Analysis of cobalt (Co) in the soil of Antang Landfill, Makassar City, South Sulawesi Province, Indonesia by use of ICP-OES

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Abstract. This study analyzed the content of cobalt (Co) heavy metal in the soil conducted around the Final Disposal Sites landfill of Antang Makassar, Indonesia. There were 12 sampling points such as points A1, A2, and A3 (line A); points B1, B2, and B3 (line B); points C1, C2, and C3 (line C); and points D1, D2, and D3 (line D). Every sampling points have a depth of 30 cm vertically, and the soil samples were divided into three layer (upper layer, middle layer, and lower layer) with a depth of 0-10 cm (upper layer), 10-20 cm (middle layer), and 20-30 cm (lower layer). The study used 36 samples all of which were analyzed using ICP-OES to measure the concentrations of heavy metals. The concentration of heavy metals in the soil around landfill of Antang had spread vertically and laterally. The analysis found that cobalt (Co) heavy metal concentrations in Line A, Line B, Line C and Line D for every depth exceeded the normal limit. However, on line B the B1 sampling point at a depth of 10-20 cm and 20-30 cm had a relatively normal concentration, which was 10 ppm. That value was the standard permitted by the General of Drug and Food Control as the level of pollution in the soil. Soil pH varies from 4.82 to 6 and is considered acidic. Soil pH significantly affects the solubility and mobility of metals, because most metals dissolve in acidic soils. Thus, remediation or appropriate precautions were needed to prevent risks to humans and the environment.

1. Introduction

Heavy metals are divided into two types. First, essential heavy metals, which have a certain amount and are needed by organisms. However, the metal may be toxic if it concentrates in excessive amounts, for example, Zn, Cu, Fe, Co, Mn, etc. The next type (second type) is not essential heavy metals. This metal is in the body and toxic. The benefits of this metal are still unknown. Examples of non-essential metals include Hg, Cd, Pb, Cr, and others. Heavy metals that pollute environmental components like air, water, and soil come from natural processes and industrial activities. The natural process can be from volcanic rocks that contribute to air, water, and soil. Human activities increase environmental pollution in the form of the industrial process, mining, burning of fuels, and other domestic events [1].

A Final Disposal Sites landfill for people of Makassar city is an essential necessity to create a comfortable environment in a big city. The landfill of Antang located in the Antang district area is the center of the landfill of all areas in the Makassar city. In its operation, landfill of Antang used the Open Dumping method, so that it had the potential to pollute groundwater. Based on data from the Spatial Unit and the Environmental Management Unit of Makassar in 2006, from the opening of the landfill of Antang to moment, it was estimated that there were already 1,240,000 tons of organic waste being disposed [2].

The community has utilized the landfill of Antang since 1995 with an area of 18.8 Ha. This disposal site was actually designed to accommodate garbage for ten years. But in fact, the landfill of Antang has been used for at least 24 years. Therefore, the assumption that the landfill of Antang Makassar had polluted the environment in the form of soil and groundwater pollution was likely to be true. The pollution certainly affected sanitation, air pollution, and unpleasant smells. The pollution itself had spread to the Northwest - Southeast with a distance of about 300 meters - 450 meters from the landfill of Tamangapa [3]. More dangerously, landfill of Antang is located around residential areas. If it is proven that cobalt (Co) metal were having very strong concentration in the soil around landfill of Antang, then the population may be in danger because this metal is toxic.

This study aims to analyze cobalt (Co) heavy metals around the landfill of Antang Makassar vertically and laterally. The study focuses on the impacts caused by the spread of cobalt (Co) around the landfill of Antang, Makassar, on the lives of people around the landfill. The soil analyzed was at depths of 0 to 10 cm (upper layer), 10 to 20 cm (middle layer), and 20 to 30 cm (lower layer), vertically and on the distance of 0, 5, to 10 m laterally for every sampling point.
2. Research Method

2.1. Research Area

Administratively, the research area is in Bangkala, Manggala District, Makassar City, South Sulawesi Province, Indonesia. Geographically, this region is located at coordinates 119°, 29', 10" to 119°, 29', 40" East Longitude and 5°, 10', 20" to 5°, 10', 40" South Altitude. The location of the study can be seen in Fig. 1.

2.2. Soil Samples

The samples in this study were the topsoil collected from the landfill of Antang. Soil sampling points were determined by dividing 12 points, namely points A1, A2, A3 (line A), points B1, B2, B3 (line B), points C1, C2, C3 (line C), and points D1, D2, D3 (line D), at a depth of 0-10 cm, 10-20 cm, and 20-30 cm vertically and the distance of sample points from 0, 5, to 10 m laterally (Fig. 1).

2.3. Sample preparation and analysis

Before being tested, the soil was roasted for 48 hours at a temperature of 106°C, [4]; [5]; [6], before hand to facilitate the screening process so that the granules were not attached to each other, then crushed with a wooden hammer or ceramic pestle [6], sieved using 2 mm stainless steel sieve [7]; [8], stored in a desiccator before being analyzed [4]. Soil samples that have been prepared were then taken to the laboratory for analysis.

2.4. ICP-OES Working Principles

The sample was weighed as much of 1 gram and inserted into the porcelain crucible, then sprinkled with 2 grams of Na2CO3, before being put into the furnace at a temperature of 800°C for 2 hours. After that, the aqua regia was added to the decomposed sample. Let it stand for ± 12 hours. Transfer it into a beaker and heat it to almost dry. Soluble samples were added with aquabidest as needed during filtration. The filtrate from the filtration process was put into mL and squeezed with aquabidest to the boundary mark using ICP-OES.

3. Results and Discussion

3.1. Results

The results of the analysis of cobalt heavy metal (Co) concentration using the ICP-OES method for line A, line B, line C and line D at a depth of 0-10 cm, 10-20 cm and 20-30 cm for 36 samples can be seen in Table 1. The results of cobalt (Co) heavy metal analysis vertically for line A, sampling points (A1, A2, and A3) at a depth of 0-10 cm, 10-20 cm, and 20-30 cm, around landfill of Antang Makassar are shown in Fig. 2.
Table 1. The results of the analysis of cobalt (Co) heavy metal concentrations for line A, line B, line C and line D vertically and laterally at depth of (0-10, 10-20 and 20-30) cm with distance of sample points 0.5, and 10 m around the landfill of Antang Makassar.

| Line | Point | Depth (cm) | Heavy metal concentration (ppm) | pH | Temperature Degree (°C) |
|------|-------|------------|---------------------------------|----|------------------------|
| A    | A1    | 0-10       | 45                              | 6  | 26                     |
|      |       | 10-20      | 42                              | 5  |                        |
|      |       | 20-30      | 44                              | 6  |                        |
|      | A2    | 0-10       | 42                              | 6  | 25                     |
|      |       | 10-20      | 48                              | 5  |                        |
|      |       | 20-30      | 45                              | 6  |                        |
|      | A3    | 0-10       | 39                              | 5  | 25                     |
|      |       | 10-20      | 39                              | 5  |                        |
|      |       | 20-30      | 39                              | 6  |                        |
| B    | B1    | 0-10       | 11                              | 5  | 30                     |
|      |       | 10-20      | 10                              | 4.78 |                    |
|      |       | 20-30      | 10                              | 4.82 |                    |
|      | B2    | 0-10       | 11                              | 5  | 28                     |
|      |       | 10-20      | 14                              | 4.82 |                    |
|      |       | 20-30      | 12                              | 4.82 |                    |
|      | B3    | 0-10       | 11                              | 5  | 26                     |
|      |       | 10-20      | 16                              | 4.82 |                    |
|      |       | 20-30      | 14                              | 4.84 |                    |
| C    | C1    | 0-10       | 13                              | 4.82 |                    |
|      |       | 10-20      | 12                              | 4.83 |                    |
|      |       | 20-30      | 12                              | 4.84 |                    |
|      | C2    | 0-10       | 28                              | 4.83 |                    |
|      |       | 10-20      | 30                              | 4.83 |                    |
|      |       | 20-30      | 22                              | 4.83 |                    |
|      | C3    | 0-10       | 29                              | 4.83 |                    |
|      |       | 10-20      | 29                              | 5   | 26                    |
|      |       | 20-30      | 23                              | 5   |                        |
| D    | D1    | 0-10       | 53                              | 4.83 |                    |
|      |       | 10-20      | 46                              | 4.84 |                    |
|      |       | 20-30      | 42                              | 4.84 |                    |
|      | D2    | 0-10       | 50                              | 4.83 |                    |
|      |       | 10-20      | 61                              | 4.85 |                    |
|      |       | 20-30      | 27                              | 5   | 26                    |
|      | D3    | 0-10       | 49                              | 4.84 |                    |
|      |       | 10-20      | 46                              | 5   | 27                    |
|      |       | 20-30      | 40                              | 4.85 |                    |

**Fig. 2** The results of analysis of cobalt (Co) heavy metals vertically for line A, sampling points (A1, A2, and A3) at a depth of 0-10 cm, 10-20 cm, and 20-30 cm, around the landfill of Antang, Makassar.

**Fig. 2** shows that at point A1 at depths of 0-10 cm, 10-20 cm and 20-30 cm, the irregular concentrations from the upper layer to the lower layer orderly (45, 42, 44 ppm), have exceeds the normal limit. A2 points at depth (0-10, 10-20 and 20-30) cm indicates irregular concentrations from the top layer to the bottom layer in a
continuous manner (42, 48 and 45 ppm) surpasses the normal limit. A3 point at depth (0-10, 10-20 and 20-30) cm presents a fixed concentration (39 ppm). Starting from the top layer to the bottom layer outpaces the normal limit. Vertical cobalt (Co) heavy metal analysis results for line B, sampling points (B1, B2, and B3) at a depth of 0-10 cm, 10-20 cm, and 20-30 cm, around the the landfill of Antang, Makassar, are presented in Fig. 3.

Fig. 3 The results of cobalt (Co) heavy metal analysis vertically for line B, sampling points (B1, B2, and B3) at a depth of 0-10 cm, 10-20 cm, and 20-30 cm, around the the landfill of Antang, Makassar.

Fig. 3 shows that, in the point B1 at depths (0-10, 10-20 and 20-30) cm, irregular concentrations from the upper layer to the lower layers (11, 10, 10 ppm), exceed the normal limit. However, at depths of 10-20 and 20-30 cm, the concentration is at the normal level (10 ppm). Point B2 in the depths of 0-10, 10-20 and 20-30 cm shows irregular concentrations from the top to the bottom layer in a continuous manner (11, 14 and 12 ppm) and surpass the normal limit. B3 points at depths of 0-10 cm, 10-20 cm and 20-30 cm show irregular concentrations in a continuous manner (11, 16, and 11) ppm, from the top layer to the bottom layer; already over the normal limit.

The results of cobalt (Co) heavy metal analysis, vertically for line C at a depth of 0-10 cm, 10-20 cm, and 20-30 cm, on the soil around the landfill of Antang, Makassar, are shown in (Fig. 4).

Fig. 4 the results of cobalt (Co) heavy metal analysis vertically for line C, sampling points (C1, C2, and C3) at a depth of 0-10 cm, 10-20 cm, and 20-30 cm, around the the landfill of Antang, Makassar.

Fig. 4 above shows that, in the point C1 at depths (0-10 cm, 10-20 cm, and 20-30 cm), irregular concentrations from the upper to the lower layers, respectively (13, 12 and 12 ppm) exceeds the normal limit. C2 points at depth (0-10 cm, 10-20 cm and 20-30 cm) are irregular concentrations. From the top layer to the bottom layer, respectively (28, 30 and 22 ppm) the normal limit is exceeded. C3 points at depth (0-10, 10-20 and 20-30) cm indicates irregular concentrations, orderly (29, 29 and 23 ppm) from the upper layer to the lower layer, it surpasses the normal limit.

The results of cobalt (Co) heavy metal analysis, vertically for line D at a depth of 0-10 cm, 10-20 cm, and 20-30 cm, in the soil around the landfill of Antang, Makassar, are shown in Fig. 5.
Fig. 5 the results of analysis of cobalt (Co) heavy metals, vertically for line D sampling points (D1, D2, and D3) at a depth of 0-10 cm, 10-20 cm and 20-30 cm, around the landfill of Antang, Makassar.

Fig. 5 above presents that, at point D1 at a depth of 0-10 cm, 10-20 cm, and 20-30 cm, the concentration decreases from the top layer to the bottom layer. Orderly (53, 46 and 42) ppm, it exceeds the normal limit. D2 point at depth of 0-10 cm, 10-20 cm, and 20-30 cm shows irregular concentrations from the top layer to the bottom layer. Respectively (50, 61 and 27 ppm) has exceeded the normal limit. D3 points at a depth of 0-10 cm, 10-20 cm and 20-30 cm shows decreased concentration. Respectively (49, 46 and 40) ppm, from the top layer to the bottom layer, it has surpassed the normal limit.

The results of cobalt (Co) heavy metal analysis, laterally for line A sampling point (A1, A2, and A3), at a depth of 0-10 cm, 10-20 cm, and 20-30 cm, in the soil around the landfill of Antang, Makassar, is shown in Fig. 6.

Fig. 6 The results of analysis of cobalt (Co) heavy metals, laterally for line A sampling points (A1, A2, and A3) at a depth of 0-10 cm, 10-20 cm and 20-30 cm and with a distance of 5 m for every sampling point, around the landfill of Antang, Makassar.

Line A shows the concentration of Co heavy metal has exceeded the normal limit. This is in accordance with the provisions of the sampling point A1 at a depth of 0-10 cm (upper layer) with concentrations ranging from 45 ppm, the concentration A2 sampling point ranging from 42 ppm, and the A3 sampling point concentration ranging from 39 ppm; concentration decreases from the deepest point to the outermost point (A1, A2, and A3). At a depth of 10-20 cm (middle layer), the A1 sampling point produces concentrations starting from 42 ppm, concentration A2 sampling points of 48 ppm, A3 concentration sampling points about 39 ppm. That means the concentration is irregular from the deepest point to the outermost point (A1, A2, and A3) and the concentration has exceeded the normal limit. At a depth of 20-30 cm (lower layer), the A1 sampling point has a concentration ranging from 44 ppm, A2 sampling point around 45 ppm, A3 sampling point of 39 ppm. This shows an irregular concentration from the deepest point to the outermost point (A1, A2, and A3), which is over the normal limit.

The results of the heavy metal analysis of cobalt (Co) laterally for line B, sampling points (B1, B2, and B3) at a depth of 0-10 cm (upper layer), 10-20 cm (middle layer), and 20-30 cm (lower layer), from the soil around the landfill of Antang, Makassar, is presented in Fig. 7.
Fig. 7 The results of analysis of cobalt (Co) heavy metals, laterally for line B sampling points (B1, B2, and B3) at a depth of 0-10 cm, 10-20 cm and 20-30 cm, with a distance of 5 m for every sampling points around the landfill of Antang, Makassar.

Line B shows cobalt (Co) heavy metal concentration has exceeded the normal limit. The conclusion is based on the findings that the sampling points B1, B2 and B3 at a depth of 0-10 cm (upper layer) have fixed concentrations ranging from 11 ppm, from the deepest point to the outermost point (B1, B2, and B3). At a depth of 10-20 cm (middle layer), the sampling point B1 shows concentrations around 10 ppm and is still within the normal range. B2 sampling point produces concentrations of 14 ppm. B3 sampling points get concentrations starting from 16 ppm. Concentration increases from the deepest point to the outermost point (B1, B2, and B3) which means it has exceeded the normal limit. At a depth of 20-30 cm (lower layer), the sampling point B1 indicates concentrations ranging from 10 ppm and is still within the normal range. B2 sampling points produce concentrations starting from 12 ppm. The B3 sampling point contains concentrations of 14 ppm. Concentration increases from the deepest point to the outermost point (B1, B2, and B3) and has exceeded the normal limit.

The results of lateral heavy metal concentration analysis for line C sampling points (C1, C2, and C3) at a depth of 0-10 cm (upper layer), 10-20 cm (middle layer), and 20-30 cm (lower layer) in the soil around the landfill of Antang, Makassar, are shown in Fig. 8.

Fig. 8 The results of analysis of cobalt (Co) heavy metals, laterally for line C sampling points (C1, C2, and C3) at a depth of 0-10 cm, 10-20 cm and 20-30 cm, with a distance of 5 m for every sampling points around the landfill of Antang, Makassar.

Line C is the concentration of heavy metal Co, for sampling point C1 at a depth of 0-10 cm (upper layer) and with concentrations ranging from 13 ppm; C2 sampling point concentration ranges from 28 ppm; and the C3 sampling point concentration ranges from 29 ppm; concentration increases from the deepest point to the outermost point (C1, C2 and C3). It has exceeded the normal limit. At a depth of 10-20 cm (middle layer), it has exceeded the normal limit. The C1 sampling point produces concentrations ranging from 12 ppm. The C2 sampling point shows a concentration of 30 ppm. The C3 sampling point gets a concentration of around 29 ppm. This means that the concentration is irregular from the deepest point to the outermost point (C1, C2, and C3). At a depth of 20-30 cm (lower layer) C1 sampling point the concentration ranges from 12 ppm has also exceeded the normal limit, C2 sampling point produces concentrations ranging from 22 ppm and point C3 sampling ranged from 23 ppm. The concentration increased from the deepest point to the outermost point (C1, C2, and C3).

The results of lateral heavy metal concentration analysis for line D sampling points (D1, D2, and D3) at a depth of 0-10 cm (upper layer), 10-20 cm (middle layer), and 20-30 cm (lower layer) in the soil around the
location of landfill of Antang, Makassar, is shown in Fig. 9.

Fig. 9 the results of analysis of cobalt (Co) heavy metals, laterally for line D sampling points (D1, D2, and D3) at a depth of 0-10 cm, 10-20 cm and 20-30 cm, with a distance of 5 m for every sampling points around the landfill of Antang, Makassar.

Line D shows that the concentration of heavy metal Co have exceeded the normal limit. For the D1 sampling point at a depth of 0-10 cm (upper layer), the concentration ranges from 53 ppm; the sampling point D2 concentrates around 50 ppm; and the D3 sampling point concentration ranges from 49 ppm. The concentration decreases from the deepest point to the outermost point (D1, D2 and D3). At a depth of 10-20 cm (middle layer), D1 sampling point is already over the normal limit. It has the concentration ranging from 46 ppm; the D2 sampling point concentration ranging from 61 ppm, the D3 sampling point concentration ranging from 46 ppm, indicating irregular concentrations from the deepest point to the outermost points (D1, D2, and D3). At a depth of 20-30 cm (lower layer), D1 sampling point is over the normal limit. It gets the concentration ranging from 42 ppm; the sampling point D2 concentration around 27 ppm; the sampling point D3 concentration ranging from 40 ppm, indicating irregular concentrations from the deepest point to the outermost points (D1, D2 and D3).

3.2. Discussion

The 12 sampling points of landfills of Antang Makassar consisting of points A1, A2, A3 (line A), points B1, B2, B3 (line B), points C1, C2, C3 (line C), and points D1, D2, D3 (line D) contained cobalt (Co) heavy metal elements far exceeding the normal limit set [9]. The results of the analysis indicated the total concentration of cobalt (Co) heavy metals in the soil around the landfill of Antang Makassar had spread both vertically and laterally. The distribution varied for each point and depth of the soil surface (topsoil). The concentration had gone through an enrichment level that exceeded the expected normal level by the soil environment. Hence, this certainly raises concerns especially for the people who live around the landfill of Antang Makassar, because the location is in the middle of a residential area.

The increase in heavy metal content in the soil around the landfill of Antang showed the contamination had been concentrated in the soil. The cause of this concentration was long contamination and continuous metal accumulation. Therefore, the existing organic compounds experienced a process of degradation and the metal content in the soil increased with time.

Based on the results of the observation, the waste disposed to the landfill of Antang Makassar contained many organic materials. Waste containing cobalt (Co) and mixed with organic substance could increase the potential of heavy metals on the soil surface [10]; [11]. The concentration of Co heavy metal in the soil might be caused by anthropogenic [12], such as household waste. The Co heavy metal is widely used as a mixture for making household appliances such as cutting tools, glass dyes, ceramics, and paint.

The results of the analysis (Table 1) depicted the concentration of cobalt (Co) heavy metal, which was on the soil surface (topsoil) or decomposed waste, still had a heavy metal content that continued to accumulate, if there was high and continuous rainfall. The contamination had the potential to sink into the bottom [11]. Heavy metals were carried by Leachate and settled in the soil, so heavy metals such as cobalt (Co) would continue to accumulate in the soil [13]. These heavy metals would affect the quality of the soil and groundwater environment around the landfill. This greatly affected the lives of people around the landfill of Antang Makassar, because most people near the disposal sites used dug wells as a source of drinking water [14]. The landfill of Antang Makassar, besides liquefying seepage into swamps, could also affect the quality of the environment around the site.

The high mobility of cobalt (Co) heavy metals on line A, line B, line C and line D (Table 1) was caused by low soil pH (acid). Increased soil reduction was due to the addition of organic matter, as well as an increase in the concentration of organic acids produced by organic matter. Mercury (Hg) metal in this study was mostly contained on the soil surface (Top soil). Low soil acidity increased the accumulation of organic acids in the soil.
The low retention or binding capacity of the soil to cobalt (Co) on line A, line B, line C and line D, was due to low clay content. This was in accordance with the opinion [1], which stated that clay fraction was an important soil characteristic in absorbing heavy metal ions.

The mobility of cobalt (Co) metal in the soil depends on humic acid and the availability of organic matter, because all heavy metals such as cobalts (Co) are very strong to absorb organic matter on the ground. Cobalt (Co) can bind organic components. The 12 sampling points locations of the landfill of Antang Makassar that were line A, line B, line C and line D contained cobalt (Co) heavy metal elements, which had exceeded the normal limit. This was probably because line A, line B, line C and line D were still actively receiving waste/garbage and were close to the highway. Waste/garbage was still in the process of decomposition and there was a lot of waste/garbage thrown into the landfill without sorting.

The landfill of Antang Makassar stands on the land of Ultisol (reddish-colored soil that contains a lot of clay), so it demonstrating plasticity, encouraging flooding and surface water pollution [8]. The color of the soil appears from the metal content, especially iron and oxidized aluminum (weathered soil). The average soil pH in the landfill of Antang Makassar analyzed ranged from 4.82-6 (acidic) with an average value of 4.84 and the average temperature ranged from 25°C-31°C (Table 1). The pH plays an important role in the bioavailability of heavy metals and soil toxicity to the surrounding area [15]; [16]. The pH also affects the mobility of metals in the soil [8]; [17]. At low pH or acidic pH will help the availability, mobility, and redistribution of mercury (Hg) heavy metals in various fractions due to an increase in ion solubility in acidic soil environments [17].

Relatively, acidic soils have increased solubility and mobility of micronutrients so that the concentration of heavy metals in the soil rises [17]; [18]. If the solution is too acidic, the plants cannot use the N, P, K and other nutrients they need. In acidic soils (low pH), it is dominated by Al, Fe and Mn ions. These ions will bind nutrients needed by plants, especially elements of P, K, S, Mg. Therefore, plants cannot absorb food properly even though the nutrient content in the soil is large.

Cobalt (Co) is a toxic heavy metal to organisms. In certain uses or activities, cobalt (Co) heavy metals will be distributed to the environment in the form of agricultural materials, medicines, paints; paper, mining, and industrial waste [11]. Heavy metal cobalt (Co) is very dangerous for the health of the population, especially those who live around the landfill because it triggers cancer and damage to the lungs. In addition, this metal element also risks reducing a child's IQ. This disease is a human threat that causes death [18]; [19]; [20].

4. Conclusion
The heavy metal content of cobalt (Co) had the potential to spread widely on the soil surface (topsoil) both vertically and laterally. The results of this study indicated that the location of the landfill of Antang Makassar, namely line A (points A1, A2, A3), line B (points B1, B2, B3), line C (points C1, C2, C3), and line D (points D1, D2, D3) contained cobalt (Co) heavy metal elements far exceeding the normal limit at each depth. However, for line B at the B1 sampling point with a depth of 10-20 cm (middle layer) and 20-30 cm (lower layer), it was within the normal range permitted by the General of Drug and Food Control. The pH value of 4.82-6 was categorized as acid. The heavy metal content of cobalt (Co), at the location of the landfill of Tamangapa, Antang, Makassar was influenced by organic matter content, temperature, texture and soil pH. Co metal, which continued to accumulate especially when the rainfall was high, could extend to permeate Co to the bottom of the landfill site. Thus, the big risk was that heavy metals could contaminate the community's dug wells in Bangkala and surrounding areas. In addition, seepage water, which flowed into swamps, might affect the local environment because the landfill site was located between settlements and operated for 24 years.

Acknowledgments
We would like to thank the Head of Health Laboratory of Makassar, the Laboratory assistant, and the Head of soil Science Laboratory of Agriculture Faculty of Muslim University of Indonesia for all the facilities provided, for our togetherness, their support and assistance during our research. Our special thank goes to LP2S of Muslim University of Indonesia and the dean of Faculty of Industrial Technology who have provided research fund and given support so that we can finished our research and prepared the manuscript. The authors also thank to editor and anonymous reviewers for their comments on the manuscript.

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