

# Heavy Metals Distribution in the Artisanal Gold Mining Area in Wonogiri

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**Abstract** Artisanal and small gold mining activity in Wonogiri Regency has long been done and gives the benefit of the people's economic support, but this activity has the potential to decrease the quality of the environment. This study was aimed to analyze the levels and spatial distribution of heavy metals in the mining area. Survey of mining and amalgamation sites, sampling the soil and tailings had been conducted. There were 66 samples of soil and tailing were collected, analysis of heavy Fe, Mn, Pb, Hg, As and Co, using X-ray fluorescence (XRF). Normal distribution test of data was conducted using the Kolmogorov-Smirnov and Shapiro Wilk. The spatial distribution of heavy metals was described using Krigging method. Contents of most heavy metals in the area studied were high, except for Co. According to the distribution pattern of heavy metals indicated that the contamination caused by the mining.

**Key words:** Artisanal mining, gold, heavy metals

**Abstrak** Pertambangan rakyat dengan skala kecil di Kabupaten Wonogiri telah lama dilakukan dan memberikan kemanfaatan dukungan ekonomi masyarakat, namun aktivitas ini berpotensi menurunnya kualitas lingkungan. Penelitian ini bertujuan untuk menganalisis kandungan dan distribusi spasial logam berat di daerah pertambangan. Survei dilakukan di areal pertambangan dan amalgamasi, sampel tanah dan tailing telah dilakukan. Ada 66 sampel tanah dan tailing dikumpulkan, analisis logam berat Fe, Mn, Pb, Hg, As dan Co, menggunakan X-ray fluorescence (XRF). Uji distribusi normal data dilakukan dengan menggunakan Kolmogorov-Smirnov dan Shapiro Wilk. Distribusi spasial dari logam berat digambarkan menggunakan metode krigging. kadar logam-logam berat di lingkungan pertambangan rakyat adalah tinggi, kecuali Co. Menurut pola distribusi logam berat menunjukkan bahwa pencemaran akibat pertambangan.

**Kata kunci :** emas, logam berat, tambang rakyat

## 1. Introduction

The problem of heavy metal contamination in soil is already understood to be harmful to the environment. The existence of contaminants in the soil may be caused by natural processes, but mostly due to human activities. Natural process that led to the emergence of contamination in the soil include: in volcanic activity and andesitic minerals alteration. As caused by human activities may include mining, industry, households, agriculture, etc. [Bless et al., 2016; Hu et al., 2013; Iorfa, et al., 2011]. Gold mining activities consisting of material mining and processing to separate the gold from the tailings, both of which can potentially lead to the emergence and heavy metal contamination in the soil. The spread of contaminants in the soil and in the area around the source of the contaminant is determined

by the basic characteristics of the soil [Iorfa et al., 2011] landform and land use. While the amount of Fe and Mn in soil is naturally at abundant levels [Hu et al., 2013]. Artisanal mining activity in Wonogiri Regency Central Java Province has been going on since about a century ago. Mining activities they do to increase revenue from the main work as a farmer. Mining community does not understand very well the characteristics of the soil and the water flow which can lead to the spreading of heavy metal contamination. The main environmental effects of artisanal mining are soil erosion, sedimentation of water bodies, mercury pollution, and a total lack of land reclamation after closure [McMahon et al., 2000]. Of these, the most common problem causing cationic metals (metallic elements whose forms in soil are positively charged cations e.g., Pb<sup>2+</sup>) are mercury, cadmium, lead, nickel, copper, zinc, chromium, and manganese [NCRS, 2000].

Heavy metals (HM) are considered to be metals with a density/specific mass above 5 g.cm<sup>-3</sup> [Nies, 1999; Hooda, 2010], and include: copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), iron (Fe), nickel (Ni), silver (Ag), thorium (Th), uranium (U), mercury (Hg) and arsenic (As).

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Untill now, there is no sufficient in the studied area about the spread of heavy metals in the soil in the mining and processing of gold in the mine area of the people at this location, while artisanal gold mining was already done from about one century ago.

Based on the problems that exist in this area, then the purpose of this study was to analyze the distribution of heavy metals as contaminants in the soil associated with alteration minerals, gold mining activities and processing in artisanal mining village of Boto village Wonogiri Regency.

## 2. The Methods

The study was conducted in the area of artisanal mining, as artisanal and small scale mining, which is located in the village of Boto, Jatiroto, Wonogiri. The location is part of mountainous region known as Gunung Mas. Mining is done by open pit mining that is in Tapel site, which is located at the peak of Gunung Mas Mountains. Mineral processing was performed by the amalgamation using mercury (Hg) which is locally termed as “gelondong”, that there were more than fifteen units located in the village. Sampling was carried out in the area, and there were for 66 samples that were distributed from: 1) alteration of rocks from open pit mines, 2) the tailings and the soil surrounding the amalgamation site, 3) soil on the rice field that were potentially received contaminant from the liquid

waste result in amalgamation processing. Analysis of heavy metals includes Fe, Mn, Hg, Pb, Co, As from soil and tailing samples that were conducted using X-ray Fluorescence (XRF). Statistical analysis included: mean, median, mode, standard deviation, testing for normality, skewness, kurtosis number and frequency distribution curve along with the normal expectation. Spatial distribution of heavy metals Fe, Mn, Hg, Pb, Co, As presented in the form of a contour map metal levels in the soil with the slope correction factor to determine the pattern of spread of contaminants.

A normality test is generally used to determine whether sample data has been drawn from a normally distributed population (within some tolerance). A number of statistical tests, such as the Kolmogorov-Smirnov and Shaphiro Wilk can be perform to the normality of data distribution. In this research, normality test of the data distribution for the contents of heavy metals was done to identify spatial changes of these metals. In an environment of relatively uniform, the concentration of heavy metals will tend to be normally distributed indicated by the low value of skewness. Then the mode is small or even conveniently indicates the mode not found metal content is not worth striking. Besides, the shape of the normal distribution curve which has a peak that is not too high or low value of kurtosis which shows the distribution of content value is relatively uniform.

## 3. Result and Discussion

### Land Characteristics

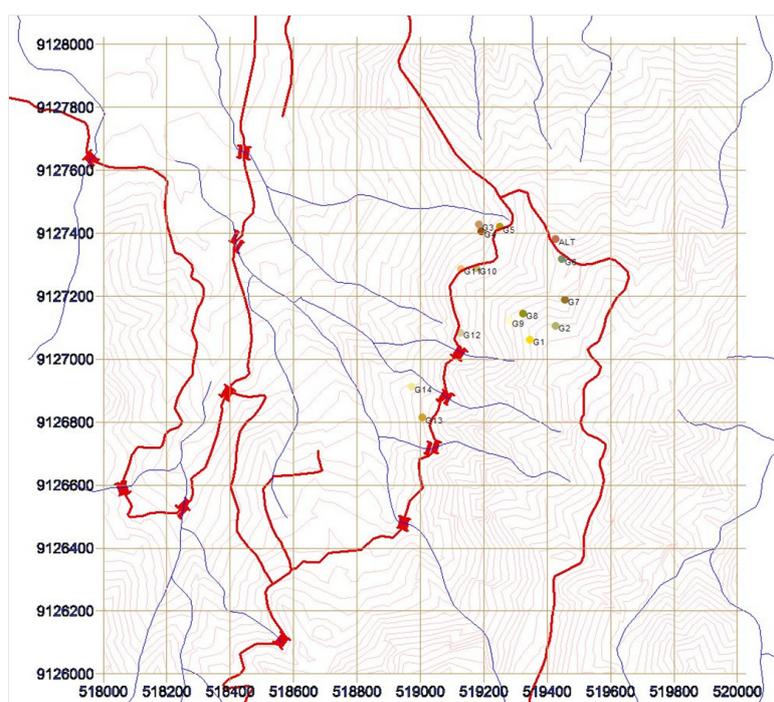


Figure 1. Sites of artisanal and small gold mining

The research location was land that is mountainous in nature and with very steep slope. According to the regional geology, lithology of this area is composed by old volcanic breccia and that have undergone alteration by hydrothermal process. Land surface was characterized by dissected slopes surface by runoff that form the rill and gully erosion and landslides in several locations. Source water flow comes from rain water or spring water that appeared from the top of the mountains and on the slopes of the mountains. Land surface was covered by abundant of rocks and stone with varies size that from small to very large. The existence of these rocks is potentially very dangerous in case of falling rocks (rock fall). In the classification of land capability and space utilization, research sites should be protected areas with land use constraints of the form factor of the slope. But according to the history of land use since prolong time as the use of land for cultivation. Existing land use on the research area is as a natural forest, mixed farming, and village settlements with the pattern of spread. In the middle altitude of the mountains there were some agricultural activity for rice cultivation in paddy fields, and it is done in the field with a steep slope with a terrace system. So that rice field as paddy field is made up as bench terraces that the pattern is in direction of the contour lines. For irrigation of paddy fields farmers use various sources of water that comes from the top flows as creeks, and also a source of water that comes out on the slopes. Livestock are commonly found in communities consisting of cattle, goats and poultry (mainly chickens). Local people raise cattle and goats by impound their animals, while the chicken which they raise are allowed to roam outside during the day, and at night the chicken are back and entered their house.

### **Mining location**

Gold mine site is located in a mountainous complex of Gunung Mas located in Wonogiri Regency, which is referred to as Tapel rural community. There were three types of mining that were operated by artisanal miner, i.e. open-pit gold mines, underground mining, and combination of open pit mine followed by underground mining. The existence of mineral prospects of the gold content is only about one meter below the soil as overburden that it may facilitates local communities easy to open land cover. Artisanal mining operations are generally defined as those using little or no mechanization or heavy equipment [McMahon et al., 2000].

Operational of gold mining is generally done by open pit with activity using manual simple equipments, and it is classified as artisanal and small scale gold mining [Arifin et al., 2015; McMahon et al., 2000]. Sorting material containing gold prospect is conducted by using the flowing water that coming from the water spring. With the provision of mining technique

that has been owned by the locals they do mining collectively and interchangeably. To reduce sediment transported by surface runoff and allow it to do sorting of returned materials prospects, a mini settling pond was constructed to facilitate suspended solid settling.

After mining was done by artisanal miners there was appearance of land surface that forming an irregular excavated land. This is because the miners only did quarrying activities and the post mining land was left without any reclamation process. Even the post open pit mining land was then followed by digging up if there was a prediction of the prospect ore present in the deep site from surface, as it was then used the underground mining technique.

The open pit gold mines are developed at the surface, because of that these mines are also called surface gold mines. The overburden, i.e.: the rock or soil overlaid the gold ore, are removed before extraction of gold ore. This overburden is dumped on surface, preferably on mined-out area. Therefore, this type of mining requires quite large area on surface. Many a times, large forest areas are transferred for gold mining purpose. The land degradation is the result of creation and expansion of open pit gold mines. The environmental aspect of land degradation in underground gold mines is due to subsidence over the underground cavities resulted from underground caving.

There are times during mining when hazardous materials can affect the environment by becoming bioavailable to downstream ecosystems. The most common pathway is from mine wastes, ore stockpiles and mine operations into surface water or groundwater. Spills during the mineral processing circuit are another potential pathway, but are less common [Australian Government 2016].

In addition to the mining was done in open pit, they also conduct underground mining by making holes in the points that the prospect for gold is obtained. The location is at the point of making the holes is estimated the presence of alteration in the form of mineral veins containing gold. So many holes underground mining might be found in Boto village, either still active or who are not mined anymore as abandoned mine.

### **Amalgamation Process**

In this village there are twenty units of mill and amalgamation to process ore to get the gold. The unit processing gold in the village called *gelundung* as the form set cylinder actuated using a dynamo with electric drive. In the processing of the material is made of split, which is then inserted into *gelundung* with addition of water, mercury and plant leaves, such as *lamtoro* leaves from *leguminosae* plant types. The process uses the *gelundung* with rotator electricity and requires for 2 hours and then fed and the result is an amalgam. Waste water is then collected in a bucket and then it

would be proceed for second step of amalgamation. The amalgamation process in general as much as 2 times, and it resulted the waste is in the form of tailing included in tubs or stacked. After the teilling had been drying then it was stored in sacks. An important consideration is the chemistry of the waste rock material being disposed of. Potential long-term impacts of weathering and subsequent release of deleterious liquors and dissolved metals determine how waste is handled and stored [Hitch et al. 2010]. The present study showed that there was businessman from outside the area that collects tailings then collect and process to be able to recover the gold taken mercury so that it can be retrieved. Most of the old mines have dumps and tailings containing appreciable amount of gold, and this may be due to the primitive technologies existed at that time or due to sudden shut down of mines [Abouzeid & Khalid, 2011]. Total absence of environmental management, health effects from mercury pollution [Hitch et al., 2010; McMahon et al., 2000]. Also the most probable source of the elevated mercury level in inhabitants of the ASGM site is the mercury vapor from smelting processes, which mainly occurs outside, in gold shops and sometimes inside houses [Arifin et al., 2015]. If hazardous materials used in the mining industry are mismanaged, they can poison humans, animals, plants and aquatic ecosystems, disrupt their reproductive processes or their habitat, and it will be very costly to remedy [Australian Government 2016].

### Heavy metals the soil

Heavy metals contamination in the soil on the gold mining might be resulted from the process of minerals alteration, mining and amalgamation processing include Fe, Mn, Pb, Hg, As and Co. The results of the analysis of all types of metals using XRF presented are in the Table 1. Metals found in water

draining from mine sites. Metal concentrations increase in waters at lower pH. Once released, metals will persist in the environment. Their concentration in water can be reduced through physical removal such as sorption, precipitation, biological uptake [Smith, 2007]. Metals as ions or complexes may be derived from metal- sludge or metal-solutions. Recovery of the metal is usually the object of the mining project, but hazards may arise from the presence of toxic by-products (for example, arsenic and cadmium) or metals released as a result of developing acidification, as described in Managing acid and metalliferous drainage [Australian Government 2016].

### Iron (Fe)

The result of the present research shows that Fe content in the soil was the highest levels among the other metal elements. In general this element is the dominant element in weathered rocks and also it evolved into the soil. In the early development of soil process Fe element is still dominant in the soil parent material and it occupy as series of primary mineral compounds. Along the process of rock weathering the elements Fe and others liberated into a soluble form, particularly on the environment with acidic reaction and oxidation state. In this condition Fe can react to form oxides, hydroxides or salts depending on the environmental elements of Fe. In environments mineral alteration in the location studied is characterized by a high degree of oxidation resulted by a very fast internal drainage of soil as it is supported by the surface land with a steep to very steep slopes.

By field observation to the soil profile that had been conducted at surveying period, it was identified that Fe in soil as iron oxides. Fe content of all samples analyzed showed in the range that is not too sharp, a minimum value of 1.65% and a maximum of 7.04%.

Table 1. Basic statistical analysis

Analysis	Elements					
	Fe (%)	Mn (%)	Pb (ppm)	Hg (ppm)	As (ppm)	Co (ppm)
Min	1,65	0,04	1,00	1.00	1,00	Nd
Max	7,04	0,60	598,00	874.00	238,00	Nd
Mean	4.69	0.16	83.76	79.45	32.00	Nd
Median	4.75	0.12	1.00	1.00	1.00	-
Mode	No	0.26	1.00	1.00	1.00	-
Numbers of mode	0	2	35	41	43	-
Std.dev	1.14	0.11	120.95	180.53	62.45	-
Skew	-0.89	2.09	1.91	3.10	2.06	-
Kurt	3.24	4.80	4.49	9.51	3.02	-
CV	24.31	68.75	144.01	227.72	194.85	-

Table 1 shows that the average value of Fe content in all samples is 4.69%, or it is approximately in the middle between the minimum and maximum values. High content of Fe in the soil and its form of iron oxide and it may play a role as coloring of the soil, which is generally red in color. Fe and Mn are major elements and they

occur naturally at abundant levels [Hu et al., 2013]. The median value of the Fe content in the present study is 4.75%, but the data distribution did not show any mode. The standard deviation of the distribution of the data content of Fe is 1.14 and the coefficient of variance (CV) value was 24.31%.

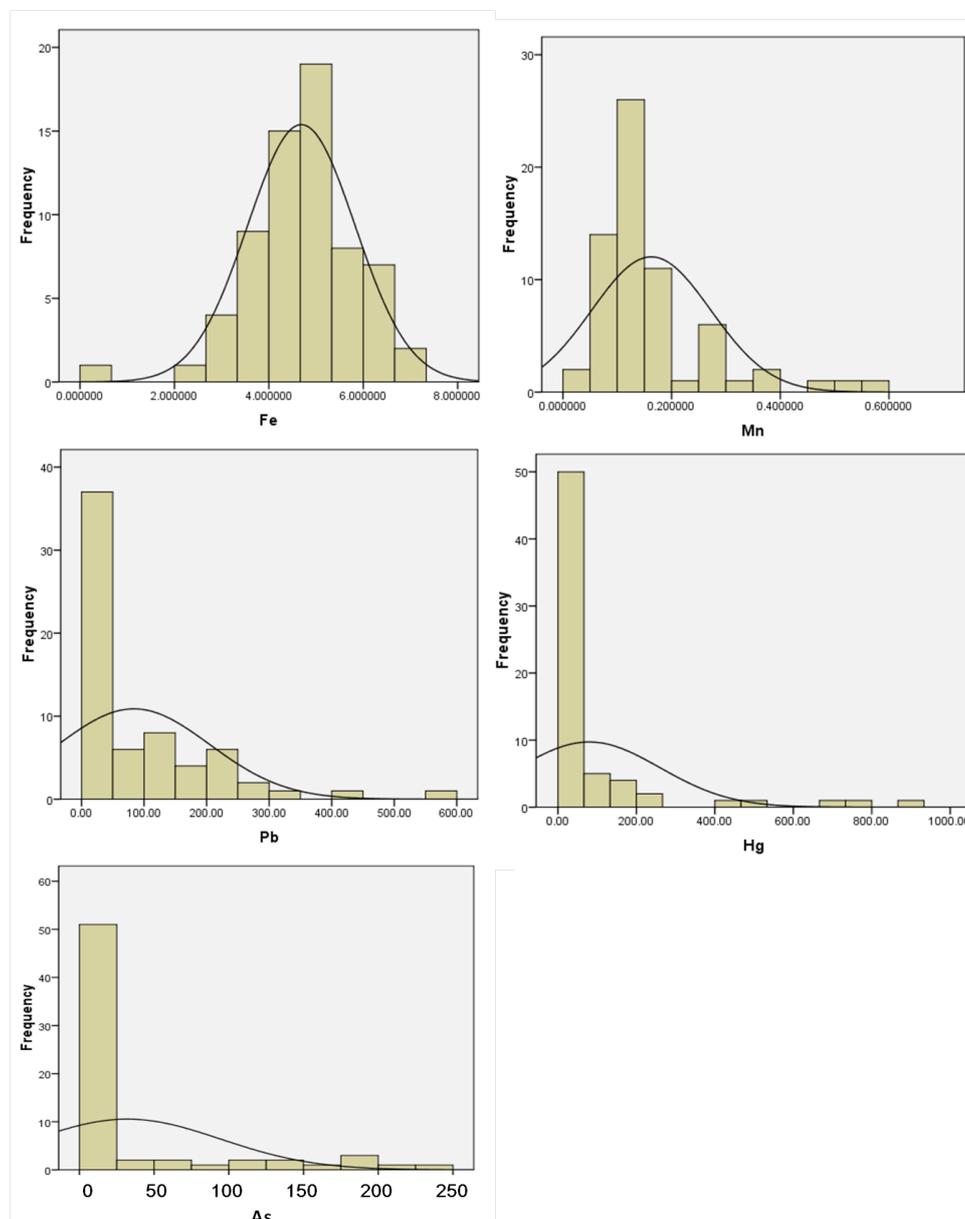


Figure 2. Distribution frequencies, kurtosis and skewness of normal distribution of heavy metals contamination in soil

### Manganese (Mn)

The results of the present analysis of 66 samples that were examined showed the minimum value was 0.04% and the maximum value was 0.60%, while the average levels of manganese in the soil was 0.16%. The median and mode values of the data were 0.12% and 0.26%, respectively. According to the value of the mode that is higher than of the average and median, it can be

stated that the frequency distribution curves of data tend to skewing right side. The standard deviation of the distribution of the data content of Mn is 0.11 and coefficient of variability (CV) is 68.75%. Manganese element in mineral soil derived from weathering rocks then it forms Mn-oxides when reaction in soil is oxidation in nature. In soil environment, Mn generally shows as a concentrate in part of the soil profile, and

it is often found as mottle of dark-colored soil. The development of mottle of manganese in the soil and then crystallized to form nodules Mn oxides. In the Mn oxide minerals of some soils developed in Java many elements of heavy metal such as Co, Ba, Sr, Cu, Cr, Zn, were found and they were fixed in the crystal structure of the mineral nodules Mn-oxides [Nurcholis et al., 1997].

### Lead (Pb)

In the studied soil, minimum content of Pb was 1.00 ppm and the maximum was 589.00 ppm with an average of 83.76 ppm. According to this result, it can be said that Pb concentration increase sharply in the alteration materials comparing with the original igneous rocks as parent materials of the developing soil. However the median and the mode values of distribution of the frequency distribution of the data to 1.00 ppm, respectively. According to the result there was high variability of the Pb content in the area of gold mining environment. Some of the studied sites might be lowering the Pb, and the value was around 1.00 ppm, but on the other site was 598.00 ppm as the maximum value. The high value of maximum concentration in the soil studied expressed that there were high contamination of Pb in soils as Pb was absorbed in clay minerals. Study on the Pb retention was conducted in Michigan US, by spiking the clay materials using solution containing metal, and the result showed that Pb was immobilized by clay materials [Salim et al., 1996]. The average value of Pb in soils was 83.76 ppm, then the median and mode were respectively 1.00 ppm. Based on the mean, median and the mode of data frequency distribution curves of Pb is likely to be skewed to the left. Occurrences mode values (1.00 ppm) was the 35 of the total of data is 66, then more than 50% of the data shows the value of Pb is 1.00 ppm (Table 1).

Presence of lead in soils is generally derived from the product of weathering of rocks. The source of Pb content in the igneous rocks is in the range of 2-30 ppm [Bradl, 2004]. Their weathering causing elements, including Pb, and the content of this element may be distributed soil body depending on the environment of the soil genesis and development. Accumulation of Pb element in the environment in gold mining area is generally occurred on rocks mineralization, and it can be formed as galena (PbS), cerussite (PbCO<sub>3</sub>) and also some in anglesite (PbSO<sub>4</sub>), so the content of Pb in environment may increase.

### Mercury (Hg)

The existence of mercury in the mine environment is very important to be analyzed. The main sources of Hg are from the natural process of alteration of rocks and from human activity or anthropogenic processes [Malm, 1998], namely the addition of mercury in the

amalgamation to separate gold from rock. The existence of Hg in the soil unstable since Hg has a very high volatility. Mercury has three forms of oxidation number is zero (element), one (mercurio) and two (mercury). In soil, sediment, water and organisms, mercury forms as salt or complex of an organic compound, currently in atmospheric mercury as an element of Hg.

Hg content in the soil studied show varies between 1.00 and 874.00 ppm (Table 1). The high difference in minimum and maximum values of Hg content in the soil at the site of artisanal mining has demonstrated their enormous addition of mercury into the soil as a contaminant. In the amalgamation process, mercury is necessary added to separate and bond the gold from the rock for gold properties that reacts with Hg to form amalgams. Amalgamation technique in the present study was simple and waste handling systems in this process was not good cause potential contamination of the soil in the vicinity of the amalgamation site. Mercury in tailing as solid residual containing Hg might potentially contaminated soil by water runoff after rainfall. The worst handling technique to liquid waste from amalgamation process may also cause Hg contaminated the soil in the vicinity of the amalgamation site. The average value of Hg content in the soil studied is 79.45 ppm, while the median and mode are respectively 1.00 ppm (Table 1). Based on the mean value greater than the value of the median and mode, it shows the frequency distribution curve is skewed to the left. Kurtosis value of the frequency distribution of soil Hg content in the highest compared with values for Fe, Mn, Pb, As and Co. Mode value of the present result was 1.00 ppm with the numbers of mode value was 41 from 66 data, the maximum value of Hg level was 874.00 ppm, and the mean value was 79.45 ppm (Table 1). Accordingly, it can be considered that Hg contamination of the soil surrounding the gold mining activities in location studied is very high. The presence of mercury in soils is highly affected by the nature of clay minerals that is the ability of these constituents to absorb Hg [Sarkar et al., 1999]. Very much area of soil that contaminated by Hg in the present study is thought as a role of clay fraction in ability to absorb Hg. Indeed, very long period of mining and amalgamation processes in this area may cause accumulation of this element in soil.

### Arsenic (As)

The results of analysis of the content of As in soil and solid waste or tailings resulted from amalgamation process in this research is in the range between 1 to 238 ppm, with an average value is 32 ppm (Table 1). Presence of arsenic in nature is determined by the source is the content of the rock, the rock weathering process and the reaction conditions in the soil environment. Generally the arsenic content in the bedrocks ranges from 1.5 to 3.0 ppm, and in the soil that normal 7.2 ppm [Adriano, 2001]. In this study, from the data numbers of 66 the

median value was 1.00 ppm and mode value was 1.00 ppm with the appearance of the mode was 43 data and maximum level of As content in soil was 238 ppm. Analysis of the normal distribution of the 66 values of As data using Kosmogolov Smirnov and Shapiro-Wilk tests (Table 1) shows that the curve of the spread of arsenic levels is not normal value. It is also presented in this table that average value was 32.00 ppm with a median and mode are respectively 1.00 ppm, so that it is not normal distribution curve with skewed to the right and the value of skewness is 2.06. Based on these results it can be said that the environmental gold mining and processing locations has been already showing contamination with arsenic. In the nature, arsenic can be in the form of arsenate of salt Pb, Cu, Ca or other cations. In the gold mine that also marked the mineral galena (PbS), the presence of As at this location is quite significant.

Retention of arsenic in soils is related to the content of oxides of Fe and Al, exchangeable Ca, and type and content of clay fraction in soils, and kaolinite absorbed more As from solution than vermiculite and montmorillonite [Onken & Adriano, 1997]. Study on Multivariate analysis of soil heavy metal pollution and landscape pattern in Changhua county in Taiwan showed that variables together explained 34.5% of the variation in the concentration of the soil heavy metals and landscape indices the data of this study area [Lin et al., 2002].

**Normality Test**

The distribution of the value of Fe content in the soil tends to lead normal (Figure 2.), although based on the data normality test results showed that the Fe content distribution did not normal (Table 2). As for the metals Mn, Pb, Hg and As did not show a

normal distribution. This suggests that heavy metal contamination were examined, except Fe, derived from the alteration of rocks. In addition, Hg levels increase in the soil was also caused by the addition of Hg in the amalgamation process. Similar results were also obtained on heavy metal distribution maps that were made in the USA, which indicates that the sample populations that have very high levels of heavy metals only slightly compared moved at a relatively low level [White et al., 1997]. Accordingly it can be said that the gold mine environments might cause increased levels of heavy metals sharply compared with the levels of heavy metals in a common environment.

In Romania already created a classification for potential heavy metal pollution in the soil [Suciu et al., 2008] sequentially from very tight to very loose, as follows: RSV (Reference value in the sensitive area), ALS (Alert level in the sensitive area), RVLS (Reference value in the less sensitive area), ALLS (Alert level in the less sensitive area) and AIT (Area intervention threshold).

**Spatial analysis**

Spatial analysis was conducted to determine the spatial distribution of metals in the environment of the gold mines, the mine site, the amalgamation process and environment. Application of geostatistics and geographic information system was successfully describe the level of zinc in soil as map for characterizing the spatial variability of heavy metals [Li et al., 2004; Liu et al., 2006; White et al., 1997; Xie et al., 2011]. Significant amounts of metals, singly or in combination, are introduced into the environment from both natural and anthropogenic sources [Duruibe et al., 2007]. In this study, the spatial analysis is performed to find out distribution of heavy metals content in soils around the environment of the sites of alteration and the amalgamation process.

Table 2. Normality analysis of the heavy metal distribution in the soil studied

Normality analysis	Elements					
	Fe (%)	Mn (%)	Pb (ppm)	Hg (ppm)	As (ppm)	Co (ppm)
Skewness	-0.89	2.09	1.91	3.10	2.06	-
Kurtosis	3.24	4.80	4.49	9.51	3.02	-
Kolmogorov-Smirnov <sup>a</sup>						
Statistic	0.080	0,233	0,283	0.332	0.355	-
dF	66.000	66.000	66.000	66.000	66.000	-
Sig	0.200	0.000	0.000	0.000	0.000	-
Shapiro Wilk						
Statistics	0,948	0,768	0.730	0.498	0.566	-
dF	66.000	66.000	66.000	66.000	66.000	-
Sig	0,007*	0,000	0.000	0.000	0.000	-

- a. Lilliefors Significance Correction
- \*. This is a lower bound of the true significance
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- \*. This is a lower bound of the true significance

The Figure 3 shows that the distribution of Fe content in the studied soil in artisanal mining environment is relatively evenly distributed, i.e. minimum value with a maximum difference is not too great. Based on this figure, total Fe content at the mine activities and amalgamation process of Fe content is relatively low. Fe content in the soil increases with decreasing altitude of location. It is in accordance with the behavior of Fe in minerals of igneous rocks and after weathering processes so that it becomes the soil constituents. Iron is an element that occupies in igneous

rocks in large quantities, and it is usually in the ferrous ( $Fe^{2+}$ ) form. Weathering of the rocks results in the release of Fe and then this element may change oxidation to  $Fe^{3+}$  as the reaction is generally in oxidation state. Iron oxide in the soil can form various types of oxides that are visually different in color, that are: goethite, limonite, or hematite, each of which is brown, yellow, or red. In general, the iron in the soil may play a role as a soil coloring. Under oxidative conditions may result in soil with red color, but instead of reductive conditions result in soil with gray color. In the mature soil, Fe oxide levels in the soil increase if soil development occurs in neutral to alkaline environment. In this environment many Si is soluble and it is then leached out from soil, while Fe will be in the soil body as a residue so that the Fe content will increase.

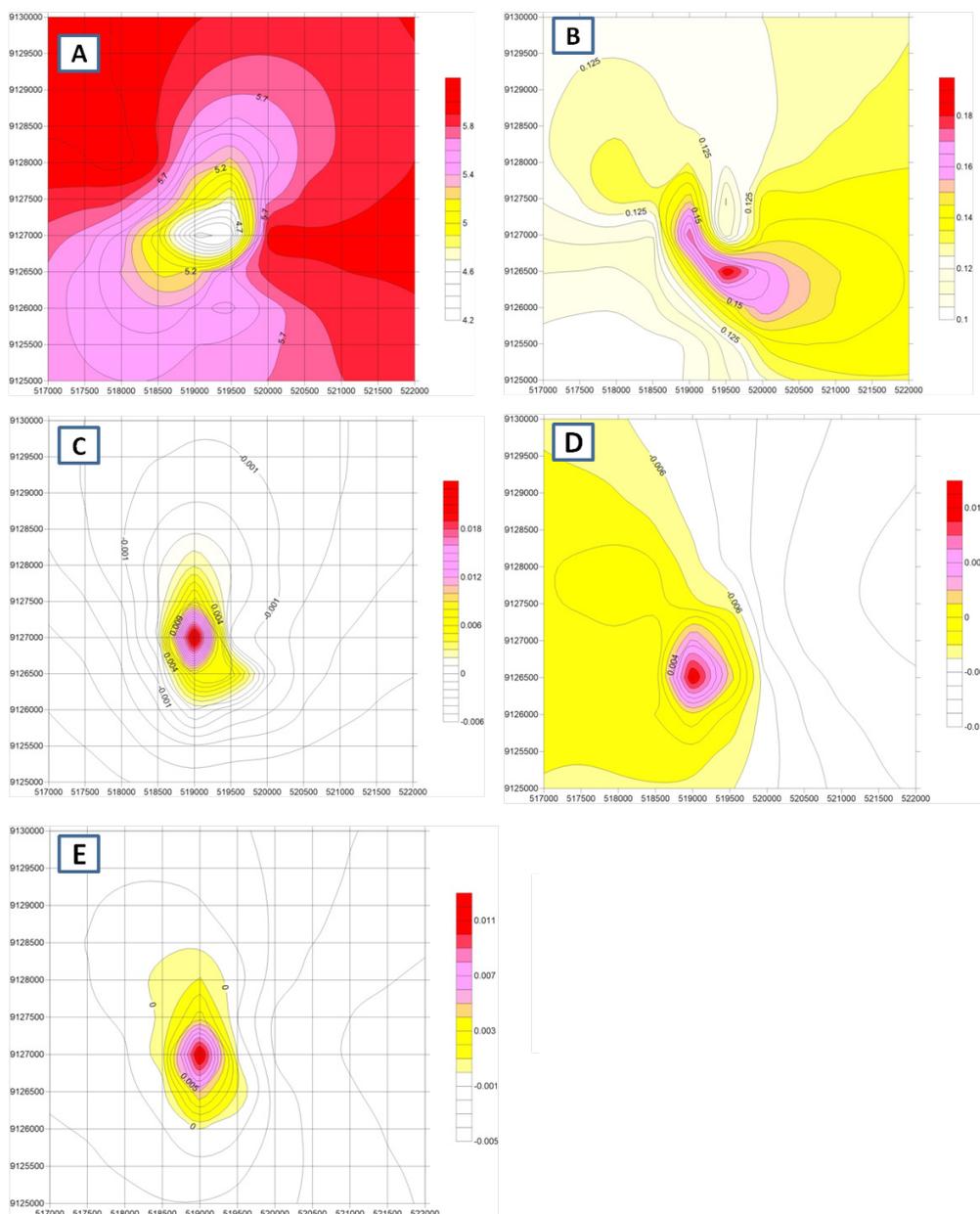


Figure 3. Distribution pattern of heavy metals contamination in soil: (A) Fe, (B) Mn, (C) Pb, (D) Hg and (E) As

**Manganese (Mn)**

The distribution of Mn in the surface soil is slightly different from Fe (Figure 3). Minerals which had been shown alteration due to weathering release elements, include heavy metal elements, which then become constituents forming soils. With this process, the Mn also like Fe that may role as the coloring soil which is black-colored of soil is expressed by Mn-oxides. Presence of Mn-oxides in the soil profile is initially shaped as mottle-colored black. On soils that have been developed advanced resulting Mn-oxide concretions formation together with Fe-oxides. The presence of Mn oxide in soils can also fix to heavy metals such as Co, Pb, As, Ba [Nurcholis et al., 1997]. In the present study showed that these oxides in gold mine area that using open pit techniques would be exposed to the surface of the soil. The material is then drawn into the material to be processed gold separation.

Mn levels in soil of the amalgamation sites, located in the upper site of mountainous area, show greater than in the lower location (Figure 3). This is because in the amalgamation process the extracted material containing heavy metal elements of the extracted metals, including Mn. Manganese that is an undesirable element in the amalgamation process that is to be a waste material or tailings, so that the tailings were then dispersed around the site of amalgamation process. Activities of amalgamation process in the present study has been going on for many decades, so the tailings that had been produced and spread on the soil surface can increase metal contents in the soil environment.

**Lead (Pb)**

Distribution pattern of the Pb content in soils studied showed of which also centered on a specific location, which is around the amalgamation process (Figure 3). Pb in the environment in general resulted from alteration of galena (PbS) minerals. In the process of mining this element are also carried in the material being processed, so the element of Pb which is in the waste can increase the content of Pb in the soil surface. Pb can also be fixed in Mn oxide minerals with three kinds of processes, namely: absorbed, special affinity, or forming minerals with Mn [Han et al., 2006;

Nurcholis et al., 1997]. In addition, the presence of Pb is also associated with other types of minerals so that Pb is also spread in the mine environment. Based on the analysis of the correlation between elements that were examined (Table 3), Pb had no correlation with Mn, this is because the current research was conducted on the waste material that had undergone a process of extraction on the amalgamation and then it was spread to the surface soil. Accordingly, these results also give the same result of the distribution of Mn element on the general soil surface.

**Mercury (Hg)**

The Hg distribution in the mine site and in the amalgamation process is presented in Figure 3. Hg in this area was originated from two different sources, namely the alteration of minerals in rocks and the addition of mercury in for the amalgamation process. Gold ore of rocks that was taken from the mine site by miners then it would be crushed manually using hammer, and following process of gold separation from ore by addition with mercury to bind gold as amalgam. The amalgamation process produced two types materials are solids and liquids in the form of colloids. Gold-bound in the mercury was then separated by heating, being the remainder in the form of colloidal and solid materials is processed to reduce the content of the materials and elements that are dangerous to the environment. But if the process of waste management has not been better for the amalgamation process, the environment is still has the potential to be contaminated with mercury (Figure 3). Based on the properties of Hg which is not solid, volatile and easily transported by flowing water, the contaminants Hg in nearby amalgamation can be easily reduced because transported by water flow. [Arbestain et al., 2008] reported that extent of contamination of soils and vegetation close to an abandoned Hg-fulminate production plant. A highly contaminated area was identified close to the former discharge zone for the wastewater produced during the washing procedures at the plant, where the concentrations of Hg in the surface horizons were higher than 1 g kg<sup>-1</sup>. The same result was also reported by Arifin [Arifin et al., 2015] that higher mercury concentration was close to the artisanal

Table 3. Correlation values among heavy metals

x\y	Fe (%)	Mn (%)	Pb (ppm)	Hg (ppm)	As (ppm)
Fe (%)		0,683	0,001	0,036	0,159
Mn (%)			0,004	0,042	0,081
Pb (ppm)				0,148	0,013
Hg (ppm)					0,034
As (ppm)					

processing units, and the levels gradually decrease downstream. The lowering concentration of mercury in water occurs as it is diluted by river system. In this research it was found that the waste spill in the form of colloidal tailings, resulting from amalgamation process, flows and enter into surface water bodies in the form of water course. Water flows on the soil surface as small stream or gravity flow that accumulated to be a small river. The joining of small rivers becoming larger stream, and river water is used as a source of irrigation water for paddy rice crops that located in the middle and bottom of the mountains. So that the source of irrigation water is also potentially containing heavy metals contaminants.

### Arsenic (As)

The problem of arsenic in gold mining is crucial because the element is abundant, mobile in acidic reactions, and this element is very dangerous for human life. Arsenic concentration in the fluvial water storage ponds ( $265 \mu\text{g L}^{-1}$ ), soil (in the range of 19–17 384  $\text{mg kg}^{-1}$ ) and dry sediment (in the range of 29–28 600  $\text{mg kg}^{-1}$ ) was identified in the area of the historical and recent mining site of Villa de la Paz-Matehuala in Mexico [Razo et al., 2004]. Adsorption by Fe- and Al- oxides and also sulfide minerals the soil around the mining areas have led to reduced levels of As in the water. It is widely accepted that surface area, pore volume, pore volume distribution, and pore network of clay can be altered by the acid activation. Acid activated laterites or AAL with concentration of 0.2 N shows higher arsenite/arsenate adsorption with respect to raw laterites or RL [Maiti et al., 2010].

### 5. Conclusions

Gold mining in Gunung Mas area, Boto village, Wonogiri regency have an impact on exposure of heavy metals of the rock into the environment. Soils around the mining area have been contaminated by heavy metals of Mn, Fe, Pb, Hg and As. The amalgamation process that by adding Hg also increase the levels of Hg in the soil, besides that it also extracted ore rocks containing heavy metals as elements that were dissolved in liquid waste. Tailings of the amalgamation process as solid wastes that were exposed on the soil surface gave a role on increase the levels of these metals in the soil. The land is located at the bottom of the mountains of Gunung Mas potentially gaining heavy metals contamination, especially for rice field which always receives irrigation water from the river that carries with it heavy metals.

The findings of this study show that the soil in the community gold mining area contains the metals of Fe, Mn, Hg, Pb, As. Levels of Fe and Mn in the soil studied with content of 4.69%, and 0.16% are prevalent as dominant elements in the soil, and do not have the potential to negatively impact the environment. The

levels of Hg, Pb, and As which respectively are 83.76 ppm, 79.45 ppm, and 32.00 ppm has the potential to have a negative impact as a pollutant in the soil.

Spatial distribution determined by krigging method indicates that Fe content is increasing with increasing distance from mining location and amalgamation activity, as source of contaminant. In contrast, the spatial distribution of metals Hg, Pb, and As decreases further and further from the source of contaminants.

Mercury is not biodegradable and, if inappropriately discarded, often combines with other elements in more toxic forms. River dumping can result in dramatic loss of plant and wildlife for considerable distances downstream. To overcome these problems is necessary to design appropriate technology in an effort to mitigate contamination of heavy metals in soil and water.

It is required the study on the characteristics of the waste, the topography, and the climatic conditions are so variable that may role on the environmental impact of artisanal and small gold mining in this area. Accordingly, it is impossible to make a design guide to cover all situations. Each tailings embankment should be designed to suit the conditions as they exist. Indeed, it is needed deep thinking to tailings disposal methods and design the appropriate technology for its storage.

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