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Dynamics of nutrient release rate and pattern from pyroclastic material due to the influence of humic substances and potassium-solving bacteria

Kurniati[1,2*], Suwardi[1], Budi Mulyanto[1], Budi Nugroho[1]

[1] Department of Soil Science and Land Resource, IPB University, Indonesia
[2] Agroecotechnology Study Program, Faculty of Agriculture and Forestry, Sulawesi Barat University, Indonesia
* Corresponding author's e-mail: kurniati25atikah@gmail.com

ABSTRACT

Indonesia has many areas with volcanic soils, especially pyroclastic materials that are rich in minerals important for plants such as calcium, potassium, and magnesium. These nutrients are bound to the minerals that are difficult for plants to access, so the soil is often less productive. The use of organic materials, such as humic substances and potassium-solubilizing bacteria can help accelerate the release of nutrients from pyroclastic materials, because humic substances increase the solubility of minerals and provide essential nutrients. This study investigated how humic substances and potassium-solubilizing bacteria work together to increase the release of nutrients from pyroclastic materials. This study was conducted by collecting pyroclastic samples at Mount Merapi and using soil from Mamuju, West Sulawesi, with a specific procedure (percolation). The results showed a pattern of nutrient release from pyroclastic materials, where Ca was always the most released element, followed by K and Mg, and this pattern was formed in all treatments. The combination (pyroclastic + humic substances + PSB) is the best treatment for nutrient release. The increase in nutrient release from the control and combination (pyroclastic + humic substances + PSB): Ca 788.84–1157.26 mg, K 123.96–206.69 mg, and Mg 50.65–59.65 mg. Humic substances improve the chemical properties of the soil and increase the activity of microorganisms, which helps in dissolving minerals, whereas bacteria produce organic acids that dissolve the potassium from minerals.

Keywords: nutrient release, pyroclastic, humic, potassium solubilizing bacteria.

INTRODUCTION

Indonesia is one of the countries with high volcanic activity, so it has many areas covered by volcanic soil, such as pyroclastic materials. Pyroclastic materials are the result of volcanic activity that are rich in primary minerals and contain various essential nutrients needed by plants (Conceicao et al., 2024), such as calcium, potassium, magnesium, and phosphorus (Toscani and Santos, 2017; Melo et al., 2012; Silva et al., 2012; Ribeiro et al., 2010). However, most of these nutrients are bound in primary minerals such as Feldspar, Pyroxene, Olivine, Amphibole, Biotite, and Quartz which are classified as easily weathered minerals (Gillman et al., 2001). Although classified as an easily weathered mineral, it is still difficult to be directly available to plants, because the release of these nutrients is often slow and does not support optimal plant growth. This causes the soil formed from pyroclastic materials to have low productivity without proper nutrient management (You and Muhrizal, 2012).

The eruption process has a negative impact on society, but on the other hand, there are great benefits, namely, the natural re-fertilization of the existing soil. The process of rejuvenating soil with nutrient-rich materials is known as rejuvenation. Shortly after the pyroclastic flow occurs, the soil formation process begins through the weathering of the elements and minerals contained in it. In agriculture, in addition to providing new materials in the soil formation process, pyroclastic material provides a suitable place for plants to grow by supplying plant nutrients in the minerals it contains (Fiantis et al., 2009; Gillman et al., 2001; Luchese et al., 2022).

A unique phenomenon and a challenge that is often found in the areas affected by volcanic materials is that farmers always carry out intensive fertilization, as do the farmers who cultivate land in non-volcanic areas. This happens because the process of releasing nutrients from pyroclastic material which requires a long time. One promising approach is the use of organic materials such as humic substances. Humic substances is a complex organic compound that can improve the chemical properties of the soil, increase the activity of microorganisms, and affect the dissolution of minerals by changing their structure and accelerating the release of nutrients. In addition, humic substances can also increase the cation exchange capacity (CEC) of the soil, allowing it to hold and release nutrients more efficiently according to plant needs. In addition to organic matter, microorganisms, such as potassium-solubilizing bacteria (PSB), play an important role in supporting the release of nutrients from mineral materials (Yang et al., 2021; Shah et al., 2018; Roulia, 2014; Gerke, 2018). Potassium-solubilizing bacteria such as *Bacillus* spp. and Pseudomonas spp. produce organic acids and enzymes that can dissolve the potassium from primary minerals. These microorganisms not only accelerate the release of potassium but also increase soil biological activity, which ultimately supports overall soil productivity (Basak and Biswas, 2008).

Several previous studies have reported on nutrient leaching from minerals and rocks. Iskandar and Irwanti (2003) found that the addition of ammonium sulfate (ZA) to Cimangkok and Ciapus sands significantly increased the release of Ca, Mg, and K. Simaremare et al. (2011) reported that the addition of chicken manure compost to volcanic ash from Mount Merapi, both with grain sizes ≤ 100 µm and > 100 µm, more effectively accelerated the release of cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) compared to pine litter and peat. Ahmad (2011) explained that the humic compounds in salt form can enhance nutrient release from igneous rocks more effectively than the humic compounds in acid form. Among the various types of silicate rocks, porphyry basalt is considered the most suitable for use as a rock fertilizer.

During nutrient release, it is important to consider the rate of nutrient release and pattern of nutrient release. The rate of nutrient release refers to the speed at which nutrients are released from minerals and become available to the plants. This rate is important, because it affects whether plants can obtain sufficient nutrients at the critical stages of their growth. The nutrient release pattern refers to the release of nutrients over time. A stable and sustainable release pattern is highly desirable for plants to obtain a consistent supply of nutrients throughout their growth cycles. An uneven release pattern, such as high nutrient release at the beginning but decreasing drastically later, can cause an imbalance in nutrient supply; therefore, knowing this is one of the basics in managing fertilizer application to plants. To study the dynamics of the rate and pattern of nutrient release, this study provides in-depth insight into the effectiveness of the combination of humic substances and potassium-solubilizing bacteria in supporting optimal nutrient release from pyroclastic materials. The results of this study are not only important in increasing the fertility of volcanic soil but also support the development of more efficient, sustainable, and environmentally friendly soil management technologies, especially in the areas with volcanic soil.

MATERIAL AND METHODS

Time and place

This study was conducted from November 2023 to June 2024. Pyroclastic materials were obtained from Mount Merapi, Yogyakarta, with sampling points at 7°32’5″S and 110°26’5″E. Soil was collected from Mamunyu Village, Mamuju District, Mamuju Regency, West Sulawesi, at sampling points at 2°42’03″S and 118°55’28.1″E. The incubation process and percolation treatment to observe the solubility level of nutrients from pyroclastic materials were conducted at the Laboratory of the Department of Soil Science and Land Resources, Faculty of Agriculture, IPB.

Research procedures and stages

1. Soil sampling was performed by taking the topsoil at a depth of 0–30 cm. The soil was air-dried, pounded, and sieved using a 2 cm sieve so that the grain size was the same.
2. The pyroclastic sand was sampled from the top at a depth of 0–10 cm. The sand was then dried and ground into a fine size and passed through a 0.5 mm sieve.

3. The sifted soil and sand were then placed into a percolation pipe/tube according to the previously determined treatment, as shown in (Table 1), All samples had the same weight (1.5 kg), and the illustration of the percolation tool is in accordance with (Figure 1), with a tube diameter of 8.5 cm and height of 27 cm.
4. When the media were inserted into the tube under field capacity conditions (soil and sand), each sample was tapped 100 times to produce the same or almost the same density level.
5. The doses of pyroclastic materials included (0, 12.5, 25, 50, 100, and 200 tons) per hectare, each equivalent to (0, 9.375 g, 18.75 g, 37.5 g, 75 g, 150 g). The reference dose of humic substances was 80 L/ha with a humic content of 36%; therefore, for a humic content of 20%, it was equivalent to 0.108 g/1.5 kg of soil sample. The dose of potassium-solubilizing bacteria was 1.2 mL/sample based on previous research (Mutmainnah, 2018).
6. After all samples were inserted and installed on the research rack, they were incubated for 15 days.
7. The nutrient elements were then washed daily with distilled water for five months. The total water provided was 124 mL/sample/day based on the rainfall in the Mamuju area in 2021, which was 2000 mm/year.
8. Every month, the percolation water was harvested, and the pH and leached elements (Ca, Mg, K, Na, Fe, Mn, Cu, Zn, and Si) were measured.
9. Observation of nutrient solubility using atomic absorption spectrophotometry (AAS) and a Flame Photometer.

RESULTS AND DISCUSSION

Calcium, potassium and magnesium nutrient release patterns

Figure 2 illustrates the release pattern of calcium, magnesium, and potassium nutrients from pyroclastic material during the 5-month leaching process, with various treatments: pyroclastic alone (control), a combination of pyroclastic and humic substances, a combination of pyroclastic and potassium-solubilizing bacteria (PSB), and a combination of pyroclastic + humic substances + PSB. In the pyroclastic treatment, calcium showed the highest release value (788.84 mg, indicating that this element is more easily released from the pyroclastic material than the other two elements. This is in line with the nature of calcium, which is more soluble or easily weathered, making it susceptible to leaching. After calcium in second place, potassium has a release value of 123.96 mg, while magnesium shows the lowest release value of 50.65 mg, indicating that this element is more difficult to leach. This may be due to its complex chemical nature or strong interaction with soil particles.

The nutrient release pattern from the pyroclastic materials treated with the addition of humic substances showed that calcium had the highest

Table 1. Percolation treatment (nutrient leaching) of pyroclastic materials

Treatment code	Fine pyroclastic (passed through 0.05 mm sieve)		
M0	Soil	M13	Soil+Humic substances+ Pyroclastic 150 g
M1	Pyroclastic 1500 g	M14	Soil+PSB+Pyroclastic 9.375 g
M2	Soil + Pyroclastic 9.375 g	M15	Soil+PSB+Pyroclastic 18.75 g
M3	Soil + Pyroclastic 18.75 g	M16	Soil+PSB+Pyroclastic 37.5 g
M4	Soil + Pyroclastic 37.5 g	M17	Soil+PSB+Pyroclastic 75 g
M5	Soil + Pyroclastic 75 g	M18	Soil+PSB+Pyroclastic 150 g
M6	Soil + Pyroclastic 150 g	M19	Soil+Humic substances+PSB
M7	Soil+Humic substances +Pyroclastic	M20	Soil+Humic substances+PSB+pyroclastic 9.375 g
M8	Soil +PSB+Pyroclastic	M21	Soil+Humic substances+PSB+pyroclastic 18.75 g
M9	Soil+Humic substances+Pyroclastic 9.375 g	M22	Soil+Humic substances+PSB+pyroclastic 37.5 g
M10	Soil+Humic substances +Pyroclastic 18.75 g	M23	Soil+Humic substances+PSB+pyroclastic 75 g
M11	Soil+Humic substances +Pyroclastic 37.5 g	M24	Soil+Humic substances+PSB+pyroclastic 150 g
M12	Soil+Humic substances +Pyroclastic 75 g		

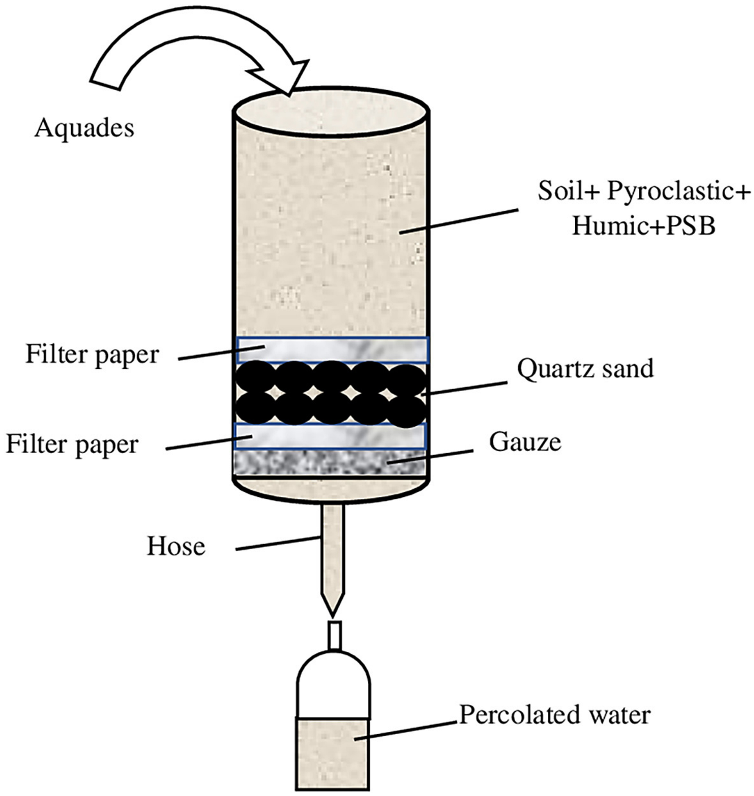

Figure 1. Illustration of percolation apparatus (leaching of nutrients)

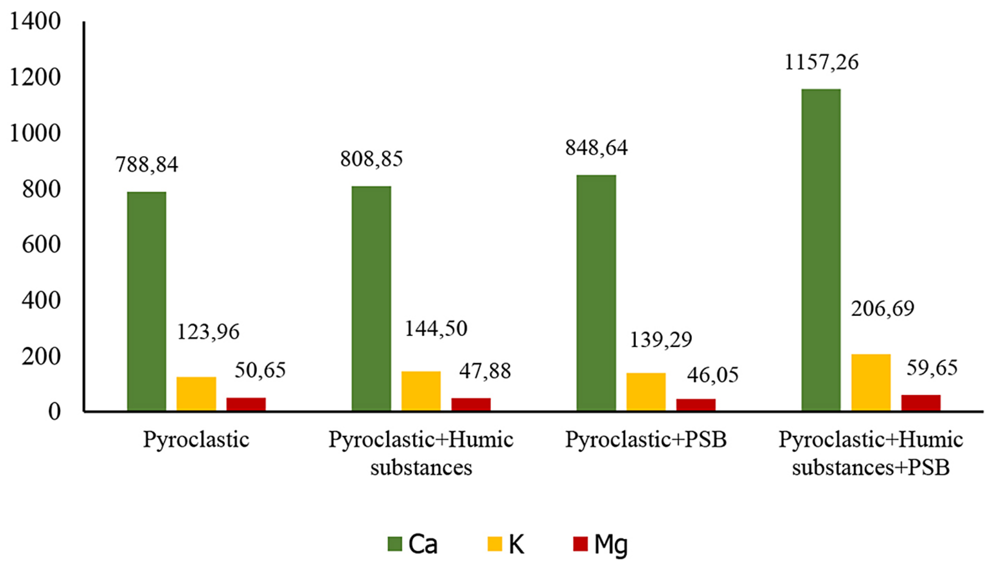

Figure 2. Nutrient release patterns from pyroclastic material with and without humic substances and potassium-solubilizing bacteria application

solubility level among other elements, reaching 808.85 mg. This indicates that calcium played a dominant role in nutrient release in combination with pyroclastic humic substances. The significant role of calcium may be due to the high calcium content in pyroclastic or humic substances or its ability to dissolve faster under certain conditions. The release of potassium nutrients was recorded at 144.50 mg, which is much lower than that of calcium, and still makes an important contribution to plant growth, indicating sufficient potassium availability in this combination. The lowest magnesium release was recorded, at 47.88 mg. This may be due to the lower concentration of magnesium in pyroclastic or humic substances or a slower release mechanism. The dominance of calcium indicates that this combination is highly effective in improving calcium-deficient soils, especially in the areas requiring liming. The moderate potassium content indicates that this combination can support the potassium needs of plants, although additional potassium fertilizer may still be required. Meanwhile, the low Mg release indicates that for Mg-deficient soils, this combination may require additional supplementation to ensure its availability to plants.

The release pattern of nutrients (Ca, K, and Mg) from the pyroclastic materials treated with potassium-solubilizing bacteria (PSB) indicated that each element exhibited a different level of release. Ca had the highest release (848.64 mg, almost six times higher than K and approximately 18 times higher than Mg). The high release of Ca indicates that the pyroclastic material used contained calcium-rich minerals, and potassium-solubilizing bacteria were effective in dissolving this element. Significant Ca release can contribute to improving soil quality, especially in neutralizing acidic soils. Potassium (K) was in second place with a release of 139.29 mg, indicating the effective role of potassium-solubilizing bacteria in dissolving this element. Potassium is important for plant metabolic processes, including osmotic pressure regulation and protein synthesis; therefore, moderate potassium release is sufficient to support plant needs, although it is much lower than calcium. The release of magnesium (Mg) was recorded as the lowest among the three elements, which was 46.05 mg, or only about 5.4% of calcium release. The low magnesium release may be due to the low initial concentration of magnesium in the pyroclastic material and the possibility that potassium-solubilizing bacteria are more effective at dissolving potassium than magnesium. Although small amounts of Mg are present, it is important, because it plays a role in chlorophyll formation and photosynthesis.

The combination of the three treatments (pyroclastic + humic substances + PSB) for the release pattern of nutrients from pyroclastic materials showed a different and significant release rate compared to the control and other treatments. Calcium (Ca) had the highest release, which was 1157.26 mg, indicating that the addition of potassium-solubilizing bacteria was very effective in dissolving and releasing Ca from the minerals in pyroclastic materials. This is likely because Ca is the main component of many pyroclastic minerals, and high Ca release can provide great benefits for increasing soil fertility, especially in balancing soil pH. Potassium (K) was in second place, with a release of 206.69 mg, although much lower than Ca (only about 18% of Ca release). This indicates that, although potassium-solubilizing bacteria are effective, their effect on K release is not as strong as that on Ca. Potassium is an important element in plant growth, especially in the regulation of osmotic pressure and energy metabolism. The significant release of K remains relevant in supporting the availability of K in plants. Mg showed the lowest release, which was 59.65 mg, only approximately 5% of the release of Ca. This may be due to the lower concentration of magnesium in the pyroclastic material compared to that of Ca and K, as well as the lower effectiveness of potassium-solubilizing bacteria in dissolving magnesium. However, Mg still plays an important role in photosynthesis and chlorophyll formation; therefore, Mg release still makes a positive contribution to soil fertility.

Nutrient release rate of Ca, K, and Mg

Figure 3a shows the release rate of nutrients in the form of Ca, K, and Mg from pyroclastic material over a period of five months. These data provide an overview of the dynamics of nutrient release from pyroclastic materials, which play an important role in soil fertility. Calcium showed the highest release rate compared to the other elements. In the first month, the Ca concentration was 119.3 mg and increased significantly to reach a peak of approximately 198.4 mg in the second month. After that, there was a gradual decrease in concentration until the fifth month, when the Ca value was below 100 mg. This pattern indicates that Ca was released rapidly in the early stages owing to the dissolution of pyroclastic material rich in calcium minerals, but the release rate decreased over time. The K release was relatively stable in the first and second months, with a concentration of approximately 24.1–26.9 mg. In the third month, there was a slight increase in the K release to a peak of 35.8 mg, which then decreased again and stabilized in the fourth and fifth months. This pattern indicates that the release is slower than that of Ca. Magnesium has a release pattern similar to that of K, but at lower concentrations. In the first and second

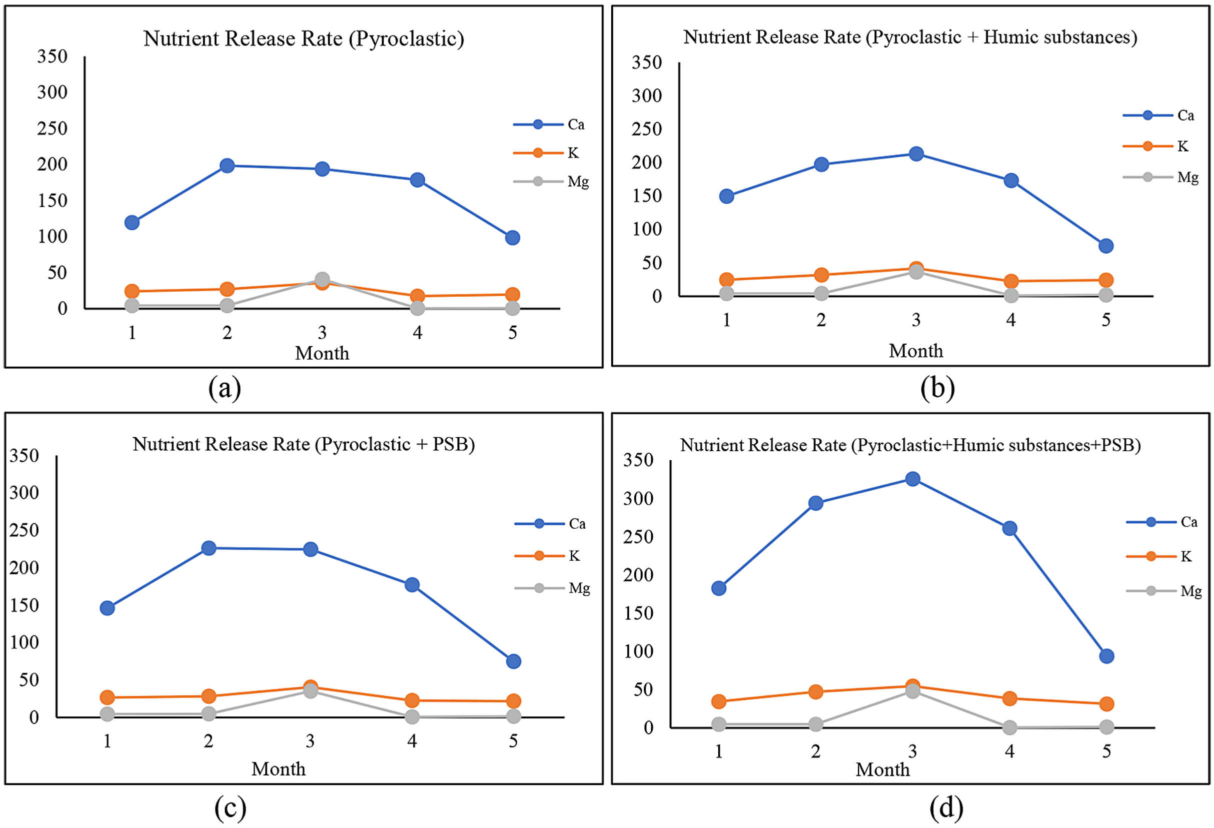

Figure 3. Rate of release of Ca, Mg, and K nutrients from pyroclastic materials with various treatments

months, The Mg release was only 4.4 mg. A significant increase occurred in the third month, reaching a peak of 40.8 mg, before experiencing a significant decrease in the fourth and fifth months of 0.4–0.7 mg. This suggests that the Mg release tends to occur slowly, most likely due to its involvement in minerals such as olivine or pyroxene, which take longer to weather.

The release of nutrients from the pyroclastic material treated with humic substances (Figure3b) shows the release rate of three main nutrients (Ca, K, and Mg) for five months. Calcium showed a significant release for five months; in the first month, the release of Ca nutrients was 149.77 mg, which gradually to reach 197.11 mg in the second month. The peak nutrient release occurred in the third month at a concentration of 213.14 mg. Subsequently, there was a gradual decrease in the fourth month (173.37 mg) and a sharp decrease in the fifth month (75.46 mg). The addition of humic substances increased the solubility of Ca through the chelation process, where compounds of humic substances bind Ca ions, making them more available in the soil solution. The decrease in concentration after the third month indicates that the mineral reserves rich in Ca are starting to run low.

Potassium has a more stable release pattern than Ca, in the first month, the K concentration was 24.53 mg, gradually increasing to 31.65 mg in the second month, and reached a peak of 41.57mg in the third month. After that, the K concentration decreased to 22.50 mg in the fourth month, before increasing slightly to 24.25 mg in the fifth month. Humic substances play a role in increasing the release of K by accelerating the weathering of silicate minerals through microbial activity. However, the lower K release rate compared to that of Ca indicates that K-producing minerals are more resistant to dissolution. The release of Mg showed a unique pattern with significant fluctuations. In the first and second months, the Mg concentration remained low at approximately 4.28–4.29 mg. There was a spike in release in the third month, with the concentration reaching 36.55 mg, which was the peak Mg release during the observation period. After that, the Mg concentration decreased drastically to 0.89 mg in the fourth month and increased slightly to 1.88 mg in the fifth month. The combination of pyroclastic and humic substances has proven effective in providing nutrients sustainably, particularly in the newly formed volcanic soils.

On the basis of Figure 3c, pyroclastic material combined with potassium-dissolving bacteria shows potential as a source of nutrients for plants. Calcium shows a release pattern in the first month reaching 145.90 mg, which then increased sharply in the second month to 226.24 mg. The concentration of Ca remained high in the third month (224.54 mg, but began to decline in the fourth month (177.27 mg) and reached its lowest point in the fifth month (74.69 mg). In contrast, K showed a more stable release pattern than Ca, the concentration of K was 26.57 mg at the beginning of the observation, increasing slightly to 28.00 mg in the second month. Peak release occurred in the third month at a concentration of 40.48 mg. After that, there was a decrease in concentration to 22.62 mg in the fourth month and 21.63 mg in the fifth month, respectively. Magnesium showed a slightly different release pattern from that of K; in the first and second months, the Mg released remained low at 4.47 mg and 4.49 mg respectively. There was a spike in the release in the third month, with a concentration reaching 35.05 mg which was the peak of Mg release. After that, the Mg concentration decreased drastically to 0.62 mg in the fourth month and increased slightly to 1.41 mg in the fifth month.

In general, compared to all other treatments, the combination of pyroclastic, humic substances, and potassium-solubilizing bacteria showed a higher nutrient release for all nutrients (Ca, K, and Mg). Nutrient release showed variations in the release of the three nutrients over five months (Figure 3d). Calcium showed the most significant release rate compared to the other elements. The initial value in the first month was 182.85 mg, which increased sharply to 293.83 mg in the second month and peaked in the third month at 325.70 mg. After the third month, Ca release began to decrease significantly, to 260.96 mg in the fourth month and decreased more drastically in the fifth month to reach 93.92 mg. Potassium showed a more moderate release pattern than calcium. The K release increased from 34.77 mg in the first month to 47.26 mg in the second month. This concentration peaked in the third month at 54.69 mg, but then decreased to 38.47 mg in the fourth month and 31.50 mg in the fifth month. Mg exhibited a fluctuating release pattern. In the first and second months, the Mg release remained low and stable at 4.85 mg. However, there was a significant spike in release in the third month, when the Mg concentration increased to 48.02 mg. After that, the Mg concentration decreased drastically to 0.76 mg in the fourth month and only 1.18 mg in the fifth month.

The presence of humic substances in the weathering process, which can release the nutrients that can be utilized by plants, plays a major role in accelerating the process of dissolving cations in minerals through the process of attachment to the mineral surface. Humic substances, especially humic acid and fulvic acid, can dissolve minerals through chelation activity against metal ions. Carboxyl (-COOH) and phenolic (-OH) groups in humic substances interact with the metal ions on the mineral surface, causing the release of ions and mineral degradation. This is in line with the findings of Das et al. (2014), who found that humic substances accelerate the dissolution of cations from minerals by forming strong complexes with ions such as $Fe^{2+}/^{3+}$, Al^{3+}, and Ca^{2+}. These cations are released more easily than Si^{4+}, which has a very stable Si-O bond. Humic substances influence the transformation of primary minerals, such as feldspar and mica into secondary minerals, such as clay. This process is often accompanied by the release of essential nutrients (e.g. as K, Mg, and Si). Humic substances act as an effective chemical weathering agent mainly through cation complexation and differentially affects silicate minerals. Hornblende is more susceptible to weathering than biotite, indicating the influence of the mineral structure on the effectiveness of weathering by humic substances. The interaction of humic substances with soil minerals increases the solubility of minerals, such as feldspar, dolomite, and apatite, so that more nutrients are released. In line with Canellas et al. (2015), humic substances have the ability to bind and solubilize nutrients from poorly soluble minerals such as phosphorus, iron, and potassium. The authors discussed that humic substances act as chelating agents that can mobilize nutrients and make them more available to plants. This helps plants obtain essential nutrients in less fertile soil conditions or when the mineral content is strongly bound to soil particles.

Potassium-dissolving bacteria can produce organic acids, such as citric acid, oxalic acid, and gluconic acid. These acids interact with minerals and dissolve potassium through acidification and chelation processes, where H^+ ions replace the

K^+ present in minerals. Some bacteria can mediate the ion exchange process between mineral cations and protons released by organic acids so that potassium ions are released from the mineral structure. In line with (Basak et al., 2009; 2010), in addition to dissolving potassium, potassium-dissolving bacteria also accelerate the physical and chemical weathering of minerals. The production of enzymes, other secretions, and cellular exudates released by bacteria causes erosion of the mineral surface microstructure, facilitating the release of potassium. Potassium-dissolving bacteria such as *Bacillus mucilaginosus*, *Paenibacillus* sp., and *Pseudomonas* spp. have the ability to dissolve potassium from minerals such as mica, feldspar, and illite. Sheng et al. (2006) research results showed that natural strains of Bacillus edaphicus and its mutants are able to dissolve potassium from biotite and feldspar minerals. These bacteria produce organic acids, such as citric acid and malic acid, which break down the mineral structure and release the potassium contained therein.

The results of the study showed that the combination of humic susbtances and potassium-solubilizing bacteria showed maximum results in the pattern and rate of releasing nutrients such as Ca, K, and Mg from pyroclastic materials. This is because humic also act as a substrate for soil microorganisms, which in turn produce enzymes that accelerate mineral weathering. These microorganisms often use the energy produced from the decomposition of humic susbtances to support their metabolic activities (Nardi et al., 2021). The interaction between humic susbtances and microbes enhances the biogeochemical weathering process through oxidation-reduction reactions. In addition to dissolving potassium, potassium-solubilizing bacteria also accelerate the physical and chemical weathering of minerals. The production of enzymes, other secretions, and cellular exudates released by bacteria causes erosion of the microstructure of mineral surfaces, making potassium more easily released.

CONCLUSIONS

The pattern of nutrient release from pyroclastic material from Merapi for five months showed that Ca was always the most released element, followed by K and then Mg, and this pattern was formed in all treatments. The increase in nutrient release from the control and combination (pyroclastic + humic substances + PSB) of Ca, K and Mg are: Ca 788.84–1157.26 mg, K 123.96–206.69 mg, and Mg 50.65 –59.65 mg.

The rate of nutrient release generally showed that Ca in the 2nd and 3rd months was the peak of nutrient release, followed by a significant decrease in the following month. For K, the pattern tends to be stable, Mg the pattern is like Ca in the first and second months stable, then in the third month there is an increase, which subsequently decreases in the 4th and 5th months.

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