Improving Volcanic Soil Chemistry After the Eruption of Mt. Sinabung, North Sumatera in 2020

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Abstract. Volcanic activity produces pyroclastic deposits when erupted and cover the surrounding area. The minerals contained in these deposits are the source of plant nutrients. The volcanic deposits weathered, release nutrients to the environment, and improve soil chemical properties. The eruption of Mt. Sinabung in 2018 covered an area of 30,320 ha, while in 2019 was 1,371 ha. The study aims to investigate the status of nutrient content and the volcanic ash weathering level in 2020. There were 16 samples taken from ash deposits at various depths, with a total area of 1,585.31 ha. Samples were analyzed to determine the total elemental composition using X-ray fluorescence (XRF) spectrometer, nutrient reserves, and weathering indices.

The results showed that the total elemental composition of SiO₂ is 51.51-67.51% classified as mafic (basalt) to felsic (dacite) materials, Al₂O₃; 15.54-23.41%, Fe₂O₃; 2.84-10.02% and CaO; 3.94-6.46%. Mount Sinabung’s volcanic ash has a nutrient reserve capacity of MgO, CaO, P₂O₅, K₂O, and SO₃, respectively with the amount of 37,384.17 kg/ha, 235,794.99 kg/ha, 34,293.12 kg/ha, 72,357.39 kg/ha, and 70,352.22 kg/ha. The weathering indices of volcanic ash of 2020 were determined with a value of 2.76-4.19 for Ruxton ratio and Product of Weathering Index (PWI) of 67.39-76.13, indicates the weathering rate of silicates from volcanic ash are still at initial stage and are still in the fresh condition.

Keywords: Pyroclastic Materials; Tephra Distribution; Nutrient Reserves; Weathering Indices

1. Introduction

Mount Sinabung is one of the active volcanoes in North Sumatera with a history of eruptions in 2010, 2013, 2014, 2016, and 2019 [1, 2, 3]. Volcanic activity produces pyroclastic deposits when erupted and covers the surrounding area. The tephra materials from pyroclastic material deposits have various size fractions, such as bomb/block, lapillus, coarse, and fine ash [4]. Besides, volcanic materials also contain various mineral compositions. Silica (SiO₂) is the main constituent component of volcanic materials [5].

Based on the SiO₂ content in the ash material, Shoji [6] classified it into mafic (alkaline), intermediate, and felsic (acid) materials. Tephra eruption material from Mt. Sinabung in 2017 and 2016 contained 61% and 49.33% SiO₂, both of which were classified as intermediate materials with andesite to basaltic-andesite minerals [7, 8]. The types of minerals in volcanic ash deposits depend on
the chemical content of the magma, temperature, and pressure during crystallization. Therefore, apart from silica, some minerals that are almost always present are Al, Fe, K, Na, Ca, and Mg [9, 10].

Volcanic material has different nutrient content, which are considered as nutrient reserves. The volcanic deposits weathered, release nutrients to environment, and improve soil chemical properties [11]. Chemical compounds resulting from weathering can differ depending on the thickness of the ash, the composition of the parent mineral, and the weathering process of the material released by volcanoes [10, 12]. Various types of oxides in primary minerals, which act as nutrient reserves, can release elements such as Al, Fe, Ca, Mg, K, P, S, and Na when the volcanic material is weathered [13, 14, 15].

The assessment of the weathering index and geochemical components can be used to show the progress of Andisols development (soil formation) from tephra material. From the results of this research, it was explained that the weathering traces of Mt. Talang volcanic ash between leached and unleached increased by 4%, identifying that the rate of weathering has released large amounts of silica from pure volcanic ash [14]. This assessment is called the Ruxton Index, which is the simplest assessment based solely on the concentration of silica and alumina [16]. The Ruxton ratio is highly recommended for measuring the weathering index of acid and intermediate bedrock [17]. Besides, to track the movement of less mobile elements such as Si, Al, Fe, and Ti in the weathering of ash deposits, a Product Weathering Index (PWI) can be used [14, 18, 19]. This research aimed to investigate the status of nutrient content and the weathering level of volcanic ash in 2020.

2. Materials and Methods

2.1. Study area
The research was conducted at the Mt. Sinabung in Karo Regency, North Sumatra Province, Indonesia, with a height of approximately 2,460 m above sea level (a.s.l.) (figure 1). It is at geographical coordinates of 3° 10' 16.7” N and 98° 23’ 24.66”. Mount Sinabung has experienced eruptions several times, namely in 2010, 2013, 2014, 2016, and 2019, so that the distribution of pyroclastic material has a different deposit thickness.

The observed of Mt. Sinabung volcanic material distribution in 2018 was 30,320 ha [20], and shrank to 1,371 ha in 2019 was monitored through remote sensing. ArcGIS software is used to create a digital map of the distribution of pyroclastic materials and record the area of ash distribution. Ash distribution of Mt. Sinabung erupted in 2019 was monitored through remote sensing from Landsat satellite images (figure 2). The distribution of ash deposit mapping has done by tracing and digitizing the flow limits from Figure Sentinel-2 (the image is available on the Google Earth Pro Engine) [21]. Then, ArcGIS software is used to create several digital maps such as pyroclastic material distribution maps, field observation maps, and research results maps.

2.2. Sampling and morphology of volcanic ash
Samples from volcanic ash deposits were collected in March 2020, namely after several months of the eruption of Mt. Sinabung in June 2019. The ash samples studied were taken at a distance of 3-5 km (disaster-prone zone) to the southeast of the eruption center, covered an area of 1,585.31 Ha (figure 2). There were 16 samples taken as a composite and several samples intact ash samples from the top ash layer until the color difference boundaries between the ash deposits were visible. Intact ash sampling was used to obtain the bulk density value of ash. The thickness of the top layer of ash was measured in the field using a meter, while the color was identified using the Munsell Soil Color Chart by matching the volcanic ash samples after sampling.

2.3. Analysis and volcanic ash data processing
The total elemental compositions of the ashfall deposit samples were identified using X-ray fluorescence (XRF) spectrometer PANalytical Epsilon 3 for geochemical analysis. The ash samples
were air-dried, homogenized by grinding and sieving using a sieve to obtain a fine fraction of 200 µm or less before analysis. Total elemental oxides from XRF analysis can explain the geological characteristics of volcanic ash deposits [12].

Figure 1. (a) Location of Mt. Sinabung and research area, (b) Topography of Mt. Sinabung.

Figure 2. The distribution of pyroclastic materials in 2019.
The intact samples of ash with a known volume of ring samples, oven-drying at 105 °C for 2 x 24 hours, then weighed before and after oven-drying to obtain bulk density data. The calculation of nutrient reserves uses data on ash density, a nutrient composition from XRF analysis, and the thickness of the top layer of ash (figure 3). The weathering rate of volcanic ash deposits in 2020 is determined through a weathering index assessment. Elemental concentration from the analysis with a spectrometer is used to determine the weathering index value of different calculation methods, according to the geochemical composition and data mineralogy that is measurable. The indexes used in this study are the Ruxton Weathering Index (R) and the Product of Weathering Index (PWI).

The Ruxton Ratio \( R = \frac{SiO_2}{Al_2O_3} \) shows the weathering rate of silica associated with immobile alumina during the weathering of volcanic ash [22]. The Ruxton index has criteria optimal weathering with a value of 0, and a value of 10 indicates the degree of fresh weathering. Product of Weathering Index \( PWI = (SiO_2/TiO_2 + Fe_2O_3 + SiO_2 + Al_2O_3) \times 100 \) can track the movement of less mobile elements such as Si, Al, Fe, and Ti in the weathering of ash deposits [18]. Furthermore, it has a scale of > 50 for fresh weathering and a scale of 0 for optimal weathering. The analysis has used JMP Pro 11 software for the measured variables for the presentation of statistical data.

**Figure 3.** Method of calculating nutrient reserves from volcanic ash of Mt. Sinabung 2020.
3. Results and Discussion

3.1. Characteristic and morphology of volcanic ash

The characteristics and morphology of the Mt. Sinabung tephra deposits are summarized in Table 1. The distribution of ash-falls from the eruption of Mt. Sinabung in 2020 has different deposit thicknesses ranging from 2-32 cm (medium to thick) in the top layer (Figure 4). It's the same with the distribution of the volcanic ash Mt. Sinabung in February 2014 have various thicknesses be classified into are < 2 cm (thin), 2-5 cm (medium), and > 5-10 cm (thick) groups [23].

With time, the ash deposits after weathered to harder and denser so that the thickness of the ash getting shrunk, but do not affect our homogenous (just fine-ash) mass or ash volume measured [24, 25]. However, the result in this research has of bulk density value > 1 Mg/m³ because containing materials of tephra with various grains size. Some of these deposits contain large fractions such as bomb/block, lapillus, and coarse ash [4]. Thus, part of the sample cannot be collected or the sample becomes heavier because it contains rocks.

Primary silicate minerals are the main ingredients in the formation of tephra materials that have various colors. Table 1 shows that the color difference is shown in the volcanic ash deposits in this study have gray (10 YR 6/1) to dark grayish brown (10 YR 4/2) colors. The composition of rhyolite, dacite, andesite in the tephra layer is generally white to gray due to the colorless volcanic glass that dominates, and a few mafic minerals [26]. Colored silicate minerals contain high iron in the form of ferrihydrite (brown to red) are formed during the weathering process. It can also be caused by a gray to light yellowish-brown in color due to the color of uncoated rhyolite, dacite, and andesite tephras materials mixed with small amounts of iron oxide and hydroxide coatings [9, 27].
Table 1. Volcanic ash characteristics.

| Samples | Location                              | Elevation (m.a.s.l.) | Top Ash Layer (cm) | Bulk Density (Mg/m³) | Colours          |
|---------|---------------------------------------|----------------------|--------------------|----------------------|------------------|
| 1       | Berastepu village, Simpang Empat Sub-district | 1228                | 26                 | 1.49                 | 10 YR 6/1        |
| 2       | Berastepu village, Simpang Empat Sub-district | 1222                | 20                 | 1.12                 | 10 YR 6/2        |
| 3       | Naman Teran Sub-district Simacem village, Simacem village | 1266                | 3                  | 1.36                 | 10 YR 6/1        |
| 4       | Naman Teran Sub-district Simacem village, Simacem village | 1319                | 6                  | 1.30                 | 10 YR 5/1        |
| 5       | Naman Teran Sub-district Suka Meriah village, Simacem village | 1343                | 7                  | 1.58                 | 10 YR 5/2        |
| 6       | Payung Sub-district Berastepu village, Simpang Empat Sub-district | 1145                | 15                 | -                    | 10 YR 3/1        |
| 7       | Berastepu village, Simpang Empat Sub-district Gamber village, Simpang Empat Sub-district | 1128                | 18                 | -                    | 5 YR 5/1         |
| 8       | Gamber village, Simpang Empat Sub-district Simacem village, Simacem village | 1172                | 4                  | 1.36                 | 10 YR 4/2        |
| 9       | Gamber village, Simpang Empat Sub-district Simacem village, Naman Teran Sub-district Gurukinayan village, Naman Teran Sub-district Gurukinayan village | 1245                | 32                 | 1.50                 | 10 YR 5/2        |
| 10      | Gurukinayan village, Payung Sub-district Gurukinayan village, Payung Sub-district Simacem village | 981                 | 17                 | 1.37                 | 10 YR 4/2        |
| 11      | Gurukinayan village, Payung Sub-district Gurukinayan village, Payung Sub-district Berastepu village, Payung Sub-district | 1028                | 20                 | -                    | 10 YR 5/2        |
| 12      | Berastepu village, Simpang Empat Sub-district Gamber village, Simpang Empat Sub-district Kuta Tonggal village, Naman Teran Sub-district Gurukinayan village, Payung Sub-district | 1093                | 20                 | -                    | 10 YR 3/1        |
| 13      | Gamber village, Simpang Empat Sub-district Kuta Tonggal village, Naman Teran Sub-district | 1134                | 4                  | -                    | 10 YR 4/1        |
| 14      | Kuta Tonggal village, Naman Teran Sub-district Gurukinayan village, Payung Sub-district | 1147                | 2                  | 1.03                 | 10 YR 4/1        |
| 15      | Gurukinayan village, Payung Sub-district | 1056                | 4                  | 1.07                 | 10 YR 6/2        |

3.2. Geochemical of volcanic ash

Pyroclastic materials such as ash and volcanic rock have variations type of mineral content. That is due to the different mineral composition and chemical content depending on the magma composition, temperature, pressure, and magma chamber during the crystallization process [9, 28]. The total chemical composition (geochemical characteristics) of volcanic ash from several samples analyzed using an X-ray fluorescence (XRF) spectrometer [29].

Figure 5 shows the SiO₂ content compositions of 51.51-67.51% classified as mafic to felsic materials (basalt, andesite, and dacite) [6]. However, most of the research areas have dacite and andesite material properties (figure 7). Meanwhile, in January 2016 and 2017, volcanic ash deposits of Mt. Sinabung showed that the elemental content of SiO₂ range from 61-49.33% classified as andesite to basaltic-andesite [7, 8]. Total silica (SiO₂) during the period of the year 2016 to 2017 decreased by 11.67%, which indicates that the condition is quite weathered when compared to volcanic ash deposits in 2020 has increased. That is because the volcanic eruption in June 2019 added fresh material to cover the previously existing ash deposits.
The tephra material contains several oxides such as $\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ up to 15%, CaO, TiO$_2$, MgO, and Na$_2$O with a mass of 3-8% [30, 31]. Ash deposits in this study showed the composition of $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, and CaO had levels ranging from 15.54-23.41%, 2.84-10.02%, and 3.94-6.46%. Meanwhile, oxides such as MgO, P$_2$O$_5$, K$_2$O, TiO$_2$, and MnO have lower contents. The mineral composition of volcanic ash varies according to the type of rock. Andesite material from the volcanic ash of Mt. Sinabung has a high crystalline mineral content which is dominated by colorless volcanic glass. Consists of several labradorites and ferromagnetic minerals such as hornblende, augite, hypersthenes, and tourmaline. Then, it can contribute K, Ca, and Mg to the soil during weathering [13, 26, 32].

3.3. Nutrients Reserves of volcanic ash

The total element in volcanic ash from XRF analysis showed that the content of Mg, Ca, P, K, and S had been varying concentrations in all samples (figure 6). Therefore, the prediction of the amount of nutrient reserves in volcanic ash at all research locations varies according to the composition of the elemental source. Nutrient reserves from volcanic ash deposits of Mt. Sinabung in 2020 are summarized in table 2.
The primary mineral content in volcanic ash is a reserve source that can increase soil nutrients for the soil and plant fertility in the future [9]. Oxides in primary minerals released from weathering can contribute essential nutrients such as S, Ca, Mg, P, and K to the soil of volcanic origin as Andisol [13]. Based on the research results of Lubis [33] and Fiantis [34], the temporal volcanic ash deposits of Mt. Sinabung (2010-2020) during its weathering can increase the concentration of Ca, Mg, Na, and K bases in the soil in the high category.

The total elemental composition of volcanic ash (figure 6) has the number of elements Ca> K> S> Mg> P will release the constituent elements as potential plant nutrients during the weathering process. The high content of volcanic glass in ash will release several alkaline elements such as Ca, Mg, and K [35]. Most of the volcanic ash deposits are classified as dacite (acid), having a higher total Ca content than other alkaline elements (K, Mg, and Mn). The CaO contents to be a result of plagioclase feldspar (labradorite) content with basaltic andesitic composition [36]. However, it is still in the low category compared to silicates as the main constituent of volcanic ash.

![Figure 7. The distribution of silica oxide (SiO<sub>2</sub>) in volcanic ash deposit of Mt. Sinabung.](image)

The Ca content is found in basaltic and andesite rocks, especially in alkaline rocks. Besides, minerals such as augite, diopside, pyroxene, anorthite, and hornblende are also sources of the total Ca content in volcanic ash [14, 26, 37]. High K<sub>2</sub>O elements in ash are also found, especially in the mineral sanidine from alkaline feldspar and biotite from mica. Furthermore, the high concentration of the total K<sub>2</sub>O element compared to the elemental composition of P<sub>2</sub>O<sub>5</sub> indicates that the volcanic ash of Mt. Sinabung was derived from acidic materials [38, 39].

Magnesium is one of the constituent elements of biotite (mica) and hornblende minerals [14, 39]. This element only has at least concentration after alkaline cation like Ca, K, and Mn in the deposits of volcanic ash. Not all samples have total S content in volcanic ash, but calculated SO<sub>3</sub> is a high source
of sulfur released from the Mt. Sinabung erupted. The SO$_3$ content that settles in the tephra material is formed from sulfur dioxide is reactive with O$_2$ during a volcanic eruption [40]. When in the air, SO$_2$ will be absorbed by volcanic ash, which is likely to occur in a higher glass surface area than quartz [41].

Table 2. Nutrients Reserves of volcanic ash.

| Samples | Top ash layer (cm) | Nutrient Reserves (kg/ha) |
|---------|-------------------|---------------------------|
|         |                   | MgO | CaO | P$_2$O$_5$ | K$_2$O | SO$_3$ |
| 1       | 26                | 81,289.43 | 580,976.03 | 95,026.72 | 171,200.01 | 0.00 |
| 2       | 20                | 72,165.33 | 334,266.24 | 24,625.55 | 117,400.70 | 86,184.00 |
| 3       | 3                 | 6,235.60  | 58,645.10  | 9,690.26  | 19,397.26  | 0.00 |
| 4       | 6                 | 18,941.00 | 118,558.44 | 20,026.12 | 27,936.80  | 283,627.50 |
| 5       | 7                 | 19,373.43 | 134,602.41 | 18,896.90 | 46,703.83  | 236,241.60 |
| 6       | 15                | -     | -     | -         | -     | -     |
| 7       | 18                | -     | -     | -         | -     | -     |
| 8       | 4                 | 10,018.67 | 79,800.45 | 13,892.18 | 22,880.08 | 34,571.20 |
| 9       | 32                | 98,480.00 | 735,369.60 | 114,882.58 | 212,295.38 | 0.00 |
| 10      | 17                | 52,945.93 | 237,013.01 | 30,298.04 | 79,683.45 | 61,718.50 |
| 11      | 20                | -     | -     | -         | -     | -     |
| 12      | 10                | -     | -     | -         | -     | -     |
| 13      | 20                | -     | -     | -         | -     | -     |
| 14      | 4                 | -     | -     | -         | -     | -     |
| 15      | 2                 | 7,326.73  | 29,811.91 | 5,694.70  | 7,030.62  | 1,179.35 |
| 16      | 3.5               | 7,065.57  | 48,906.70 | 9,898.16  | 19,045.73 | 0.00 |

Average 12.97 37,384.17 235,794.99 34,293.12 72,357.39 70,352.22

The composition and chemical concentration of the results of pedogenesis are different because they are influenced by the thickness of the ash, the composition of the parent mineral, and the weathering process of the material released by volcanoes [10, 12]. The surface thickness of volcanic ash deposits in table 2 plays an important role in determining the amount of nutrient reserves, the thicker the ash layer, the greater the nutrient reserves. In addition to using data on nutrient concentration and thickness/depth of material, data processing of ash weight in hectares in hectares of ash density is also required to calculate nutrient reserve capacity.

Based on table 2, the nutrient reserve capacity of the volcanic ash deposits of Mt. Sinabung is quite high in the form of CaO > K$_2$O > SO$_3$ > MgO > P$_2$O$_5$ with an average value of 235,794.99 kg/ha, 72,357.39 kg/ha, 70,352.22 kg/ha, 37,384.17 kg/ha, and 34,293.12 kg/ha. The nutrients reserve capacity of the distribution of volcanic materials deposits is presented in figure 8.

3.4. Weathering indices of volcanic ash

Geopedogenesis rate of volcanic ash material weathering of Mt. Sinabung can be identified through evaluation using weathering index analysis. Two weathering indices were evaluated, namely Ruxton index (R), and Product of Weathering Index (PWI) were adapted from [18, 22]. There are several purposes for measuring these two indices, namely measuring conditions volcanic ash against weathering rate, know mobility of immobile elements such as Si, Al, Fe, and Ti during weathering, and prediction of the conversion of primary minerals [14].
Figure 8. The nutrient reserves distribution in volcanic ash of Mt. Sinabung in 2020.
Table 3 presents the potential chemical weathering index of volcanic ash in 2020 from eruptions in 2019. The weathering indices in this study have diverse values for the Ruxton ratio value ranging from 2.76-4.19 and the PWI 67.39-76.13. However, because the index value range is > 0, it is in the initial weathering criteria. The Ruxton ratio identifies that a large amount of the silica-to-alumina has been released from pure volcanic ash in all ash deposit samples. However, its weathering rates are at the initial weathering criteria. The PWI ratio of all samples > 50 indicated that they are at the fresh stage of weathering criteria. This index shows that the movement of silica is related to the elements Al, Fe, and Ti move less during the weathering of volcanic ash [14, 19].

Based on the results presented, the smaller the weathering indices value, it is assumed that the sample is in a more weathered/optimal weathering condition. The amount of secondary minerals will also increase with increasing weathering [19].

Table 3. Weathering indices of volcanic ash.

| Samples | Ruxton Index (R) | Product of Weathering Index (PWI) |
|---------|-----------------|----------------------------------|
| 1       | 3.46            | 74.06                            |
| 2       | 3.93            | 75.89                            |
| 3       | 3.54            | 74.73                            |
| 4       | 3.32            | 71.05                            |
| 5       | 3.68            | 72.99                            |
| 6       | 3.26            | 71.31                            |
| 7       | 3.61            | 74.72                            |
| 8       | 3.31            | 71.60                            |
| 9       | 3.43            | 73.48                            |
| 10      | 2.76            | 70.82                            |
| 11      | 3.58            | 73.40                            |
| 12      | 3.27            | 67.68                            |
| 13      | 4.19            | 76.13                            |
| 14      | 3.43            | 67.39                            |
| 15      | 3.01            | 67.84                            |
| 16      | 3.43            | 73.91                            |
| Average | 3.43            | 72.34                            |

4. Conclusion
The total elemental content of Mt. Sinabung has variations from mafic (base) to felsic (acid) with several material properties such as basalt, andesite, and dacite. However, most of them have dacite material properties with the total elemental content of Si ranging from 62-70%. Over time, volcanic ash containing various minerals can increase soil nutrients, with nutrient reserves currently stored at CaO > K₂O > SO₃ > MgO > P₂O₅. Since the 2019 eruption until now, we have seen traces of weathering from volcanic ash deposits of Mt. Sinabung is still in a fresh weathering condition.
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