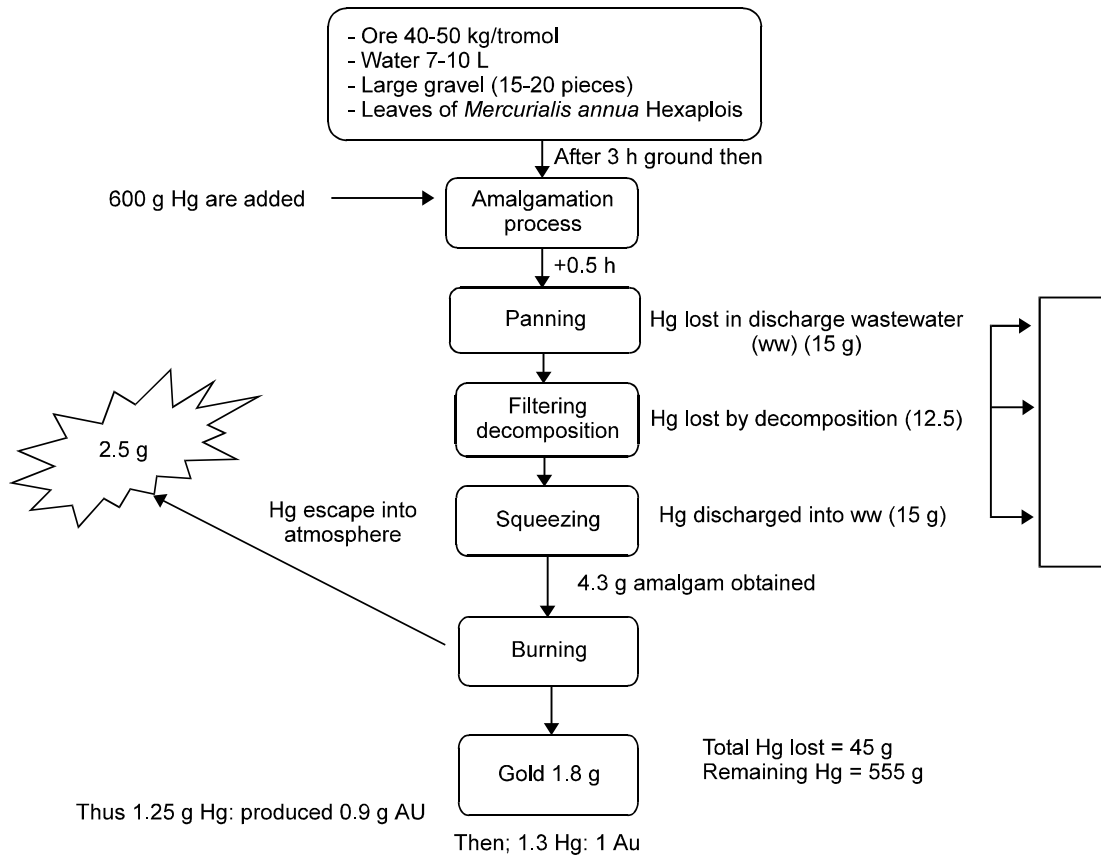


Fig. 2: Mercury mass balance of amalgam gold recovery in Buladu gold mine

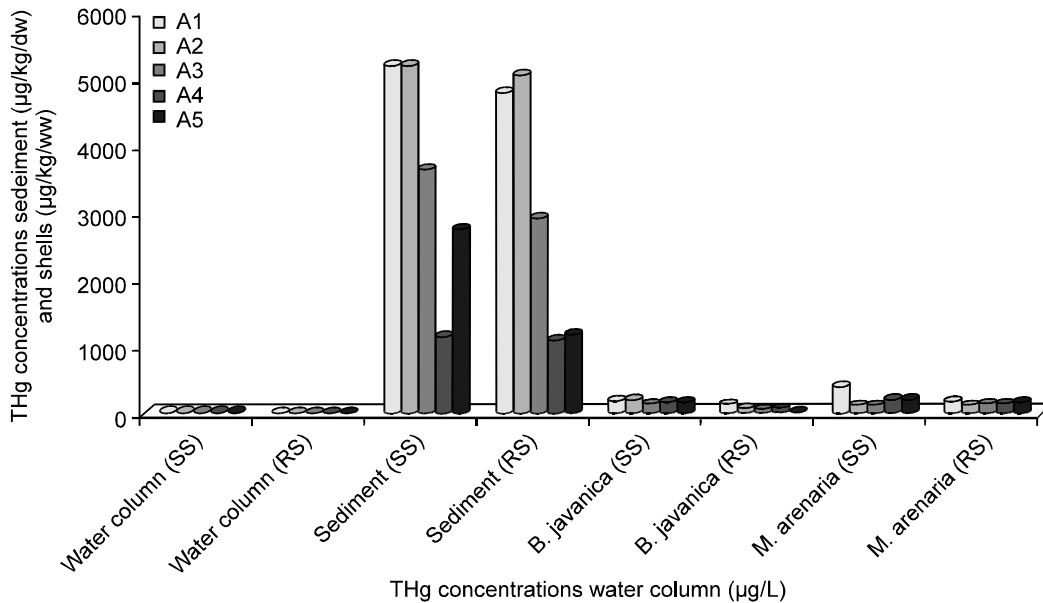


Fig. 3: THg in water, sediment and shellfish in uncontaminated aquatic tracks of the Buladu River. A1-A5 = Uncontaminated track, SS: Summer season (Sep. 2011), RS: Rainy season (Feb. 2012)

resulting from the hilly geographic area. Generally, in flat areas the CEC mostly found lower.

Sediment texture of the Buladu river was investigated and found that the content of the sediment has much of

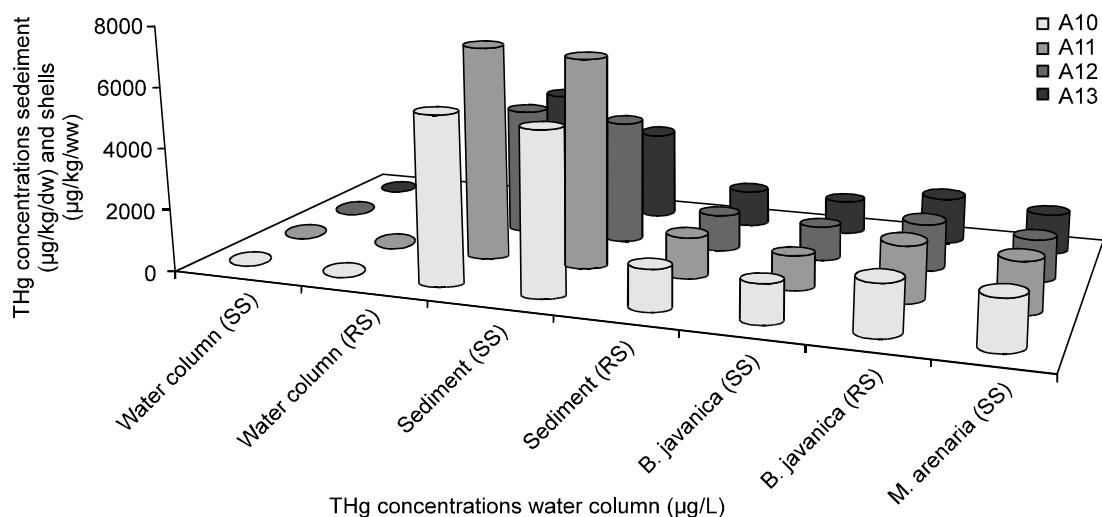


Fig. 4: THg in water, sediment and shellfish in contaminated aquatic tracks of the Buladu River. A10-A13 = Contaminated track. SS: Summer Season (Sep. 2011), RS: Rainy season (Feb. 2012)

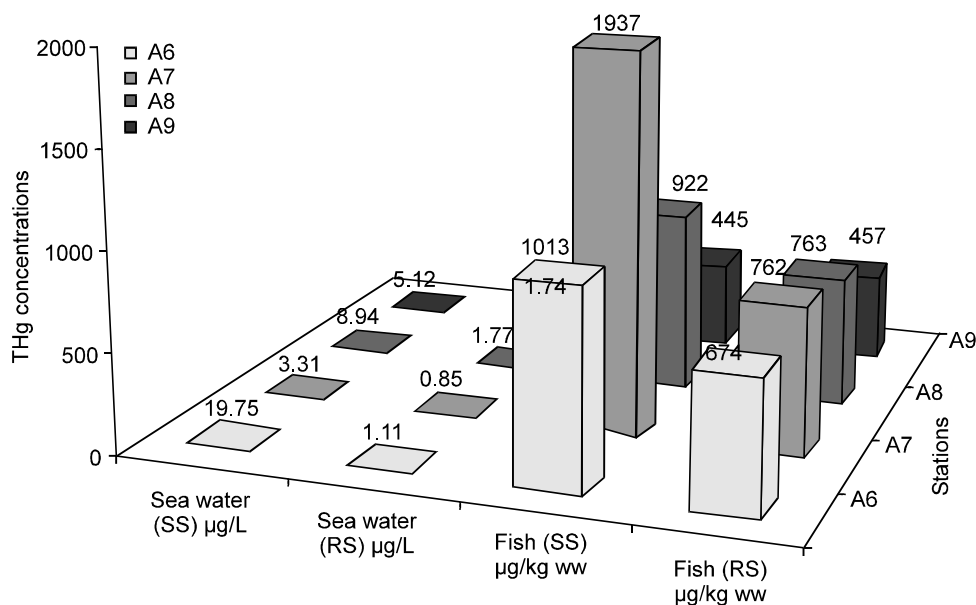


Fig. 5: THg in sea water and tuna fish in the Sulawesi Sea in summer and rainy seasons (September, 2011 and February 2012). SS: Summer season, RS: Rainy season

sand which nominates the percentage in the range of 50-52 to 66-68%. Higher content of sand mainly come from the material and mineral ore that was disposed into the water bodies as a result of gold ore separation processing at stations A1-A4. At the river mouth, the greater silt loam containing sediment was reflecting the original material of the estuary. Silt however, at all stations has a lower content within the range of 21-22 to 37-38% whereas clay content was ranged from 11-13 to 23-24%, respectively.

THg in the buladu river

THg in water column: THg concentrations in the river were moderately high elevated upstream at stations A1 with the concentrations ranged of 32-41 µg/L and 20-24 µg/L in summer and rainy seasons, respectively. Lower concentrations were found downstream at stations A5 with the concentrations ranged of 11 µg/L in dry season and 8.7 µg/L in rainy season, respectively. All those stations have exceeded the value of maximum contaminant level (2.0 µg/L) accepted by the U.S. Environmental Protection Agency (USEPA). At station A1

Table 8: Estimated Weekly Intake (EWI) of Hg through consumption of shellfish and fish in summer and rainy seasons (September, 2011 and February, 2012)

----- EMI for shellfish -----									
Bellammya javanica (µg/kg ww)					Mya arenaria (µg/kg ww)				
Stations	Locations (Buladu river)	SS	RS	SS	RS	Stations	Locations (Sulawesi sea)	SS	RS
A1	Upstream, 200 m from A3	2.97	2.11	5.96	2.69	A6	About 100 m from A5 in Sea	20	13
A2	Upstream, 100 m from A3	3.23	1.16	1.97	1.97	A7	About 500 m from A6 to East	39	15
A3	Central community	2.19	0.90	2.00	2.26	A8	About 500 m from A6 to West	18	13
A4	Downstream, 100 m from A3	2.76	1.22	3.05	2.29	A9	About 1000 m from A6 to East	8.90	9.13
A5	Downstream, 200 m from A3	2.73	0.54	3.31	2.54	-	-	-	-
----- Permitted concentration (FOA, 1996) -----									
SS: Summer season, RS: Rainy season									
----- PTWI 5.0 µg/kg/bw for Bivalve and fish -----									

Table 9: Target hazard quotient (THQ) for Hg through consumption of shellfish and tuna fish in summer and rainy seasons (September, 2011 and February, 2012)

----- EMI for shellfish -----									
Bellammya javanica (µg/kg ww)					Mya arenaria (µg/kg ww)				
Stations	Locations (Buladu river)	SS	RS	SS	RS	Stations	Locations (Sulawesi sea)	SS	RS
A1	Upstream, 200 m from A3	0.06	0.04	0.11	0.05	A6	About 100 m from A5 in the Sea	0.36	0.24
A2	Upstream, 100 m from A3	0.06	0.02	0.04	0.03	A7	About 500 m from A6 to the East	0.69	0.27
A3	Central community	0.04	0.02	0.04	0.04	A8	About 500 m from A6 to the West	0.33	0.24
A4	Downstream, 100 m from A3	0.05	0.02	0.06	0.04	A9	About 1000 m from A6 to the East	0.16	0.16
A5	Downstream, 200 m from A3	0.05	0.01	0.06	0.05	-	-	-	-
----- Permitted concentration -----									
THQ>1 = at risks									
SS = Summer season, RS = Rainy season									

and A2 the THg concentrations were significantly high elevated due to the closer distance to the gold mine and amalgam processing centre. A relevant study associated with THg accumulation in the area near gold mine in Asturias in Spain, showed that THg concentrations in the local stream varied from <0.5 to 90.8 g/L and tended to elevate near point source (Loredo *et al.*, 2006). Samples from the Idrija Rivers in Slovenia showed the clear evidence of contamination that Hg levels raised up to several hundreds of ng/L even in downstream away from main point sources (Bonzongo, 2002).

THg in sediment: The magnitude of THg concentrations in sediment had a similar trend with those in surface water. Elevated THg in uncontaminated track at A1 and A2 were considerably high with the concentration of 5225 and 5238 µg/kg dw in summer season and also 4826 and 5077 µg/kg dw in rainy season, respectively. Likewise, in contaminated aquatic track at A10 and A11, sediment THg concentrations were very high ranged from 5612 to 7124 µg/kg dw and 6950 to 5373 µg/kg dw in summer and rainy seasons, respectively. These high elevated concentrations could be explained by the historical function of this river in the past. This site has been used as a part of panning activity by those miners in the area and located close to amalgamation centre (Department of Mining and Forestry, 2008) in addition, the elevated concentration on sediment due to the slow flow as particulate matter contained Hg settled out and accumulated on the bottom in higher size. Thus, the Hg in sediment may not be easily remobilized back to the water due to the accumulated heavier clay texture (USGS, 2003; Pataranawat *et al.*, 2007). Relevant reported study in the Songhua River in China, mercury distribution resulting from the gold mining activities were found that in sediment>soil>plant>water and this indicated the concentration of atmospheric mercury in summer was higher than that in autumn (Zou, 2010). Also, a significant positive relationships of mercury bioaccumulation with intensity of hydraulic gravel mined were found in the Sierra Nevada (Hunerlach *et al.*, 2005).

THg in shellfish: In summer season, *B. javanica van den bush* and *M. arenaria* were the major species of shellfish found in this area and analyzed for THg accumulation. *M. arenaria* and *B. javanica van den bush* with sizes ranged from 5-9 cm long and 6-12 cm long, respectively, were collected randomly in the sampling plot of 30 m² for 15-20 individuals. The results showed that the accumulation of THg in *B. javanica* from uncontaminated track at A2 was highly elevated with the value of 215 µg/kg ww compared to the lower contaminated station at A3 (146 µg/kg ww) and had no any significant difference (Table 3). Likewise, *M. arenaria* at station A1 had the highest THg concentration (397 µg

kg ww) which was twofold when compare to the lowest values of 132-133 µg/kg ww at stations A2 and A3 with significant difference. All stations in contaminated track, A10 to A13, THg concentrations in shellfish for *B. javanica van den bush* and *M. arenaria* have far exceeded the guideline of 100 µg/kg ww (Table 6).

This study suggested that the elevated THg concentration and accumulation in shellfish decreased as increasing distance from point source. Stations A1 and A2 as the nearest points to the workplace (tromol processing centre) have the highest THg concentrations. The results obviously confirmed that the closer of distance from the point source, the higher of THg in shellfish accumulation. It is also revealed that THg and methyl-Hg contents in sediment and water were elevated over local uncontaminated baselines. In addition, THg (10-930 ng/L) and methyl-Hg (0.02-3.8 ng/L) were found highly elevated in mine water (Gray, 2002).

THg accumulation in shellfish has linear association with the THg concentration in water and significant correlation with those in sediment as well (Fig. 3 and 4). Both species of *Bellamny javanica* and *Mya arenaria* contained elevated Hg levels that were consumed by local people in Buladu and surrounding as food sources. This result was relevant with the study in the Phanom Pha gold mine, Thailand with high elevated THg in water (0.4 to 4 µg/L), sediment (96 to 402 µg/kg) and bivalve (15 to 584 µg/kg) at the mining operation site and were much higher than those stations outside the work place (Pataranawat *et al.*, 2007).

THg in the sulawesi sea

THg in sea water: THg concentrations in sea water at mid depth about 17-20 m depth at station A6 to station A9 were varied with the values of 3.3, 5.1, 18.9 and 19.8 µg/L in summer and 0.9, 1.1, 1.8 and 1.7 µg/L in rainy season, respectively. Of those four stations in the Sulawesi Sea, the highest THg concentration was found at the river mouth with the value of 19.8 µg/L. This THg concentration is above than what would be expected since the accumulation of THg in the sea usually lower with the respect of the mobilization of pollutants. This finding was insignificantly difference from the study of THg concentrations in the Napoleon Gulf with the averaged of 4 ng/L at 13 m depth and 0.3 ng/L in the Michigan Lake (Mason and Sullivan, 1997; Ramlal, 2003).

THg in fish: THg concentrations in fish were ranged from 445 to 1937 µg/kg ww and 457 to 762 µg/kg ww in summer and rainy seasons, respectively. The highest THg concentration in the biggest fish was in fact forth folds than the national standard. The results revealed that accumulation of THg in fish tended to be higher in bigger fish both in summer and rainy seasons compare

with the smaller one due to the biomagnifications level in their life span of higher trophic level. It was then followed by the closer stations at the river mouth where Hg contaminated waste and wastewater from some panning activities and tailing at tromol centre discharged directly into the receiving river to accumulate in sediment. Consequently, the elevated Hg level in the sea was generated.

This result is consistent with the report of the Rio Ramis-Lake of the Titicaca Watershed, Peru, that mercury levels of pejerrey fish increased with its size, although this relationship was less apparent for the smaller carachi fish. Approximately, 27% of pejerrey and 75% of carachi had the accumulation exceeded the US EPA fish tissue-based water quality criterion level of 0.30 µg/g (Gammons, 2006). In addition, initial study also revealed that the elevated mercury concentrations in fish muscle were positively correlated with sediment mercury concentrations (Munn and Short, 1997). Tuna fish containing high elevated Hg concentration found in this area are consumed by local people as the main protein sources. Results from the analyzed THg and health risk assessment suggested that the fishes living in the sea near the artisanal gold mine would not be safe for consumption among community in the area. Almost the fish samples from stations of the Sulawesi Sea (except station A9) exceeded Indonesian National Standard guidelines for human consumption (0.5 mg/kg) and the WHO recommended limit for vulnerable groups (0.2 mg/kg). The bigger the fish size, the higher the Hg concentration in tuna fish. This is relevant with the survey in the Atlantic Ocean where Hg levels were positively correlated with the length of fish in populations of freshwater piscivore fish such as *Serrasalmus rhombeus*, *Hoplias malabaricus* and *Plagioscion squamosissimus* and also in estuarine species as *Arius couma*, *Cynoscion virescens* and *Macrodon ancylodon* and also in marine such as *S. guachancho* (Mol, 2001). Mercury also contaminates water as metallic liquid (Hg⁰), which is trapped in sediments as inorganic mercury. In anaerobic conditions, it can be biotransformed to organic mercury compounds (e.g., MeHg and monovalent MeHg) by sulfate reducing bacteria (Compeau and Bartha, 1984; Mercury Source Protocol, 2008). Hg bioaccumulation sequences might occur as it is known that organic mercury can be taken up from sediments by phytoplankton, which are eaten by invertebrates and small fish, which at the end are eaten by large predatory including fish. Next, in this way mercury is transported through aquatic food chains from sediment to humans. Another potential way of bioaccumulation is the runoff water from soils containing mercury is an important source of mercury to fish life span transformation (Mercury Source Protocol, 2008; Lindqvist, 1984). Particularly, the organic form (MeHg) is bioavailable and accumulates in fish through the aquatic

food web and nearly 100% of the mercury found in fish muscle tissue is methylated (Bloom *et al.*, 1991). Moreover, accumulation of THg through food chain also due to the accumulation in sediment, as it play a key role in controlling the metal including Hg concentration in biota, (Lasut and Yasuda, 2008; Blanchette, 2001) this led to accumulation in the marine biota of the sea. The sources of THg included indirect deposition from watershed runoff, direct atmospheric deposition, point sources and internal recycling mechanisms such as sediment resuspension (WHO, 2004).

Potential environmental risks: Potential environmental risk assessment was calculated using hazard quotient (HQ) equation. The objective of this evaluation earmarked for the estimation of potential environmental risks to the receptors that were performed in both terrestrial and aquatic habitats. For sediment in this study, the screening benchmark accepted by Canadian environmental standard was used with the maximum limit of 174 µg/kg dw (Environment Canada, 1995).

The results revealed that high elevated Hg for water column in the Buladu River were accumulated in most of the stations (A1-A4) in summer and exceeded the screening benchmark value (2.0 µg/L) whereas in rainy season the measured values were found lower than the standard (except in A2). It was indicated that the Hg distribution in this area was initiated by the disposal tailing waste from the gold recovery process that directly released Hg containing wastewater into the river as well as Hg emission from open burning of amalgam and the fall out of atmospheric dry deposition. In addition, Hg accumulation in the sediment tended to be correlated to the Hg in water (Acquavita, 2012). At the river mouth, the Hg accumulation is obviously high with respect of the long period of Hg exposure of the sediment. The results showed that the potential environmental risks in water column of both uncontaminated and contaminated aquatic tracks were ranged from 6 to 21 and 43 to 91 in summer season and also 4 to 12 and 36 to 83 in rainy season, respectively. All stations indicated high values of Hg and were at risks (HQ>1) particularly in the contaminated track. Likewise, Hg concentration in sediment in the study area exceeded the standard accepted by the Canadian (174 µg/kg dw). This level lead to toxicological effects on sediment that might be biological significance. The sediment characteristics with consideration at site that pH ranged from 6.2 to 7.3, OM within the range of 0.7 to 4.3 clay content with 11 to 50% provided adsorption ability for Hg in less toxic to living organisms. In addition, all HQ values of water column in the Sulawesi Sea in summer season exceeded the risk standard, it were ranged from 1.7 to 10.0 whereas in rainy season, however, the values were lower within the range of 0.4 to 0.9, respectively.

Potential health risks

Estimated weekly intake (EWI): The provisional tolerable weekly intake (PTWI) guideline recommended by the Joint Food and Agriculture Organization (FAO)/the World Health Organization (WHO) Expert Committee on Food Additives (JECFA) shows appropriate safe exposure levels of 5 µg/kg bw, which were used to estimate the amount of contaminants ingested over a lifetime without appreciable risk among people living in there (FAO, 1996; IPCS, 1991). In the area of study, local people consume shellfish and fish as the main source of protein daily and the average daily intake for the adult in the region is 350 g shellfish per week and tuna fish 700 g per week. In comparison with other foods, tuna in the Sulawesi Sea accumulate the high elevated concentration of THg and all values have exceeded the PTWI guideline. It indicated that those people who consumed fishes in the area of concern might be posed to the risks. Fortunately, the Hg accumulated in shellfish was still less than the guideline and there is no risk to consume with.

The estimated PTWI concentration of THg in shellfish and fish in two seasons showed the magnitude of EWI of *B. javanica*, *M. arenaria* and *T. sp* consumption per week for body weight of 70 kg in the range of 2.19 to 3.23 µg/kg bw, 1.97 to 5.96 µg/kg bw and 8.90 to 39 µg/kg bw in summer season, respectively. Likewise, the EWI for this biota were 0.54 to 2.11 µg/kg bw, 1.97 to 2.69 µg/kg bw and 9.13 to 15 µg/kg bw in rainy season, respectively. Of those two different shellfish, none of them was higher than PTWI level in rainy seasons. However, the value of EWI for *M. arenaria* at station A1 was higher than the guideline in summer season. Most of these values indicated that they are still safe and might not be at risk except those at station A1. By contrast, almost all the degree of EWI for *T. sp* both in summer and rainy seasons exceeded the standard (>5 µg/kg/bw) and indicated a risk for consumption. Relevant association study by Hines and Gray (2005) suggested that fish samples collected in the areas of artisanal gold mining contain THg concentrations >4.0 µg/g, significantly have exceeded the 0.5 µg/g safe level recommended by the WHO for human consumption of fish (Hines and Gray, 2005).

Target hazard quotient (THQ): The results showed that the highest THQs were 0.06 for both *Bellamnya javanica* and *Mya arenaria* in summer season whereas the lower values of 0.04 and 0.05 were found in rainy season, respectively. Likewise, the higher THQ values of fish were found in the values of 0.69 and 0.27 in summer and rainy seasons, respectively (Table 9). Although these values are still less than 1, the potential risks might be posed due to the continual bioaccumulation and long term exposure. Similar experience was found in municipality of Montecristo, Colombia, which the THg

mean level for all fish samples (0.407±0.360 µg/g ww) did not exceed the recommended limit ingestion level. However, the risk assessment based on the hazard index was suggested that a fish intake of 0.12 kg/day could increase the potential health effects related to Hg exposure in the local human population (Marrugo-Negrete *et al.*, 2008).

In addition, limited consumption of shellfish and fish from mercury contaminated water was recommended because most current health risks associated with seafood safety originate in the environment. It is in fact that absolute residue limits are difficult to derive because of the lack of direct evidence for critical levels in seafood. Since the HQ of majority of tuna fish exceeded current human health criteria for Hg, the contaminated fish consumption from the Sulawesi Sea which was the main route of human exposure appears to be risky for human health (Ullrich, 2007). The magnitudes of detectable Hg concentrations were used to estimate potential total lifetime cancer and non-cancer risks based on scenario of an exposure of one meal per week.

Fish consumption level data can be procured and evaluated for potential risk. It may be advisable to alert the people to consume the smaller fish with respect of the biomagnifications factor as well as the recommendations for optimizing monitoring and outreach to the concerned local government (Watanabe, 2003; Katner *et al.*, 2010). The positive correlation between fish length and Hg contaminated concentration is well established. Fish consumption showed a positive relation and so did occupation, particularly in small-scale gold mining (Barbieri *et al.*, 2009). Another potential risk which remains to be assessed is the possible runoff transfer of Hg-rich particles from the upper layer soil to downstream aquatic habitats during rainy season (Guedron, 2013). Further studies focusing the long term exposure and measurement repetition still need to be delivered.

Conclusion: The presence of THg in aquatic habitat is the primary environmental concern due to its accumulation in all environmental compartments and the potential impact to environment and human surrounding the gold mine. High elevated THg concentrations were found in living organisms in aquatic ecosystems such as water, sediment, shellfish and fish near and adjacent to the mining area. Also, all of those aquatic contaminated food sources that are consumed by local people are also sold out to other provinces. Furthermore, the elevated THg concentrations might be found in the long distance vicinity areas which the accumulation of Hg in aquatic biota can be merely generated from the Hg dry deposit as a result of atmospheric fall out that occur continuously.

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