Preliminary Study of Atmospheric Mercury Contamination Assessment Using Tree Bark in an ASGM Area in North Gorontalo Regency, Indonesia

Hendra Prasetia*, Masayuki Sakakibara1,2, Koichiro Sera3.

1 Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Ehime, Japan; hendra@sci.ehime-u.ac.jp
2 Faculty of Collaborative Regional Innovation, Ehime University, Matsuyama, Ehime, Japan; sakakibara.masayuki.mb@ehime-u.ac.jp
3 Cyclotron Research Centre, Iwate Medical University, 348-58 Tomegamori, Takizawa, Iwate 020-0173, Japan; ksera@iwate-med.ac.jp

* Corresponding Author: hendra@sci.ehime-u.ac.jp

Abstract. Mercury (Hg) atmospheric contamination have been analysed using several indicators. In this study, the tree bark was used to indicate Hg contamination of the atmosphere in ASGM area. This study aimed to determine the potential species to assess Hg atmospheric contamination by using tree bark. The Hg concentration was determined in the tree bark from various tree species. The tree bark was collected at Diameter Breast Height (DBH) which is about 130 cm. The fine powder of tree bark was analysed by PIXE to detect Hg concentration. The results show that Mangifera indica, Lansium domesticum, Syzygium aromaticum and Artocarpus heterophyllus species accumulate Hg concentration about 4.90 to 10.3, ND to 1.10, ND to 4.42 and 2.43 mg/kg-DW, respectively. This suggests that M. indica, L. domesticum, S. aromaticum, and A. heterophyllus show high toxic of Hg contamination in the tree bark compared to tolerable toxic level in the plant. This study indicates that the surface condition of tree bark probably effects on the detection of Hg contamination in each tree species. The tree plant, especially tree bark, is a good candidate to assess Hg atmospheric contamination.

Keywords: Mercury; atmospheric contamination; tree bark.

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 [8-10]. 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 pollution, arising from the amalgamation process in an ASGM area. Tree bark was used for the environmental assessment in this study because it attaches and absorbs Hg vapor. The aim of the study was to determine the potential species to assess Hg atmospheric contamination by using tree bark in an ASGM area in the North Gorontalo Regency, Indonesia.

Figure 1. Tree bark sampling point in an ASGM area, North Gorontalo Regency, Indonesia. 1: S. aromaticum; 2: M. indica; 3: M. indica; 4: L. domesticum; 5: L. domesticum; 6: G. arborea; 7: L. domesticum; 8: L. domesticum; 9: S. aromaticum; 10: S. aromaticum; 11: S. aromaticum; 12: M. indica; 13: A. heterophyllus.

2. Materials and Methods
This is preliminary study to investigate the potential species on atmospheric Hg contamination. We performed a field survey and laboratory analyses to determine the heavy metal concentration (especially Hg) in tree bark to assess the environmental contamination in the study area. We obtained tree bark samples from the various species such as, M. indica, S. aromaticum, L. domesticum, G. arborea, and A. heterophyllus 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. The diameter
of *M. indica* number 2, 3 and 12 were 33.8, 87.3, and 72.6 cm. The diameter of *S. aromaticum* number 1, 9, 10, and 11 were 28.0, 30.7, 30.6, and 36.9 cm. The diameter of *L. domesticum* number 4, 5, 7, and 8 were 30.7, 10.5, 9.20, and 37.3 cm. The diameter of *G. arborea* and *A. heterophyllus* were 28.3 and 54.8 cm.

2.1. Analytical methods
The tree bark samples were dried at ~80ºC 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 HNO₃ in a ratio of 3:100, before the heavy metal concentration of Hg were determined with PIXE [18][19][20] at Iwate Medical University (Iwate, Japan).

2.2. 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 (p < 0.05) were determined with one-way ANOVA.

3. Results

3.1. The Hg concentration in the tree bark
In this study, we screened *M. indica*, *S. aromaticum*, *L. domesticum*, *G. arborea*, and *A. heterophyllus* bark in an ASGM area for heavy metal contamination, using a bioindicator approach to evaluate atmospheric contamination. The Hg concentration of *M. indica*, *S. aromaticum*, and *L. domesticum* in the tree bark samples ranged from 4.90 to 10.3, not detected (ND) to 4.42, and ND to 1.10 mg/kg-DW (Table 1). In the tree bark of *G. arborea* and *A. heterophyllus*, Hg concentration were ND and 2.43 mg/kg-DW (Table 1). In this study, the ND results are probably attributable to the leaching of Hg during the weathering processes [20].

| No | Samples       | Hg conc. (mg/kg-DW)±SD |
|----|---------------|------------------------|
| 1  | *S. aromaticum* | ND                     |
| 2  | *M. indica*   | 6.79±3.90              |
| 3  | *M. indica*   | 4.90±2.85              |
| 4  | *L. domesticum* | 1.10±1.81              |
| 5  | *L. domesticum* | 0.74±1.81              |
| 6  | *G. arborea*  | ND                     |
| 7  | *L. domesticum* | ND                     |
| 8  | *L. domesticum* | ND                     |
| 9  | *S. aromaticum* | 4.07±4.70              |
| 10 | *S. aromaticum* | ND                     |
| 11 | *S. aromaticum* | 4.42±3.50              |
| 12 | *M. indica*   | 10.3±3.34              |
| 13 | *A. heterophyllus* | 2.43±2.83              |

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 *M. indica*[20], *S. aromaticum*, and *A. heterophyllus* can accumulate a high concentration of Hg from atmospheric contamination through its bark. It also demonstrates that the bark of *M. indica*, *S. aromaticum* and *A. heterophyllus* can be used as a bioindicator of atmospheric Hg contamination in environmental assessments of ASGM areas. Therefore, this study demonstrates that the bark of *M. indica*, *S. aromaticum*, and *A. heterophyllus* can be used as a biomarker for atmospheric contamination with Hg in environmental assessment projects.
3.2. Tree characteristic based on species

In this study, each of tree species has different characteristic. This result shows that the characteristic trees is based on the species. The characteristic of *M. indica* was tree 10-40m tall, rough bark, and root depth about 6m. The characteristic of *S. aromaticum, L. domesticum, G. arborea, and A. heterophyllus* were 10-15m tall, medium roughness bark, branch diameter 1-2.5cm; 10-20m tall, smooth bark, brownish and grey stem; 30-40m tall, smooth bark; 20-30m tall, rough bark, stem diameter about 1m, respectively. The tree bark on each species has a different condition. In this study, the surface condition of tree bark has probably important role to attach Hg contaminant in the atmosphere. The *M. indica, S. aromaticum* and *A. heterophyllus* have a rougher bark surface compared to *G. arborea* and *L. domesticum*, shown in Figure 2.

![Figure 2](image_url)

**Figure 2.** Tree bark condition of the highest three Hg concentration. *A: M. indica; B: S. aromaticum; C: A. heterophyllus.* Scale: 260 mm

4. Discussion

4.1. The Hg concentration distribution based on distance to the amalgamation house

No analysis of *S. aromaticum, L. domesticum, G. arborea, and A. heterophyllus* 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 Hg concentration in the trees at the height of 130cm. This study shows that Hg concentration detected in the tree species of *M. indica, S. aromaticum, L. domesticum,* and *A. heterophyllus*(Table 1). Heavy metals are absorbed into plant tissue through the phloem, in conjunction with nutrient absorption. 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 sample location and its topography are shown in Figure 1 and 3. The concentration 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 1m height was not influenced by the 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 *M. indica, S. aromaticum,* and *A. heterophyllus* have great potential utility as a bioindicator of atmospheric contamination in an ASGM area.
Figure 3. Distribution map of Hg concentration in the tree bark. 1: *S. aromaticum*; 2: *M. indica*; 3: *M. indica*; 4: *L. domesticum*; 5: *L. domesticum*; 6: *G. arborea*; 7: *L. domesticum*; 8: *L. domesticum*; 9: *S. aromaticum*; 10: *S. aromaticum*; 11: *S. aromaticum*; 12: *M. indica*; 13: *A. heterophyllus*

4.2. *The correlation of Hg concentration to the tree’s diameter*

In this study, the diameter of tree bark was measured. The diameter of tree bark shows the age of the tree. The result shows that there is a positive correlation between the diameter of the tree and Hg concentration in the tree bark. 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 the plants metabolic process [20]. The Hg concentration has a heterogeneities within the tree bark tissue [20]. The Hg is entering the bole of the 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].

Figure 4. The correlation of Hg concentration to the diameter of the tree.
5. Conclusions

We have shown the concentration and distribution of atmospheric Hg contamination in tree bark of *M. indica*, *S. aromaticum*, *L. domesticum*, *G. arborea*, and *A. heterophyllus*. The *M. indica* species has the highest concentration of Hg in the tree bark compared to other species. The Hg concentration of *M. indica*, *S. aromaticum* and *A. heterophyllus* has a higher concentration than the toxic tolerable level in the plant. The Hg concentration in the tree barks has no correlation to the distance of amalgamation house. There is an indication that Hg concentration in the tree bark depends on the tree bark surface condition. This study suggests that *M. indica*, *S. aromaticum*, and *A. heterophyllus* are good candidate bioindicators of atmospheric Hg contamination in an ASGM area and can be used as a utility for the environmental assessment of air pollution studies.

Acknowledgments

Hendra Prasetia, one of the authors in this studies wishes to thank 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.

References

[1] Fitzgerald W F, Engstrom D R, Mason R P and Nater E A 1998 The case for atmospheric mercury contamination in remote areas *Environ. Sci. Technol.* **32** 1–7

[2] Rasmussen P E 1994 Current methods of estimating atmospheric mercury fluxes in remote areas *Environ. Sci. Technol.* **28** 2233–41

[3] Taylor H, Appleton J D, Lister R, Smith B, Chitamweba D, Mkumbo O, Machiwa J F, Tesha A L and Beinhoff C 2005 Environmental assessment of mercury contamination from the Rwamagasa artisanal gold mining centre, Geita District, Tanzania *Sci. Total Environ.* **343** 111–33

[4] Peng K J, Luo C L, Chen Y H, Wang G P, Li X D and Shen Z G 2009 Cadmium and other metal uptake by Lobelia chinensis and Solanum nigrum from contaminated soils *Bull. Environ. Contam. Toxicol.* **83** 260–4

[5] Brookes P C 1995 The use of microbial parameters in monitoring soil pollution by heavy metals *Biol. Fertil. Soils* **19** 269–79

[6] Adriano 2001 *Trace Elements in Terrestrial Environments* vol 32 (Springer-Verlag)

[7] Tlustoš P, Pavlíková D, Száková J and Balík J 2006 Phytoremediation of Metal-Contaminated Soils ed J-L Morel, G Echevarria and N Goncharova (Dordrecht: Springer Netherlands) pp 53–84

[8] Vtorova V N 1987 Quantitative evaluation of the chemical similarity of needles of Picea schrenkiana with other spruce species in natural and artificial growth conditions *Biol. Bull. Acad. Sci. USSR*

[9] Vtorova V N 1991 Substantiation of methods and objects of observations over chemical composition of plants during monitoring of forest ecosystem *Inf. Bull. Probl. III Counuc. Mutual Econ. Help*

[10] Kabata-Pendias A, Pendias H and others 1984 *Trace elements in soils and plants* vol 315 (CRC press Boca Raton)

[11] Geagea M L, Stille P, Millet M and Perrone T 2007 REE characteristics and Pb, Sr and Nd isotopic compositions of steel plant emissions *Sci. Total Environ.* **373** 404–19

[12] Catinon M, Ayrault S, Clocciati R, Boudouma O, Asta J, Tissut M and Ravanel P 2009 The anthropogenic atmospheric elements fraction: a new interpretation of elemental deposits on tree barks *Atmos. Environ.* **43** 1124–30

[13] Olajire A A and Ayodele E T 2003 Study of atmospheric pollution levels by trace elements analysis of tree bark and leaves *Bull. Chem. Soc. Ethiop.* **17**

[14] Markert B 1992 Presence and significance of naturally occurring chemical elements of the
periodic system in the plant organism and consequences for future investigations on inorganic environmental chemistry in ecosystems Plant Ecol. 103 1–30
[15] Markert B 1994 Plants as biomonitors for heavy metal pollution of the terrestrial environment
[16] Ryan C G, Cousens D R, Sie S H, Griffin W L, Suter G F and Clayton E 1990 Quantitative pixe microanalysis of geological material using the CSIRO proton microprobe Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 47 55–71
[17] Folkmann F, Borggreen J and Kjeldgaard A 1974 Sensitivity in trace-element analysis by p, Sα$ and 16O induced X-rays Nucl. Instruments Methods 119 117–23
[18] Sera K, Yanagisawa T, Tsunoda H, Futatsugawa S, Hatakeyama S, Saitoh Y, Suzuki S and Orihara H 1992 Bio-PIXE at the Takizawa facility (Bio-PIXE with a baby cyclotron) Int. J. PIXE 2 325–30
[19] Prasetia H, Sakakibara M, Sueoka Y and Sera K 2016 Pteris cretica as a Potential Biomarker and Hyperaccumulator in an Abandoned Mine Site, Southwest Japan Environments 3 15
[20] Prasetia H, Sakakibara M, Omori K, Laird J S and Sera K Mangifera indica as Bioindicator of Mercury Atmospheric Contamination in an ASGM Area in North Gorontalo Regency, Indonesia
[21] Kabata-Pendias 2011 Trace elements in soils and plants
[22] Lomonte C, Wang Y, Doronila A, Gregory D, Baker A J M, Siegele R and Kolev S D 2014 Study of the spatial distribution of mercury in roots of vetiver grass (Chrysopegon zizanioides) by micro-PIXE spectrometry Int. J. Phytoremediation 16 1170–82
[23] Kumar P B A N, Dushenko V, Motto H and Raskin I 1995 Phytoextraction: the use of plants to remove heavy metals from soils Environ. Sci. Technol. 29 1232–8
[24] Siwik E I H, Campbell L M and Mierle G 2010 Distribution and trends of mercury in deciduous tree cores Environ. Pollut. 158 2067–73