Study of Mineralogy Composition, Total, and Exchangable Content of K, Ca, and Mg of Volcanic Ash from Sinabung Mountain Eruption in North Sumatera, Indonesia

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Abstract

Purpose – The research was carried out in order to study the composition of minerals, content of total-K, total-Ca, total-Mg, and exchangeable of K, Ca, Mg in volcanish ash from Sinabung volcano eruption.

Design/Methodology/Approach – The volcanic ash material in amount of 5 kg was collected from the depth of 0–20 cm and 21–41 cm. Mineral composition was determined by using line counting method; total contents of K, Ca, and Mg were measured by HCl 1N extraction, and exchangeable of K, Ca, and Mg was measured by NH_4OAc 1N pH 7.0 extraction.

Purpose – The results depicted in volcanic ash layer at the depth of 0–20 cm found some minerals such as plagioclase (34%), hypersthene (9%), augite (3%), hornblende/amphibole (5%), and volcanic glass (1%). These minerals were also found in different amounts at a depth of 21–41 cm. Hypersthene and amphibole were higher and augite was lower at a depth of 0–20 cm than 21–41 cm. The total content of K, Ca, and Mg was found to be 2.27%, 8.12%, and 2.28%, respectively, at a depth of 0–20 cm. The exchangeable of K, Ca, and Mg was found in an amount of 1.89 me/100 g, 20.71 me/100 g, and 1.62 me/100 g, respectively. The total content of K, Ca, and Mg was not available to plants but could potentially be as a source of plant nutrient after weathering while exchangeable form can be uptaken by plant directly.

Research Limitations/Implications – Based on the composition of the minerals, total, and exchangeable of K, Ca, and Mg that the material of volcanic ash, it could potentially be used as source of fertilizers.

Originality/value – The composition of primary minerals contained in volcanic ash and to know the amount of elements K, Ca, and Mg-associated minerals either in total or exchange.

Keywords Mineral composition, Vulcano sinabung, North Sumatera

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1. Introduction

Indonesia has 129 volcanoes, 83 volcanoes belong to the active category. The active and inactive volcanoes are spread around the islands of Sumatera, Java, Bali, Nusa Tenggara, Sulawesi, Maluku, and Papua. In Sumatera, there are still some active volcanoes. In the province of North Sumatera, there are two active volcanoes namely Sibayak volcano and Sinabung volcano. Sibayak volcano erupted in 1881, while Sinabung volcano in the past seven years alone had three times experienced a major eruption and produced volcanic ash. These eruptive activities occurred in 2010, 2013/2014, and the end of 2016 even in 2017. Volcanic ash is a material which resembles cloud clumps, formed during an explosion which is spread into the air, <2 mm (0.079 in) in size. This material is relatively hard, insoluble in water, can be very rough and quite easy to crush.

The volcanic ashes fall to the ground to a distance of hundreds of kilometers when carried by the wind. Volcanic ash contains a number of primary and secondary minerals as well as various chemical elements partly known as nutrients. The types and amounts of minerals, especially the primary minerals which found in volcanic ash, may be the same or vary from each volcano and this condition depends on its rocks. In volcanic ash from Redoubt volcano, an active volcano located in Alaska, the United States for example, the mineral found is dominated by feldspar, about 70%. Besides, there are also mineral quartz, calcite, magnetite, gypsum/anhydrite, mica, and amphibole (Bayhurst *et al.*, 1992). Volcanic ash in southern east Baltic does not only produce K-feldspar minerals but also some macro- and micro-elements such as P, K, Ca, Mg, S, Mn, Fe, Zn, Cl, and Cu (Kiipli *et al.,* 2012). Volcanic ash from several volcanoes in Japan also contains primary minerals feldspar, plagioclase, hornblende, amphibole, biotite, quartz, cristobalite, tridymite, pyroxene, mica, gypsum, anhydrite, olivine, opaque, and phyropillite (Nanzyo *et al.*, 1993; Nakagawa and Ohba, 2002; Minami *et al.*, 2016). Some active volcanoes in Indonesia such as Merapi, Kelud, and Sinabung also have varied types and amounts of primary minerals in their volcanic ashes. Volcanic ashes from volcanoes in Java Island contain minerals quartz, cristobalite, feldspar, magnetite, volcanic glass, and also amphibole, pyroxene, hematite, and tridymite in sufficient quantities (Supriyo *et al.*, 1992). The dominant minerals found in volcanic ash of Volcano Merapi are molibate and cristobalite. Kelud is dominated by leucite minerals, diobsite-subsilisic, almarudite, whereas in volcanic ash of volcano Sinabung, albite and quartz were found (Latif *et al.*, 2016).

Volcanic ash also contains certain chemical elements, such as potassium, calcium, magnesium, aluminum, iron, and silica in addition to minerals (McDaniel and Wilson, 2007). Volcanic ash from Fujivolcano in Japan contains elements Na> Ca> K> Mg> P> Si> Ti, Fe> Al> Mn (Shikazono *et al.*, 2005). Volcanic ash from Merapi volcano in Central Java contains K, Ca, Mg, Na, P, Si, Al, Fe, Mn, Ti, and other elements (Wahyuni *et al.,* 2012). Volcanic ash from Merapi volcano has low Mg content, but it has high Ca content (Suriadikarta *et al.*, 2011). The volcanic ash of Sinabung volcano is also estimated to contain chemical elements such as K, Ca, Mg, and various other chemical elements. The presence of these elements is the result of mineral decomposition contained in volcanic ash. Therefore, the amounts of nutrients that will be presenting in the soil depend on the mineral decomposition of volcanic ash. This level of decomposition is influenced by various conditions such as the mineral type, the silica–oxygen bond of the mineral, and its environmental conditions (Tan, 1998; Wilson, 2004). It is important to have knowledge about mineral and chemical elements especially K, Ca, and Mg in volcanic ashes, as this will determine the nature of the soil and its fertility rate against plant growth. If there are many nutrients in the volcanic ash, especially nutrients such as alkaline, then the volcanic ashes can be used as an alternative material for fertilization. Therefore, this study was conducted to examine the composition of primary minerals contained in volcanic ash and to know the amount of elements K, Ca, and Mg associated minerals either in total or exchange.

2. Materials and Methods

The research site was within the area of Sinabung volcano, Karo District, North Sumatera Province, Indonesia (Figure 1). Sinabung volcano is located at the coordinates of 03^{o}10″N and 98^{o}23″E, with a height of 2,460 m above sea level. The study began from field observation and sampling of volcanic ash material in May 2017 to obtain the results of analysis of material samples from the laboratory in September 2017. Determination of location and sampling point of volcanic ash material is considered quite appropriate because it referred to the map of the spread of volcanic ash and using purposive sampling methods. Map of volcanic ash distribution was obtained from the Center of Meteorology, Climatology and Geophysics (BMKG) Tanah Karo Regency, North Sumatera Province (Figure 2).

A total of 5 kg of volcanic ash is taken at the eruption site from a depth of 0–20 cm and 21–41 cm. Each sample of volcanic ash has been dried and sieved with a mesh sieve of 10 meshes. Analysis of volcanic ash samples done in the laboratory comprised sand mineral fraction analysis and analysis of potassium (K), calcium (Ca) and magnesium (Mg) contents in total and exchangeable forms. Sand mineral fraction analysis was conducted in Soil Chemical and Mineralogy Laboratory, Agriculture Faculty, Bogor Agricultural University, using sand fraction material derived from the texture determination. Sand fractions were washed, dried and then filtered. The sand section of 0.25–1.00 mm was used as an example to determine the type of mineral. The type of mineral was observed by sprinkling a number of sand samples evenly with the object glasses/microscope slides until evenly distributed. A few drops of nitrobenzol were applied as medium and stirred until there is no sand floating. Object glasses/microscope slides were placed under a polarized microscope to be observed. The calculation of the amount of minerals is done using the method *line counting*, which is 100 grains (Lynn *et al.*, 2008; Pramuji and Bastaman, 2009).

The analysis of total of K-, Ca-, and Mg- were performed by extraction of 1N HCl, whereas the analysis of K-, Ca-, and Mg- can be exchanged through NH_4OAc extraction 1N

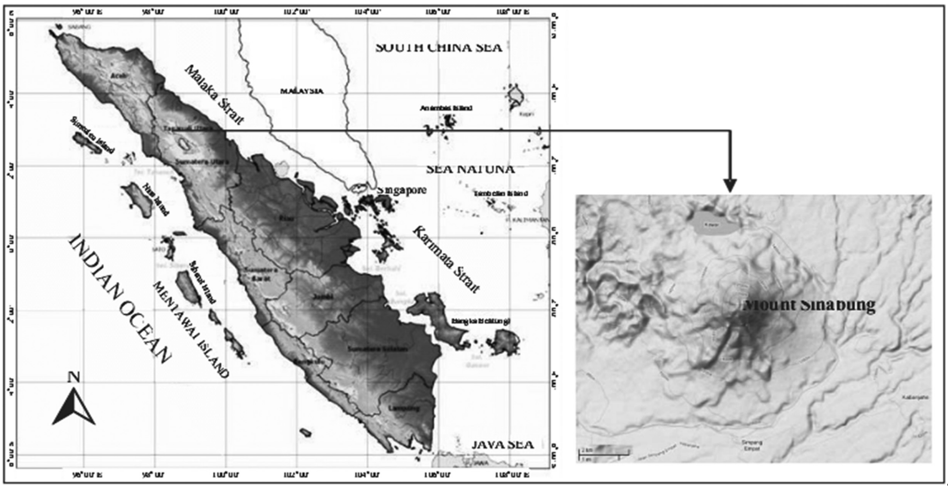

Figure 1.
Position of Sinabung Volcano in North Sumatera, Indonesia

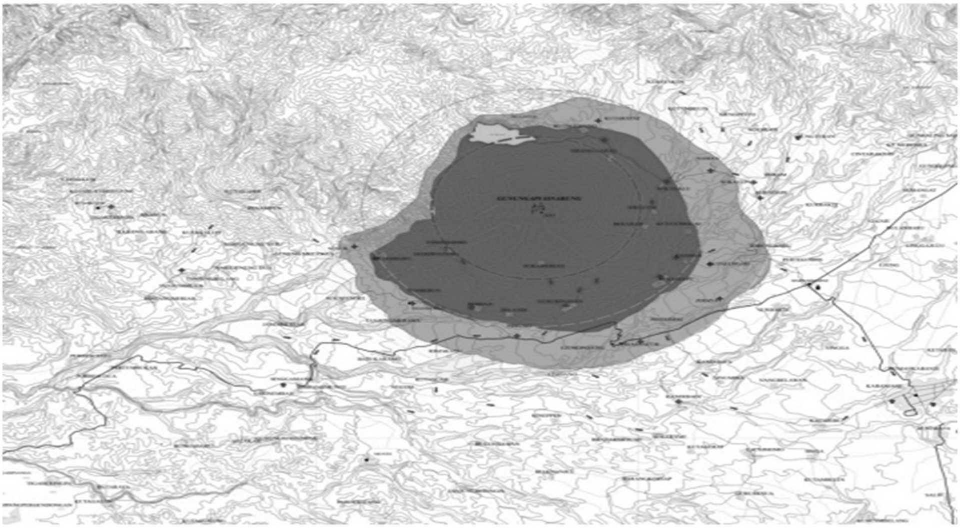

Figure 2.
Distribution of Material Volcanic Ashes from the Eruption of Volcano Sinabung

pH 7.0. Ca and Mg elements were measured using Atomic Adsorption Spectrophotometry, while the K element used Flamephotometry.

3. Results and discussions

3.1. Mineral composition of volcanic ashes

The primary compositions of mineral from volcanic ashes of Sinabung volcano in North Sumatera Province are described in Table 1. Data in Table 1 showed that several different primary minerals such as Plagioclase (34%), Hypersthene (4–9%), Augite (3–5%), Hornblende/Amphibole (3–5%), Volcanic Glass (0–1%), Magnetite (1–2%), and Quartz (0–2%) have been found in volcanic ashes. The first four primary minerals contain elements such as K, Ca, and Mg in it. Therefore, if the structure of minerals were destroyed by decomposition, it will release the elements into the soil solution into an exchangeable form and available for collection by plants. This is believed to be because the minerals contained in volcanic ash contain a number of both macro- and micro-nutrients (Shikazono *et al.*, 2005, Kiipli *et al.*, 2012; Wahyuni *et al.,* 2012). Plagioclase, hypersthene, hornblende/amphibole and

Table 1.
Mineral Compositions of Volcanic Ash from Sinabung Volcano Eruption in North Sumatera

Minerals Composition	Amount (%) 0–24 cm	Amount (%) 24–41 cm
Plagioclase	34	34
Hypersthene	9	4
Augite	3	5
Hornblende/amphibole	5	3
Volcanic glass	1	0
Magnetite	2	1
Quartz	0	2
Weathered volcanic glass	5	6
Weathered material	41	45

augite are minerals commonly found in volcanic ash and their presence would increase the amount of K, Ca, and Mg in the soil (Shoji and Takahashi, 2002).

These primary minerals were also found in different amounts of volcanic ash in depths of 21–41 cm. Hypersthene and hornblende/amphibole were higher and augite was lower at a depth of 0–20 cm rather than a depth of 21–41 cm. The amount of amorphous as a result of decomposition of volcanic glass and lapel material was also found with the amount of 5–6% and 41–45%, respectively. These data indicated that the laps of volcanic and lapel glasses were higher at a depth of 21–41 cm than a depth of 0–21 cm. The difference in the amount of minerals between 0–21 cm and 21–41 cm depth was very likely to occur considering that the eruption of volcanic ash from the eruption occurred at different times. In addition, the minerals contained in volcanic ash can then form a single mineral, disappeared from the system by washing, or reacting in the system to form various crystalline and amorphous products.

3.2. Total Contents of K, Ca, and Mg

The content of elements K-, Ca-, and Mg-total in volcanic ash are the elements contained within the mineralized structure and the elements in exchangeable form. The results of volcanic ash analysis from Sinabung volcano eruption that had K-, Ca-, and Mg-total content are presented in Table 2. The total or total content of K, Ca, and Mg was found to be, respectively, 2.27%, 8.12%, and 2.28%. The amount is relatively indifferent between a depth of 0–20 cm and a depth of 21–41 cm. This fact revealed that although the deposition time of volcanic ash material was different, the total content of these elements between those found in the volcanic ash material in the upper layer and the material in the lower layers were the same.

Although the total element content of K, Ca, and Mg contained in the mineral was not a form which can be taken or absorbed by the plants, it could be a potential source of nutrients after the mineral has been decomposed, as it is understood that nutrients that can be absorbed by plants are nutrients in exchangeable form and are present as free ions in soil solution (Tan, 1998).

3.3. Contents of exchangeable of K, Ca. and Mg

The present of exchangeable of K, Ca, and Mg is a part of elements released from the weathering of the primary minerals. The results of analysis of the contents of K, Ca, and Mg exchangeable in volcanic ash from Sinabung volcano eruption in North Sumatera Province are reported in Table 3. The exchangeable of K, Ca, and Mg were found in different amount and can be arranged from high to low such as Ca (20.71–21.8 me/100 g) > Mg (8.21–8.44 me/100 g), and K (1.62–1.89 me/100 g).

The high content of Ca was correlated with the mineral species as a source of the element, plagioclase [$NaAlSi_3O_8$ to $CaAl_2Si_2O_8$] and/or amphiboles [$NaCa(Mg,Fe)_5\ AlSi_4O_{22}(OH)_2$]. The primary minerals (plagioclase, amphibole, and hypersthene) were more weatherable as

Table 2.
Total Contents of K, Ca, and Mg in Volcanic Ash from Sinabung Volcano Eruption in North Sumatera

Elements	Total Content (%)	
	0–24 cm	24–41 cm
K	2.27	2.21
Ca	8.12	8.19
Mg	2.28	2.22

a source of Ca and Mg, meanwhile the lower content of K may be correlated with orthoclase/ felsdpar felsdpar-orthoclase [$KAlSi_3O_8$] and/or augite [$Ca(Mg,Fe,Al)(Si,Al)_2O_6$] as more resistance minerals limited the weathering process. The rate of release of each element can be described by hypothetic reaction of minerals weathering based on the formula below (Brady, 1990; Tan, 1998).

Calcium (Ca) source from Ca-plagioclase:

$$CaAlSi_2O_8 + H_2CO_3 + \frac{1}{2}O_2 = Al_2Si_2O_5(OH)_4 + Ca^2 + CO_3^{2-} \quad (1)$$

Magnesium (Mg) source from hypersthene:

$$MgFeSiO_3 + 2H_2CO_3 = Mg^{2+} + Fe^{2+} + 2HCO^{3-} + SiO_2 + H_2O \quad (2)$$

Potassium (K) source from feldspar or orthoclase :

$$2KAlSi_3O_8 + 2H^+ + 9H_2O = HAl_2Si_2 + \quad 4H_4SiO_4 + 2K^+ \quad (3)$$

The concentration of K, Ca, and Mg to be exchangeable form and/or available to the plants depends on the reaction rate that is controlled by some factors such as minerals species, temperatures, soil acidity, and soil moisture. According to Bowen Series, the rate of weatherable minerals was deteriorated from amphibole, biotite until K-felsdpar (Bowen, 1928). Under the condition of high temperature and low pH, it could support promoting the rate of dilution process resulted the minerals destroyed and release exchangeable cations. Soil moistures are responsible to control the hydration and reduction–oxidation process. By this process, iron (Fe) in mineral structure, pyroxene can be reduced or oxidized so that the mineral was destroyed and some cations are released (Schott *et al.*, 1981). All the process are able to increase the concentration of exchangeable cations.

In order to improve the concentration of exchangeable K, Ca, and Mg, the volcanic ashes can be treated by promoting the decomposition of mineral such as heating, boiling, acidification, and fermentation. All of this study needs to be conducted in the future research.

3.4. Ratio of Exchangeable and Total of K, Ca, and Mg

The ratio of exchangeable to total of K, Ca, and Mg in volcanic ash from Sinabung volcano eruption in North Sumatera is described in Table 4. The ratio can be used to indicate the rate of the release of the element in exchangeable from mineral structure by weathering process.

Table 3. The Contents of K, Ca, and Mg exchangeable in Volcanic Ash from Sinabung Volcano Eruption in North Sumatera

Elements	Exchangeable Content (me/100 g)	
	0–24 cm	24–41 cm
K	1.89	1.62
Ca	20.71	21.08
Mg	8.44	8.21

The weathering of calcium minerals was higher than the others as shown by E/T ratio value, for example Ca (0.051), Mg (0.044–0.046), and K (0.029–0.032).

The content of exchangeable K, Ca, and Mg was too low as shown by data 5.1% Ca, 4.6% Mg, and 2.9% K from total form (Figure. 3). To indicate the content of exchangeable K, Ca, and Mg relative to the total amount of K, Ca, and Mg, the percentage of exchangeable of K, Ca, and Mg relative to total of K, Ca, and Mg in volcanic ash from Sinabung volcano eruption in North Sumatera are reported in Table 5. The table describes the minerals that

Table 4. The Ratio of Exchangeable to total of K, Ca, and Mg in Volcanic Ash from Sinabung Volcano Eruption in North Sumatera

Elements	Exchangeable (*E*) (%) 0–24 cm *(1)*	Exchangeable (*E*) (%) 24–41 cm *(2)*	Total (*T*) (%) 0–24 cm *(3)*	Total (*T*) (%) 24–41 cm *(4)*	Ratio: *E/T* 0–24 cm *(1)/(3)*	Ratio: *E/T* 24–41 cm *(2)/(4)*
K	0.073	0.063	2.27	2.21	0.032	0.029
Ca	0.414	0.421	8.12	8.19	0.051	0.051
Mg	0.101	0.098	2.28	2.22	0.046	0.044

Table 5. Percentage of Exchangeable of K, Ca, and Mg Relative to Total of K, Ca, and Mg in Volcanic Ash from Sinabung Volcano Eruption in North Sumatera

Elements	Exchangeable (%) 0–24 cm *(1)*	Exchangeable (%) 24–41 cm *(2)*	Total (%) 0–24 cm *(3)*	Total (%) 24–41 cm *(4)*	Percentage (%) 0–24 cm *(1)/(3)×100*	Percentage (%) 24–41 cm *(2)/(4) ×100*
K	0.073	0.063	2.27	2.21	3.2	2.9
Ca	0.414	0.421	8.12	8.19	5.1	5.1
Mg	0.101	0.098	2.28	2.22	4.6	4.4

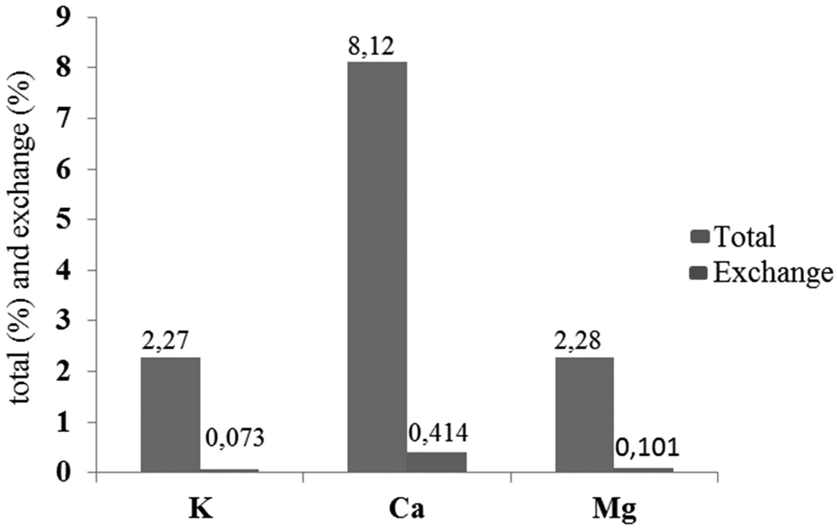

Figure 3. The Contents of Total and Exchangeable K, Ca, and Mg in Volcanic Ash from Sinabung Volcano Eruption in North Sumatera

did not decompose too much. Therefore, the elements of K, Ca, and Mg-exchangeable were low in volcanic ash of Sinabung volcano eruption.

4. Benefits of volcanic ash as source of fertilizers and soil formation

In the long term, volcanic ash can be part of the body of the soil, and, in the short term, it can act as a soil enhancer to improve soil quality. Precipitation of repeated volcanic ash eruptions in relatively large numbers tends to increase the soil layer. The process will produce the soil with distinctive new features and may differ from the previous traits, from its morphological, mineralogical, and physic-chemical features (Shoji *et al.*, 1994). Volcanic ash influences the development of soil horizon through the accumulation of humus and carbon, increasing porosity and the variable charge of soils (Nanzyo *et al.*, 1993; Imaya *et al.*, 2010).

On the other hand, the decomposition of primary minerals from volcanic ash was not only capable of releasing alkaline elements such as K, Ca, and Mg and amorphous silica materials but at the same time increasing the soil capacity to retain water and encourage the development of bacteria in the soil. This condition will have a direct impact on the increase in soil fertility needed to support the growth of cultivated plants.

5. Conclusions and recommendations

- In the material of volcanic ash at a depth of 0–21 cm, some primary minerals such as plagioclase (34%), hypersthene (9%), augite (3%), hornblende/amphibole (5%), and volcanic glass (1%) were found. These minerals were also found at a depth of 21–41 cm in different amounts.
- Hypersthene and amphibole were found to be higher and augite was lower at a depth of 0–21 cm than a depth of 21–41 cm.
- The total content of K, Ca, and Mg was found to be 2.27%, 8.12%, and 2.28%, respectively, at a depth of 0–21 cm.
- The exchangeable of K, Ca, and Mg were found in an amount of 1.89 me/100 g, 20.71 me/100 g, and 1.62 me/100 g, respectively.
- Based on the composition of minerals, it showed that the total and exchangeable of K, Ca, and Mg were relatively high so that the material of volcanic ash can be potentially used as alternative source of K, Ca, and Mg fertilizers.
- The total of K, Ca, and Mg were not available to plants but could potentially be the source of plant nutrients after weathering while exchangeable form can be absorbed by plants directly. Therefore, it is recommended to conduct future research to find the methods how to increase available forms of the exchangeable content of K, Ca, and Mg for the plants.

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