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Heavy metals concentrations in scalp hairs of ASGM miners and inhabitants of the Gorontalo Utara regency

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Abstract. We performed the Particle Induced X-ray Emission (PIXE) analysis on scalp hair samples of 115 ASGM miners and inhabitants of Gorontalo Utara regency. Along with mercury (Hg), we presented other trace elements such as Copper (Cu) and Manganese (Mn). Concentrations of Cu, Mn and Hg in the scalp hairs of ASGM miners are higher non miners. Significant and positive correlations coefficients between Cu and Hg concentration with Mn concentration may indicate that there are still unknown metabolism process related with ASGM activities.

1. Introduction

The Gorontalo Utara regency is home of the historical gold mining site Hulawa (formerly known as Buladu), the Hulawa reopen again at 1970 by local inhabitants and continues operates as ASGM. Since 2000 several new ASGM sites in the regency has been start operating. Recent estimation that ASGM sites in the regency produces 286 kg of gold and emits 572 kg of Hg per year [1]. Elevated mercury concentrations on the environments and human hairs of ASGM miners and inhabitants have been reported [2]. Arsenic (As) and lead (Pb) concentrations in human scalp hairs have been detected and positively correlate with mercury [3].

In this report, we presented the evidence of other trace elements (Cu and Mn) in scalp hair of miners and inhabitants of the Gorontalo Utara regency. Correlations of Cu and Mn with Hg in scalp hair may add information on source of contamination or fate of elements in human body.

2. Experimental

2.1. Study Area

Samples were collected from five districts in the Gorontalo Utara regency: Anggrek, Kwandang, Monano, Sumalata, and Tolinggula (Figure 1). Geographically, Tolinggula, Sumalata, Monano, Anggrek, and Kwandang are situated on hills and mountains along the coastline of the Gorontalo Utara Regency. Inhabitants of the Gorontalo Utara regency mainly work as farmers and fishermen. Marine fish is commonly a part of their diets, along with rice, corn and vegetables, which are also produced on the nearby hills alongside the coastline.

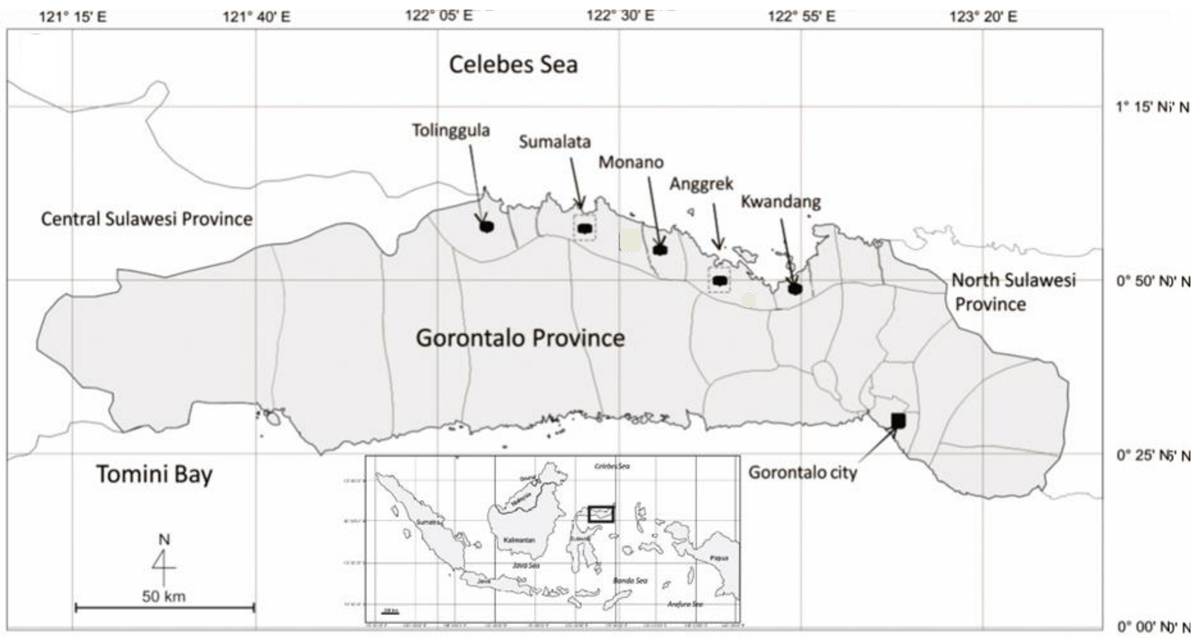

Figure 1. Sampling locations of human hair from the Gorontalo Utara regency are indicated by (●) on Gorontalo Province map, Tolinggula, Sumalata, Anggrek, Monano and Kwandang are name of subdistricts.

The ASGM activities in the Sumalata and Anggrek districts are located along the Wubudu and Anggrek riverbanks, respectively. The bioaccumulation of Hg, which may occur in living organisms such as paddy rice, corn, and marine fish, becomes agents that spread Hg contamination through the food web of inhabitants in the Gorontalo Utara regency. The Hg concentration in river sediments and fish will be used as background information about the Hg in the biotic and abiotic environments.

The Sumalata and Anggrek districts are locations with ASGM activities, while Kwandang, Monano, and Tolinggula are districts without mining activities. The residents of Anggrek and Sumalata are considered the ASGM miners group, while the residents of Kwandang, Monano, and Tolinggula are considered the control group.

2.2. Sampling

Human scalp hair samples were taken from 95 participants from inhabitants of Anggrek (n=25), Sumalata (n=24) Kwandang (n=15), Monano (n=39), and Tolinggula (n=12) between 2012 and 2013. Of the 115 participants, 66 were female, and the mean age was 23 years (range: 8 months – 63 years). Among the 115 participants, 21 were ASGM workers, 22 were housewives, 7 were officers of the regency, 6 were unemployed, 1 was a teacher, 1 was a university student and 38 were children (participants with ages below 18 years old).

The Cu, Mn, and Hg concentrations in the hair samples from Anggrek, Kwandang, Monano, Sumalata, and Tolinggula were determined to understand the status of contamination. The distribution of participants according to sex, location, and occupation is summarized in the table 1. Approximately 10-20 strands of hair were cut close to skin from the right backside (mastoidal region of the temporal bone) and then labelled and stored in a sample plastic bag [5].

The Hg concentration in hair samples will be used to characterize the risk through a comparison with reference values published by the German Human Biomonitoring Commission in 1999 (Commission Human – Biomonitoring of the Federal Environmental Agency Berlin, 1999) [6]. The German Human Bio-Monitoring (HBM) commission established toxicology threshold limits, which can be put into three categories. The first category is below normal or HBM I, where the Hg level in hair is below 1 μg/g. The above normal category is an alert level between HBMI and HBM II, where the Hg hair content is from 1 to 5 μg/g. Meanwhile, above 5 μg/g is categorized into the high level or over HBM II. Cu and Mn are essential elements for human body, however at certain conditions their excess concentrations are related to disturbance in organ functionalities [7-9].

Table 1. Number of scalp hair donor distribution related to their job, sex and living place in Gorontalo Utara regency.

Residence	Sex	N	Job	N
Anggrek	F	13	Miner	8
	M	12	Non Miner	17
	Total	25	Total	25
Kwandang	F	7	Miner	0
	M	8	Non Miner	15
	Total	15	Total	15
Monano	F	24	Miner	1
	M	15	Non Miner	38
	Total	39	Total	39
Sumalata	F	12	Miner	12
	M	12	Non Miner	12
	Total	24	Total	24
Tolinggula	F	10	Miner	0
	M	2	Non Miner	12
	Total	12	Total	12
Total	F	66	Miner	21
	M	49	Non Miners	94
	Total	**115**	**Total**	**115**

2.3. Analytical Procedure

Elemental analysis for the scalp hair samples was performed by particle induced x-ray emission (PIXE) in the Cyclotron Research Center, Iwate Medical University, Japan. The precision and accuracy of this method have been reported elsewhere [10-12] and will be described as follows. We used Zinc with known concentration (256 ppm) as internal standard; PIXE detects peak count of K_{α} about 2,325.2 ±50 (2% error). Hair samples were washed using Milli-Q water and shaken in an ultrasonic bath for 1 minute. Then, the samples were dried by wiping them with a tissue. The dried hair samples were washed again by being stirred in acetone for 5 minutes. Then, they were washed again using Milli-Q water, wiped well with tissue and left to dry at room temperature. The hair samples (approximately seven hairs per person) were stuck on a target holder. A 2.9 MeV-proton beam hit the target after passing through a beam collimator of graphite, whose diameter was 6 mm. X-rays of energy higher than that of the K- K_{α} line were detected by a Si(Li) detector (25.4 mm thick Be window; 6 mm active diameter) with a 300 mm-thick Mylar absorber. For measurements of X-rays lower than the K-K_{α} line, a Si(Li) detector (80 mm Be; 4 mm active diameter), which has a large detection efficiency for low energy X-rays, was used. Descriptions of the data acquisition system and the measuring conditions are reported elsewhere [8]. The typical beam current and integrated beam charge were 100 nA and 25 μC, respectively. The procedure for the standard-free method for untreated hairs is almost the same as that reported in the previous studies [6].

3. Result and discussion

Table 2 shows the summary of statistical results of Cu, Mn, and Hg concentrations in hairs of the inhabitants in the Gorontalo Utara regency. There is clear indication that means concentrations of Cu, Mn and Hg for ASGM miners are higher than miners. But there were no clear trends of mean concentrations of Cu, Mn, and Hg as functions of distance of living place to ASGM locations.

We perform the Spearman correlation on the total sample, and we found the tree coefficients (see the Table 3). There are strong and significant correlations of Hg and Mn concentrations to Cu concentration in hairs of inhabitants of the Gorontalo Utara regency. While weak and non-significant correlation is found between Cu and Hg.

Table 2. Cu, Mn, and Hg concentrations (μg/g) in hairs of inhabitants in the Gorontalo Utara regency.

Region	**Cu**		**Mn**		**Hg**	
	Mean ± SD	range	Mean ± SD	range	Mean ± SD	range
Anggrek	32.2±2.1	14.9-136.1	14.0±2.6	1.3 – 56.7	16.9 ± 29.2	2.1 – 144.8
Kwandang	15.0±1.7	6.6 - 34.8	3.9±5.7	0.4 - 103.4	6.5 ± 1.5	3.5 – 14.6
Monano	11.9±1.6	1.5 - 26.9	10.3±2.7	0.9 - 63.8	5.6 ± 2.8	2.8 – 28.1
Sumalata	16.6±1.5	6.2 - 45.7	4.5±4.8	1.0 – 58.6	8.2 ± 1.9	2.5 – 69.8
Tolinggula	11.4±1.3	1.3 - 16.1	12.1±3.0	1.8 - 87.9	5.1 ± 0.8	4.3 – 6.0
Miners	22.6 ± 1.9	6.2 – 89.3	13.6 ± 1.7	1.6 – 136.1	8.2 ± 1.7	2.7 – 17.9
Non miners	13.6 ± 1.7	1.5 – 136.7	8.5 ± 3.4	0.4 – 88.0	6.3 ± 2.0	1.1 – 144.8
Total	**1.3±2.7**	**0.0 - 19.9**	**8.7±10.4**	**0.0 - 67.6**	**10.2 ± 16.9**	**2.1-144.8**

Table 3. Correlation coefficient between elements.

Element	**Mn**		**Hg**	
	Coeff.	Sig.	Coeff.	Sig.
Cu	0.12	0.06	0.14	0.15
Hg	0.25	0.007		

4. Conclusion

Concentration of Cu, Mn, and Hg in average of miners and inhabitants of exposed group (Anggrek and Sumalata) are less elevated than control group (Kwandang, Monano, and Tolinggula). While according to HBM: inhabitants of the Gorontalo Utara regency have elevated Hg concentration (already in the alert level), while mean value for inhabitants exposed groups are in the danger level. The amount of Pb in hair of inhabitants of the Gorontalo Utara regency are still in the safe level, while As are already higher than the limit.

We also found the significant and strong correlation between concentrations of Cu and Hg to Mn in scalp hairs of inhabitants of the Gorontalo Utara regency. Such correlation may reveal the unknown sources of contamination, routes of contamination, and impact on health status of individual hair donors.

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