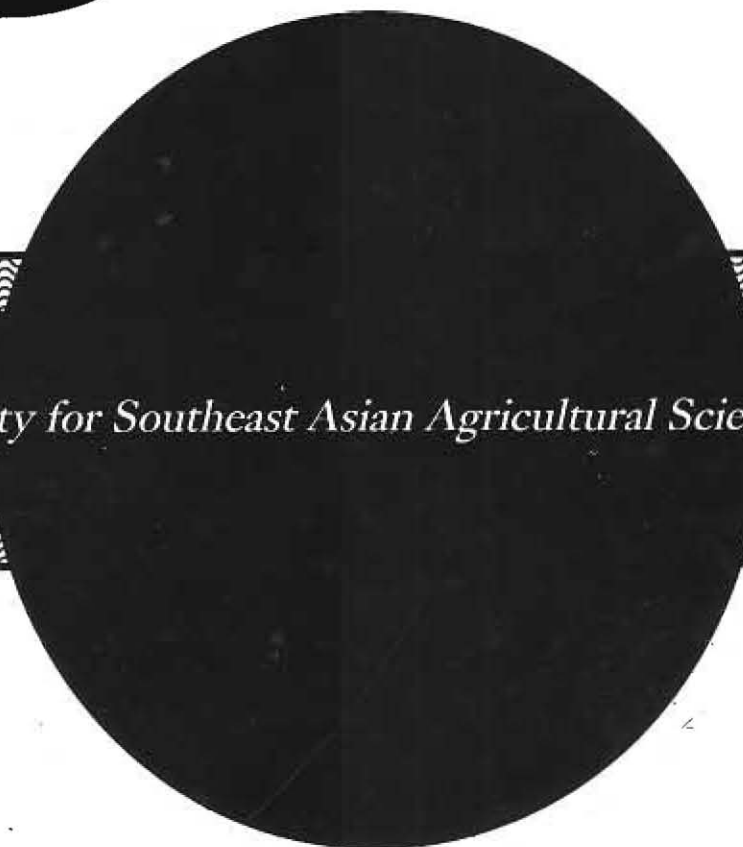


ISSN 0859-3132

Volume 20, Number 2, December 2014



Journal of ISSAAS



The International Society for Southeast Asian Agricultural Sciences

EFFECTS OF SILICATE APPLICATION ON THE RELEASE PATTERN OF NATIVE INORGANIC PHOSPHORUS FROM ANDISOL SOIL IN LEMBANG, INDONESIA USING SUCCESSIVE RESIN EXTRACTION

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(Received: December 27, 2013; Accepted: November 28, 2014)

ABSTRACT

Andisol is soil order which covers a wide area in Lembang, West Java, Indonesia. Lembang is a horticultural crops area with intensive phosphorus fertilization for years. The efforts to mine phosphorus in Andisol soil in Lembang is necessary to increase the efficiency of phosphorus fertilization and to decrease phosphorus enrichment in water bodies. Trials on the effect of silicate application on the release pattern of native inorganic phosphorus from Andisol soil in Lembang using successive resin extraction were conducted in the laboratory of Department of Soil Science and Land Resource, Faculty of Agriculture, Bogor Agricultural University from March to July 2011. Sodium silicate (Na_2SiO_3) with the rates 0, 18, 45, 90 g were added to the three hundred g (oven-dry weight) soil and incubated for one month. After one month of incubation, ten times successive resin extraction and phosphorus fractionation were conducted. Data of successive resin extraction were simulated using first order kinetic equation. The results showed that application of sodium silicate increased maximum phosphorus release. The application of sodium silicate with the rate of 90 g resulted in the highest maximum phosphorus release. However the application of sodium silicate decreased the rate constant of phosphorus release. The changes of phosphorus fractions after successive resin extraction showed that NaOH-phosphorus inorganic (Al-P and Fe-P) and HCl-phosphorus inorganic (Ca-P) were P fractions contributed to phosphorus release. The results suggested that silicate can be used to mine phosphorus from Andisol soil in Lembang.

Key words: contribution, fractionation, maximum, mining, rate constant

INTRODUCTION

Andisol is soil order which covers wide area in Lembang, West Java, Indonesia. The land in Lembang is mostly cultivated for horticultural crops. The application of phosphorus fertilizers is very intensive in Andisol soil in Lembang. It is indicated by relatively high total phosphorus (Hartono, 2007). Hartono (2007) reported that total phosphorus of Andisol in Lembang was about 5000 mg phosphorus kg^{-1} and distributed mostly in inorganic phosphorus fractions namely Al-P, Fe-P and Ca-P. Similar results concerning the phosphorus accumulation in inorganic phosphorus were reported in Chilean volcanic soils (Briceño et al. 2004). The value of total phosphorus in Andisol soil in Lembang was very high compared to that of other upland soils in Indonesia (Hartono *et al.*, 2005). Therefore efforts to mine phosphorus in this soil is very important to increase phosphorus fertilization efficiency and to decrease phosphorus eutrophication in water bodies.

The parent material of Andisol soil in Lembang is tuff andesitic derived from mount Tangkuban Perahu. The clay fractions are short-range-order minerals dominated by allophane (Hartono, 2007; Tan, 1984; Wada, 1959). Theoretically, phosphorus mostly sorbed by hydrous oxides of aluminium (Al) and iron (Fe) on allophane, however the excess phosphorus sorbed on allophane was supposed to decrease the bonding energy of sorption. Meason et al. (2009) reported that addition of triple super phosphate (TSP) increased the sodium hydroxide phosphorus (Al-P and Fe-P)- and hydrochloric acid-extractable phosphorus (Ca-P) pools suggesting that phosphorus sorption sites were blocked by phosphorus from TSP decreasing the phosphorus sorption capacity and bonding energy.

One way to mine phosphorus is to replace phosphorus position on sorption sites with the ion relatively having the same behaviour with phosphorus. It was reported that the sulfate was only significant at pH < 4.5 to compete with phosphorus on the sorption sites. At pH > 4.5 the ability of sulfate to compete with phosphorus on sorption site was not significant (Pigna and Violante, 2003). The humic substances extracted from peat soil and Andisol were inconsistent in decreasing phosphorus sorption maxima and bonding energies of the soils high in Al and Fe oxides (Hartono et al. 2013) meaning that the humic substances were inconsistent to compete with phosphorus on sorption sites. On the other hand, the use of silicate markedly reduced phosphorus sorption maximum of low pH Greenville soil from the Coastal Plain of Georgia (Owino-Gerroh and Gascho, 2005). The silicate was also reported to enhance the phosphorus transformation from moderately resistant phosphorus (Al-P and Fe-P) to labile phosphorus (Hartono, 2007). These reports indicated that silicate could compete with phosphorus and it could replace previously sorbed phosphorus on sorption sites.

The research on how silicate replaces phosphorus on sorption sites and the amount of total phosphorus replaced by silicate in Andisol soil in Lembang is not yet evaluated. Therefore the objective of this research was to evaluate the effect of silicate on the native inorganic phosphorus releasing pattern in Andisol soil in Lembang and which inorganic phosphorus fractions contribute to the phosphorus released.

MATERIALS AND METHODS

Soil sample

Soil sample of Andisol soil was collected in plots belonging to Indonesian Vegetables Research Institute, Lembang, West Java in March 2011. The trials were conducted in the laboratory of Department of Soil Science and Land Resource, Faculty of Agriculture, Bogor Agricultural University from March to July 2011. Soil samples were air-dried and crushed to pass through a 2-mm mesh sieve. Prior to experiments, initial analyses of the soil samples were carried out to determine soil pH, total organic carbon (C), total phosphorus, cation exchange capacity (CEC), exchangeable calcium (Ca), exchangeable magnesium (Mg), exchangeable potassium (K), exchangeable sodium (Na), and oxalate-extractable iron and aluminum (Fe_o and Al_o).

Methods of initial analyses

Initial analyses were described by Hartono (2007). The pH was measured in a 1:1.5 (w/v) water solution using a pH meter (EUTECH INSTRUMEN type pH 2700). Soil texture was determined by the pipet method (Gee and Bauder, 1986). Total organic C in soil was determined by a NC analyzer (Sumigraph NC analyzer NC-800-13 N, Sumika Chem. Anal. Service). Total phosphorus was obtained by digesting the soil sample using concentrated perchloric acid and nitric acid as described by Kuo (1996). Their absorbance at 693 nm was determined using a UV-VIS spectrophotometer (UV-1200, Shimadzu Corporation, Japan). Cation exchange capacity was determined by extraction with 1 mol L⁻¹ NH₄OAc pH 7.0 and the contents of exchangeable bases

calcium (Ca^{2+}) and magnesium (Mg^{2+}) were obtained by atomic absorption spectrophotometry (AA-640-12, Shimadzu Corporation, Japan) while those of exchangeable potassium (K^+) and sodium (Na^+) were obtained by flame emission spectrophotometry (AA-640-12, Shimadzu Corporation, Japan). Base saturation was defined as the ratio of total exchangeable bases to cation exchange capacity, expressed as a percentage. Oxalate-extractable iron and aluminum (Fe_o and Al_o) were obtained by extraction with 0.3 mol L^{-1} ammonium oxalate, at pH 3 for 4 h in a dark room (McKeague and Day, 1966). The extracted iron and aluminum of Fe_o and Al_o were filtered through a syringe filter with a $0.45 \mu\text{m}$ pore size (Minisart RC 15, Sartorius, Hannover, Germany). The extracted iron and aluminum were then determined by inductively coupled plasma-atomic emission spectroscopy (SPS1500, SEIKO Instruments Inc., Tokyo, Japan).

Incubation experiment

Three hundred g (oven-dry weight) soil was weighed into a plastic pot and incubated with sodium silicate, with the rates 0, 18, 45 and 90 g for one month. A completely randomized design in double replication was set up. Deionized water was added to the pots to maintain the soil moisture around 85 % of water holding capacity every second day gravimetrically. After the period of incubation, the soil samples were air-dried.

Successive resin extraction experiment

Successive resin extraction experiment was performed to release phosphorus from sorption sites. Successive resin extraction mimics the phosphorus uptake by plant root (Mc Kean and Warren, 1996). Two resin strips oversaturated with bicarbonate were put into the 50 mL centrifuge tubes containing 1 g soil and 30 mL distilled water. It was shaken for 16 h, after which the resin strips were removed and washed with distilled water. Any soil trapped in the resin strips was collected and dried. This lost soil was weighed and taken into account in the calculations of the amount of phosphorus extracted. Resin strips were placed in a clean 50 mL tube and applied $20 \text{ mL } 0.5 \text{ mol L}^{-1} \text{ HCl}$ and shaken for 16 h. After that resin-phosphorus inorganic was determined. The resin strips were removed, washed and regenerated for further use as described by Saggar *et al.* (1990) and Tiessen and Moir (1993). The extraction of phosphorus from each sample was continued by placing a regenerated resin strip in the original centrifuge containing the soil and water suspension and the procedure was repeated. A set of ten successive extractions was performed.

Phosphorus fractionation

Initial phosphorus fractionation were conducted before successive resin extraction experiment. phosphorus fractionation after successive resin extraction experiment was conducted to evaluate the changes of phosphorus fractions. phosphorus fractionation procedure was described in Figure 1 (Hartono, 2008). Characterization of sequential soil phosphorus extraction was explained as follows: (i) resin-phosphorus inorganic was interpreted as phosphorus that is readily available to plant, (ii) NaHCO_3 -phosphorus inorganic, were interpreted as phosphorus which are strongly related to phosphorus uptake by plants and microbes and bound to mineral surface, (Mattingly, 1975; Tiessen and Moir, 1993) (iii) NaOH -phosphorus inorganic, were interpreted as phosphorus which are more strongly held by chemisorption to Fe and Al components of soil surface (Fe-P and Al-P) and (iv) HCl -phosphorus inorganic was interpreted as Ca-P of low solubility.

Calculation of contribution of NaHCO_3 -Phosphorus inorganic, NaOH - Phosphorus inorganic and HCl - Phosphorus inorganic to the total P released as resin- Phosphorus inorganic

Contribution of $\text{NaHCO}_3\text{-P}_i$, NaOH -Phosphorus inorganic and HCl -Phosphorus inorganic to the total phosphorus released as resin-Phosphorus inorganic in percentage was determined by the

values of initial NaHCO_3 -Phosphorus inorganic, or NaOH - Phosphorus inorganic or HCl - Phosphorus inorganic was subtracted by the values of NaHCO_3 - Phosphorus inorganic, or NaOH - Phosphorus inorganic or HCl - Phosphorus inorganic after successive resin extraction of each treatment and divided by the total P released as resin- Phosphorus inorganic of each treatment.

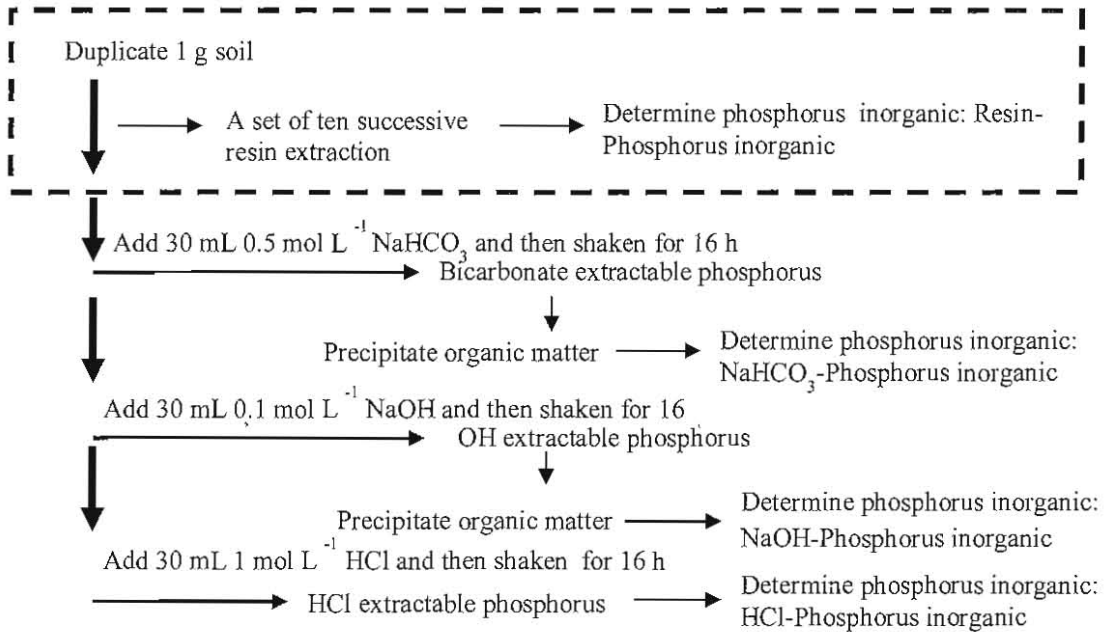


Fig. 1. Flow chart of the phosphorus fractionation into various inorganic phosphorus fractions

Data analyses

Data from successive resin extraction were simulated using first order kinetic as written below:

$$\text{Resin- Phosphorus inorganic} = a (1 - e^{-k(\text{number of extraction})})$$

where the constant a is the maximum phosphorus released and k is the rate constant. Analyses of variance followed by a Tukey's test were applied to evaluate the effect of silicate to the parameters.

RESULTS AND DISCUSSION

Physico-chemical properties of Andisol soil in Lembang

Physico-chemical properties of Andisol soil in Lembang are presented in Table 1. The status of selected chemical properties was based on the methods as described by Hartono (2007) and classified according to the criteria published by Soepratohardjo et al. (1983). Soil pH of Andisol soil in Lembang was acid. Total organic carbon was very high. Cation exchange capacity was high however the base saturation was low. Sum of percentage of aluminum plus half of iron extracted by ammonium oxalate acid more than 2% typifies for Andisol soil. Total phosphorus were very high indicating that phosphorus in Andisol soil in Lembang was very accumulated.

The initial phosphorus fractionation showed that phosphorus was accumulated in the NaOH-Phosphorus inorganic, HCl-Phosphorus inorganic, NaHCO₃-Phosphorus inorganic and resin-Phosphorus inorganic. The values of NaOH-Phosphorus inorganic, HCl-Phosphorus inorganic, NaHCO₃-Phosphorus inorganic and resin-Phosphorus inorganic were 968, 790, 391, 97.9 mg phosphorus kg⁻¹, respectively.

Table 1. Physico-chemical properties of Andisol soil in Lembang (Hartono, 2007).

Soil Properties	Value	Status
pH (H ₂ O)	4.74	acid
Total Organic Carbon (C) (%)	6.06	very high
Total-Phosphorus (P) (mg kg ⁻¹)	4783	very high
Total-Nitrogen (N) (%)	0.44	medium
Calcium (Ca) (cmol _c kg ⁻¹)	2.64	low
Magnesium (Mg) (cmol _c kg ⁻¹)	0.34	low
Potassium (K) (cmol _c kg ⁻¹)	0.1	low
Sodium (Na) (cmol _c kg ⁻¹)	0.21	low
Cation Exchange Capacity (CEC) (cmol _c kg ⁻¹)	30.1	high
Base saturation (BS) (%)	10.9	low
Clay (%)	24.9	-
Oxalate:		-
Aluminium (Al _o) (%)	5.97	-
Iron (Fe _o) (%)	2.11	-
Al _o +1/2Fe _o (%)	7.03	-

Successive resin extraction

The pattern of phosphorus released is presented in Figure 2. Maximum phosphorus released and the constant rate of first order kinetic is presented in Table 2. The increasing rates of silicate in the form of sodium silicate increased phosphorus release. The application of silicate in the form of sodium silicate significantly increased maximum phosphorus release. The application of sodium silicate with the rate 90 g resulted in the highest maximum phosphorus release compared to other treatments. The maximum phosphorus released from the application of sodium silicate, with the rates 0, 18, 45 and 90 g, were 274, 479, 744 and 1050 mg phosphorus kg⁻¹, respectively.

Table 2. Maximum phosphorus release (*a*) and rate constant (*k*) derived from first order kinetics

Rates of sodium silicate (g pot ⁻¹)	<i>k</i> (number of extraction ⁻¹)	<i>a</i> (mg Phosphorus kg ⁻¹)	R ²
0 (control)	0.442 a*	274 a	0.99
18	0.311 ab	479 a	0.99
45	0.283 bc	744 b	0.99
90	0.248 bc	1050 c	0.99

*Means followed by the same letter within a column are not significantly different (Tukey's test, *P* < 0.05)

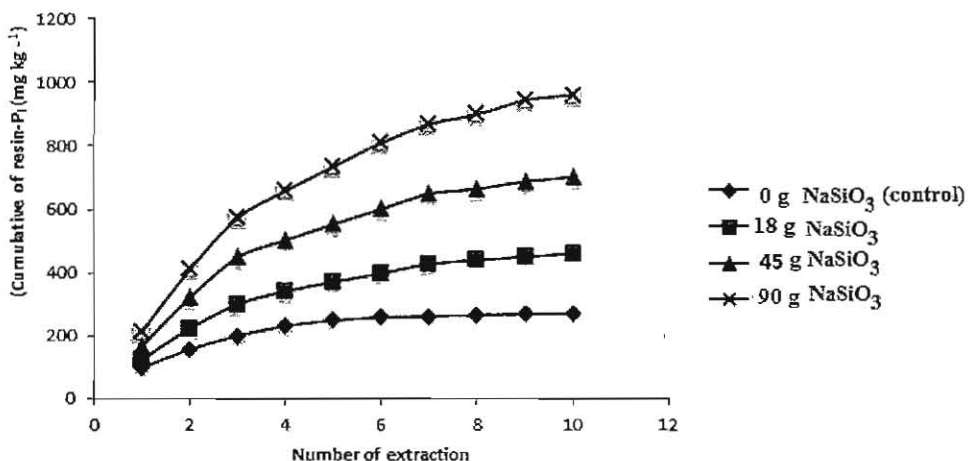


Fig. 2. Phosphorus release pattern (mg kg^{-1}) of Andisol soil in Lembang after successive resin extraction as influenced by the amount of Na_2SiO_3

The maximum phosphorus released by application of sodium silicate with the rate 90 g was about 22% of total phosphorus. This finding confirmed that silicate could be used to mine phosphorus in Andisol soil in Lembang. The application of silicate in the form of sodium silicate significantly decreased the rate constant. The least value of rate constant was the application of sodium silicate with the rate 90 g. It indicated that slow release of phosphorus sorbed in sorption sites occurred with the presence of silicate. Although the application of silicate increased the maximum phosphorus release but the rate of phosphorus release was slow. It could increase the efficiency of phosphorus uptake by plant. The results also confirmed that the transformation of resistant phosphorus to labile phosphorus occurred with the application of silicate (Hartono, 2007).

Phosphorus fractionation after successive resin extraction

Phosphorus fractionation after successive resin extraction is presented in Table 3. Compared to initial phosphorus fractionation the values of NaHCO_3 -Phosphorus inorganic, NaOH -Phosphorus inorganic and HCl -Phosphorus inorganic in Table 3 decreased after successive resin extraction experiment. It indicated that those fractions contributed to the phosphorus release. The samples treated by sodium silicate showed the higher decrease of those phosphorus fractions compared to those of the control sample.

Table 3. Phosphorus fractionation after successive resin extraction.

Rates of sodium silicate (g pot^{-1})	NaHCO_3 - Phosphorus inorganic	NaOH - Phosphorus inorganic	HCl - Phosphorus inorganic
mg Phosphorus kg^{-1}		
0 (control)	316	851	689
18	238	758	583
45	282	682	461
90	175	564	466

Percentage of the contribution from NaHCO₃-Phosphorus inorganic, NaOH-Phosphorus inorganic and HCl-Phosphorus inorganic is presented in Table 4. NaOH-Phosphorus inorganic fraction and HCl-Phosphorus inorganic fraction which are interpreted as phosphorus strongly held by chemisorption to iron and aluminum components of soil surface and Ca-P of low solubility respectively were the main contributors for phosphorus release. Their contribution varied from 33.7% to about 46.9%. It indicated that NaOH- Phosphorus inorganic and HCl-Phosphorus inorganic were not stable phosphorus fractions. Phosphorus was released when phosphorus in the soil solution decreased.

Table 4. The percentage of contribution to the value of resin-P_i from NaHCO₃- Phosphorus inorganic, NaOH- Phosphorus inorganic and HCl- Phosphorus inorganic

Rates of sodium silicate (g pot ⁻¹)	NaCHO ₃ - Phosphorus inorganic	NaOH- Phosphorus inorganic	HCl- Phosphorus inorganic
%.....		
0 (control)	28.0	43.7	37.7
18	33.3	45.7	45.0
45	15.6	40.8	46.9
90	22.5	42.1	33.7

CONCLUSIONS

Total phosphorus of Andisol soil in Lembang were very high. They mostly accumulated in NaOH-Phosphorus inorganic (Al-P and Fe-P) and HCl-Phosphorus inorganic (Ca-P). The application of silicate increased maximum phosphorus release in successive resin extraction. However the application of silicate decreased the rate constant of phosphorus release.

Successive resin extraction experiment suggested that silicate could be used to mine phosphorus in Andisol soil in Lembang to save phosphorus fertilizer. NaOH-Phosphorus inorganic and HCl-Phosphorus inorganic were phosphorus fractions which contributed to phosphorus release. Materials containing silicate are promising to be used as ameliorant for releasing native phosphorus of Andisol soil. It is necessary to make calibration experiments in the field to select which materials are good as ameliorant in Andisol soil.

ACKNOWLEDGEMENT

The authors thank the Indonesian Vegetables Research Institute, Lembang West Java, for helping in the soil samples collection and the Graduate School of Agriculture, Kyoto University for funding the chemical reagents.

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