Distribution Pattern of Volcanic Ash Essential Elements on the Top Layer of Agricultural Land Post Merapi Eruption in Sleman

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Abstract: Volcanic ash contains essential elements to the soil fertility of agricultural land which is important to be investigated. The aim of this study was to determine the distribution pattern of volcanic ash essential elements as a result of volcanic eruption disaster using Surfer software. Soil samples of volcanic ash at 10 sampling locations in Sleman at a radius of 14 to 26 km towards the south from a peak of Merapi were collected for data input of Surfer software. Data of wind direction, humidity and ground level at the time of sampling were also collected. The concentrations of the essential element in samples were measured using NAA (neutron activation analysis). The pH of volcanic ash samples in each sampling locations was also measured. The results showed that volcanic ash for all sampling locations contained Al, Fe, Na, K, and Si as major elements and Zn, Co, and Se as trace elements. The concentration distribution pattern of the Zn, Si, Co and Fe elements tends to decrease towards the peak of Merapi, on the other hand, the Na, and K elements showed that their distribution concentration tends to decrease away from the peak of Merapi. The wind's speed affects the distribution range of an element contained in volcanic ash samples. The pH of volcanic ash samples seemingly only affect the concentration of Zn elements in the distribution pattern of elements.

Keywords: volcanic ash; essential elements; distribution pattern; NAA; Surfer software

INTRODUCTION

In the year 2010, Mount Merapi in Yogyakarta Indonesia erupted, and almost all areas of Yogyakarta and surrounding areas were covered with volcanic ash. The total amount of ash produced in the eruption reached 160 million tons [1]. Volcanic ash contains many of the essential elements in abundance so that those ash provide additional essential elements to soil fertility of agricultural land surrounding Mount Merapi.

A soil fertility is an important factor that determines the growth of plants. It refers to the ability of the soil to supply availability of essential nutrients in a sufficient and balanced amount. Thus, fertility is determined by the presence or absence of macro and micronutrients, namely nutrition [2-4]. A soil fertility level varies depending on the geographical location of soil The content of essential elements in the soil is also influenced by natural events either by nature or by human activities. One of the many natural phenomena that provide an abundant supply of essential ingredients in the environment is volcanic eruptions.

In general, the soil of the volcanic area is more fertile than in other areas. This is influenced by the addition of the essential elements either primary or secondary micronutrients from a volcanic ash postvolcanic eruption. By the winds, pyroclastic material (volcanic ash) distribute to various surrounding few kilometers to a thousand kilometers from volcanoes [5-7]. The presence of volcanic ash aids the availability of essential elements especially elements of micronutrients in the soil. Research on volcanic ash has been done by Canion et al. [1] in cooperation with BATAN Yogyakarta in 2012. In their research, trace element analysis was conducted for 5 sampling locations using NAA Thermal and NAA Ephytermal Method [1]. Their study has only examined the trace element contents in volcanic ash from the eruption of Mount Merapi. Volcanic ash research from the eruption of Mount Merapi was also carried out by Budianta et.al. [7]. Their study has examined the impact of volcanic ash on public health.

However, the distribution pattern of volcanic ash essential elements as a result of volcanic eruption disaster in 2010 in Sleman has not been explored yet. As mention previously, volcanic ash contains essential elements to the soil fertility of agricultural land which is an important factor for the growth of plants. Therefore, the distribution pattern of volcanic ash essential elements as a result of volcanic eruption disaster in 2010 in Sleman is very important to be determined. The aim of this study was to determine the distribution pattern of volcanic ash essential elements as a result of volcanic eruption disaster using Surfer software. This study is expected to complete the previous research and will be useful for agriculture service division in Yogyakarta.

EXPERIMENTAL SECTION

Materials

The materials used in this study were soil samples of volcanic ash and their environmental data to be investigated, standard radioactive sources of Co-60, Cs-137 and Eu-152 to calibrate the energy and efficiency of gamma spectrometer, Standard Reference Material (SRM) 1633b Trace Elements Coal Fly Ash from NIST for control and validation of the measurement, and the secondary standard of fly ash for quantitative analysis of soil samples.

Instrumentation

Kartini Nuclear Research Reactor of PSTA-BATAN

Yogyakarta was used to do neutron activation by irradiating volcanic ash samples. Gamma spectrometer was used to detect the gamma spectra and to measure their concentration from irradiated samples. Semimicro digital analytical weight was used to weigh a sample. The surfer software trial version was used to determine the distribution pattern of essential element concentration of volcanic ash samples.

Procedure

Soil samples of volcanic ash from 10 sampling locations in Sleman at a radius of 14 to 26 km scattered to the south of the peak of Mount Merapi were collected. The collections of volcanic ash samples were taken from a relatively flat, clean, dry, hard surface soil with consideration of no contamination from surface dust (for example, copper, chromium, and arsenic from tanalized fence posts or zinc from galvanized roofing materials). Always record the surface of each sample which is collected [8]. Environmental data of 10 sampling locations such as ground level, wind direction, and humidity at the time and place of sample collecting were also recorded. The sampling location and its environmental condition were depicted in Table 1. Samples were then sieved using stainless steel sieves of 200 mesh (grain size < 0.074) in order to have the same grain size as that of SRM and secondary standard. After that, samples were input into a sterilized polyethylene vial of 0.3 mL and they were weighted using a semimicro digital analytical weight where each sample has 100 mg

| Locations | GPS | Wind Speed (km/h) | Height (m) |
|-----------|--------------------------------|-------------------|------------|
| Ι | SL 07°41'59" EL 110°26'43" | 0.0-0.2 | 309 |
| II | SL 07°39'54" EL 110°25'03" | 0.0-0.3 | 435 |
| III | SL 07°39'13" EL 110°22'47" | 0.0 | 428 |
| IV | SL 07°39'07.5" EL 110°19'34.6" | 0.0 | 346 |
| V | SL 07°36'35.1" EL 110°18'08.9" | 0.0-3.1 | 400 |
| VI | SL 07°39'47.9" EL 110°29'20.3" | 0.5-3.3 | 419 |
| VII | SL 07°39'42.7" EL 110°30'30.1" | 2.0 | 410 |
| VIII | SL 07°40'25.3" EL 110°31'54.8" | 0.36-7.12 | 311 |
| IX | SL 07°35'23" EL 110°33'16.6" | 0.32-4.16 | 543 |
| Х | SL 07°33'52.2" EL 110°32'15.8" | 0-1.6 | 716 |

Table 1. The sampling location data of post-Merapi volcano eruption 2010

weight. Each sampling locations was prepared for 5 samples to get better uncertainty.

Before doing elemental analysis using NAA (Neutron Activation Analysis), a sample in the vial in each sampling location was given the identity in order to ease data analysis. Most elemental analysis of samples is analyzed by using thermal neutron except the elemental analysis of Si used epithermal neutron. Detail NAA analysis technique such as principle, formulation, absolute and relative method are described elsewhere [9].

Two kinds of the standard were used in NAA, namely, dry secondary standard for quantitative analysis and SRM NIST 1633b (Trace Elements Coal Fly Ash) as control as well as validation of measurement. The secondary standard of the dried drops was made from a single standard solution of 1000 μ g of Al, 1000 μ g of Si, 10 μ g of Co, 20 μ g of Se, 50 μ g of Zn, 500 μ g of K, 500 μ g of Na and 1000 μ g of Fe. The SRM NIST 1633b was weighted of 100 mg using a semimicro analytical weight then it was put in a 0.3 mL sterilized polyethylene vial. The sample, standard, and SRM were irradiated together using flux neutron from Kartini nuclear research reactor in the same position of layer and hole.

Neutron irradiation of the element Al and Si were conducted in the pneumatic facility for 5 min irradiation time, however K and Na were conducted at Lazy Susan facility for 6 h of irradiation time, as well as Zn, Se, Co, and Fe were conducted at Lazy Susan facility for 2×6 h of irradiation time. The Si element was activated using epithermal neutrons, so it required Cd cover. The irradiated samples were then measured using a gamma spectrometer. The qualitative analysis was based on the characterization of the energy of gamma rays, and the quantitative analysis was based on the comparative analytical method by comparing the counting gamma spectrum of a sample with a secondary standard. Before doing the qualitative and quantitative analysis, the gamma spectrometer was calibrated by using standard radioactive sources of Co-60, Cs-137, and Eu-152. Al and Si elements were measured with cooling time 5 min, K and Na were measured with cooling time of 3 days and counting time of 20 min, Zn, Se, Co, and Fe were measured with a cooling time of 16 days and counting time and 90 min.

RESULTS AND DISCUSSION

The results of qualitative and quantitative analysis of essential elements in the sample volcanic ash are presented in Table 2. From the analysis results of volcanic ash samples, it is known that the elements of Al, Fe, Na, K, and Si are major elements, while Zn, Co, Se are trace elements. All sampling location contained the same essential elements except the sampling location of the number VI where the Se was not detected. The result of the validation method can be seen in Table 2.

Essential elements are needed for plant growth, but some elements become toxic when they are overstepped. Elements of Al, Zn, Co, and Se at certain concentrations are indispensable in the growth of plants and animals, whereas they are toxic to the environment at high concentrations [10]. The elements of Na, K, Fe, and Si are needed by living organisms both of plants and

| Table | 2. Validation of | f methods for tl | ne measurement | of the essential | elements u | using the NIST | 1633 c trace e | elements in |
|----------|------------------|------------------|----------------|------------------|------------|----------------|----------------|-------------|
| coal fly | 7 ash | | | | | | | |

| Elements | Analysis value | Certificate value | Accuracy (%) | Precision (%) |
|----------|--------------------|---------------------|--------------|---------------|
| Al | 12.582 ± 0.757 | 13.28 ± 0.61 | 94.744 | 2.410 |
| Si | 19.654 ± 0.763 | 21.30 ± 0.57 | 92.272 | 3.386 |
| Κ | 1.684 ± 0.068 | 1.773 ± 0.066 | 94.980 | 0.303 |
| Na | 0.163 ± 0.006 | 0.1707 ± 0.0059 | 95.489 | 0.169 |
| Zn | 217 ± 16.749 | 235 ± 14 | 92.340 | 1.964 |
| Se | 12.618 ± 0.755 | 13.9 ± 0.5 | 90.777 | 5.100 |
| Со | 44.104 ± 4.011 | 42.9 ± 3.5 | 97.193 | 1.460 |
| Fe | 10.156 ± 0.451 | 10.49 ± 0.39 | 96.816 | 1.564 |

| | ne results o | n anarysis of | | cincinto in | the volcame | sample at 1 | o sampning | locations |
|-----------|--------------|---------------|-------|-------------|-------------|-------------|------------|-----------|
| Locations | Al (%) | Si (%) | K (%) | Na (%) | Zn (µg/g) | Se (µg/g) | Co (µg/g) | Fe (%) |
| Ι | 11.560 | 25.991 | 1.628 | 2.440 | 108.877 | 4.251 | 18.265 | 6.250 |
| II | 11.646 | 13.113 | 1.731 | 2.524 | 90.892 | 3.192 | 15.307 | 5.423 |
| III | 12.211 | 21.209 | 1.761 | 2.543 | 90.505 | 1.232 | 14.943 | 5.229 |
| IV | 11.419 | 22.192 | 1.498 | 2.518 | 94.906 | 0.979 | 15.447 | 5.183 |
| V | 12.267 | 22.592 | 1.670 | 2.601 | 82.821 | 2.351 | 14.256 | 4.891 |
| VI | 7.856 | 10.795 | 1.645 | 2.712 | 91.462 | 0ND | 13.646 | 4.609 |
| VII | 7.435 | 14.734 | 1.658 | 2.534 | 123.415 | 1.607 | 19.194 | 6.565 |
| VIII | 8.788 | 14.850 | 1.384 | 2.445 | 103.502 | 1.313 | 17.264 | 5.636 |
| IX | 8.994 | 16.852 | 2.079 | 2.797 | 94.426 | 4.533 | 18.491 | 5.769 |
| Х | 8.861 | 17.133 | 2.094 | 2.832 | 86.951 | 1.959 | 16.746 | 5.701 |

Table 3. The results of analysis of essential elements in the volcanic sample at 10 sampling locations

Note : ND = $< 0.1 \, \mu g/g$

animals [11], but these elements are less toxic in large quantities.

The distribution pattern of essential elements was simulated using surfer software. Its simulation was based on the quantitative analysis data from Table 3 and secondary data from Table 1. These simulation results are presented in Fig. 1. In Fig. 1, the X-Y axis is the GPS (Global Positioning System) where the X-axis represents east longitude, the Y-axis represents south latitude, the curve in the graph represents the wind's speed, star symbol represents sampling locations, and the color degradation represents the concentration of an element.

From Fig. 1, the concentration distribution of the essential elements in volcanic ash showed different patterns. The elemental concentrations of Al and Se are randomly distributed but the elemental concentrations of Si, Na, K, Zn, Co, and Fe show a certain distribution pattern. For Zn, Si, Co and Fe elements, the distribution pattern of their concentration tends to decrease towards the peak of Merapi. Meanwhile, the concentration tends to decrease away from the peak of Merapi.

Moreover, at low-speed wind, the concentration distribution pattern of Al elements tends to be accumulated a certain location than that of high-speed wind. This is due to the relatively light of the atomic weight of Al elements (26.98154 g mol⁻¹) that makes it easier to get carried away by the wind. Similarly, the Si element has the same distribution pattern with an Al element based on the wind's speed.

In contrast, the Na element with the atomic weight of 22.9895 g mol⁻¹ and the K element with the atomic weight of 39.0983 g mol⁻¹ have almost the same pattern. The further away from the peak of Merapi, the higher their concentration is more increasing. It may be related to the elements with the light atomic weight that are easily carried out by the wind so that its distribution range is wider.

The elements of Fe, Zn, Se, and Co have the opposite pattern with Na and K elements. It is due to the elements of Fe, Zn, Se, and Co that have relatively heavier atomic weights than Na and K elements, so the distribution ranges are centered around the peak of Mount Merapi. In Fig. 1, it can be seen that the distribution pattern of essential elements is strongly influenced by the wind velocity and the atomic weight of elements. The height of the sampling location does not significantly influence the distribution pattern of essential elements is volcanic ash.

The contents of essential elements in volcanic ash are not all absorbed in the soil. Several factors greatly affect the washing of volcanic ash into the environment. Washing experiments with pure volcanic ash in water have been widely performed to determine the release of various sulfate and halide compounds in addition to essential elements such as N, P, Si, Fe, Co, and Zn [12]. Several studies indicate the adsorption of volcanic salt on the surface of volcanic ash as the main mechanism for the production of soluble compounds in volcanic ash. In addition, sulfuric acid condensation to volcanic ash can



Fig 1. The distribution pattern of essential elements in various sampling locations around Yogyakarta

induce dissolution reactions, thus providing a soluble cation source. The removal of essential elements from volcanic ash into the environment is influenced by soil physical chemistry conditions, one of them is the pH value. Compare to the experiment result of Canion et al., qualitatively the experimental results done in this study were mostly in agreement except Se element was not reported in the results from Canion et al. [1]. They reported that more than 20 elements were identified;



Fig 2. Measurement of volcanic ash pH at 10 sampling locations

however, we are only interested in essential elements about 8 elements (Al, Si, Na, K, Se, Zn, Co, Fe). From Table 3, the quantitative data of this study were in agreement with Canion et al. results except for Se element we got the concentration of Se element in the ranges 0.979 to 4.533 µg/g. The condition of soil physical chemistry that easily observed is the pH value of volcanic ash. The pH value is a factor that can affect whether or not the essential element in volcanic ash is absorbed by the surrounding soil. The pH value of soil is known to affect the mobilization of cations and the solubility of a metal [13]. Therefore, pH value affects the presence and accumulation of a metal in the soil. The measurement of pH in volcanic ash samples from various locations was also conducted in this research to determine the effect of volcanic ash for the surrounding environment. From the measurement result of pH, it is known that the highest of pH is 9 at location VIII, while the lowest of pH is 5 at location V (Fig. 2).

Based on the value of pH, it is known that the volcanic ash is more acidic at the sampling location of V and X. In the case of volcanic ash sample, it showed from Table 3 the concentration of Zn element is lower than other location. It causes the essential elements to be bioavailable and soluble in the soil. Meanwhile, essential elements are less soluble in the soil at locations VI, VIII and IX than other sampling location because volcanic ash tends to be alkaline [14-15]. The bioavailable properties of the essential elements in volcanic ash are related to pH. In

acidic conditions, most elements with multi-valency are easily soluble so they can seep into the soil better [16].

In general, most of the trace elements can be activated at under acidic conditions, so their presence in the soil can be increased. However, it is very easy to accumulate trace elements in the soil under alkaline conditions. Therefore, the enrichment of essential elements in agricultural land derived from volcanic ash can be attributed to alkaline conditions. Acid conditions in the soil can reduce the number of essential elements because it can increase their solubility and mobility. But the relationship is not for a single. Besides the pH of the soil, there are other factors that control the accumulation of essential elements throughout the area affected by the distribution of volcanic ash [13,17].

CONCLUSION

The distribution pattern of volcanic ash essential elements as a result of volcanic eruption disaster has been successfully mapped using Surfer software. In this study, several elements in volcanic ash such as major elements of Al, Fe, Na, K, Si and trace elements Zn, Co, Se were detected. The distribution of the essential elements in volcanic ash as a result of volcanic eruption disaster showed a different pattern. The concentration distribution pattern of the Zn, Si, Co and Fe elements tends to decrease towards the peak of Merapi. Meanwhile, the concentration of Na and K elements of their distribution concentration tends to decrease away from the peak of Merapi. The wind's speed affects the distribution range of an element contained in volcanic ash samples. Lighter elements have a wider distribution range than that of heavier elements. The pH of volcanic ash samples seemingly only affected the concentration of Zn elements in the distribution pattern. The distribution data of essential elements in the volcano ash will be useful for agriculture service division in Yogyakarta.

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REFERENCES

- Canion, B., Jacques, C., Landsberger, S., and Taftazani, A., 2012, Trace analysis of Indonesian volcanic ash using thermal and epithermal neutron activation analysis, *Nukleonika*, 57 (4), 585–589.
- [2] Salam, A., Khattak, R.A., Ahmed, S., and Ahmed, N., 2013, To study the micronutrients status of Kowga area district Buner, *Pure Appl. Biol.*, 2 (1), 38–41.
- [3] Pirzadeh, M., Afyuni, M., Khoshgoftarmanesh, A., and Schulin, R., 2010, Micronutrient status of calcareous paddy soils and rice products: Implication for human health, *Biol. Fertil. Soils*, 46 (4), 317–322.
- [4] Xia, H., Zhao, J., Sun, J., Xue, Y., Eagling, T., Bao, X., Zhang, F., and Li, L., 2013, Maize grain concentrations and above-ground shoot acquisition of micronutrients as affected by intercropping with turnip, faba bean, chickpea, and soybean, *Sci. China Life Sci.*, 56 (9), 823–834.
- [5] Yaroslavtseva, T.V., and Raputa, V.F., 2013, Analysis of particle size distribution in fields loss volcanic ash, *Bull. Nov. Comp. Center*, 1–5.
- [6] Wilson, T.M., Stewart, C., Sword-Daniels, V., Leonard, G.S., Johnston, D.M., Cole, J.W., Wardman, J., Wilson, G., and Barnard, S.T., 2012, Volcanic ash impacts on critical infrastructure, *Phys. Chem. Earth*, 45-46, 5–23.
- Budianta, W., 2011, The potential impact of ash Merapi volcano eruption 2010 in Yogyakarta, Indonesia, for the environment and human health, *J. SE Asian Appl. Geol.*, 3 (2), 111–115.
- [8] Stewart, C., Horwell, C., Plumlee, G., Cronin, S., Delmelle, P., Baxter, P., Calkins, J., Damby, D., Morman, S., and Oppenheimer, C., 2013, Protocol for analysis of volcanic ash samples for assessment of hazards from leachable elements, United States Geological Survey - USGS, June 2013.
- [9] Sunardi and Darsono, 2017, Performance test of K_o

NAA and relative method for analysis of Al, Mg, K nuclides in SRM lake sediment sample, *Indones. J. Chem.*, 17 (2), 175–181.

- [10] Kiliç, K., Doğan, H.M., Yalçin, H., Bilim, M., and Karahan, G., 2015, Potentially toxic elements of volcanic ash soils in the Cappadocia region of central Turkey, *Carpath. J. Earth Environ. Sci.*, 10 (1), 171–181.
- [11] Gislason, S.R., Hassenkam, T., Nedel, S., Bovet, N., Eiriksdottir, E.S., Alfredsson, H.A., Hem, C.P., Balogh, Z.I., Dideriksen, K., Oskarsson, N., Sigfusson, B., Larsen, G., and Stipp, S.L.S., 2011, Characterization of Eyjafjallajökull volcanic ash particles and a protocol for rapid risk assessment, *PNAS*, 108 (18), 7307–7312.
- [12] Langmann, B., 2013, Volcanic ash versus mineral dust: Atmospheric processing and environmental and climate impacts, *IRN Atmos. Sci.*, 2013, 245076.
- [13] Li, L., Wu, J., Lu, J., Min, X., Xu, J., and Yang, J., 2018, Distribution, pollution, bioaccumulation, and ecological risks of trace elements in soils of the northeastern Qinghai-Tibet Plateau, *Ecotoxicol. Environ. Saf.*, 166, 345–353.
- [14] Njinga, R.L., Moyo, M.N., and Abdulmaliq, S.Y., 2013, Analysis of essential elements for plants growth using instrumental neutron activation analysis, *Int. J. Agron.*, 2013, 156520.
- [15] Rassam, G., Dashti, M., Dadkhah, A., and Khoshnood Yazdi, A., 2015, Root yield and quality of sugar beet in relation to foliar application of micronutrients, *Annals of West University of Timişoara, ser. Biology*, XVIII (2), 87–94.
- [16] Nanzyo, M., 2002, Unique properties of volcanic ash soils, *Global Environ. Res.*, 6, 99–112.
- [17] He, H., Dong, Z., Peng, Q., Wang, X., Fan, C., and Zhang, X., 2017, Impacts of coal fly ash on plant growth and accumulation of essential nutrients and trace elements by alfalfa (*Medicago sativa*) grown in a loessial soil, *J. Environ. Manage.*, 197, 428–439.