Soil Environ. 37(2): 95-102, 2018
DOI:10.25252/SE/18/51414
Online ISSN: 2075-1141
Print ISSN: 2074-9546

Effect of nanoparticle of volcanic ash and rock phosphate on some soil chemical properties of variable charge Andisols, Indonesia

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Abstract

Andisols is a variable charge soil where fertilizations to the soil do not give the same result as that to the soils with permanent charges. Therefore, amelioration is needed to improve the soil chemical properties. The purpose of this research was to find out the influence of nanoparticles of volcanic ash and rock phosphate as ameliorants on pH_w, pH_0, P-retention and available P on variable charge Andisols, Indonesia. This research used a complete randomized experimental design on factorial pattern with two factors. The first factor was nanoparticle of volcanic ash consisting of four levels i.e. 0, 2.5, 5.0 and 7.5% of soil weight (w/w). The second factor was nanoparticle rock phosphate, also consisting of 4 levels like nanoparticle of volcanic ash. The treatments were repeated 3 times. The results showed that there was an interaction between nanoparticle of volcanic ash and rock phosphate in increasing pH_w to 5.37 and increasing availbale P to 330 mg kg^{-1}. However, there was no interaction in pH_0 and P-retention. Nanoparticle of volcanic ash and rock phosphate was found effective to improve some soil chemical properties after one month of incubation.

Keywords: Nanoparticle, pH_w, pH_0, P-retention, available P

Introduction

Andisols is the soil order derived from volcanic ash, differentiated by andic soil properties and dominated by the noncrystalline minerals like allophane. Allophane is one of the short range order of alumino hydrous silicate minerals formatted by the Si-O-Al group. Allophane has a very wide and amphoteric surface area of aluminum hydroxide (Al-OH) group which has retained capabilities of phosphate and result in high P-retention (Shoji *et al*., 1993; Dahlgred *et al*., 2004; Parfit, 2009; McDaniel *et. al*., 2012). According to Arifin (1994), Andisols in Ciater, Subang West Java Indonesia has 90-98% P-retention.

Volcanic ash and phosphate rocks are some of the most negatively charged ameliorants that can decrease P-retention. Volcanic ash dominated by SiO_2 (53%) was reported to decrease P-retention (Van Ranst *et al*., 1993) to make it available for plants. Phosphate ions in rock phosphate also can decrease P-retention in Andisols (McDaniel *et al*., 2012).

Nanotechnology has been used to address several problems in agriculture. Applications of nanotechnology in agriculture have offered as a new tool for increasing yield production (De Rossa *et al*., 2010). Application of nanotechnology in the form of nanoparticle of volcanic ash and rock phosphate as ameliorant will be one of a new tool in improving soil characteristics of Andisols.

Materials and Methods

Andisols for this research were obtained from tea plantation area of Nusantara Plantation VIII, Block Mojang, Ciater Subang, West Java, Indonesia referred to Arifin (1994). The location was 1250 m above sea level (asl) and about 30 km from Bandung Capital City to the north. The soil samples for experimental work were taken compositely at several points from the depth of 0-60 cm and mixed evenly to have the homogeneity. The soils for chemical and physical characteristics were taken from the minipit to the depth of 60 cm and the results are presented in Table 1. Prior to the treatments, the soils were analyzed for pH_0 (Uehara and Gillman, 1981), pH H_2O (pH_w) and pH KCl and delta pH (Van Reeuwijk, 2002), bulk density (Bielders *et al*., 1990), organic C (USDA, 1972), P-retention (Blakemore *et al.,* 1987), available P (Van Reeuwijk, 2002) and aluminum and iron oxalate (Blakemore *et al*., 1987).

The volcanic ash was collected from Mt. Sinabung, North Sumatera after the eruption of January 2016. The rock

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phosphate was from Egypt and packaged in East Java Province, Indonesia. The nanoparticle of volcanic ash and rock phosphate were processed in Nanotechnology and Graphene Research Centre of Universitas Padjadjaran with top-down method by bead milling machine and particle size analyzer (PSA) was used to test the size.

The research used a complete randomized experimental design in factorial with two factors. The first factor was nanoparticle of volcanic ash (a) with four doses on soil weight percentage (w/w) each 0, 2.5, 5.0 and 7.5%. The second factor was nanoparticle of rock phosphate (p) also with four doses on soil weight percentage (w/w) of 0, 2.5, 5.0 and 7.5%. Ameliorant treatments and soils (each 1 kg) were put into a 3 kg size polybag. The combined treatments were replicated three times, organized into 4 × 4 ×3 of polybag treatments. The soils and treatments were watered to the soil field capacity, fit tightly and incubated for four months. During incubation, the soils were taken after one, two, three and four months of incubation to be analyzed for the pH_0, pH_w, P-retention and available P. The Duncan's New Multiple Range Test was used for testing the mean differences.

Results and Discussion

Data of soil, volcanic ash and rock phosphate prior to the treatmens

The soils were derived from andesitic parent material of Mt. Tangkuban Parahu (Arifin, 1994). The data of soil chemical and physical soil characteristics is presented in Table 1. The data of analyses revealed that to the depth of 0-60 cm, the organic carbon content was in range of 3.61-4.141%, bulk density was 0.32-0.59 g cm^{-3}, P-retention was 89.3-97.3% and Al plus ½ Fe with acid ammonium oxalate was 2.36-4.48%. All the data fullfill the requirements of andic soil properties as a prerequisite of Andisols as written in Soil Survey Staff (2014). The value of pH_w showed that the soil was acid (3.61-4.13). The value of Δ pH was -0.03 to -0.31, less than 0.5 as prerequisite as a variable charge soil (Uehara and Gillman, 1981). The high P-retention (89.3

Table 1: Chemical and physical characteristic of the soil

Horizons[a)]	Depth (cm)	pH		Δ pH[b]	BD ⅓bar (g cm^3)	C (%)	Feo (%)	Alo (%)[c]	Feo+½Alo (%)[d]	P-retention (%)	Available P (mg kg^{-1})
		H_2O	KCl								
Ap	0-17	3.61	3.81	-0.20	0.59	9.11	3.14	0.79	2.36	89.30	1.53
Bw	17-31	4.08	4.11	-0.03	0.47	7.18	4.27	0.98	3.12	94.30	2.22
BC	31-43	4.14	4.45	-0.31	0.32	7.52	3.27	0.80	2.44	96.40	2.34
2Ab	43-60	4.13	4.43	-0.30	0.42	5.92	6.29	1.33	4.48	97.30	2.01

a: Taken from Minipit of Block Mojang; b: pH H_2O- pH KCl; c: Fe extracted by acid amonium oxalate; d: Al extracted by acid amonium oxalate

Table 2: Analyses of volcanic ash and rock phosphate prior to the treatment

No	Parameters	Unit	Value
Volcanic Ash			
1	SiO_2	%	53.26
2	Al_2O_3	%	18.10
3	Fe_2O_3	%	10.05
4	CaO	%	9.62
5	MgO	%	3.23
6	K_2O	%	1.54
7	Na_2O	%	2.65
8	TiO_2	%	0.93
9	MnO	%	0.21
10	P_2O_5	%	0.34
11	H_2O^-	%	0.07
Rock Phosphate			
12	Total phosphorus in P_2O_5	%	28.76
13	P_2O_5 (in citric acid 2%)	%	21.87
14	Water content	%	2.46
15	Bulk Density	g cm^{-3}	1.98

-97.3%) resulted in low available P (1.53-2.34 mg kg^{-1}).

The characteristics of volcanic ash and rock phosphate are presented in Table 2. The SiO_2 content of Mt. Sinabung was 53.26%. The content was a bit lower compared to basic ash from Mt. Merapi in Central Java Indonesia, erupted in November 2010 which consisted of about 55-57% of SiO_2 (Anda and Sarwani, 2012). Nevertheless, the SiO_2 content of Mt. Sinabung was high enough of the silicate source for ameliorating Andisols. Related to rock phosphate, the phosphate content of rock phosphate indicated that there was 28.26% total P in P_2O_5, in which 21.87% was available P. During incubation period, the silicate and phosphate from volcanic ash and rock phosphate were expected to release the phosphorus from the retention of the short-range-order minerals in Andisols. These processes were expected to decrease pH_0 and P-retention, but increase pH_w and available P.

The particle size analyses showed that the particle of volcanic ash and rock phosphate after being processed with bead milling machine in top-down method, were dominantly 500 nanometers (0.5 µm) as presented in Figure 1.

pH_w

Application of nanoparticle of volcanic ash and rock phosphate significantly interacted (p<0.05) in increasing pH_w after 1, 2 and 4 months of incubation (Table 3). The combined treatments of nanoparticle of volcanic ash with or without rock phosphate increased the pH_w value compared to the control (4.54) after one month of incubation (Table 3). The highest pH_w values were obtained from 5.0 and 7.5% of rock phosphate combined with 2.5, 5.0 and 7.5% of volcanic ash which ranged from 5.30 to 5.48. A different phenomenon was found after two months of incubation (Table 3). The combined treatments also increased the pH_w value compared to the control (4.23). However, the highest pH_w value were obtained by the treatments of 5.0 and 7.5% of rock phosphate which ranged from 5.24 to 5.41. An almost similar finding was found after 4 months of incubations (Table 3). The combined treatments increased the pH_w value compared to the control (4.32), and the highest pH_w values were provided by the treatments of 7.5% of rock phosphate, combined with and without 2.5% of volcanic ash, ranged from 5.53 to 5.56.

The findings after 3 months of incubation showed different phenomenon, where nanoparticle of volcanic ash and rock phosphate had no significant interaction; however, rock phosphate independently increased the value of pH_w (Table 4) compared to without rock phosphate (4.74). The doses of 2.5, 5.0, and 7.5% of rock phosphate provided the same level of increase, ranged from 5.21 to 5.27.

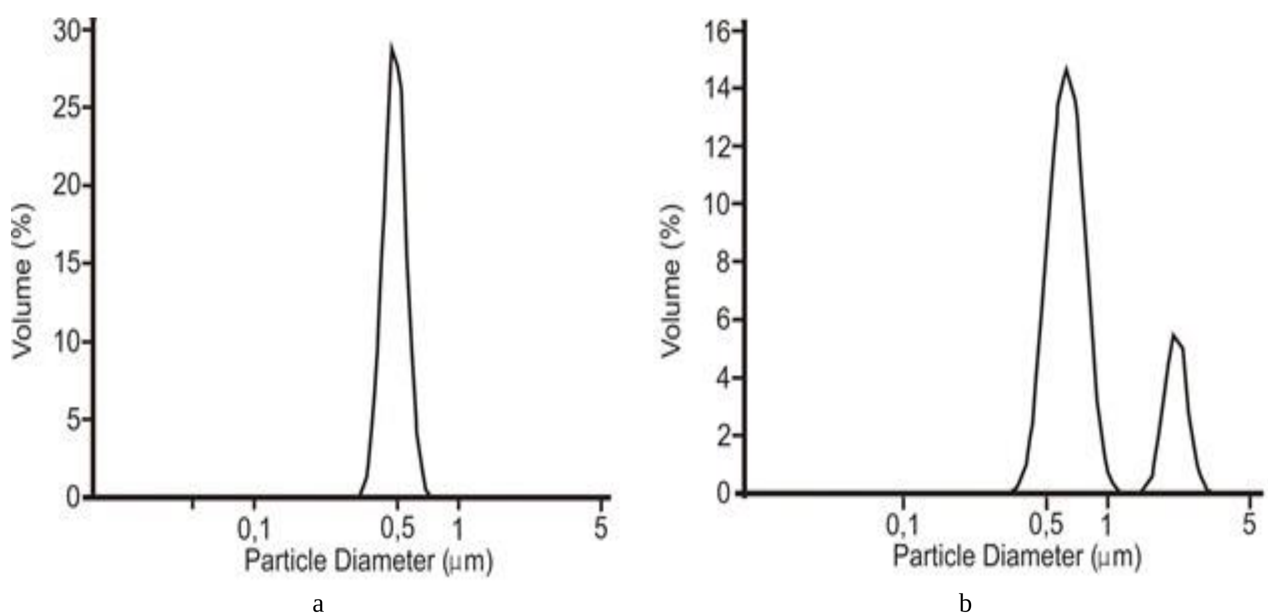

Figure 1: Particle Size Analyzer result of volcanic ash (a); and rock phosphate (b)

Table 3: The interaction of nanoparticle volcanic ash and rock phosphate on pH_w after 1, 2, and 4 months of incubation

Nanoparticle of Volcanic Ash (%)	Nanoparticle of Rock Phosphate (%)			
	0	2.5	5.0	7.5
After 1 month of incubation				
0	4.54 a (a)	5.30 a (b)	5.41 a (b)	5.45 a (b)
2.5	4.90 b (a)	5.11 a (b)	5.38 a (c)	5.34 a (c)
5.0	4.90 b (a)	5.10 a (b)	5.30 a (c)	5.48 a (c)
7.5	4.90 b (a)	5.14 (b)	5.23 a (bc)	5.37 a (c)
After 2 months of incubation				
0	4.23 a (a)	4.80 a (b)	5.45 a (c)	5.41 a (c)
2.5	4.90 b (a)	5.22 b (a)	5.28 a (a)	5.11 a (a)
5.0	4.89 b (a)	5.04 ab (a)	5.26 a (ab)	5.44a (b)
7.5	4.95 b (a)	5.03 ab (a)	5.06 a (a)	5.12a (a)
After 4 months of incubation				
0	4.32 a (a)	5.19 a (b)	5.25 a (b)	5.56 a (c)
2.5	4.81 b (a)	5.42 a (bc)	5.16 a (b)	5.53 a (c)
5.0	5.10 b (a)	5.39 a (ab)	5.37 a (ab)	5.49 a (b)
7.5	5.09 b (a)	5.17 a (ab)	5.43 a (b)	5.37 a (ab)

Note: The letters in parentheses are read horizontally, the letters without parentheses are read vertically. Same letters indicate no difference of value among the treatments with Duncan New Multiple Range Test 5 %.

Table 4: The independent effect of volcanic ash and rock phosphate nanoparticle on pH_w after 3 months of incubation

Nanoparticle of Volcanic Ash (%)	Average
0	5.15 a
2.5	5.15 a
5.0	5.18 a
7.5	5.00 a
Nanoparticle of Rock Phosphate (%)	
0	4.74 a
2.5	5.27 b
5.0	5.21 b
7.5	5.25 b

Note: Same letters indicate no difference of value among the treatments with Duncan New Multiple Range Test 5 %.

The phenomenon discovered in Tables 3 and 4 indicated that nanoparticle of volcanic ash was in conjunction with nanoparticle of rock phosphate in increasing pH_w value; however, the combined treatments caused different level of increase. It seemed that nanoparticle of rock phosphate was more pronounced in increasing the pH_w value. Hawthorne (1998) reported that the basic chemical of natural rock phosphate contained $Ca_{10}(PO_4)_6F_2$. The calcium content in rock phosphate influenced the increasing of pH_w and acted as lime. Opala (2017) reported that material containing Ca increased soil pH.

pH_0

The application of nanoparticle of volcanic ash and rock phosphate had no significant interaction on pH_0 value. Effects on independent treatments of nanoparticle of volcanic ash or rock phosphate were given in Table 5. The table showed that neither nanoparticle of volcanic ash nor the nanoparticle of rock phosphate after 1 and 2 months of incubation had significant effect on the increase or the decrease of pH_0 value. The interesting phenomenon was found after 3 and 4 months of incubation, where there were significant effects ($p<0.05$) of nanoparticle rock phosphate independently in increasing the pH_0 value.

Table 5: The independent effect of volcanic ash and rock phosphate nanoparticle on pH_0 after incubation of 1, 2, 3 and 4 months

Treatment (Doses)	pH_0				P-retention (%)			
	1	2	3	4	1	2	3	4
Nanoparticle of Volcanic Ash (%)								
0	5.10 a	4.15 a	5.31 a	4.36 a	76.00 a	93.91 a	17.23 a	91.33 a
2.5	5.22 a	4.31 a	4.42 a	4.34 a	75.90 a	94.91 a	19.15 a	91.73 a
5.0	5.39 a	5.00 a	4.75 a	4.50 a	76.19 a	96.66 a	18.93 a	89.74 a
7.5	5.11 a	4.45 a	5.10 a	4.35 a	71.49 a	97.29 a	20.41 a	89.61 a
Nanoparticle of Rock Phosphate (%)								
0	4.94 a	3.91 a	4.60 a	3.87 a	76.23 a	97.44 a	17.83 a	93.29 b
2.5	5.15 a	4.68 a	4.44 a	4.54 b	76.47 a	94.96 a	18.28 a	92.00 b
5.0	5.23 a	4.50 a	4.98 ab	4.67 b	75.26 a	96.33 a	19.13 a	88.37 a
7.5	5.50 a	4.80 a	5.57 b	4.47 b	71.63 a	94.04 a	20.48 a	88.76 a

Note: Same letters indicate no difference of value among the treatments with Duncan New Multiple Range Test 5 %.

Table 6: The independent effect of volcanic ash and rock phosphate nanoparticle on available P after incubation of 1 and 2 months

Treatment (Doses)	Available P (mg kg^{-1})	
	1	**2**
Nanoparticle of Volcanic Ash (%)		
0	121.79 a	188.63 a
2.5	162.92 a	184.63 a
5.0	141.84 a	233.90 a
7.5	170.50 a	149.43 a
Nanoparticle of Rock Phosphate (%)		
0	5.56 a	16.45 a
2.5	111.20 b	96.55 a
5.0	207.18 c	146.92 a
7.5	273.11 c	496.65 b

Note: Same letters indicate no difference of value among the treatments with Duncan New Multiple Range Test 5 %.

The increasing of pH_0 value was in contrary to the aim of this study. Ameliorating with nanoparticle of volcanic ash and rock phosphate was expected to decrease, not to increase, the pH_0 value. Both nanoparticle of volcanic ash and rock phosphate normally release silicate and phosphate ions during incubation period, and the ions will influence the soil colloid in reducing pH_0 as mentioned by Qafoku *et al.* (2004) and Van Ranst *et al*. (2017).

Compared to pH_w, the combined treatments of nanoparticle of volcanic ash and rock phosphate or nanoparticle of rock phosphate independently increased pH_w value. The increase of pH_w is usually followed by the decrease of pH_0, but it in fact increased in this study. This finding, however, was in line with Arifin (1994) where without any treatments pH_w value had positive correlation with pH_0. It indicated that the higher the pH_w, the higher the positive charge of the soils. It was opposite to the existing theory of permanent charge soils where the higher the pH_w the higher the negative charge. Nevertheless, Andisols as a variable charge soils showed a different behaviour. Based

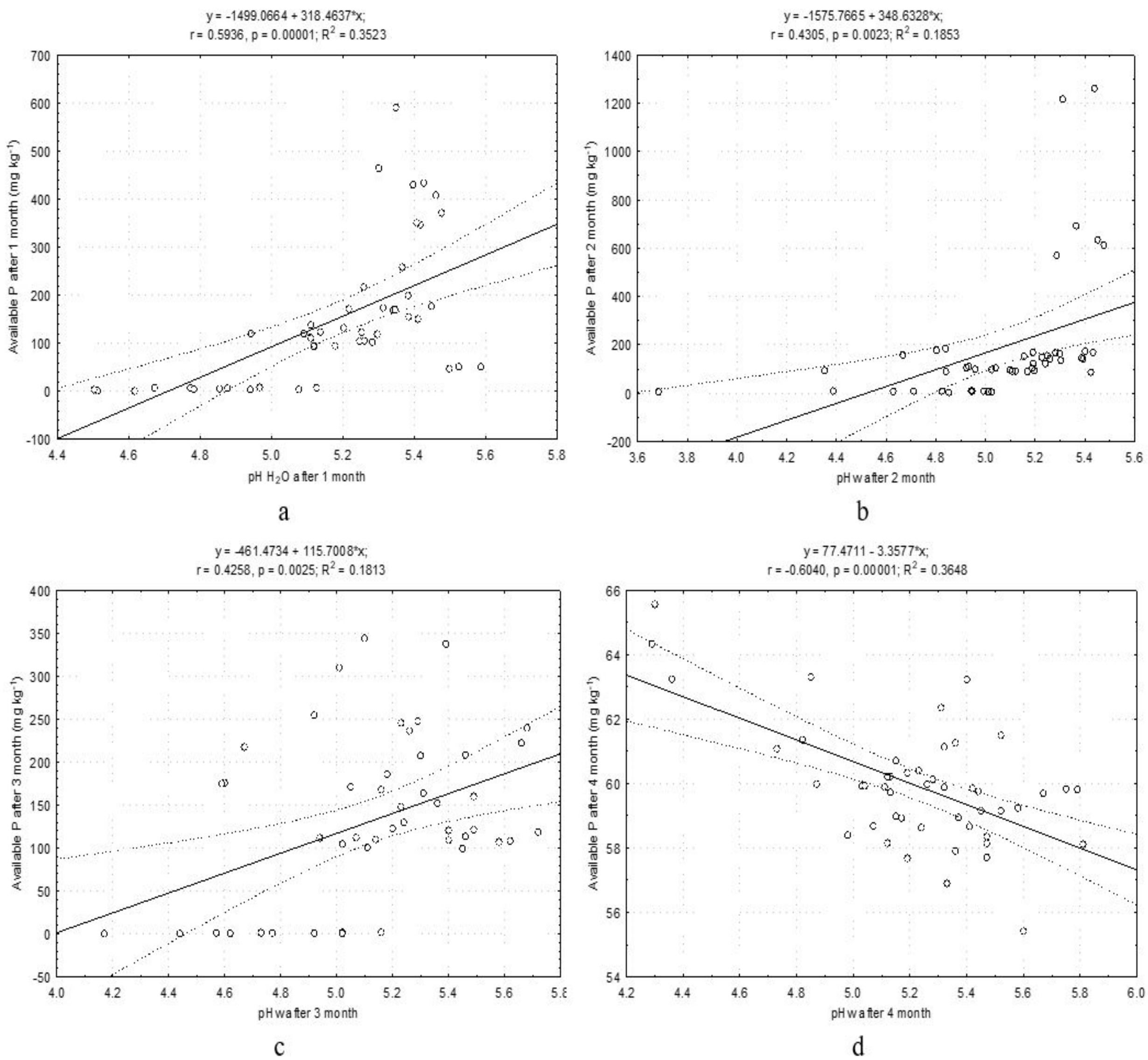

Figure 2: The relationship of pH_w and available P after one month (a); two month (b); three month (c), and four month (d) of incubation

on the data of pH_w and pH_0, the higher the pH_w the higher the pH_0 or the higher the positive charge. Justification and scientific verification related to this phenomena need a more detailed research.

P-retention

The application of nanoparticle of volcanic ash and rock phosphate had no significant interaction (p<0.05) on P-retention after 1, 2, 3 and 4 months of incubation. Meanwhile nanoparticle of rock phosphate significantly decreased (p<0.05) the P-retention after 4 months of incubation as indicated in Table 5. The high Ca content in rock phosphate increased the OH^- ion and consequently increased the pH_w value (Tables 3 and 4). The increase of OH^- ions have triggered the amorphous colloid of noncrystalline minerals releasing the retained P and decreasing the P-retention as found in Utami (1998).

An interesting phenomenon appeared in the time sequence of P-retention value due to its irregular increase and decrease. The initial value of P retention in the upper 60 cm ranged from 89.3-97.3% (Table 1). After one month of incubation the P-retention decreased to 71.4-76.4% (Table 5). After 2 months of incubation the P-retention value increased to close of the initial value of 94.25%. After 3 months of incubation the value decreased sharply to 20%

level. While after 4 months of incubation the value increased again to the preliminary value and exceeded the average value after 1 month.

This phenomenon occurs presumably because after 3 months incubation, nanoparticle of rock phosphate weathered further and worked effectively in changing the amorphous colloid and decreased P-retention drastically approaching 20%. However, this process did not last longer because P-retention increased again to 90% after 4 months, closer to the result of preliminary soil analysis (95%). Presumably after 4 months nanoparticle of volcanic ash have produced silica and amorphous aluminum compounds that retain P. The result of this study indicated that silica content of Sinabung volcanic ash tends to increase the pH_0 and decrease the pH_w. The used of Sinabung volcanic ash as ameliorant for Andisols should be avoided in the future. Therefore, an alternative ameliorant with lower silica content can be used to improve soil chemical properties of variable charge Andisols.

Available P

The application of nanoparticle of volcanic ash and rock phosphate had no significant interaction ($p<0.05$) on available P after 1 and 2 months of incubation. Meanwhile, only rock phosphate that significantly increased available P ($p<0.05$) as indicated in Table 6. The high phosphate content in rock phosphate as indicated in Table 2 (total P_2O_5 28.76%) caused the increase of available P.

Available P had positive correlation with pH_w after 1, 2 and 3 months of incubation as presented in Figure 2. Phosphorus was precipitated and retained by the noncrystalline minerals like allophane in low pH value. As the pH increased, the available P increased as well. The available P improved as the pH approaches nearly neutral. However, a different phenomenon was found after 4 months incubation where it had a negative correlation. This contradiction further needs deep investigation.

Conclusion

Nanoparticle of volcanic ash and rock phosphate interacted in increasing pH_w to 5.37 and increasing available P to 330 mg kg^{-1}. However, there was no interaction in decreasing pH_0 and P-retention. Nanoparticle of volcanic ash and rock phosphate were effective to improve pH_w and P-available after only one month of incubation. The research of amelioration of variable charge Andisols needs futher deep investigation.

Acknowledgement

The authors are thankful to the Rector of Universitas Padjadjaran for funding this research through Academic Leadership Grant (ALG).

References

Anda, M. and M. Sarwani. 2012. Mineralogy, chemical composition, and dissolution of fresh ash eruption: new potential source of nutrients. *Soil Science Society of America Journal* 76: 733-747.

Arifin, M. 1994. Pedogenetic of Andisols Derived from Andesit and Basalt Volcanic Ash in Some Agroclimatic Zones of Tea Plantation in West Java. Ph.D. Thesis. Bogor Institute of Agriculture. P.202.

Bielders C.L.L., W. De Backer and B. Delvaux. 1990. Particle density of volcanic soils as measured with a gas pycnometer. *Soil Science Society of America Journal* 54: 822-826.

Blakemore, L.C., P.L. Searle and B.K.Daly. 1987. Methods for chemical analysis of soil. Lower Hutt, New Zealand. P.103.

Dahlgren, R.A., M. Saigusa and F.C. Ugolini. 2004. The nature, properties, and management of volcanic soils. *Advances in Agronomy* 82: 113-182.

DeRosa M.C., C. Monreal, M. Schnitzer, R. Walsh and Y. Sultan. 2010. Nanotechnology in fertilizers. *Nature Nanotechnology* 5: 9-97.

Hawthorne, F.C. 1998. Structure and chemistry of phosphate minerals. *Mineralogical Magazine* 62(2): 141-164.

McDaniel, P.A., D.J. Lowe, O. Arnalds and C.L. Ping. Andisols. 2012. In: Handbook of Soil Sciences. P.M. Huang, Y. Li, and M.E. Sumner (eds). 2nd edition Vol. 1: Properties and Processes. CRC Press (Taylor & Francis), Boca Raton, United States. P. 33.29 – 33.48.

Opala, P.A. 2017. Influence of lime and phosphorus application rates on growth of maize in acid soil. *Advances in Agriculture* 2017: 1-5.

Parfitt, R.L. 2009. Allophane and imogolite: role in soil biogeochemichal processes. *Clay Minerals* 44: 135-155.

Qafoku, N. P., E., Van Ranst, A. Noble dan G. Baert. 2004. Variable charge soils: their mineralogy, chemistry and management. *Advances in Agronomy* 84:159-215.

Shoji, S, M. Nanzyo and R.A Dahigren. 1993. Volcanic Ash Soils: Genesis, Properties and Utilization. Elsevier, Developments in Soil Science 21. P.288.

Soil Survey Staff. 2014. Keys to Soil Taxonomy 12th Ed. Natural Resource Conservation Service, United State Development of Agriculture. 360 p.

Uehara, G. and G.P. dan Gillman, 1981. The Mineralogy, Chemistry, and Physics of Tropicals Soils with Variable Charge Clays. Westview Press, Colorado. P.170.

Utami, S.R. 1998. Properties and Rational Management Aspects of Volcanic Ash Soils from Java, Indonesia. Ph.D. Thesis. University of Ghent, Belgium.P.388.

USDA, Soil Conservation Service. 1972. Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples. US Goverment Printing Office, Washington D.C. USA. P.63.

Van Ranst, E, F.DE. Coninck, and J. Debaveye. 1993. Implication of charge properties and chemical management of volcanic ash soils in West Cameroon. *Proceedings of 2nd African Soil Science Society Conference on Soil and Water Management for Sustainable Productivity:* 255-264.

Van Reeuwijk, L.P. 2002. Procedures for Soil Analysis. 6th Ed. ISRIC. Wageningen. The Netherlands. P.112.

Van Ranst, E., N.P. Qafoku, A. Noble and R. Xu. 2017. Variable charge soils: mineralogy and chemistry. p.2432-2439. In: Encyclopedia of Soil Science. R. Lal (ed). 3rd Ed. Taylor & Francis Oxford, United Kingdom.