Phosphorus Sorption by Al(Fe)-Humus Complexes in Volcanic Ash Soils

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Introduction

In volcanic ash soils, large amounts of phosphorus sorption have been attributed to the abundant presence of amorphous aluminosilicates and hydrous Al(Fe) oxides. It has been universally recognized that among these constituents, greater roles in phosphorus sorption are assigned to those inorganic constituents dissolved with dithionite-citrate treatment, rather than allophane (imogolite) dissolved with 0.5 N NaOH treatment[5,6,14]. Dithionite-citrate treatment dissolves, in general, free Fe(Al) hydrous oxides and allophane-like constituents, in addition to organic complexed Al(Fe)[2,11]. Allophane-like constituents were referred to as the amorphous inorganic constituents dissolved with dithionite-citrate and 2% Na_2CO_3 treatments, having infrared spectra similar to those of allophane and lower SiO_2/Al_2O_3 molar ratio than in allophane[13]. However, their relative importance in contribution to phosphorus sorption by each constituents, i.e., free hydrous Al(Fe) oxides, allophane-like constituents and organic complexed Al(Fe), has not been investigated.

In the present study, the emphasis is placed on the phosphorus sorption by Al(Fe) in the forms of humus complexes in volcanic ash soils. Amounts of Al(Fe) in humus complexes, in other words, organic complexed Al(Fe), were estimated by 0.1 M $Na_4P_2O_7$ extraction[2,12]. For the purpose of this study, it seems to be one of the more favorable approaches to use the samples which are free from allophane (imogolite), as well as allophane-like constituents. Appelt *et al.*[1] showed that the complexes synthesized from humic acids and $Al_x(OH)^{3x-y}$ ions were active in phosphorus sorption and their reactivity depended on the OH/Al ratio of the complexed $Al_x(OH)^{3x-y}$ ion species. This suggests that Al, possibly Fe, associated with humus plays an important role in phosphorus sorption.

Materials and Methods

Soil samples

Brief descriptions, some analytical data and the composition of amorphous inorganic constituents in clay separates of the samples are shown in Table 1. The compositions of the clay separates of the samples were obtained by the method of selective dissolution-differential infrared spectroscopy analysis[2,9,10]. S-1-1 is originated from ash deposits ejected from Mt. Sakurajima in Kagoshima since 1914. This sample contains no allophane, as well as allophane-like constituents in clay fraction (Higashi and Takahashi, unpublished). H-1-1 and H-1-2 are from the same profile at Daikanbo (lat. 33 00'47"N, long. 131 03'21"E), Aso-gun, Kumamoto. The amounts of allophane-

Table 1.   Brief descriptions, some analytical data of the samples and the compositions of amorphous inorganic constituents in their clay separates

Soil number	Horizon	Depth (cm)	Total carbon (%)	Clay content (%)	Composition of clay separates[1]			Reference[2]
					Dithionite-citrate	2% Na_2CO_3	0.5 N NaOH	
S -1-1	A_1	0-10	3.6	4	A'(?)(14)	O.S. (14)	O.S. (28)	
M-5-1	A_1	0-13	7.8	6	A'(n.d.)		O.S. (n.d.)	a)
M-6-1	A_1	0-25	11.6	13	A'(38)		O.S. (51)	a)
H-1-1	A_1	0-25	16.6	19	A'(53)	O.S. (7)	O.S. (16)	b)
T -1-1	A_1	0-25	15.0	21	A'(34)	A'(12)	O.S. (23)	c)
M-7-1	A_1	0-30	9.5	47	Al-gels, Gb(42)		L.S., Gb(21)	a)
T -1-8	uA_1	130-80	14.6	37	A'(37) X(6)		L.S. (9)	c)
H-1-2	uA_1	25-45	24.1	42	A'(?)(68)	A'(8)	O.S. (8)	b)
H-1-3	uA_1	45-80	16.9	42	A'(44)	A'(29)	A-Im. (21)	b)
H-1-4	uA_1	80-105	16.4	36	A'(46)	A'(27)	A-Im., O.S. (18)	b)
H-1-5	uA_1	105-120	2.1	21	A'(22)	A'(29)	A-Im. (43)	b)
H-1-6	uA_1	120-135	11.4	44	A'(32)	A'(28)	A-Im. (34)	b)

1) Abbreviation;   A-Im.=allophane (imogolite),   A'=allophane-like constituents,   O.S.= opaline silica,   L.S.=layer silicates,   Gb=gibbsite,   X=unidentified.   Figures in the parentheses are the contents of each soluble freactions.

2) a); Mizota (1977),   b); Higashi and Shinagawa (1980),   c); Tokashiki and Wada (1975).

like constituents in these samples were assumed to be very small[3]. M-5-1 and M-6-1 are from Kamisatsunai and Asahiyama, Tokachi-shichyo, Hokkaido, respectively, and the age of the samples is less than 1000 years B.P.[8]. M-7-1 was taken from a profile at Togeyama (lat. 33 28'58"N, long. 130 32'26"E), Chikushino, Fukuoka and has been strongly weathered with an age of more than 10000 years B.P.[7]. For M-5-1, M-6-1 and M-7-1, the presence of allophane was not positively detected in 0.5 N NaOH soluble fractions of the clay separates from these samples[8]. Analytical data of the composition of these samples are shown as the sum of dithionite-citrate plus 2% Na_2CO_3 treatments, and 0.5 N NaOH treatment (Table 1). M-7-1 contains Al-gels and gibbsite. T-1-1 and T-1-8 are from the same profile at Asahidai (lat. 33 10'06"N, long. 131 15'04"E), Kusugun, Oita and both samples contain no allophane[9]. The amounts of allophane-like constituents were assumed to be slightly higher in T-1-1 clay separate than in the other samples. For T-1-8, unidentified, poorly defined infrared spectra were obtained for dithionite-citrate and 2% Na_2CO_3 soluble fractions, and these materials were referred to as aluminum-rich constituents[9].

On contrast to the samples mentioned above, four clay separates from H-1-3 to H-1-6 were used as the reference samples containing clearly allophane in 0.5 N NaOH soluble fractions[3]. These four samples are from the sublayers at the Daikanbo profile.

Methods

a)   *Na-pyrophosphate extraction and the determination of Al and Fe in the extracts*

The detailed procedures of the extraction and the determination of Al and Fe in the extracts were shown in the previous paper[12]. Twice extractions were carried out on air-dried samples of less than 65 mesh.

b)   *Phosphorus sorption (P-sorption)*

Twenty five ml of two different concentrations (4 and 20 Mm) of H_3PO_4 or NaH_2PO_4 were

added to 500 mg of samples (less than 65 mesh) in a 50 ml glass centrifuge tube. The tube with fitted stopper, containing the sample and phosphorus solution, was then allowed to stand for 24 hours at about 30°C with an occasional shaking. After the reaction of the phosphorus with the soil sample, the supernatant was collected by centrifuging to measure the equilibrium pH and P concentration. The amount of P-sorption was calculated as the difference between P added and P found in the supernatant and is shown as milliatom % per oven-dried soil basis. These procedures for P-sorption were repeated until no sorption of P was to be observed.

Results and Discussions

1. *P-sorption by soil samples containing no allophane*

Amounts of P-sorption in four different systems were in the following order on all of the samples containing no allophane; 20 mM $H_3PO_4 > 4$ mM $H_3PO_4 > 20$ mM $NaH_2PO_4 > 4$ mM NaH_2PO_4 (Table 2). Since the dominant ion species of P is considered to be $H_2PO_4^-$ in both H_3PO_4 and NaH_2PO_4 systems under their equilibrium pH ranging from 2.3 to 5.8 (Table 2), the differences in

Table 2. Amounts of P-sorption, equilibrium pH values of supernatants and the amounts of extractable Al and Fe with Na-pyrophosphate on the samples

Soil number	P-sorption[1]					Pyrophosphate extraction		
	H_3PO_4 20 mM(a)	4 mM(b)	b)/a)	NaH_2PO_4 20 mM	4 mM	Al[2] (%)	Fe[2] (%)	(Al+Fe)[3]
S –1–1	6.1 (2.3)[4]	5.2 (3.0)	0.85	3.8 (4.4)	2.1 (4.3)	0.28	0.13	12.7
M–5–1	10.4 (2.3)	8.2 (3.2)	0.79	5.3 (4.5)	3.3 (4.8)	0.45	0.25	21.2
M–6–1	29.5 (2.6)	24.8 (3.3)	0.84	19.6 (5.2)	9.7 (5.1)	1.11	0.40	48.3
H –1–1	47.9 (2.6)	37.1 (3.8)	0.77	30.7 (5.3)	16.0 (5.7)	1.46	0.99	71.8
T –1–1	51.9 (2.7)	43.8 (4.1)	0.84	33.3 (5.5)	18.8 (5.7)	1.58	0.85	73.8
M–7–1	60.3 (2.7)	52.4 (4.2)	0.87	41.2 (5.5)	24.7 (5.8)	1.88	0.70	82.2
T –1–8	76.8 (2.6)	62.8 (4.3)	0.82	49.4 (5.5)	26.8 (5.4)	2.18	1.42	106.2
H –1–2	104.4 (2.7)	79.9 (4.6)	0.77	69.9 (5.5)	41.3 (5.6)	2.99	1.74	142.0
H –1–3	154.4 (2.8)	81.2 (4.5)	0.59	n.d.	n.d.	1.06	0.28	44.3
H –1–4	140.5 (2.8)	92.3 (4.6)	0.66	n.d.	n.d.	1.49	0.38	62.0
H –1–5	115.5 (2.8)	70.1 (4.7)	0.67	n.d.	n.d.	0.32	0.06	13.0
H –1–6	155.7 (2.8)	89.0 (4.8)	0.57	n.d.	n.d.	0.82	0.08	31.8

1) shown as milliatom % P on oven-dry soil basis (less than 65 mesh)
2) shown as % on oven-dry soil basis
3) shown as milliatom % (Al+Fe) on oven-dry soil basis
4) Figures in the parentheses denote the equilibrium pH values of supernatants.

the amounts of P-sorption among four different systems on the same sample might be attributed to the differences in equilibrium pH and P concentration, the higher the concentration of P and the lower the equilibrium pH value, the higher are the amounts of P-sorption (Table 2). A similar effect of equilibrium pH on P-sorption was shown on a sample from volcanic ash soils[14]. They showed maximum amounts of P-sorption at pH of about 2.7, which roughly corresponds to the range of pH in the 20 mM H_3PO_4 system of the present study (Table 2).

As for the absorbents of P in the samples, Al(Fe) in humus complexes, free Al(Fe) hydrous oxides and small amounts of allophane-like constituents might be responsible, since these samples

contain no allophane, and layer silicates and opaline silica are considered to have low P-sorption capacities (Table 1). Among active absorbents of P mentioned above, Miyauchi and Nakano[6] showed P-sorption by free Al(Fe) hydrous oxides, probably including allophane-like constituents, dissolved with dithionite-citrate and 2% Na_2CO_3 treatments from a (B) horizon sample of volcanic ash soils. This was estimated from the difference in the amounts of P-sorption between non- and dithionite-citrate plus 2% $NaCO_3$-treated samples, where amounts of P-sorption increased with the increasing of P concentration of H_3PO_4 from 10 to 500 mM at several equilibrium pHs buffered with Na-acetate and acetic acid. Since they used a (B) horizon sample, Al(Fe) in humus complexes could not be dominant and important absorbents. However, on the studied samples containing no allophane, only a slight difference in the amounts of P-sorption between 4 and 20 mM H_3PO_4 systems was obtained, as shown by the ratios of b)/a) in Table 2. This suggests that dominant absorbents in the samples might be different from allophane-like constituents and/or Al(Fe) hydrous oxides, that is, they are probably Al(Fe) in humus complexes. It is presumed that Al(Fe) in humus complexes have a ready and high reactivity in P-sorption at even a relatively low concentration of P as 4 mM in the present study.

It was observed, moreover, that the larger the amounts of P-sorption, the higher are the values of equilibrium pH after 24 hours of reaction in the respective systems, especially in case of the 4 mM H_3PO_4 system (Table 2). This might be interpreted in terms of specific adsorption of $H_2PO_4^-$ ion species[4], resulting in the release of OH^- ion located on the amorphous inorganic constituents mentioned before.

2. P-sorption by soil samples containing allophane(imogolite)

The amounts of P-sorption by the samples containing clearly allophane(imogolite) were larger than those by the samples containing no allophane (Table 2). This is probably due to the presence of allophane (imogolite), allophane-like constituents and free Al(Fe) hydrous oxides, which predominate in the samples of H-1–3, 4, 5 and 6 (Table 1). And, a proportion of the amounts of P-sorption of 4 mM relative to those of 20 mM H_3PO_4, indicated by b)/a) ratio in Table 2, was higher in the samples containing no allophane than in those containing allophane (imogolite). It suggests that Al(Fe) in humus complexes have a higher affinity for phosphorus at a very low concentration of P such as 4 mM, compared with those in the other amorphous inorganic constituents as mentioned above.

3. Relationship between the amounts of P-sorption and pyrophosphate extractable Al plus Fe

As shown in Figure 1, a linear relationship was obtained between the amounts of P-sorption and those of pyrophosphate extractable Al plus Fe in the samples containing no allophane (imogolite) in both the 20 mM H_3PO_4 and NaH_2PO_4 systems. The regression curves for the 20 mM H_3PO_4 and NaH_2PO_4 were $Y = 0.71X - 1.4$ (closed circle) and $Y = 0.47 - 1.2$ (half closed circle), respectively. This suggests that Al and Fe in humus complexes are active in P-sorption and react with phosphorus with an atomic ratio of $\left(\dfrac{P}{Al+Fe}\right)$ of about 0.7 and 0.5 for the H_3PO_4 and NaH_2PO_4 systems, respectively (see Fig. 1). The difference in the value of $\left(\dfrac{P}{Al+Fe}\right)$ might be explained as follows; Al or Fe in humus complexes extractable with pyrophosphate are stable in their structure as absorbents under the equilibrium pH from 4.4 to 5.5 in the 20 mM NaH_2PO_4 system, while they are unstable under lower pH of less than 4 as in the 20 mM H_3PO_4 system, resulting in their depolymerization of complexed Al(Fe) which reacts with phosphorus by a higher

P(milliatom %)

Y = 0.71 X - 1.4

● : H₃PO₄

○ : NaH₂PO₄
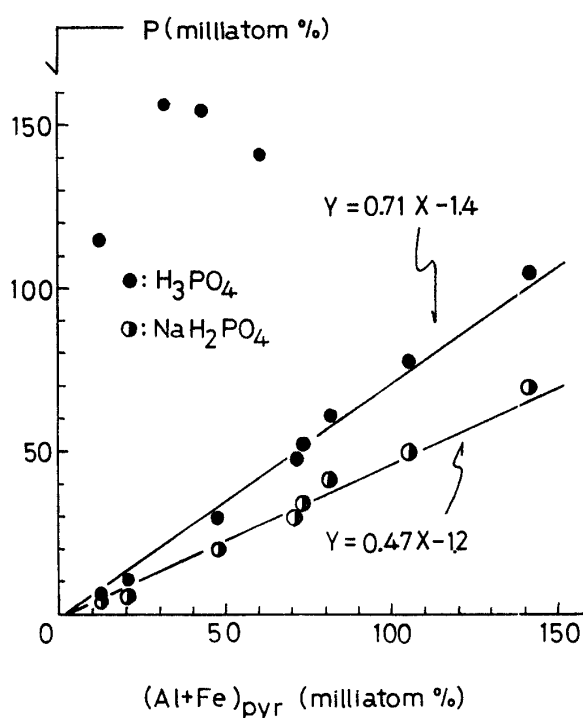
Y = 0.47 X - 1.2

(Al+Fe)pyr (milliatom %)

Fig. 1.   Relationship between the amounts of P-sorption and those of Al plus Fe extracted with Na-pyrophosphate.

value of $\left(\dfrac{P}{Al+Fe}\right)$.   Moreover, considering the increase in pH with the increase of the amounts of P-sorption (Table 2), there might be a possibility that co-ordination shells of Al(Fe) atoms in humus complexes may not be perfectly combined with the ligands of humus molecules, leaving OH^- ions on atoms.   The product of the reaction between $H_2PO_4^-$ and Al(Fe) in humus complexes would be expected to be such an insoluble compounds as $Al(Fe)(OH)_2H_2PO_4$.

In contrast to the samples containing no allophane, the samples clearly containing allophane (imogolite), H-1-3, 4 and 6, showed a large deviation from the regression curves (Fig. 1).   This is certainly related with the predominance of allophane (imogolite) and/or allophane-like constituents, in addition to Al(Fe) hydrous oxides in these samples, indicating that the contribution of pyrophosphate extractable Al plus Fe in humus complexes for phosphorus sorption is relatively small.

Summary

Phosphorus sorption by Al(Fe)-humus complexes in volcanic ash soils was studied on 8 samples containing no allophane, and 4 samples clearly containing allophane (imogolite) as the reference. Al or Fe in humus complexes showed a ready and high reactivity for phosphorus sorption from such a low concentration of P as in the 4 mM H_3PO_4 solution.   And, a linear relationship was obtained between the amounts of phosphorus sorption and those of Al plus Fe extractable with Na-pyrophosphate, with an atomic ratio of $\left(\dfrac{P}{Al+Fe}\right)$ of about 0.7 in case of 20 mM H_3PO_4 system.

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