Effect of organic ligands on phosphate adsorption and availability in Andisols of eastern Hokkaido, Japan

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Abstract
Andisols usually fix large amounts of phosphate on surface-reactive sites. Competitive effects of natural organic ligands, like citric acid and water-soluble organic matter (WSOM), on phosphate adsorption and availability to plants in Andisols were studied. Three types of Andisols were selected and soil samples were collected from surface horizons of upland fields. Phosphate adsorption isotherms were measured to evaluate effects of organic ligands on phosphate adsorption. Pot experiments were also conducted to investigate effects of the combined application of fertilizer and manure on phosphate availability. A suppressive effect of concurrent addition of citrate on phosphate adsorption was observed for all Andisols. Previous addition of citrate was more effective to suppress the phosphate adsorption in humic Andisols. Effects of the WSOM from cattle manure on phosphate adsorption could be observed clearly at the low concentration of phosphate. The most significant effect of WSOM on phosphate adsorption in the Andisols was to severely reduce the binding strength of phosphate and possibly induce subsequent phosphate desorption. The combined application of manure and inorganic phosphate fertilizer could improve the availability and efficiency of phosphate, by reducing phosphate adsorption and increasing phosphate solubility in the Andisols.

Key Words
Andisols, organic ligand, phosphate adsorption, phosphate availability, citrate, manure.

Introduction
Phosphates are a limited non-renewable resource, which cannot be replaced by other substances, as an essential plant nutrient (Franz 2008). Phosphates are mostly obtained from mined rock phosphate and its existing reserves could be exhausted in the next 50-100 years. Efficient use and alternative management of phosphate fertilizers are critical to ensure global food production and security (Cordell *et al.* 2009). Most of the arable land of eastern Hokkaido, which is one of the largest agricultural areas in Japan, is widely covered with volcanic ash and the soils are often classified as Andisols. The availability of phosphate fertilizer for plant uptake is extremely low in Andisols due to increased phosphate sorption and retention onto Al-humus complexes and amorphous to para-crystalline clay minerals, such as allophane and imogolite (Wada 1989). Andisols usually fix large amounts of phosphate by ligand exchange reaction with Al-OH and Al-H_2O functional groups on these constituents. There is considerable evidence that naturally-derived organic matter may influence soil chemical and biological processes, and enhance phosphate availability (Schefe *et al.* 2009). Natural organic ligands in soils, which consist of a mixture of well-defined organic acids and organic compounds that do not have a defined chemical structure like humic and fulvic acids can block some surface-reactive sites on minerals and hydroxides, thereby reducing the phosphate adsorption and increasing phosphate availability (Antelo *et al.* 2007). Although the competitive adsorption of phosphate and organic ligands by synthetic and natural clay minerals, iron oxides, and highly weathered acidic soils, such as Oxisols and Ultisols, have been studied (Hu *et al.* 2001; Antelo *et al.* 2007; Schefe *et al.* 2009), there is limited information on the fate of phosphate in the presence of organic ligands in Andisols. The aims of this study are to identify the effects of organic acid (citrate) and water-soluble organic matter extracted from aerobically composted cattle manure on phosphate adsorption and availability to plants in Andisols and to increase the efficiency of phosphate and contribute to the sustainable food production.

Materials and Methods
Soil samples and their characterization
Soil samples were collected from three upland fields in and around Obihiro, Hokkaido, Japan. The soils are classified into three subgroups of Andosols in the Japanese cultivated soil classification, which are Haplic Wet Andosols (Typic Melanaquands), Cumulic Andosols (Typic Melanudands), and Low-humic Andosols

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Table 1. Several physico-chemical and mineralogical properties of the soil samples.

Soil subgroups	$pH(H_2O)$[a]	PAC[b]	Total C[c]	Al_p[d]	Al_o[e]	Si_o[e]	Allophane[f]	CEC[g]	AEC[g]
			(g/kg)					(cmol$_c$/kg)	
Haplic Wet Andosols	5.4	1670	87.5	9.50	19.4	5.71	40.3	36.4	0.35
Cumulic Andosols	5.3	1650	53.2	7.36	28.1	13.0	87.1	34.5	1.33
Low-humic Andosols	5.7	1650	29.6	5.12	37.9	17.9	131	26.9	2.42

[a]Soil/water ratio of 1:2.5. [b]Phosphate absorption coefficient obtained by a Japanese conventional method. [c]Total carbon determined by the dry-combustion method. [d]Aluminium extracted with sodium pyrophosphate. [e]Aluminum and silicon extracted with acid ammonium oxalate, respectively. [f]Estimated from Al_p, Al_o and Si_o. [g]Cation and anion exchange capacity at pH5.5 determined by a centrifugation method, respectively.

(Typic Hapludands). Although the fields were located on the same volcanic ash terrace, slight differences in the micro topography and subsequent moisture conditions in the subsoils affected their formation processes and soil physico-chemical properties (Table 1). The surface soil samples at the depth of 0-20 cm were collected from each field, air-dried, and passed through a 2 mm pore-size sieve.

Adsorption isotherms of phosphate in the presence of citric acid

Phosphate adsorption isotherms were measured to evaluate the effects of citric acid on phosphate adsorption. One gram of the air-dried soil sample was placed in a 50-mL plastic centrifuge tube. 15 mL of 0.2 mol/L KNO_3 at pH5.5 was added to each tube. After shaking for 1 h at 25 ˚C, the pH of the suspension was readjusted to 5.5. 0-5 mL of 0.1 mol/L KH_2PO_4 and 5 mL of 0.05 mol/L citric acid were added to each tube. Soil/solution ratio was adjusted to 1:25. Initial concentration of phosphate and citrate was 0 to 20 mmol/L and 10 mmol/L, respectively. The tubes were shaken for 24 h at 25 ˚C, centrifuged at 10,000 G for 10 min, filtered through a 0.45-μm membrane filter, and the P concentration in the supernatant was determined by ICP-AES. The experiments were conducted in duplicate. The linear form of the Langmuir adsorption equation was used to describe phosphate adsorption maxima (b) and binding strength (k) on the Andisols. The effects of additional sequences of citric acid and phosphate on phosphate adsorption were also examined. Experiments were conducted as follows: (1) addition of citrate after phosphate adsorption for 24 h at 25 ˚C; (2) addition of phosphate after citrate adsorption for 24 h at 25 ˚C. Other procedures for shaking and determination of P in the supernatant were also the same as mentioned above.

Adsorption isotherms of phosphate in the presence of water-soluble organic matter from cattle manure

The effects of water-soluble organic matter (WSOM) extracted from aerobically composted cattle manure on phosphate adsorption were examined. The well-composted manure sample was oven-dried and ground finely. One gram of the air-dried soil sample and 0.1 g of the oven-dried manure sample were placed in a 50-mL plastic centrifuge tube. 20 mL of 0.15 mol/L KNO_3 at pH5.5 was added to each tube. After shaking for 1 h at 25 ˚C, the pH of the suspension was readjusted to 5.5. 0-5 mL of 0.1 mol/L KH_2PO_4 was added to each tube. 0-5 mL of 0.02 mol/L KH_2PO_4 was also added to each tube to examine the effects of WSOM on phosphate adsorption at lower phosphate concentration (0 to 4 mmol/L). Other procedures for shaking and determination of P in the supernatant were also the same as mentioned above. The experiments were conducted in duplicate.

Pot experiments of the combined application of manure and inorganic phosphate fertilizer

The pot experiment was conducted to investigate the effects of mixing cattle manure with a phosphate fertilizer on the availability of phosphate for plant uptake. Soil sample was collected from an upland field at Obihiro University of Agriculture and Veterinary Medicine, air-dried and passed through 2-mm sieve. The soil is classified as Low-humic Andosols (Typic Hapludands). The soils were amended with 100 mg N/pot from $(NH_4)_2SO_4$, 100 mg K_2O/pot from K_2SO_4, and superphosphate at the rate of 0, 50, 100, and 150 mg P_2O_5/pot (F0, F50, F100, and F150, respectively). The soils were also amended with the same amounts of $(NH_4)_2SO_4$ and K_2SO_4, and the mixture of superphosphate with 5 g of dried and ground cattle manure at the rate of 0, 50, and 100 mg P_2O_5/pot (F0+M, F50+M, and F100+M, respectively). The experiments were conducted in triplicate. The manure contained 9.6 g N/kg, 10.5 g P_2O_5/kg, and 4.7 g K_2O/kg. The amended soil was then moistened to 50 % of water-holding capacity and distributed into the Neubauer's pots (600 mL, 0.01 m^2). Each pot was planted with nine spinach seeds and placed in a growth chamber (day/night temperature, 25/15˚C; photoperiod, 16-h light and 8-h dark; relative humidity of 70 %). After germination, the plants were thinned to three per pot. The spinach shoot and root were harvested after 20 days of growth. The plants were oven-dried at 60 ˚C to determine dry matter yields of spinach. The dried plant samples were then ground and analysed for plant tissue P concentration by the Kjeldahl digestion method and ICP-AES.

Results and Discussion

Effects of citric acid on phosphate adsorption in Andisols

Phosphate adsorption isotherms without citrate for each soil were relatively similar and indicated that the Andisols could fix large amounts of phosphate (Figure 1). The values of adsorption maxima (*b*) calculated from the Langmuir equation were 13.6, 14.7, and 13.9 g P_2O_5/kg for Haplic Wet Andosols (WA), Cumulic Andosols (CA), and Low-humic Andosols (LA), respectively. The suppressive effect of concurrent addition of citrate on phosphate adsorption was observed for all Andisols. At the highest concentration, the reduction of phosphate adsorption reached 20-40 %, and the order of reduction was WA > CA >LA. The effect of the order of addition of citrate and phosphate to the Andisols was also clearly observed. The previous addition of citrate (phosphate after citrate) was more effective to suppress the phosphate adsorption in the WA and CA, where more than 50 % of the phosphate adsorption was reduced. On the other hand, the previous addition of phosphate (phosphate before citrate) was not effective to reduce the phosphate adsorption in the Andisols. When phosphate was added first, phosphate could be adsorbed on the surface-reactive site of the Andisols more easily. In this case, the subsequent addition of citrate only results in desorption of the phosphate which was adsorbed weakly to the surface (Hu *et al.* 2001). The suppressive effect of citrate on the phosphate adsorption was higher in the WA, of which reactive sites for phosphate adsorption dominated by Al-humus complexes (Table 1). The previous addition of citrate could induce citrate adsorption and desorption of humic substances from the solid phase through ligand exchange reaction and/or Al-citrate complexation, resulting in competitive adsorption of phosphate with water-soluble humic substances.

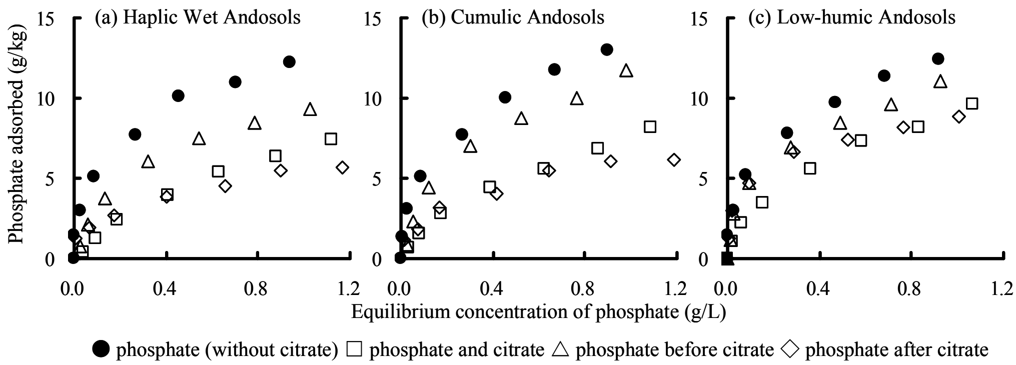

Figure 1. Phosphate adsorption isotherms of the Andisols in the absence and presence of citrate (a) Haplic Wet Andosols, (b) Cumulic Andosols, and (c) Low-humic Andosols.

Effects of water-soluble organic matter from cattle manure on phosphate adsorption in Andisols

The effects of the presence of cattle manure on phosphate adsorption at the high concentration of phosphate were not obvious compared with those of citrate (Figure 2a). However, the effects could be observed clearly at the low concentration of phosphate for all Andisols, especially for the LA (Figure 2b).

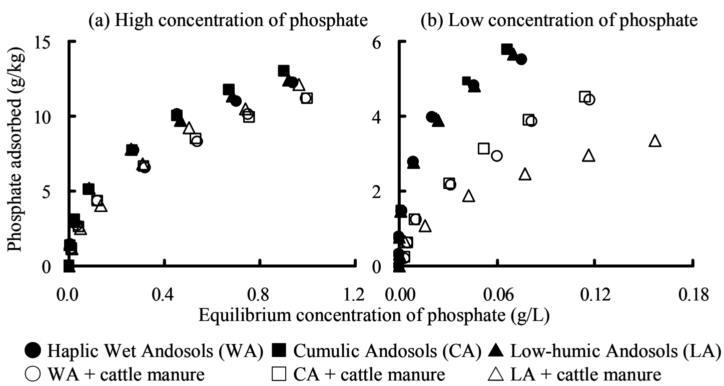

Figure 2. Phosphate adsorption isotherms of the Andisols in the absence and presence of cattle manure (a) at high concentration of phosphate (0-20 mmol/L) and (b) at low concentration of phosphate (0-4 mmol/L).

It had been confirmed that the adsorption of phosphate on the manure and desorption of phosphate from manure had only a slight influence on the phosphate adsorption isotherms from the preliminary experiments (data are not shown). The aerobically composted manure used in this study released a high concentration of water-soluble organic matter (WSOM), of which water-soluble organic carbon content was 15.2 mg C/g and dominated with humic acid (47 %) and fulvic acid (25 %). Strong competition of organic ligands, humic and fulvic acids with phosphate for adsorption sites has been identified as one mechanism by which humic substances inhibit phosphate adsorption by soil colloids (Agbenin and Igbokwe 2006). The values of the binding strength (k) calculated from the Langmuir equation were 0.16, 0.19, and 0.18 in the absence of the manure, and reduced to 0.019, 0.021, and 0.018 in the presence of manure for the WA, CA, and LA, respectively. The most significant effect of WSOM from the cattle manure on phosphate adsorption in the Andisols at the low P concentration was to severely reduce the binding strength (k) of phosphate and possibly induce subsequent phosphate desorption and solubility.

Availability of phosphate in the presence of mixture of cattle manure and phosphate fertilizer

Dry matter yields of spinach and amounts of phosphate absorbed by the plants increased significantly with increase in the amounts of phosphate applied to the pots from an inorganic fertilizer (Table 2). Since sufficient amounts of inorganic nitrogen and potassium were applied to the pots, these results apparently indicate that the phosphate availability was one of the most critical limiting factors for plant growth in the Andisols. When the phosphate fertilizer was mixed with cattle manure, the dry matter yields of spinach shoot increased significantly. At the same level of applied phosphate from the fertilizer and manure, for example, comparing F150 and F100+M, the dry matter yields were not different significantly; however, the amounts of phosphate absorbed by the shoot and whole plants were significantly different. These results indicated that the combined application of manure and inorganic phosphate fertilizer could improve the availability and efficiency of phosphate, by reducing phosphate adsorption and increasing phosphate solubility in the soils.

Table 2. Dry matter yield of spinach and amount of phosphate absorbed by spinach in the pot experiment.

Plot	Phosphate applied ($mg\ P_2O_5$/pot)			Dry matter yield (mg/pot)			Phosphate absorbed ($mg\ P_2O_5$/pot)		
	Fertilizer	Manure	Total	Shoot	Root	Whole	Shoot	Root	Whole
F0	0	0	0	0.10 a	0.05 a	0.15 a	0.25 a	0.12 a	0.37 a
F50	50	0	50	0.22 ab	0.16 b	0.38 ab	0.77 ab	0.83 b	1.60 ab
F100	100	0	100	0.38 bc	0.29 c	0.66 cd	1.96 c	1.68 c	3.63 c
F150	150	0	150	0.65 cd	0.41 d	1.06 e	4.27 d	2.57 d	6.83 e
F0+M	0	52	52	0.34 b	0.14 b	0.48 bc	1.72 bc	0.78 b	2.49 bc
F50+M	50	52	102	0.53 c	0.21 bc	0.74 d	3.68 d	1.45 c	5.12 d
F100+M	100	52	152	0.81 d	0.27 c	1.08 e	5.92 e	2.40 d	8.33 f

Means followed by the same letter within each column are not significantly different at $P < 0.05$ by Tukey's test.

Conclusion

Natural organic ligands, such as organic acids and water-soluble humic substances in the organic amendments, could be interposed between phosphate and reactive sites in Andisols, protecting phosphate from direct interaction or bonding with soil surface-reactive sites, and reducing phosphate adsorption. Phosphate availability and efficiency could be improved by combination of inorganic phosphate fertilizer and manure, probably due to the effects of organic-ligands to reduce phosphate adsorption and increase phosphate desorption in Andisols.

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