Atmospheric mercury contamination assessment using various tree bark in an ASGM area in North Gorontalo Regency, Indonesia

Hendra Prasetia[1], Masayuki Sakakibara[1,2] and Koichiro Sera[3]

[1]Graduate School of Science and Engineering, Ehime University
2-5 Bunkyo-cho, Matsuyama 790-8577, Ehime, Japan

[2]Faculty of Collaborative Regional Innovation, Ehime University
2-5 Bunkyo-cho, Matsuyama 790-8577, Ehime, Japan

[3]Cyclotron Research Centre, Iwate Medical University
348-58 Tomegamori, Takizawa, Iwate 020-0603, Japan

1. Introduction

Artisanal and small-scale gold mining (ASGM) provides income to many poor communities predominantly in developing countries, such as Indonesia, where it is also one of the major sources of mercury (Hg) contamination. Anthropogenic Hg emissions into the atmosphere significantly interfere with the natural Hg cycle [1]. Estimates of natural global Hg emissions into the atmosphere vary by orders of magnitude [1][2]. The source of atmospheric Hg derived from ASGM is the amalgamation process, in which amalgam is burned in a small charcoal fire, releasing Hg into the atmosphere [3]. Mercury is extremely dangerous and contaminates the air, water, soil, and living organisms, including trees. The health of miners and inhabitants living within or outside an area affected by Hg contamination is affected by the inhalation of atmospheric Hg [3].

Biological methods, utilizing living organisms can be applied to assess the degree of heavy metal contamination within an environment [4] [5]. A plant's species and genotype determine its tolerance to heavy metals [6] [7]. Plants are sensitive to their environmental conditions, and their elemental compositions actively reflect changes in these conditions [8] [9] [10]. Tree bark, in particular, can be used to assess the status of the environment, especially the level of Hg contamination. The enrichment of trace elements in tree bark can also allow us to trace a pollution source. [11] Airborne particles are trapped within the structure of tree bark, where they accumulate over several years [12]. The mechanisms of trace element uptake by the plant involve both root uptake and foliar absorption, which includes the deposition of particulate matter on the plant leaves [13]. The different

uptake patterns of plants are based on three factors: the plant species, the element species, and the conditions at specific sites [14] [15].

The proton microprobe is an ideal tool for the nondestructive in situ microanalysis of mineral grains [16]. By utilizing proton-induced X-ray emissions (PIXEs), it can detect trace elements in situ with a detection sensitivity of a few ppm in individual grains for most minerals and of < 1 ppm in some cases [17].

In this study, we investigated the Hg vapor contamination due to amalgamation process of ASGM. Tree bark was used for the environmental assessment in this study due to its ability to attaches and absorbs Hg vapor. The aim of the study was to determine the potential ability of *C. petandra, S. aqueum,* and *T. grandis* tree bark to assess Hg atmospheric contamination in an ASGM area in the North Gorontalo Regency, Indonesia.

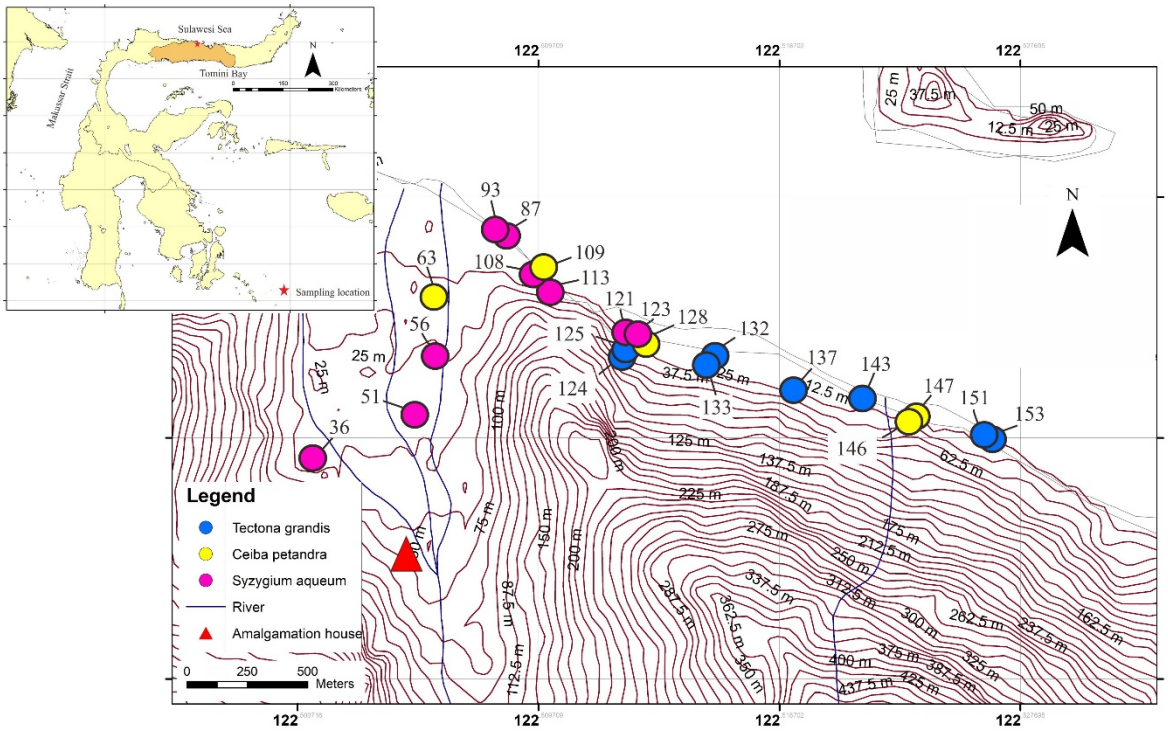

Figure 1. Tree bark sampling point in an ASGM area, North Gorontalo Regency, Indonesia.

2. Materials and Methods

This is a study to investigate the potential species on atmospheric Hg contamination. We performed a field survey and laboratory analyses to determine the heavy metal concentrations (especially Hg) in tree bark to assess the environmental contamination in the study area. The

researchers in this study obtained tree bark samples from the various species such as, *C. petandra, S. aqueum,* and *T. grandis* in the ASGM area in the North Gorontalo Regency, Indonesia, shown in Figure 1. The tree bark samples were collected at DBH (Diameter at Breast Height) about 130 cm height.

2.1. Analytical methods

The tree bark samples were dried at ~80°C for two days in a ventilated oven. Then, tree bark samples were crushed to a fine powder with a powder mill (Varian PM-2005m, Osaka Chemical Co., Ltd., Osaka, Japan) to produce homogenous samples for analysis. The tree bark powders (30 mg of each sample) were digested with a mixture of indium (In) and HNO_3 in a ratio of 3:100, before the heavy metal concentrations of Hg were determined with PIXE [18] [19] [20] at Iwate Medical University (Iwate, Japan).

2.2. Calculation of total weight

The bioaccumulation of Hg can be estimated from the total weight of mercury (THg). THg is defined as the dry weight of the sample multiplied by the Hg concentration determined by the PIXE analysis in 100 cm^2 of the sample.

$$THg = (DW \times C_{Hg}) \times (FD \times \text{real square}) \text{ [20]}$$

where DW is the dry weight of the sample and C_{Hg} is the Hg concentration, FD is fragmented dimension (100 cm^2), and real square is the result of image J measurement.

2.3. Statistical analysis

Statistical analyses were performed with SPSS Statistic 21 for Windows (IBM, Armonk, NY, USA). The tree bark data were log-normally distributed before their analysis, and statistically significant differences ($\rho < 0.05$) were determined with one-way ANOVA.

3. Results

3.1. The Hg concentrations in the tree bark

In this study, we screened *C. petandra, S. aqueum,* and *T. grandis* bark in an ASGM area for Hg vapor contamination, using a bioindicator approach to evaluate atmospheric contamination. The THg of *C. petandra* were ranged from ND to 38.2 μg-DW per weight of the sample (Table 1). In the tree bark of *S. aqueum* and *T. grandis,* the THg were ranged from ND to 84.9 and ND to 85.9 μg-DW

per weight of sample (Table 2 and 3). In this study, the ND results are probably attributable to the leaching of Hg during the weathering processes [20].

Table 1. Total weight of Hg and diameter of *C. petandra* tree barks

No	Samples	T(Hg) (μg-DW)±SD	Diameter (cm)
1	*C. petandra* 109	38.2±22.7	120
2	*C. petandra* 128	ND	99.7
3	*C. petandra* 147	ND	139
4	*C. petandra* 146	28.3±11.5	67.2
5	*C. petandra* 63	ND	60.2

DW: Dry Weight; SD: Standard Deviation; ND: Not Detected.

Table 2. Total weight of Hg and diameter of *S. aqueum* tree barks

No	Samples	T(Hg) (μg-DW)±SD	Diameter (cm)
1	*S. aqueum* 51	16.7±11.0	35.7
2	*S. aqueum* 56	1.45±2.47	40.8
3	*S. aqueum* 113	15.3±5.46	17.8
4	*S. aqueum* 93	42.3±41.6	17.5
5	*S. aqueum* 123	84.9±49.4	23.2
6	*S. aqueum* 121	60.3±35.0	38.2
7	*S. aqueum* 36	60.3±45.6	37.9
8	*S. aqueum* 87	ND	42.7
9	*S. aqueum* 108	ND	40.4

DW: Dry Weight; SD: Standard Deviation; ND: Not Detected.

Table 3. Total weight of Hg and diameter of *T. grandis* tree barks

No	Samples	T(Hg) (μg-DW)±SD	Diameter (cm)
1	*T. grandis* 133	85.9±28.6	36.0
2	*T. grandis* 137	6.89±6.99	13.4
3	*T. grandis* 151	47.8±27.6	35.4
4	*T. grandis* 132	2.82±9.79	34.7
5	*T. grandis* 143	ND	14.3
6	*T. grandis* 124	0.23±29.8	31.8
7	*T. grandis* 125	ND	29.6
8	*T. grandis* 153	30.5±17.3	35.7

DW: Dry Weight; SD: Standard Deviation; ND: Not Detected.

A plant can be categorized as toxic if the concentration of Hg exceeds 1 ppm [21]. This study shows that *C. petandra, S. aqueum* and *T. grandis* can accumulate high total weight of Hg from atmospheric contamination through its bark. It also demonstrates that the bark of *C. petandra, S. aqueum* and *T. grandis* can be used as a bioindicator of atmospheric Hg contamination in environmental assessments of ASGM areas.

4. Discussion

4.1. The THg distribution based on distance to the amalgamation house

No analysis of *C. petandra, S. aqueum* and *T. grandis* tree bark in ASGM areas have been reported until now. The ability of *M. indica* as a bioindicator for Hg atmospheric contamination in an ASGM has been reported before [20]. In this study, the tree bark analysis with PIXE detected the THg in the trees at height 130 cm. Heavy metals are absorbed into plant tissue through the phloem, in conjunction with nutrient absorption.

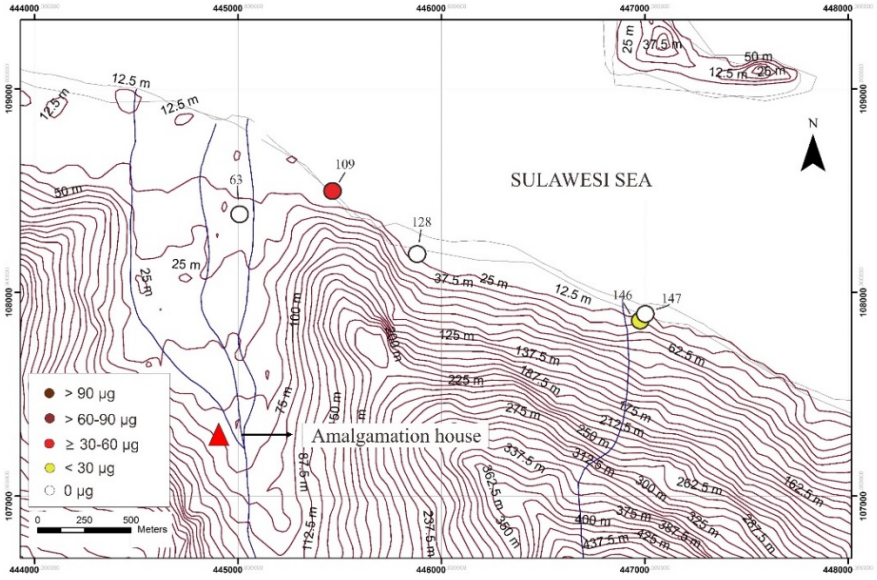

Figure 2. Distribution map of *C. petandra* THg in the tree bark.

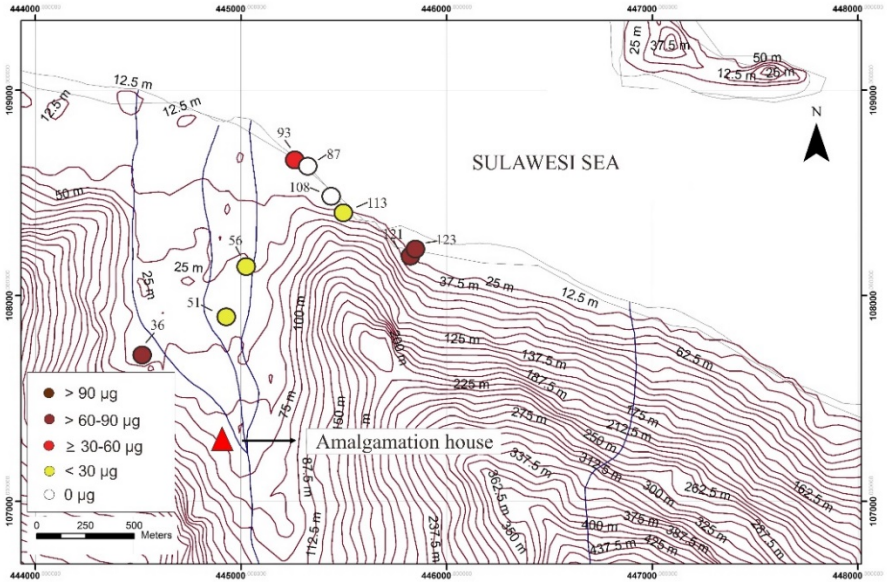

Figure 3. Distribution map of *S. aqueum* THg in the tree bark.

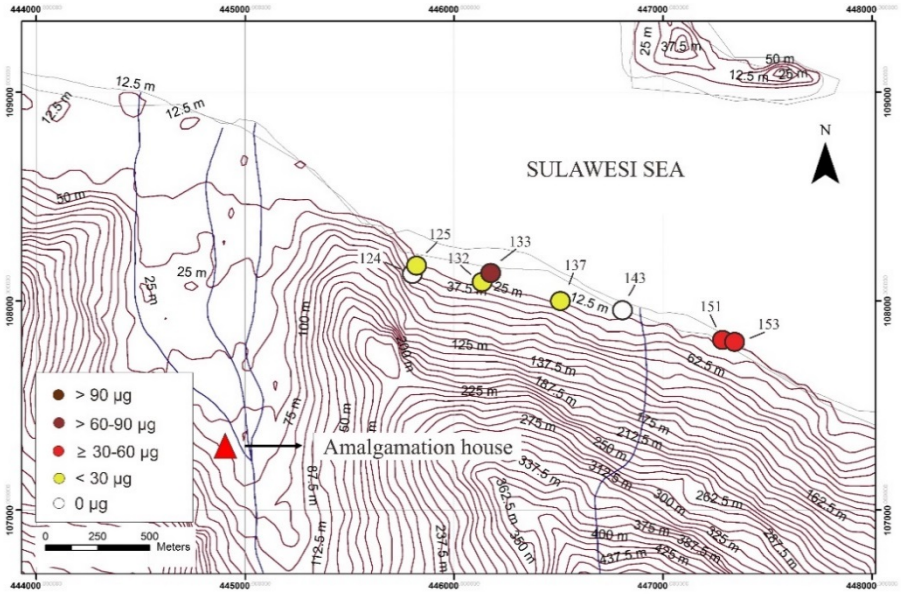

Figure 4. Distribution map of *T. grandis* THg in the tree bark.

The heavy metals are absorbed in the form of essential macro and micronutrients, induced by the selective uptake of ions by roots, or by the diffusion of elements in the soil. Hg, like other heavy metals, can be translocated to the above ground tissue along a similar pathway to that used by nutrients in solution [22]. The ability of a plant to accumulate heavy metals is considered a detrimental trait in the long term [23]. The highest THg of Hg in the tree bark of *C. petandra* is located in the lower topographic, *C. petandra* 109, and far from the amalgamation house, shown in Figure 2. This results were also shown in the tree bark of *S. aqueum* 123 and *T. grandis* 133, which is located in the lower topographic and far from amalgamation house, shown in Figure 3 and 4. This study indicates that THg in the tree bark has no correlation to the distance of contamination source, due its topographic and local weathering condition, such as wind direction.

The total weight of Hg in the tree bark suggested that topography and local weathering process significantly influence the accumulation of Hg in the tree bark [20]. The total weight of Hg in 1 m height was not influenced by distance the amalgamation house [20]. The weathering condition such as wind direction, which move the Hg in the atmosphere and deposit it at lower topographic sites [20]. Overall, this study suggests that the bark of *C. petandra, S. aqueum* and *T. grandis* have great potential utility as a bioindicator of atmospheric contamination in an ASGM area.

4.2. Boxplot of THg tree bark in various species

On determination of the THg boxplot in various species, the test was measured using IBM SPSS Statistic 21 for Windows. The result showed that the mean value of *C. petandra, S. aqueum,* and *T. grandis* are about 13.3, 31.3, and 21.8 µg-DW, respectively, shown in Fig. 5. The Fig. 5 shows that there is no significance difference ($\rho > 0.05$).

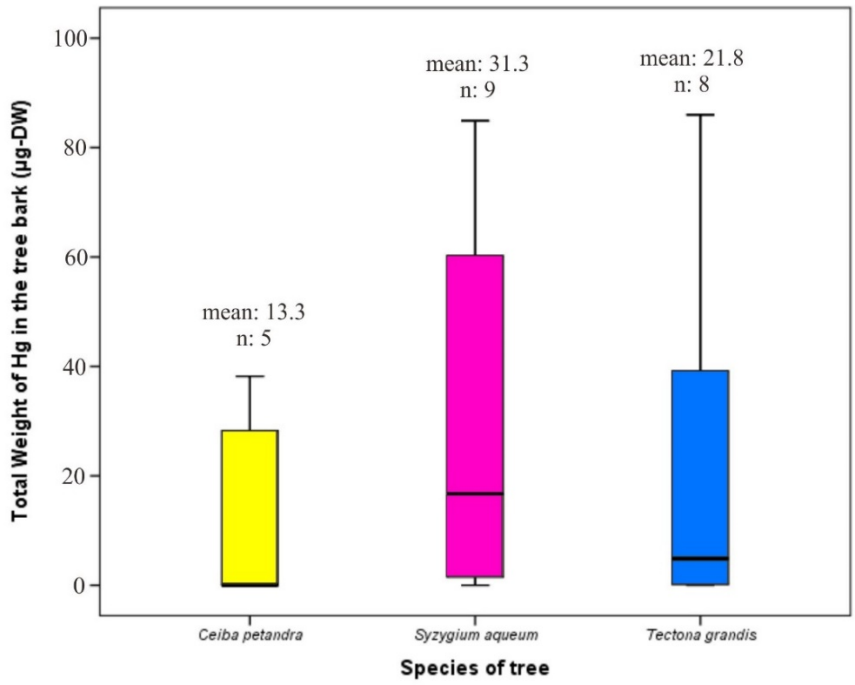

Figure 5. The correlation of the diameter of the tree to the total weight of Hg.

The atmospheric Hg contamination was absorbed into the inner part of the tree bark through the adaxial epidermis (Ead) and the vascular (V) tissue in the *M. indica* species after it attached to the outer bark [20]. The atmospheric Hg can penetrate to the inner parts of the plant through plants metabolic process [20]. The Hg concentrations have a heterogeneities within the tree bark tissue [20]. The Hg is entering the bole of tree through the bark either from atmospheric deposition directly to the bark or the transport of atmospheric Hg from the leaves through the phloem rather than uptake by root [24].

5. Conclusions

This study has showed the distribution and results of THg in tree bark of *C. petandra, S. aqueum* and *T. grandis*. The *T. grandis* species has highest total weight of Hg (THg) in the tree bark

compared to the *C. petandra* and *S. aqueum* species. The highest THg of *C. petandra, S. aqueum* and *T. grandis* accumulated in the lower topography, coastline area, of this study. The THg in the tree barks has no significance difference in various species of the tree. There is an indication that THg in the tree bark depends on the tree bark surface condition and local weathering codition. This study suggests that *C. petandra, S. aqueum* and *T. grandis* are good candidate bioindicator, in the tropical area, of atmospheric Hg contamination in an ASGM area and has utility in the environmental assessment of air pollution.

Acknowledgements: The author would like to thank to the Japanese Government for providing a Monbukagakusho Scholarship for graduate study at Ehime University, and the North Gorontalo Regency Government of Gorontalo Province that allowed the author to conduct the research activity. This research was supported by Research Institute for Humanity and Nature Project No. 14200102. This work was also supported by JSPS KAKENHI Grant Number 16H02706.

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