Impact of mercury contamination by artisanal mining on soil and the use of natural zeolite for stabilization

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Abstract. Artisanal gold mining (ASGM) commonly found in Indonesia, particularly in Banyumas, Central Java, which is still processing the gold ore by using mercury. The objective of this study to examine the concentration and mobility of mercury contamination on the soil in the study area and to investigate the potential use of natural zeolite for stabilization mercury in contaminated soil. The soil samples were obtained from the top layer and subsurface and then analyzed for mercury concentrations and mobility. Soil stabilization experiment was conducted by using natural zeolite from Gunungkidul, Yogyakarta and the effects of natural zeolites in the reduction of the concentration of mercury was investigated by assessed Jatropha curcas plant. The result shows that the higher mercury concentration was found in topsoil rather than the subsurface. The result of mobility analysis shows that most mercury fractions are associated with organic mercury followed by mercury element fractions. Soil stabilization experiment revealed that adding natural zeolites as soil additives will reduce the concentrations of Hg in plant material which of the important point leading to the entry of mercury into the food chain.

1. Introduction

Natural disasters may be caused by natural and human activity including environmental pollution that can be caused by artisanal small-scale mining (ASGM) activity. ASGM activity commonly found in developing countries such as Indonesia. One of the pressing environmental issues related to ASGM is the use of mercury during gold processing or called amalgamation process [1, 2]. One of the effects of mercury contamination is the degradation of soil quality. Soil provides plants for their roots and holds the necessary nutrients for plants to grow, it filters the rainwater and regulates the discharge of excess rainwater, preventing flooding, and it is capable of storing large amounts of organic carbon also it buffers against pollutants, thus protecting groundwater quality [3]. Several studies revealed that artisanal mining has an impact on mercury contamination in soil around the gold mining processing area [4, 5]. The study was conducted in ASGM area in Banyumas District, Central Java, Indonesia. In the research area, gold mining and processing activities are adjacent to residential or housing and community activity centers [6]. In the study area, the level of mercury concentration in river water and stream sediment is elevated and well documented in the previous study [7]. Geologically, the study area consists of limestones, claystone–siltstone, and tuff clay unit, and the ore deposits types are typical of low sulphidation epithermal especially carbonate-base metal-gold mineralization system [8]. The aim of this study is to investigate the concentration and mobility of mercury contamination on the soil and to investigate the potential use of natural zeolite for stabilization mercury in contaminated soil.

2. Material and methods
Mining waste (tailing), which as the main source of mercury, was sampled and measured for mercury concentration. The vein or ore mineral in the gold mining area was sampled as well and measured for mercury concentration in order to understand the natural background. Contaminated soil samples for this study were obtained from the most contaminated sites within the gold processing area using a hand auger made of stainless steel. The soil samples were obtained from two layers: top layer (0–20 cm) and subsurface (40–60 cm). The samples from a given layer were collected at three sites to ensure that the result would be representative of contaminated soil in the study area. The samples were placed in plastic boxes and were transported to the laboratory, where they were dried at room temperature to constant weight. The analysis of mercury was done for the soil samples that were refined in an agate mortar but not to damage the structure of the grains. The samples then were collected and sieved through a sieve of mesh size 0.150 mm. The total concentrations of the Hg were measured by Inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Furthermore, in order to identify the mobility of Hg in soil, a sequential extraction analysis method was performed. The analysis was performed with the steps referring to another study [9]. Extraction was performed to obtain the following sequences: F1 (deionized water), F2 (0.01 M HCl + 0.1 M CH3COOH), F3 (1 M KOH), F4 (12 M HNO3), and F5 (aqua regia). The analysis of mercury (Hg) content in all samples was performed with ICP AES. For the soil stabilization experiment, the zeolite sample used in this experimental work was obtained from Gunungkidul, Yogyakarta, which consists of clinoptilolite and mordenite which are the dominant zeolite minerals and clay minerals. Other minerals are also present, such as quartz, plagioclase, illite, smectite [10, 11]. The properties of the natural zeolite sample are shown in table 1.

| Component      | Value (%) |
|----------------|-----------|
| Mordenite      | 18.12     |
| Clinoptilolite | 5.66      |
| Illite         | 4.35      |
| Smectite       | 2.38      |
| Quartz         | 5.71      |
| CEC (meq/100 g) | 43.2     |
| Specific surface area (m²) | 29.8 |
| Volcanic glass | 81        |
| Rock fragment  | 4         |
| Crystal        | 2         |

The zeolite sample then was a homogenized sample and was sieved to obtain the 1-2 mm grain size fraction. The effects of natural zeolites in the reduction of the concentration of mercury in plants were investigated by assessed Jatropha curcas (Jatropha curcas L., Euphorbiaceae.) in contaminated soils with and without the addition of natural zeolites. The Hg contaminated soil was obtained from the gold processing area as mentioned in the previous section. For the experiments, pots were used containing 2 kg of soil, which were placed in a greenhouse. Natural zeolites were added at rates of 1% (treatment A), 2% (treatment B) and 5% (treatment C) by weight referred to another study [12]. Control pots without the addition of zeolites were also prepared. From each pot, three different subsets of by Jatropha curcas were harvested at three different times during the growing season for 3 months in the end. The plants were split into shoots and roots, thoroughly washed with distilled water to remove adhering soil particles, and dried at 35°C to constant weight. Plant material was then milled, weighed, and determined of mercury concentration by ICP AES after digested in 25 ml aqua regia.

3. Result and discussion
3.1 Mercury in soil and mobility

The result of the measurement of mercury concentrations on the samples of ore minerals and tailings samples were shown in table 1 as a result of the previous study [7]. The results of laboratory tests showed mercury content in 6 soils around the mining site had a range of values 6.6 – 10.9 ppm for soil with depth 0-20 cm and 4.0-7.9 ppm for 40-60 cm depth. In summary, the mercury content of the data is presented in table 2.

### Table 2. Results of mercury content measurement of samples

| No. | Samples                | Sample number | Mercury range (ppm) | Average mercury concentration (ppm) |
|-----|------------------------|---------------|---------------------|------------------------------------|
| 1   | Veins/minerals         | 3             | 0.005 — 0.012       | 0.008                              |
| 2   | Tailings               | 5             | 7,493.0 — 92,000.0  | 10,138.0                           |
| 3   | Soil (0-20 cm)         | 3             | 6.6 — 10.9          | 8.7                                |
| 4   | Soil (40-60 cm)        | 3             | 4.0 — 7.9           | 5.8                                |

The sequential extraction results of mercury can be seen in table 3. The fraction I or water-soluble (Hg-w) is performed using the extraction of pure water, carried out for the soluble bound Hg fraction without damaging other species present in the soil. This fraction has values ranging from 3.6 to 10.3%, with an average of 8.0%. Then, fraction II or human stomach acid soluble (Hg-h) is carried out by extraction of CH₃COOH which aims to extract potentially reducible metals or may be bonded with the oxide layer. This fraction ranged from 17.3 to 36.5% with an average of 26.8%. Furthermore, the fraction III or organo-chelated (Hg-o), where this fraction ranges from 30.1 to 42.0% with an average of 35.2%. In this fraction, mercury binds to organic matter. Furthermore, the fraction IV or 12 M HNO₃ or elemental mercury (Hg-e), with a range of 19.5 – 38.1% with an average of 26.8. Then, finally, the fraction V or mercuric sulfide (Hg-s) in which the fraction is intended to reduce all traces of mercury present in the sediment (residual fraction by using aqua regia extraction). The compounds in this fraction are classified as non-available because they are stable and strongly bonded with minerals-in sediments. The extracted mercury in this fraction ranges from 0.2 to 2.4% with an average of 1.5%. Table 3 shows the percentage of extracted Hg fraction in soil samples in each sample with a pattern of approximately Hg-o> Hg-e> Hg-h> Hg-w> Hg-s. In general, Hg is found in the Hg-o fraction, with an average of 35.2% of total Hg.

### Table 3. Extracted Hg Percentage in soil with different depth (%)

| Samples          | Fraction I (Hg-w) | Fraction II (Hg-h) | Fraction III (Hg-o) | Fraction IV (Hg-e) | Fraction V (Hg-s) |
|------------------|-------------------|--------------------|---------------------|--------------------|-------------------|
| S1 (0-20 cm)     | 8.2               | 17.3               | 36.4                | 35.7               | 2.4               |
| S2 (0-20 cm)     | 10.3              | 36.5               | 30.1                | 22.1               | 1.0               |
| S3 (0-20 cm)     | 6.0               | 22.0               | 33.7                | 38.1               | 0.2               |
| S1 (40-60 cm)    | 10.3              | 33.1               | 33.0                | 23.3               | 0.3               |
| S2 (40-60 cm)    | 9.7               | 24.0               | 42.0                | 22.3               | 2.0               |
| S3 (40-60 cm)    | 3.6               | 27.8               | 36.1                | 29.5               | 3.0               |
| Average          | 8.0               | 26.8               | 35.2                | 28.5               | 1.5               |

The fractions associated with sulfides (Hg-s) and elemental mercury (Hg-e) have an average of 1.5% and 28.5%, indicating that this fraction has a high adequate percentage associated with inorganic sulfur complexes to amorphous materials such as aluminum silicate and Fe and Mn oxides. The percentage of Hg-e that averages 28.5% can be presumed to be due to mercury use from the amalgamation process by traditional gold miners. For the last fraction of Hg-s, this is the most stable fraction. Fractions associated with Hg-w and Hg-h show an average of 8.0% and 26.8%, wherein the mercury in this fraction binds to the soluble and most volatile organic. This fraction is present large enough and has the possibility of being uptake by the plant. The Hg-w and Hg-h fractions found in this study indicate that the two fractions may be suspected to originate from human activities, in this case, are traditional mining activities.
3.2 Soil stabilization experiment

Tables 4 summarize the Hg concentrations in the shoots and roots concerning various zeolite additive. The results of the analysis of mercury concentration (Table 4) show reduction by 83.3% in shoots and 60.3% in roots relative to the controls when natural zeolites are added to the soil. The lowest concentrations of mercury in Jatropha curcas shoots were obtained in the treatment of 5% zeolites, while there are significant reductions in the concentrations of mercury in Jatropha curcas roots, the reductions were less evident at harvest 1. The maximum percentage reductions, compared to the controls, are less than for the shoots. Figures 1 and 2 show a progressive reduction in mercury concentrations with time.

Table 4 Concentrations of mercury (ppb) in shoots and roots of Jatropha curcas

| Plant/harvest time | Control\(^1\) | A\(^2\) | B\(^3\) | C\(^4\) | R\(^5\)% |
|--------------------|---------------|---------|---------|---------|---------|
| **Shoots**         |               |         |         |         |         |
| Harvest time (1)   | 56            | 29      | 22      | 13      | 76.8%   |
| Harvest time (2)   | 49            | 27      | 21      | 9       | 81.6%   |
| Harvest time (3)   | 48            | 26      | 23      | 8       | 83.3%   |
| **Roots**          |               |         |         |         |         |
| Harvest time (1)   | 178           | 92      | 83      | 76      | 57.3%   |
| Harvest time (2)   | 156           | 84      | 75      | 62      | 60.3%   |
| Harvest time (3)   | 158           | 81      | 67      | 65      | 58.9%   |

\(^1\)no zeolite added  
\(^2\)additive of 1\% soil weight zeolite  
\(^3\)additive of 2\% soil weight zeolite  
\(^4\)additive of 5\% soil weight zeolite  
\(^5\)R\%, maximum percentage reduction of mercury concentration in plant relative to control.

Figure 1 Concentrations of mercury (ppb) in roots of Jatropha curcas
The addition of zeolite at the rate of 5% seems to reduce mercury concentrations more than the other treatments in both shoots and roots of Jatropha curcas plant, similar findings with another study [12]. The reductions are definite in the shoots than in roots of the Jatropha curcas plant. In phytoremediation studies, mercury concentrations were higher in the roots than in the shoots is confirmed by other studies, and generally, a trend for mercury to concentrate in roots, demonstrates that the roots delivered as a barrier to Hg uptake [13].

4. Conclusion
Based on the results and discussion, the higher mercury concentration was found in topsoil rather than the subsurface. The result of mobility analysis shows that most mercury fractions are associated with organic mercury (Hg-o) followed by mercury element fractions (Hg-e) associated with amorphous nitrides such as aluminum silicate and Fe and Mn oxides, then mercury associated with Hg-h which binds to dissolved mercury. The high content of Hg-e suspects derived from the mining activities of the people due to the amalgamation process. While the fractions Hg-w and Hg-h, which is the most unstable fraction encountered with a reasonably high percentage, so that this fraction is very potential to pollute the environment directly as it will be uptake by the plant. The result of the experiment on soil stabilization by natural zeolite revealed that by adding natural zeolites as soil, additives would reduce the concentrations of Hg in plant material. Mercury concentration in shoots and roots, compared to controls with no added zeolites, was reduced up to 83.3% and 60.3%, respectively. The additive zeolite is useful to reduce Hg in the plant which is a crucial step leading to the entry of mercury into the food chain.

References
[1] Koyomi N, Nagafuchi O, Kawakami T, Inoue T, Yokota Y, Serikawa Y, Cyio B, Elvince R (2016) Human health risk assessment of mercury vapor around artisanal small-scale gold mining area, Palu city, Central Sulawesi, Indonesia. J Ecotoxicol Environ Saf 124:155–162
[2] Tomiyasu T, Kono Y, Kodamatan H, Hidayati N, Rahajoe JS (2013) The distribution of mercury around the small-scale gold mining area along the Cikaniki river, Bogor, Indonesia. J Environ Res 125:12–19
[3] Doran, J.W. and Zeiss, M.R. (2000) Soil health and sustainability: managing the biotic component of soil quality. *Applied Soil Ecology* **15**, 3–11

[4] Appleton, JD, Weeks, JM., Calvez, JPS., Beinhoff, C, (2006) Impacts of mercury-contaminated mining waste on soil quality, crops, bivalves, and fish in the Naboc River area, Mindanao, Philippines. *Sci. Total Environ.* **354**, 198–211

[5] Molina, JA, Oyarzun, R, Esbri, JM., Higueras, P (2006) Mercury accumulation in soil and plants in the Almadén mining district, Spain, one of the most contaminated sites on Earth, *Environmental Geochemistry and Health* **28**, 487–498

[6] Fahmi FL (2014) Kandungan dan Sebaran Pencemaran Merkuri (Hg) di Lokasi Penambangan Tradisional Emas Primer Desa Paningkaban, Dan Sekitarnya, Kabupaten Banyumas, Provinsi Jawa Tengah. undergraduate thesis Department of Geological Engineering Universitas Gadjah Mada (in Indonesia language) unpublished

[7] Budianta W, Fahmi FL, Arifudin, Warmada IW, (2019) The distribution and mobility of mercury from artisanal gold mining in river sediments and water, Banyumas, Central Java, Indonesia, *Environmental Earth Sciences* **78**:9

[8] Hakim F (2014) Geology, alteration, mineralization, and characteristic of hydrothermal fluid on epithermal gold deposit in Cihonje-Paningkaban area, Gumelar, Banyumas, Central Java, Indonesia, undergraduate thesis Department of Geological Engineering Universitas Gadjah Mada (in Indonesia language) unpublished

[9] Bloom NS, Preus E, Katon J, Hiltner M (2003) Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Anal Chim Acta* **479**:233–248

[10] Ardiana A, (2019) Remediasi Cd dengan menggunakan tufa zeolitik Nengahan, Tegalrejo, Gunungkidul, Yogyakarta, undergraduate thesis (in Indonesia language) unpublished.

[11] Andriyani, ND, (2019) Remediasi Pb dengan menggunakan tufa zeolitik Bantengwareng, Gedangsari, Gunungkidul, Yogyakarta, undergraduate thesis Department of Geological Engineering Universitas Gadjah Mada (in Indonesia language) unpublished.

[12] Haidouti C (1997) Inactivation of mercury in contaminated soils using natural zeolites, *Sci. Total Environ* **208**, 105–109

[13] Lindberg SE, Jackson DR, Huckabeer JW, Janzen SA, Lenin MJ, Lund JR (1979) Atmospheric emission and plant uptake of mercury from agricultural soils near the Almadén mercury mine. *J Environ Qual* **8**:572-578

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