The content of heavy metals in vegetables in the hydrothermal alteration rocks Boto Wonogiri Central Java

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Abstract. The research area was an area of hydrothermal alteration resulted of Tertiary volcanoes activity. Stratigraphically this region was composed of volcanic breccia, andesite lava intruded by andesite and then undergoes hydrothermal alteration. The result of the interaction between hydrothermal fluids and rocks produce some heavy metals. The elements will be contained also on the soil which was the result of its weathering and then the heavy metal elements were absorbed by the plant. The elements with certain level were very dangerous for human health. This phytoremediation process can also occur in alteration rocks of Quaternary volcanoes. Then some plants will have different capabilities in absorbing certain heavy metals. This research was conducted to know the characterization of vegetable plants that absorb heavy metals and this research using methodology are: petrography, X-ray diffraction (XRD), X-Ray Fluorescences (XRF) and mercury analysis using Mercury Survey meter. These methods were done to know the rocks type, alterations type and heavy metals content. The analysis yields andesitic rock type which is hydrothermally altered to argillic. These argillic rocks become soils containing heavy metals including Mn, Fe, Co, Cu, As, Hg and Pb. With the process of phytoremediation then heavy metals can be contained in plants. The results showed that vegetable plants have the character of absorbing certain heavy metals, such as: chilli (Capsium fruteceus) absorb Hg. Kale (Ipomoea aquatica), chilli, bay (Eugenia aperculata) leaf, papaya (Carica papaya) and taro (Colocasia esculenta) leaf are absorbed Fe element. It proves that the metallic minerals as result of hydrothermal alteration process are absorbed by plants or vegetables.

1. Introduction
The mining waste can be a toxin that can spread through surface water flow, thus polluting soil and ground water. This phenomenon is similar to that occurring in the former mine area in the Marrakech of South Morocco, where rivers and soils are contaminated by copper (Cu) and zinc (Zn) elements from mineral mine weathering such as: pyrrhotite, sphalerite, galena, chalcopryite, arsenopyrite, pyrite and magnetite.

The pH of the river ranges from 2.1 to 2.6, thus making the pH of the river very acidic [1]. The heavy metal toxins in the soil and rivers can be absorbed by plants. Plants absorb heavy metals by cation, so
by planting the plants, the concentration of toxins in the soil can be reduced [2]. This phytoremediation research was successfully performed by [3, 2, 4] planted sorghum on soils containing heavy metal toxins and the results showed that sorghum strongly absorbed Zn, Fe, Mo, Cu contained by the soil. So the purpose of this research was to determine the heavy metals content in vegetables that grow in alteration rocks due to hydrothermal processes.

The research area is administratively located in Jatiroto Sub-district, Wonogiri Regency, Central Java Province (Figure 1.). Based on the arrangement of the magmatic arc expressed by [5, 6], the research area is a part of the island arc Tertiary volcanoes in Java Island. The interaction between hydrothermal fluids and rocks lead to alteration and mineralization. The process produces heavy metal elements such as: Fe, Mn, Cu, Pb, Hg, As, Zn, Ag [7].

The vegetation interacted with each other and with the environment [8, 9, 10]. The presence of metal elements in nature can affect the existing vegetation. The vegetation was containing heavy metals, when consumed can accumulate in the body. If there is more accumulation, it will affect human health [11, 12].

2. Method
Measurements and sampling were conducted in alteration and residential area of Boto village, Jatiroto Wonogiri Central Java. From the Wonogiri city approximately 20 km to the southeast to Ponorogo (Figure 1). The research area was a steep hill area and in the north is a plain occupied by settlements and rice fields.

Sampling was done to know the content of heavy metal elements in soil and vegetables. The research method used was the method of observation, measurement and laboratory analysis. To know the mercury content in soil using Mercury Survey Meter. To identify the rock type and mineralogy using petrographic method, while to know the type of alteration using X-ray diffraction (XRD) method. The heavy metal content the soil and vegetables using XRF (X-Ray Fluorescence) method. The vegetables are selected to represent some of the plants that are often consumed by local people for daily purposes.

3. Result and Discussion
The research area was part of Tertiary volcanoes di Java Island that have now been altered and are one of the gold mineralized producers in Wonogiri Central Java. The formation of the Tertiary Magmatic arc was nothing else, due to the subduction between the Indian-Australian oceanic crust and the Southeast Asian continental crust. According to [13, 14], explained that the Indian-Australian oceanic crust moves relatively to the north and the Southeast Asian continental crust move relatively to the south. [5], explains that this subduction product in Java forms the magmatic arc aged from the Early Tertiary to the present. [15], the volcanic rock and acid-basic intrusion rocks that have undergone alteration and
mineralization processes. The research areas compiled by the volcanic breccia of Nglanggran Formation interbedded with andesite lava. This unit lithology is intruded by andesite. Age of this unit lithology was Miocene Early-Middle. The volcanic breccia has features: massive, graded-supported textures. The andesite fragments embedded in the volcanic material matrix that cemented by silica. This breccia was intruded by andesite and the rock was generally altered ([15, 16]).

In the study area found the volcanic breccias of Nglanggran Formation interbedded with andesite lava which was unconformity by the limestones of Wonosari Formation. The volcanic breccia of Nglanggran Formation was intruded by andesite and this intrusion has undergone alteration (Figure 2).

![Figure 2](image.png)

**Figure 2.** Geological map of research area, Mesu, Jatiroto Wonogiri Central Java.

The results of petrographic observation of volcanic breccia fragments were brownish, massif, pilotaxitic, porphyritic, hypocrystalline, medium-affanitic, subhedral-anhedral and inequigranular texture. The mineralogical composition consists of pyroxene, plagioclase and opaque minerals embedded in the groundmass of plagioclases microlite and volcanic glasses (Figure 3).

Andesite lava was found as an interbedded in the breccia. These rocks when fresh has the characteristics: brownish gray, scoria, amygdaloidal, medium fine-affanitic, subhedral-anhedral, hypocrystalline and inequigranular texture (Figure 4). The constituent mineralogy consists of pyroxene, plagioclase embedded in the groundmass of plagioclases microlite and volcanic glasses. Secondary quartz is present as amygdaloidal minerals.
The altered andesitic intrusion has the following characteristics: greenish gray, massive, medium fine-afanitic, subhedral-anhedral, hypocrystalline and inequigranular texture. The mineralogy consists of pyroxene and plagioclase embedded in the groundmass of plagioclases microlite and volcanic glasses. The alteration and mineralization due to hydrothermal processes produce secondary minerals such as sericite, calcite, chlorite, montmorillonite, hematite, pyrite, chalcopyrite, galena, gold, bornite and covellite.

3.1. Alteration zone
The type zone of surface alteration that has been found in the study area was argillic. In this type of alteration minerals of argillic found some of minerals as montmorillonite, quartz, hematite, pyrite and fine cinnabar. The type of clay minerals in this argillic zone is montmorillonite, this can be known from the results of X-ray diffraction (XRD) analysis (Figure 5.).
3.2. Heavy metal on soil

The research area was an area of hydrothermal mineralization and a gold mine that 50 years old. The mine was traditionally managed by local people. The research area was an alteration area, so it was a lot of heavy metals contained in altered rocks and the soil that was the result of weathering. Heavy metals were not dangerous, when the amount of accumulation was still within normal limits. However, if the accumulation exceeds the normal threshold that has been set, it will be dangerous. Many of the heavy metals found in soil in the research area include: mercury (Hg), manganese (Mn), arsenic (As) and lead (Pb). The distribution of heavy metals can be explained as follows:

Mercury (Hg), the mercury distribution in the research area was spread only in the central part of the Boto region and the mercury concentration in the soil was about 1-80 ppm. Moreover, this area was also mixed mercury from the former gold processing conducted by local people. Manganese (Mn), the concentration of manganese in soil samples was about 1-3579 ppm. The manganese distribution comes from alteration rocks that have undergone weathering. Arsenic (As), arsenic content in soil was ranges from 1 to 100 ppm. As with Mn, so As element was present in the andesite intrusion alteration zone. Lead (Pb), content of lead dispersion in the highest research area was 598 ppm. The highest concentration of Pb was present in the middle of the research area.

3.3. The content of heavy metals in vegetables

This research also assessed the content of heavy metals from vegetables and planted by local people. [17] explained that the Hg element derived from the gold processing using the amalgamation process and also formed naturally from the alteration rocks. The spread of Hg was controlled by the topography, bedrock and water flow. Mercury in the soil was already polluting the local people as well as animals and plants. Some plants used as research objects including several types of vegetables. The vegetables were also suspected to absorb heavy metals, as the plant grows on the alteration rocks, so the plant can be used as phytoremediation plants.

To know the content of heavy metal elements in vegetable plants, the samples taken on some leaf and fruits of vegetables such as kale (Ipomoea aquatica), chilli (Capsicum fruteceus), taro (Colocasia esculenta) leaf, papaya (Carica papaya) leaf and bay (Eugenia aperculata) leaf. These vegetable plants were very common in the local area and was consumed by local people for food needs and planted around thier house. Other than the vegetable plants, the samples plant were selected by age criteria of plants, ie: ages of about 3-6 months and plants over one year. This was to estimate the concentration of heavy metals that can be absorbed by plants. Short-term plants that are about 3-6 months commonly grown by local people are kale, chilli, taro leaf, other than that was more than 1 year old was the leaf of
papaya and bay leaf. In generally some of these vegetables absorb heavy metals, but the element of Fe was generally absorbed by these vegetable crops. Kale, chilli and taro leaf are absorbent Fe element around 0.0375-0.0603 ppm. While the bay leaf can absorb Fe (0.0228 ppm), the element absorbed by the bay's leaf was lower than that absorbed by papaya (0.0631 ppm). Hg element was only absorbed by chili and bay leaf, which was 0.0168 ppm. This suggests that the age of the chili plants, which was about 3-6 months, can absorb more mercury than the bay leaf plants that have more than 1 year of age (Figure 6-7). Medium taro leaf as the highest absorbent element Mn (0.0094 ppm) compared to other vegetable plants. Elements of Co, Cu, As and Pb are generally absorbed in small amounts (0.0001-0.0010 ppm).

4. Conclusions
Heavy metal can be accumulated in plants in the research areas starting from magmatic activities such as volcanic eruptions (pyroclastic rocks, lava) and andesite intrusions that carry heavy metals out of the earth. The hydrothermal and weathering process was a process after magmatic. With this process heavy metals can be concentrated on the soil which is then absorbed by the plants. Primary minerals producing heavy metals are pyroxene, opaque minerals, while secondary minerals producing heavy metals are chlorite, hematite, pyrite, chalcopyrite, galena, gold, manganese, bornite, sinabar and covellite. The minerals produce heavy metals such as Fe, Mn, Cu, Hg, Pb and As. Each vegetable has the character of absorbing heavy metals, such as: chilli \((Capsium fruteceus)\) absorb Hg. Kale \((Ipomoea aquatica)\) leaf, chilli, bay \((Eugenia aperculata)\) leaf, papaya \((Carica papaya)\) leaf and taro \((Colocasia esculenta)\) leaf are absorbed Fe element.

![Graph showing the concentration of heavy metals contained by vegetable plants.](image)

*Figure 6. Graph showing the concentration of heavy metals contained by vegetable plants.*
Figure 7. Shows photos of some vegetable crops found in the study area as vegetables consumed by local people. 
   a. Kale leaf, b. Chilli, c. Bay leaf, d. Papaya leaf, e. Taro leaf

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