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Analysis of Mercury Concentration on The Water and Sediment at Tiabo River, Roko, West Galela District, North Halmahera

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ABSTRACT

Gold mining activity at Tiabo river in the North Halmahera causes the water on the river is contaminated by mercury. The contamination mercury on the water can damage food chain and adverse consequences toward health of people, fish, and so on. The purpose of this study is to obtain the concentration of mercury contamination that was caused by gold mining activity. The water and sediment sample was obtained by purposive sampling. The characterization of concentration mercury in the water and sediment using mercury analyzer HG-300 in the wave length 253.72 nm. The result shows that mercury concentration of the water in the six and five sample point in the rainy session and the dry session respectively is <0.66 µg/L, and the mercury concentration in the sediment shows that the lower value in the upstream river was 1.2 mg/kg and the higher concentration in the middle of river was 8.94 mg/kg respectively in the rainy session. The result indicates that the contamination mercury in the moderate danger level according to the IADC/CEDA data standard.

Keywords: mercury, contamination, sediment, water, Tiabo river

INTRODUCTION

Mercury (Hg) is the volatile metal, dissolved in the water and fat. Hg is a liquid at 25°C, being odorless and toxic gas [1]. Mercury contaminate in environment can cause toxicity, bioaccumulation, and biomagnification that damage environmental and human health [2,3]. The organic mercury is more hazardous than inorganic mercury [4]. Organic mercury can damage food chain and adverse consequences toward health of people, such as brain cell damage, through the placenta that cause the children born with disabilities. Inorganic mercury causes damage to the liver and kidneys, while mercury vapor can damage the lung [5].

Even though the mercury is harmful, the gold miner has been using the mercury on the gold mining area using amalgamation methods. This activity causes mercury contaminate in the environmment. The nature of the heavy metal is easy to stick and settle down on the waters. And the concentration mostly depends on the physical, chemical and biological conditions [6]. According to Wilken and Hintelman [7], heavy metal concentration in the water lesser than that in the sediment. It occurs due to the heavy metal in the water is more dissolved and it acumulate on the sediment.

Tiabo river is the source of the potential water as a support system for community life in the Roko district. It is about 1.000 people living there. The Tiabo river has been recentlty used

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for taking a bath, fishing, and consuming. The case of fish death was happened over the time [8], and also skin diseases caused by consuming of the water from Tiabo river. These cases were suspected by contaminated of water by mercury in the area of gold mining. The local industries apply mercury during the amalgamation process [9]. The leaching of mercury into environment damages the ecosystem of the Tiabo river. This paper will be discosed our recent investigation toward mercury content that contaminate the water source and sediment in the Tiabo river ecosystem.

EXPERIMENT

Sampling area

Water and sediment sample were collected both in rainy and dry season. On rainy season, samples were taken on June 2019 at Tiabo river area (Figure 1). Six water samples were collected in the point area S1, S2, S3T1, S5T1, S6T1, and S7T1. Meanwhile, three sediment samples were collected from upstream area (S1), central stream area (gold mining area) (S2), and downstream area (S3). Water samples on dry session were taken at five sample points, i.e. S3T2, S4, S5T2, S6T2, and S7T2 (Figure 1). Detailed coordinates are displayed in the Table 1. The samples were stored at a cool box in 4 ^{o}C before further analysis in the laboratory.

Tabel 1. The detailed coordinates for water and sediment sampling locations

No	Sampling location	Coordinate points		Description
The water samples				
1	S1	01°49’37.0” N	127°41’35.8” E	Upstream
2	S2*	01°49’46.9” N	127°41’47.9” E	River branch
3	S3T1 dan S3T2**	01°50’40.905” N	127°43’49.973” E	After Branch
4	S4***	01°51’25.5” N	127°45’02.1” E	Gold Mining Area 1
5	S5T1 dan S5T2	01°51’31.9” N	127°44’54.5” E	Gold Mining Area 2
6	S6T1 dan S6T2	01°51’31.4” N	127°45’28.7” E	Society activity location
7	S7T1 dan S7T2	01°51’42.432” N	127°45’39.982” E	Downstream
The sediment samples				
1	S1	01°49’37.0” N	127°41’35.8” E	Downstream
2	S2	01°51’31.9” N	127°44’54.5” E	Middle
3	S3	01°49’46.8” N	127°41’49.0” E	Upstream

Note: S2* (dry season), **S3T2 (upstream in the dry season), and S4*** (strong stream area in the rainy season)

Chemicals

The chemical used for research was potassium permanganate (Merck), hydroxilamine hydrochloride (Merck), tin dichloride (Merck), nitric acid (Merck) and perchloric acid (Merck). The inorganic mercury solution in stock standard was prepared from mercury chloride (Merck) solution in 100 ppm.

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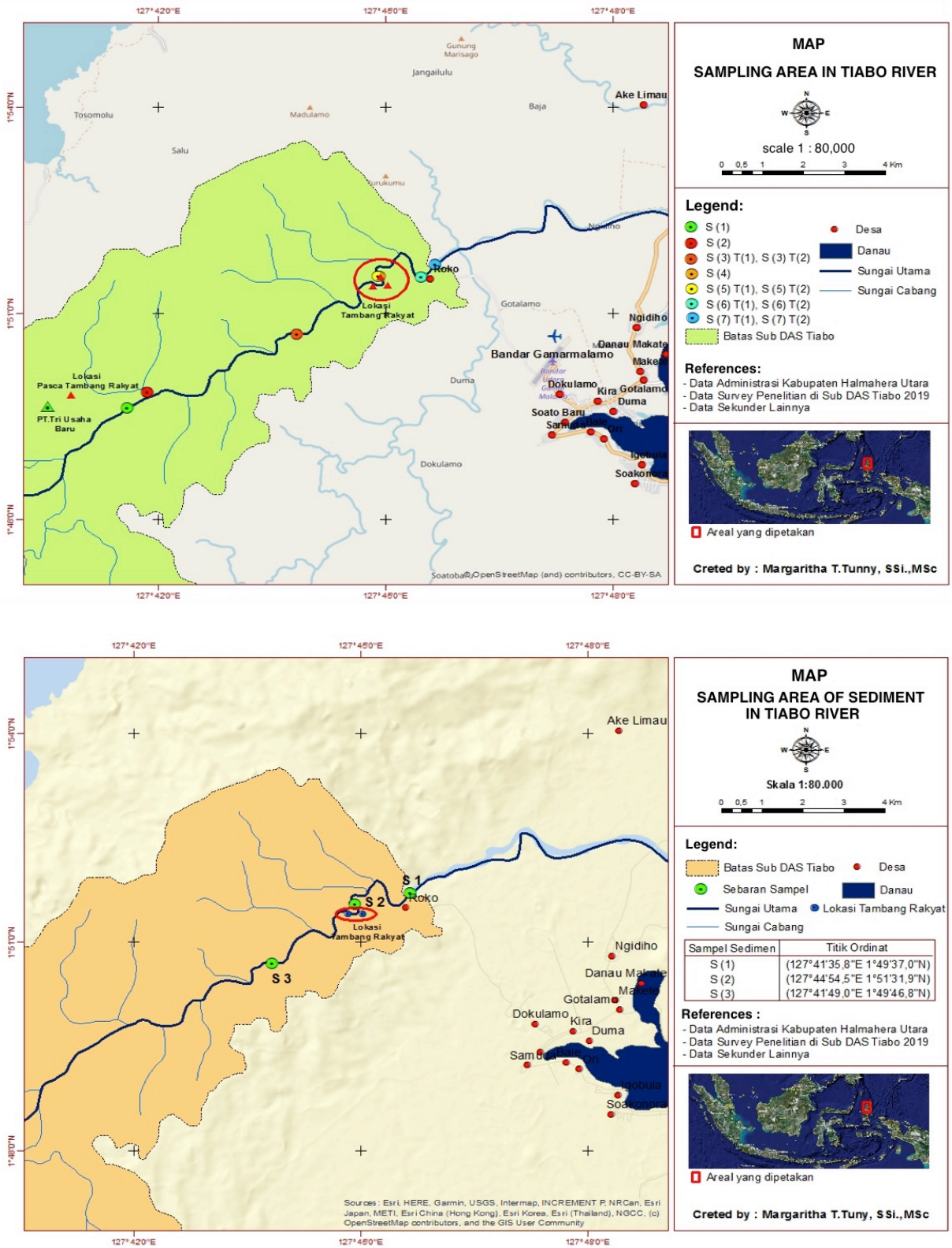

Figure 1. The map for sampling location in the Tiabo river. Sampling points for water sample (above) and sediment sample (below).

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Instruments and tools

Several instruments for analysis applied for research was mercury analyzer HG-300, analytical balance, digital pH-meter (YSI TruLab pH-1110), turbidity analyzer (Palintest) and BOD analyzer (Hanna Instrument HI-98186), hygro-thermometer, global positioning system (GPS, Garmin type 12 XL), and cool box with dry-ice blue.

Temperature measurement

The mercury thermometer (100 °C) was dipped in the river water samples, mercury will move. Wait a few moments until the mercury stops moving and shows a fixed number in the scale.

The pH measurement

The pH measurement was carried out in- and ex-situ based on the Indonesian National Standard (SNI number 06.6986.11.2004). The in-situ measurements were carried out directly at the location or at the time of sampling. The pH meter was cleaned and washed with distilled water, then it was dipped in water sample. The number provided was recorded. The ex-situ measurements were carried out in the laboratory. The sample was analyzed using similar procedure to the in-situ technique.

The dissolved oxygen (DO) measurement

The measurement of DO parameters was carried out ex-situ by dipping platinum rod from BOD analyzer (HI 98186) into water sample. The value was recorded from the display.

Standard solution of mercury

Working mercury standard solutions were prepared freshly. A 1.0 mL of mercury stock solution (100 ppm) in 100 mL of the volumetric flask was added with distilled water until the line. Then, 0.1 mL from this solution was further diluted to 10 mL in a volumetric flask. It was a 10 ppb of mercury solution. Several different mercury concentrations were prepared using similar procedure to produce mercury with concentrations 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, and 3.2 ppb, respectively.

Water sample preparation

The water sample in volumetric flask was filtered out using 0.45 µm filter sieve. Then, 10 mL of the sample was added into 0.1 mL of 0.1% potassium permanganate solution ($KMNO_4$), and stirred until homogeneous. This mixture was added with 0.1 mL of 10% hydroxylamine hydrochloride ($NH_2OH.HCl$) solution, 0.5 mL of 10% tin dichloride ($SnCl_2$) solution. This mixture was stirred until homogeneous, and further analyzed using mercury analyzer HG-300 [10].

Sediment sample preparation

A gram of sediment sample in 100 mL-erlenmeyer was added with 10 mL of a mixture solution of nitric acid-perchloric acid with 1:1 (v/v) in ratio. The samples were heated a clear solution was achieved. Then, it was filtered off using a filter paper 0.45 µm and added a 50 mL sample solution into volumetric flask. A sample aliquot was taken in vial tube, and was prepared for further mercury analysis. The procedure analysis was similar to that undertaken for the standard mercury sample [14].

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Table 2. Criterion for mercury content in sediment and its level value [13]

Heavy metal	Target level	Limit level	Verification level	Intervention level	Dangerous level
Mercury concentration (ppm)	0.3	0.5	1.6	10	15

Note: The mercury concentration contained in the sediment on the target level means its concentration value below the value is safe for environmental. The limit level means the maximum value that mercury still safe or allowable risk for human and environment. Verification level is the concentration of mercury contained in the sediment or water sample can affect negatively to the water environment. It is a medium level of mercury contamination. Moreover, for mercury concentration below in the intervention level that it has strong pollution in the sediment. Meanwhile for dangerous level is the concentration of mercury in that value seriously harmful and dangerous for both human and environment.

RESULT AND DISCUSSION

The variable of water environment

The sample collection for measurement of water quality parameter at Tiabo river in the rainy season was undertaken in six location points (S1, S2, S3T1, S5T1, S6T1, and S7T1). Collection in dry session was undergone at five location points (S3T2, S4, S5T2, S6T2, and S7T2). Meanwhile, for sediment samples were obtained in the rainy session was taken in three location points include upstream, middle stream or gold mining area, and the downstream region.

During the field sampling in Tiabo river, location temperature was recorded in about 30-31 ^{o}C, however the water temperature was recorded between 28.0 ^{o}C and 29.7 ^{o}C (Table 3). This value was within the standard temperature allowed according to the government regulation [11]. Include for dissolved oxygen and the pH level in the water. The DO was recorded in between 6.3 mg/L and 6.6 mg/mL, meanwhile the pH value was detected in the neutral level (pH 7.5- 7.8). Temperature, pH and dissolved oxygen were factors that affect the amount of mercury in the waters. According to Schuhmacher et al. [12], mercury concentrations in water tend to be at higher concentration in the lower temperature (<25 °C) compared to it in higher temperatures (> 25 °C).

Table 3. Data on environmental quality parameters of the waters at each sampling location

Location	Temperature (°C)	pH	Dissolved oxygen (DO) (mg/L)
S1	28.0	7.8	6.5
S2	28.2	7.5	6.3
S3T1	28.0	7.8	6.6
S3T2	28.4	7.8	6.6
S4	29.3	7.8	6.5
S5T1	29.7	7.8	6.6
S5T2	29.7	7.8	6.5
S6T1	28.6	7.8	6.6
S6T2	29.7	7.8	6.6
S7T1	29.7	7.8	6.6
S7T2	29.7	7.8	6.6

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Mercury concentration in the Tiabo river

The gold miners live around the Tiabo river in the Roko village since 2015 until 2019 in average about 200 people. In total, it was 120 drum containers used for amalgamation process to separate gold. The mercury concentration each container was 55-99%, and mostly the 99% mercury was preferred for high yield gold separation. Each process, the gold ore requires 2-3 kg of mercury. After this process, in average 6-10 gram of reduced weight of gold ore was resulted. However, it was also disposed the aqueous mercury waste into the ponds or an open waste storage area. The location is 3-5 m from Tiabo river area. Every 6-month the disposed mercury waste about 2-3 kg, and every period of time, the pond was full of mud or sediment. Then, the muds were displaced into surrounding area to the ponds. During rainy season, the muds was hit by flood and flow into the Tiabo river.

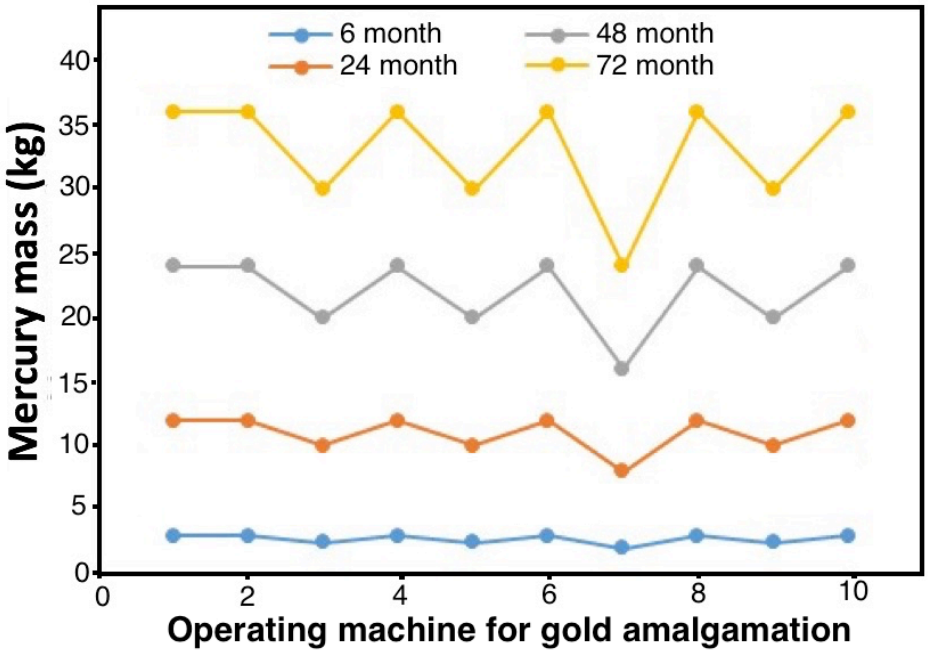

Figure 2. The estimated mercury waste disposed during gold mining activity around the Tiabo River in Roko Village

In Figure 2 is showed the estimation for mercury concentration wasted into the environment. The calculation based on the statistical approximation that each drum container was operated by processing machine in every 6-month produces 2-3 kg of mercury waste. Then, in 24, 48, and 72 months could result 8-12 kg, 16-24 kg, and 30-36 kg of mercury waste. It occurs along the years. The amount of mercury in each machine depends on the amount of mercury used by miners on each machine in the amalgamation process. The lowest amount of mercury is found in machine 7. In average, it uses a 6 kg of mercury for six months, followed by machine 3, machine 5 and 9 with an average usage each machine is 2.5 kg per 6-month operation.

The result for mercury analysis from the water sample collected in the location is summarized in Table 3. The collection was undertaken in both dry and rainy season. It shows that mercury concentration detected has the similar value. The concentration detected in all samples were below the 0.06 µg/L. Each sample was analyzed three times by mercury analyzer

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and obtained the concentration average <0.66 µg/L. This value still below the value regulated by the government. The maximum limit of mercury concentration in class II of water was 10.002 mg/L [11].

The lower of mercury concentration in Tiabo river was predicted due to the reduction process of mercury in wastewater. The reduction could occur through the settling process during the storage. The wastewater tanks or ponds were arranged in a series structure. The density of mercury 13.6 g/cm^3 is greater than the density of water 1 g/cm^3. The mercury will be settled down and adsorbed to the sediment or mud in the pond. In the rainy season, the waste pool over flows and enter the Tiabo river. However, the mercury concentration in the wastewater has been reduced by the dilution in the river, and gradually the mercury concentration decrease along the river [16]. It was also predicted that temperature around Tiabo river (28.0-29.0 ^{o}C) could affect the mercury concentrations. The volatility of mercury could spread to the air and reduce the solvation process in water but can increase its quantity in the sediment.

Tabel 4. Mercury concentration in several sampling areas at Tiabo river

Location	Rainy season (µg/L)	Dry season (µg/L)	Description
S1	<0.66	-	Upstream
S2*	<0.66	-	River branch
S3T1; S3T2**	<0.66	<0.66	After branch
S4***	-	<0.66	Gold mining area 1
S5T1; S5T2	<0.66	<0.66	Gold mining area 2
S6T1; S6T2	<0.66	<0.66	Society activity
S7T1; S7T2	<0.66	<0.66	Downstream

Note: *S2 : Sample was collected in dry season. **S3T2 : Sample was collected from upstream in the dry season, and *** S4 : sample was collected in the "dangerous area" during rainy season.

The analysis result for mercury content in the sediment along to the Tiabo river is displayed in Figure 3. Three points area for sampling was chosen. The upstream was located above to the mining area. The middle stream area, where the mining site area was located. And the downstream area, where the sediment sample was taken below the mining site along the river. The value of mercury concentration was depicted with 5% of margin error from statistical analysis. The lowest of mercury concentration was recorded in 1.2 mg/kg, and detected from the sediment sample in the upstream location. This location is denoted as S1 and about 1-2.5 Km to the east along the Tiabo river from the mining site. The second largest mercury concentration was in the downstream area. It was depicted as S3 point, and located along the river about 4 Km to the south-west from the mining site. The mercury concentration was detected in 6.63 mg/kg of sediment. And lastly, sediment sample contains the largest concentration of mercury found in the mining site, and denoted as S2 point. Mercury concentration was recorded 8.94 mg/kg of sediment. The mercury concentration at the upstream are relatively lower than those in two sampling location points. It was predicted the sediment in the upstream location was not contaminated by mercury disposal from the mining site down to the Tiabo river. But small river surrounding the Tiabo river also contribute to the sedimentation process of mercury, beside natural rock in Sinabar area can displace the mercury

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to the sediment layer [14]. However, the mercury content in the upstream location, include with both other locations, have the value above to the allowed concentration for mercury in the sediment [13].

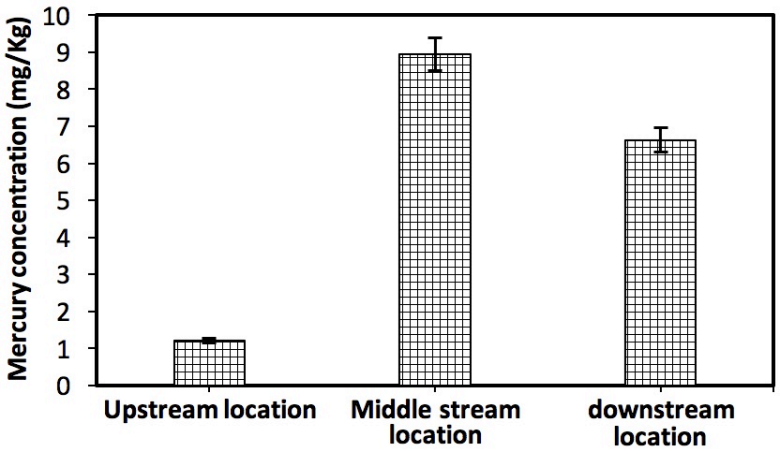

Figure 3. Mercury concentration in sediment collected from Tiabo river area

CONCLUSION

The mercury concentration from the water of Tiabo river in both rainy and dry season shows in the lower concentration to that regulated by government. The mercury concentration still below 0.06 µg/L. But the mercury concentration from the sediments collected is above the allowed quantity by regulation. Further recommendation should be undertaken by local government to strictly control and monitor in order to reduce the mercury disposal or waste of any mercury sources to the environment. Community has to be involved for inhibiting the usage of mercury for gold separation.

CONFLICT OF INTERESTS

Authors declare that there is no competing interest.

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