Releasing Pattern of Applied Phosphorus and Distribution Change of Phosphorus Fractions in the Acid Upland Soils with Successive Resin Extraction

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ABSTRACT

Releasing Pattern of Applied Phosphorus and Distribution Change of Phosphorus Fractions in the Acid Upland Soils with Successive Resin Extraction (A. Hartono): The releasing pattern of applied P in the acid upland soils and the soil properties influencing the pattern were studied. Surface horizons of six acid upland soils from Sumatra, Java and Kalimantan were used in this study. The releasing pattern of applied P (300 mg P kg^{-1}) of these soils were studied by successive resin extraction. P fractionation was conducted to evaluate which fractions released P to the soil solution after successive resin extraction. The cumulative of resin-$P_{inorganic}$ (P_i) release of soils was fitted to the first order kinetic. Regression analyses using factor scores obtained from the previous principal components analyses was applied to determine soil properties influencing P releasing pattern. The results suggested that the maximum P release was significantly ($P < 0.05$) increased by acidity plus 1.4 nm mineral-related factor (PC_2) i.e. exchangeable Al and 1.4 nm minerals (smectite and vermiculite) and decreased by oxide related factor (PC_1) i.e. aluminum (Al) plus 1/2 iron (Fe) (by ammonium oxalate), crystalline Al and Fe oxides, cation exchange capacity, and clay content. P fractionation analysis after successive resin extraction showed that both labile and less labile in the form of $NaHCO_3$-P_i and NaOH-P_i fractions, respectively, can be transformed into resin-P_i when in the most labile resin-P_i is depleted. Most of P released in high oxides soils were from NaOH-P_i fraction while in low oxides soils were from $NaHCO_3$-P_i. P release from the former fraction resulted in the maximum P release lower than that of the latter one. When $NaHCO_3$-P_i was high, NaOH-P_i was relatively more stable than $NaHCO_3$-P_i despite resin-P_i removal. $NaHCO_3$-P_i and NaOH-P_i are very important P fractions in replenishing resin-P_i in these acid upland soils.

Keywords: Acid upland soils, phosphorus, realeasing pattern, successive resin extraction

INTRODUCTION

Most of the upland soils in Indonesia are acidic in reaction and found to be deficient in available phosphorus (P). Acid soils account approximately 57% of total upland soils and are developed from different kinds of parent materials (Subagyo *et al.*, 2000). P fertilization is a key component for increasing soil productivity in these acid upland soils. Transformation study of applied P in these soils showed that much of P fertilizer in soils with high amount of oxides in one cropping season (90 days) was transformed to chemisorbed aluminum (Al) and iron (Fe) oxides while in soils with low amount of oxides was transformed not only tochemisorbed to Al and Fe oxides but also on the surface of Al and Fe oxides (Hartono *et al.*, 2006).

P forms dictate the P release to soil solution. The P release in acid upland soils from P bonded by Al and Fe oxides in these acid soils are not evaluated. It is essential to know the long-term effects of the applied P in the soil. By using successive resin extraction, there is possibility to study the long term effect due to the characteristic of anion exchange resin as reported by Amer *et al.* (1955), Sibbesen (1978), Dalal (1985), and Van Raij *et al.* (1986). They reported that in determination of available P with anion exchange resin extractions, available P correlated well with plant P uptake. The resin acts as a sink for desorbed P in the same way as plant roots. Recently it was used to evaluate the

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release pattern of P in heavily fertilized calcareous soils and limed acid soils (Delgado and Torrent, 2000) and in typical mediterranean soils (Saavedra and Delgado, 2005). Since the use of resin does not disrupt the chemical structure of the soil, it should be possible to make a series of extractions from one soil sample allowing the examination of the release characteristics of soil P from stronger P bond over time.

The P release characteristics may be different among soils with high or low amount of oxides due to difference of soil properties. The objective of the study were to evaluate the releasing pattern of P on soils with high amount of oxides and on soils with low amount of oxides using successive resin extractions and to evaluate the distribution change of P fractions after successive resin extraction.

MATERIALS AND METHODS

Soil samples. Surface horizons of six acid upland soils from Sumatra, Java and Kalimantan were used in this study. These soil samples were selected based on the results of P transformation study (Hartono *et al.*, 2006). Based on the results of that study, PDI (Sumatra), Pringsurat (Java), Darmaga (Java), Gajrug (Java) represented soils with high amount of oxides. While Kota Bangun (Kalimantan) and SM-BP (Kalimantan) represented soils with low amount of oxides. For convenience in discussion, soils with high amount of oxides is called high oxides soils and soils with low amount of oxides is called low oxides soils.

Parent materials and selected chemical and physical properties of the soils are listed in Table 1. The methods to obtain their values were described in Hartono *et al.* (2005). Dominant silicate clay minerals in soils from PDI were kaolinite and Al-interlayered vermiculite-chlorite intergrades, while soils from Pringsurat and Darmaga were kaolinite. Dominant silicate clay mineral in soil from Gajrug was smectite, while soils from Kota Bangun and SM-BP were kaolinite and vermiculite.

In the previous study, the principal component analysis (PCA) was applied and three principal components (PCs) were extracted from the chemical and physical properties of 13 original soils (Hartono *et al.*, 2005). PC_1 was interpreted as an oxide-related factor (amorphous Al and Fe oxides, crystalline Al and Fe oxides, cation exchange

Table 1. Some chemical and physical properties of the soils used.

Location	Soil order*	Parent material	Depth	pH H_2O	Organic C	Clay	Pyrophosphate		Oxalate		DCB		Base Saturation	CEC	Exch. Al	Bray 1-P
							Al_p	Fe_p	Al_o	Fe_o	Al_d	Fe_d				
			(cm)	(1:1.5)	(g kg^{-1})	%	....	................g kg^{-1}	....				%	...cmol$_c$ kg^{-1}	....	(mg P kg^{-1})
High fixing																
PDI	Ultisols	Andesite	0-14	5.61	53.9	55.5	1.41	1.93	5.65	20.7	13.2	53.9	62.5	21.1	nd	1.19
Pringsurat	Alfisols	Volcanic ash	0-9	4.56	11.0	88.6	0.39	nd	3.48	4.67	7.24	57.6	43.8	13.3	nd	0.90
Darmaga	Inceptisols	Andesite	0-13	4.37	22.2	70.0	1.89	2.45	3.24	3.64	7.46	45.1	22.6	18.1	4.21	2.91
Gajrug	Ultisols	Volcanic ash-sedimentary rock mixture	0-14	4.24	25.2	65.2	4.97	4.15	6.38	9.11	8.67	29.2	15.0	40.3	23.1	5.65
Low fixing																
Kota Bangun	Ultisols	Sedimentary rock	0-4	4.51	13.6	14.8	0.39	0.66	0.59	1.41	1.05	5.82	18.3	5.74	1.21	12.3
SM-BP	Ultisols	Sedimentary rock	0-11	4.60	17.3	16.1	0.25	1.10	0.64	5.03	1.26	12.2	19.7	6.70	1.22	10.3

*Soil Survey Staff (1998)
nd: non-detectable

Tabel 2. Factor scores of PC_1, PC_2 and PC_3 of the soils used.

Soil samples	Factor scores of PC_1	Factor scores of PC_2	Factor scores of PC_3
High fixing			
PD1	2.09	-1.55	2.89
Pringsurat	0.48	-1.06	0.96
Darmaga	0.69	-0.15	0.29
Gajrug	1.88	2.69	1.67
Low fixing			
Kota Bangun	-1.37	0.02	0.81
SM-BP	-1.05	0.01	1.09

capacity and clay content). PC_2 was interpreted as an acidity plus 1.4 nm mineral-related factor (exchangeable Al and 1.4 nm minerals i.e. smectite and vermiculite), and PC_3 was interpreted as an organic carbon (C)-related factor (organic C and organically bound Fe). They were used again to describe soil properties in this study. Factor scores of PC_1, PC_2 and PC_3 of the soils used is presented in Table 2.

Incubation procedure. Duplicate 1 g samples were treated with 300 mg P kg^{-1} soil as a solution of KH_2PO_4, mixed thoroughly, and incubated for 30 days at 25° C and 80% of field capacity. Controls without P addition were also included for each soil. 30 days was selected as a period of incubation, because most of selected soils in this study reached their equilibrium of P transformation in 30 days (Hartono *et al.*, 2006). The results of P fractionation according to Tiessen and Moir (1993) method of these selected soils after 30 days incubation based on the previous P transformation study is presented in Table 3 (Hartono *et al.*, 2006).

Successive resin extraction procedure. Two resin strips oversaturated with bicarbonate and 30 mL of deionized water were applied to 1 g of soil in 50 mL centrifuge tubes and then shaken for 16 h. Resin strips were removed and washed with deionized water over a glass vial. Any soil trapped in the resin strips and lost from the bottle was collected, dried, and the weight loss was taken into account in the calculations of the amount of P extracted. Resin strips were placed in a clean 50 mL tube and applied 20 mL 0.5 mol L^{-1} HCl and shaken for 16 h. After that resin-P_i was determined.

Table 3. P distribution of 300 mg kg^{-1} P added after 30 d of incubation.

Location	Depth (cm)	Resin-P_i	NaHCO$_3$-P		NaOH-P		HCl-P_i	Recovery (%)
			NaHCO$_3$-P_i	NaHCO$_3$-P_o	NaOH-P_i	NaOH-P_o		
		…………	…………mg kg^{-1}	…………	…………	…………	…………	
High fixing								
PD1	0-14	60	34	0	153	0	2	83
Pringsurat	0-9	72	37	0	163	19	8	100
Darmaga	0-13	108	23	2	131	4	2	90
Gajrug	0-14	144	9	5	115	39	2	100
Low fixing								
Kota Bangun	0-4	128	85	0	49	0	1	88
SM-BP	0-11	65	106	0	82	0	1	85

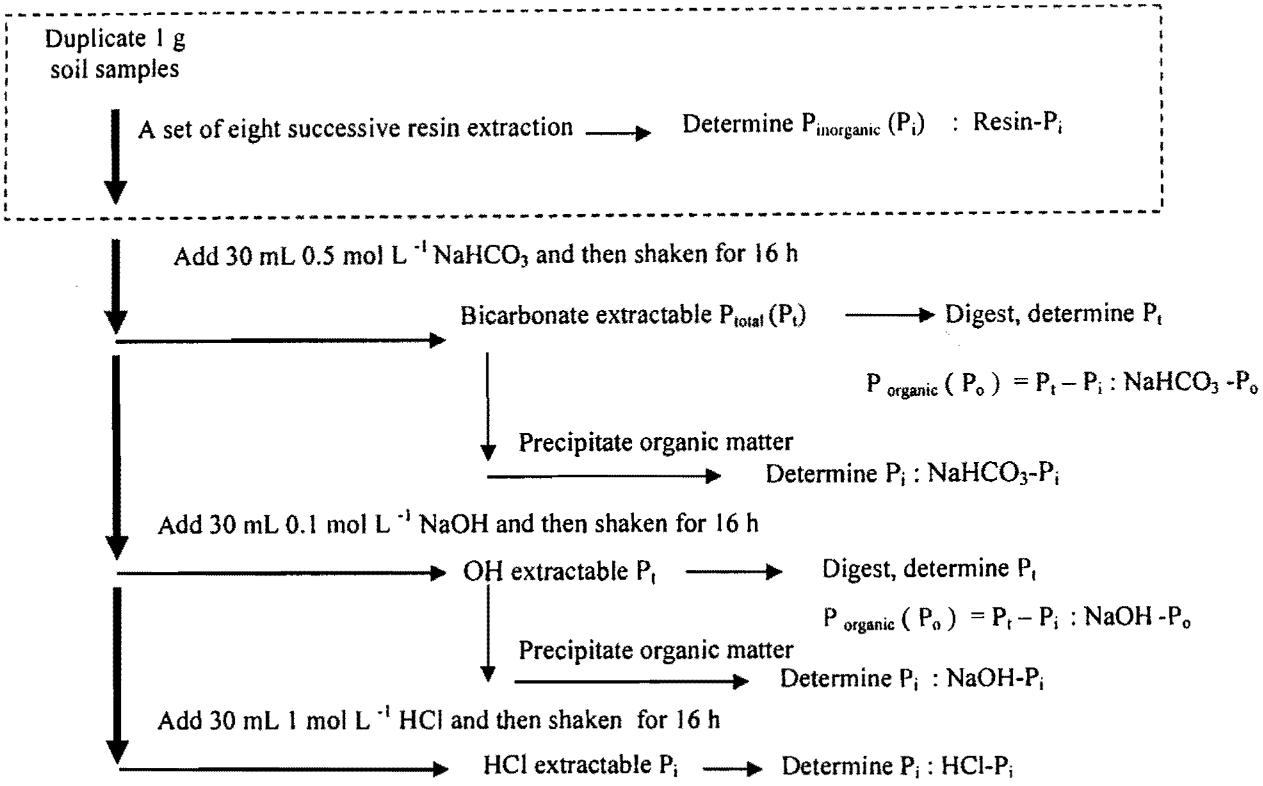

Figure 1. Flow chart of the P fractionation into various inorganic- and organic-P fractions.

The resin strips was removed, washed and regenerated for further use as described by Saggar *et al.* (1990) and Tiessen and Moir (1993). The extraction of P from each sample was continued by placing a regenerated resin strips in the original centrifuge containing the soil and water suspension and the procedure was repeated. A set of eight successive extractions was performed. The values were obtained by subtracting the release resin-P_i with those of control.

P fractionation. After a set of eight successive extractions, P fractionation was performed to evaluate the changes of P fractions. P fractionation procedure was described in Figure 1. Characterization of sequential soil P extraction was explained as follows: (i) resin-P_i was interpreted as P that is readily available to plant, (ii) $NaHCO_3$-P_i, -$P_{organic}$ (P_o) were interpreted as P which are strongly related to P uptake by plants and microbes and bound to mineral surface, (Mattingly 1975; Tiessen and Moir 1993) (iii) NaOH-P_i, -P_o were interpreted as P which are more strongly held by chemisorption to Fe and Al components of soil surface and (iv) HCl-P_i was interpreted as Ca-P of low solubility. The values were obtained by subtracting control from the recovery of P fractions.

RESULTS AND DISCUSSION

Successive Resin Extraction of Soil Samples

The cumulative of resin-P_i released by soils are presented in Figure 2. For describing the releasing of P pattern, the data was fitted to the first order kinetic as written below:

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

where the constant a is the maximum resin P_i release and k is the rate constant of cumulative resin-P_i released per resin extraction. The parameters of the equations are presented in Table 4.

The k of soil from Gajrug was the highest among the soils (Table 4). Soil from Gajrug had the highest factor score of PC_2 in the soils indicating that this soil had high exchangeable Al and the dominant silicate clay mineral was 1.4 nm mineral (smectite). Exchangeable Al and 1.4 nm minerals of which smectite and vermiculite were common in

these acid soils were reported decreased the P sorption maxima (Hartono *et al.*, 2005). It suggested that exchangeable Al associated with smectite increased *k* value of resin-P_i released from soils.

PD1 soil exhibited the lowest *a* value (Table 4). It was due to high factor score of PC_1. The stepwise regression showed that *a* value significantly ($P < 0.05$) decreased with increasing of PC_1 and increased with increasing of PC_2 as in the equation below:

$$a = 199 - 18.3\,PC_1 + 14.8\,PC_2 \quad (R^2 = 0.88^*)$$

PC_3 which is C-related factor (organic C and organically bound Fe) was considered as not component to estimate *a* value because PC_3 made the equation was not significant statistically.

P desorbability was reported to decrease with increasing Al_o + Fe_o (Lookman *et al.*, 1995; Maguire *et al.*, 2001; Vadas and Sims, 2002). This result suggested that not only oxide-related factor where Al_o + Fe_o was included but also the presence of exchangeable Al which is associated with 1.4 nm minerals should be included to estimate P desorbability in these acid upland soils. Due to low factor scores of PC_1 the *a* value of two low oxides soils Kota Bangun and SM-BP was higher than that of soil from PD1. Low factor score of PC_1 caused significant amounts of P distributed in the $NaHCO_3$-P_i fraction (Table 3).

Two high oxides soils Pringsurat and PD1, exhibited the quite different pattern in maximum P released. Although their rate constants were similar but soil from Pringsurat had a higher *a* value (maximum P release) than PD1. This is because of factor score of PC_1 of PD1 soil was higher than that of Pringsurat soil. It meant that PD1 soil had higher amount of oxides than that of Pringsurat soil.

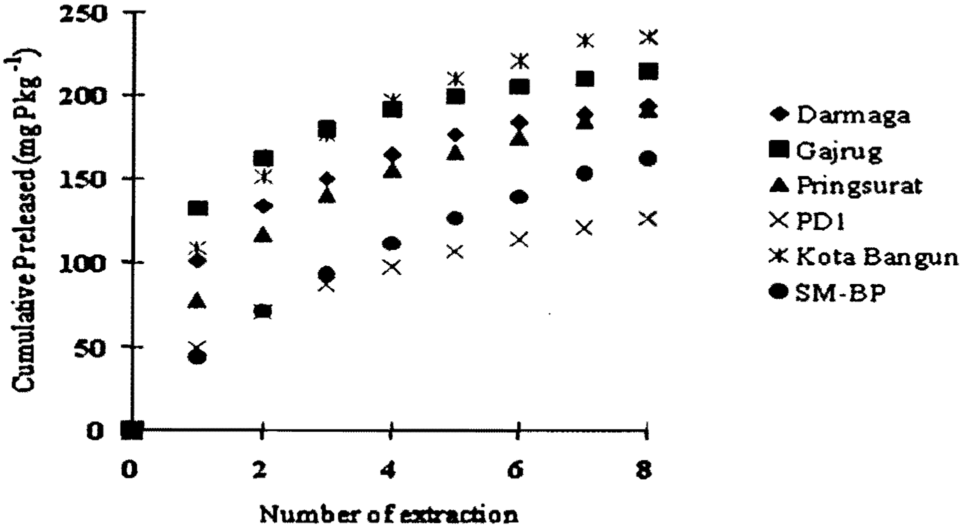

Figure 2. Cumulative of resin-P_i release extracted by successive resin extraction.

Table 4. The parameters of the equation.

Location	Depth (cm)	*k*	*A* (mg P kg^{-1})	r^2
High fixing				
PD1	0-14	0.40	128	0.975
Pringsurat	0-9	0.46	190	0.985
Darmaga	0-13	0.64	188	0.945
Gajrug	0-14	0.88	205	0.914
Low fixing				
Kota Bangun	0-4	0.53	232	0.972
SM-BP	0-11	0.21	200	0.995

Table 5. P distribution after successive extraction excluded resin-P_i of 300 mg P kg^{-1} added P.

Location	Depth (cm)	$NaHCO_3$-P		NaOH-P		HCl-P_i
		$NaHCO_3$-P_i	$NaHCO_3$-P_o	NaOH-P_i	NaOH-P_o	
		………………mg P kg^{-1}………………				
High fixing						
PD1	0-14	9	5	100	12	1
Pringsurat	0-9	7	1	72	0	3
Darmaga	0-13	4	2	64	0	2
Gajrug	0-14	3	1	46	2	2
Low fixing						
Kota Bangun	0-4	16	0	27	0	2
SM-BP	0-11	31	0	71	0	7

The Changes of P Distribution after Successive Resin Extraction of Soil Samples

The changes of P distribution after successive extraction of soil samples was evaluated to investigate how P released from P stronger bond fractions. The P distribution after successive extraction of soils samples except resin-P_i is presented in Table 5.

The amounts of $NaHCO_3$-P_i and NaOH-P_i were decreased after successive resin extraction. Compared to initial P fraction distribution (Table 3), it suggested that both labile and less labile P_i in the form of $NaHCO_3$-P_i and NaOH-P_i fractions, respectively, can transform into resin-P_i when the resin-P_i decrease. The resin-P_i, $NaHCO_3$-P_i and NaOH-P_i appeared to be in equilibrium. Most of P released in high oxides soils namely Darmaga, Gajrug, Pringsurat and PD1 were from NaOH-P_i fraction while low oxides soils, namely Kota Bangun and SM-BP were from $NaHCO_3$-P_i.

Contribution from $NaHCO_3$-P_i and NaOH-P_i to the total P released from 2nd to 8th extraction were calculated from the decrease of the data of P transformation experiment (Table 3) compared to the data of P distribution after successive extraction (Table 5).

The total P released from 2nd to 8th is presented in Table 6. The percentage of contribution of $NaHCO_3$-P_i and NaOH-P_i to the total P released from 2nd to 8th extraction is presented in Table 7.

In high oxides soils (PD1, Darmaga, Gajrug, Pringsurat) more than 60% of P release derived from NaOH-P_i while in low oxides soils (Kota Bangun and SM-BP) more than 50% P release derived from $NaHCO_3$-P_i and only small amount P release derived from NaOH-P_i fraction. In soils from Kota Bangun and SM-BP there was 28% contribution of P released from unknown fraction. This was probably derived from residual P.

Table 6. P released in the form of resin-P_i from 1st to 8th extraction and total P released from 2nd to 8th extraction.

Location	Depth (cm)	Extraction number								Total P released from 2nd to 8th extraction
		1	2	3	4	5	6	7	8	
		………………g P kg^{-1}………………								
High fixing										
PD1	0-14	49	21	16	11	9	7	7	6	77
Pringsurat	0-9	77	39	24	15	11	9	11	6	115
Darmaga	0-13	100	33	16	15	12	7	5	5	93
Gajrug	0-14	132	31	18	11	8	6	5	4	83
Low fixing										
Kota Bangun	0-4	108	43	25	20	13	10	12	3	126
SM-BP	0-11	43	28	22	18	15	13	14	10	120

Table 7. Contribution from $NaHCO_3$-P_i and NaOH-P_i fractions to total P released from 2nd to 8th extraction.

Location	Total P released from 2nd to 8th extraction (mg P kg^{-1})	Decrease of $NaHCO_3$-P_i (mg P kg^{-1})	Percentage of $NaHCO_3$-P_i contribution (%)	Decrease of NaOH-P_i (mg P kg^{-1})	Percentage of NaOH-P_i contribution (%)	Percentage of contribution of unknown fraction (%)
High fixing						
PD1	77	25	32	53	69	0
Pringsurat	115	30	26	91	79	0
Darmaga	93	19	20	67	72	9
Gajrug	83	6	7	69	83	10
Low Fixing						
Kota Bangun	126	69	55	22	17	28
SM-BP	120	75	63	11	9	28

Among the high oxides soils, $NaHCO_3$-P_i, which originally occupied a small portion, seems to be firstly depleted. According to Table 3 and 5, the amount of NaOH-P_i which was left in that fraction after the successive extraction was higher (65%) in the soil from PD1 than in the soil from Pringsurat (44%), suggesting that P in PD1 soil were more difficult to release than that of Pringsurat soil due to higher factor scores of PC_1.

Concerning two soils from Kota Bangun and SM-BP, lower amounts of P was released from NaOH-P_i fraction than that from $NaHCO_3$-P_i (Table 7), indicating that $NaHCO_3$-P_i was released first when resin-Pi decreased. These two soils accumulated 300 mg P kg^{-1} added P in significant amounts into $NaHCO_3$-P_i fraction (Table 3). When $NaHCO_3$-P_i was high, NaOH-P_i was relatively more stable than $NaHCO_3$-P_i despite resin-P_i removal as shown clearly in soil from SM-BP. The results suggested that $NaHCO_3$-P_i and NaOH-P_i are very important P fractions in replenishing the labile resin-P_i in these acid upland soils because accumulation of added P mostly in these fractions and they can be readily dissolved. It was reported by Beck and Shanchez (1994), Guo *et al.* (2000), and Zheng *et al.* (2003), NaOH-P_i was not a static fraction, instead it declined under crop. However for comparison, in Andisols the P replenishment from this fraction was very slow as reported by Beck *et al.* (1999). It suggested that chemisorbed P which partly to crystalline Al and Fe oxides in these soils was different from chemisorbed P to amorphous Al and Fe oxides in Andisols in term of bonding energy of P sorbed.

CONCLUSIONS

The study suggested that exchangeable Al which is associated with smectite increased rate constant of P released from soils.

The maximum P released was decreased by oxide-related factor i.e. aluminum (Al) plus 1/2 iron (Fe) (by ammonium oxalate), crystalline Al and Fe oxides, cation exchange capacity, and clay content and increased by acidity plus 1.4 nm minerals-related factor i.e. exchangeable Al and 1.4 nm minerals (smectite and vermiculite).

P fractionation analysis after successive resin extraction showed that both labile and less labile P_i in the form of $NaHCO_3$-P_i and NaOH-P_i fraction, respectively, can transform when in the resin-P_i is depleted. Most of P released in high oxides soils were from NaOH-P_i fraction while low oxides soils were from $NaHCO_3$-P_i where P release from the former fraction resulted in the *a* value lower than that of the latter one. When $NaHCO_3$-P_i was high, NaOH-P_i was relatively more stable than $NaHCO_3$-P_i despite resin-P_i removal.

$NaHCO_3$-P_i and NaOH-P_i are very important P fractions in replenishing the most labile P (resin-P_i) in these acid upland soils.

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