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The effect of humic acids on the availability of phosphorus fertilizers in alkaline soils

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Abstract. The effect of humic acids on transformation of phosphorus fertilizer was studied in an alkaline soil. Soil P was fractionated following 4 and 15 days incubation after humic acids were applied with phosphorus fertilizer to the soil. The availability of phosphate in the soil and total phosphorus in plants were determined at earing stage and at maturity in a pot experiment, and wheat yield was examined in a field trial. Addition of humic acids to soil with P fertilizer significantly increased the amount of water soluble phosphate, strongly retarded the formation of occluded phosphate and increased P uptake and yield by 25%.

Keywords: Humic acids, transformation, phosphorus fertilizers, soil, availability, phosphorus, uptake, wheat

INTRODUCTION

A disadvantage of using phosphorus fertilizer is that the availability of the added P can decline rapidly because of fixation in soil. Fixation is believed to be significantly influenced by iron, aluminium and calcium ions in soil (Patti, 1987). Weir & Soper (1963), Sinha (1971) and Martinez *et al.* (1984) have suggested that organic matter, especially humic (HA) and fulvic (FA) acids, may dissolve insoluble phosphates, increasing phosphorus mobility by formation of humic acid-metal-phosphate complexes.

Weir & Soper (1963) reported that humic acids can complex ferric ions, and then hold phosphate ions against an anion resin. The humic acids-iron phosphate complex was found to be nearly all exchangeable, but only a portion of the phosphate was available for plant use. Direct interaction of phosphate with low-ash humic acid or fulvic acid under laboratory conditions indicated that organo-metallic phosphates were formed only when the organic acids contained iron or aluminium (Sinha, 1971). Fulvic acid-metallic phosphate complexes should be more available to plants because of their greater mobility.

Further work by Sinha (1972) showed that fulvic acids can dissolve precipitated phosphates. Formation of complexes between iron, phosphate and fulvic acids may be one of the possible mechanisms involved in the mobilization of insoluble soil phosphate. Martinez *et al.* (1984) showed that the application of HA from lignite in an alkaline soil solubilized P from phosphorites and thus slowly contributed to the soil's available phosphorus. They suggested that instead of using soluble phosphorus fertilizers, HA from lignite should be added to alkaline soils mixed with phosphorite fertilizers. Rubinchik *et al.* (1985) showed that oxidized and ammoniated oxidized coal can increase the solubility of P added to soil as mono-, di-, and tricalcium phosphates.

Yang *et al.* (1985) reported that the addition of humic acids significantly increased plant total P and P uptake as well as yield of wheat. The efficiency of P fertilizer was thereby increased by 40%. Laboratory experiments using an alkaline soil in China (Li & Wang, 1988) also indicated that the available P content of the soil was increased by the addition of humic acids and incubation for one year; phosphate fixation was significantly retarded by mixing humic acids with ammonium dihydrogen phosphate ($NH_4H_2PO_4$).

This paper reports the effect of humic acids on phosphorus availability, P-uptake and wheat yield on an alkaline soil.

MATERIALS AND METHODS

Soil samples for the laboratory study and pot experiment were collected from the 0–15 cm layer of an alkaline soil, located on the southern margin of the Zhunger Basin, China, where a field experiment investigated the effect of humic acids on P-uptake and yield of wheat. This soil was air-dried and crushed to pass a 2 mm sieve. Its properties were: pH, 8.2; organic matter, 0.48%; total N, 0.033%; total P, 0.077%; and CEC, 10.4 meq/100 g soil. Soil pH was determined with a glass electrode (soil/water ratio 1 : 5), organic matter by wet oxidation (Nelson & Sommers, 1982), total N analysis by the regular Kjeldahl method (Bremner & Mulvaney, 1982), total P by the digestion method (Olsen & Sommers, 1982) and CEC by the method for arid land soils (Rhoades, 1982). The humic acids derived from Xinjiang brown coal were provided by Beijing Institute of Chemistry Research, Academia Sinica, China (Table 1).

Laboratory experiment

5 g soil samples were thoroughly mixed with 0.05 g ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and 0.1 g

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Table 1. The properties of humic acids used

	pH (1:2.5)	−COOH	−OH	−CO	molecular weight
		(meq/g)			
HA1	1.15	5.2	1.8	3.38	2542
HA2	3.30	5.2	2.0	3.46	5236
HA3	3.42	2.8	5.0	1.32	3370
HA4	3.35	5.2	1.8	3.38	7834
HA5	5.87	4.9	4.0	2.20	ND

ND = Not determined.

humic acid (HA1, HA2, HA3 or HA4), and watered every second day to keep soil moisture to 60% of its field water-holding capacity. The soil samples were incubated at room temperature, dried and sieved through 100 mesh screen after 4 and 15 days incubation. Soil P was then fractionated by the method of Chang & Jackson (1957). Water soluble phosphorus (H_2O-P) was extracted by 1 N NH_4Cl, aluminium phosphate (Al-P) by 0.5 N NH_4F, iron phosphate (Fe-P) by 0.1 N NaOH, calcium phosphate (Ca-P) by 0.5 N H_2SO_4, and occluded phosphate (Oc-P) by $Na_2S_2O_4$-citrate.

Pot experiment

Four treatments to examine the influence of humic acids on efficiency of P uptake by the crop and crop yield were:

(1) Control – no humic acid or phosphate
(2) P – ammonium dihydrogen phosphate alone
(3) HA5 + ammonium dihydrogen phosphate
(4) HA1 + ammonium dihydrogen phosphate.

i kg of the same alkaline soil was used for each pot. 0.2 g ammonium dihydrogen phosphate with or without 0.2 g HA were applied at 2 cm depth in pellets (2.5 mm in diameter and 2.5 mm in length). Two wheat seeds were sown in each pot. Six replicates were used for each treatment. Two replicates were harvested when earing started, four at maturity. Soil available P was determined by the colorimetric method of Olsen & Dean (1965) because this method is recommended for measuring available P in alkaline soils in China. Plant total P was determined by the same method after digesting plants with concentrated sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2).

Field experiment

This was designed to determine the effect of humic acids on wheat yield on the alkaline soil, which had been abandoned for two years because of its poor productivity. The plot layout consisted of three blocks, each of which contained six plots measuring 21 m². The treatments were:

(1) Control – no humic acid or ammonium dihydrogen phosphate
(2) P – 150 g ammonium dihydrogen phosphate broadcast as powder
(3) HA5 (300) – 300 g broadcast as powder
(4) P + HA5(150) – 150 g ammonium dihydrogen phosphate and 150 g HA5 mixed and broadcast as pellets (2.5 mm in diameter and 2.5 mm in length)
(5) P + HA5(300) – 150 g ammonium dihydrogen phosphate and 300 g HA5 broadcast as powder
(6) P + HA1(150) – 150 g ammonium dihydrogen phosphate and 150 g HA1 mixed and broadcast as pellets (2.5 mm in diameter and 2.5 mm in length).

Spring wheat seeds were sown on 5 April 1986, after application of the treatments. Urea was broadcast over all plots at the rate of 50 kg N/ha on each of 3 dates (5 April, 10 May and 15 June 1986) and followed by watering. Wheat was harvested and yield measured on 14 July.

RESULTS

Laboratory experiment

Table 2 shows the fractionation of soil P from applied ammonium dihydrogen phosphate with and without humic acids after 4 and 15 days incubation. With the addition of ammonium dihydrogen phosphate alone, water soluble P (H_2O-P) declined rapidly during the incubation, from 1450 ppm at day 4 to 851 ppm at day 15, whereas occluded P increased from 1007 ppm at day 4 to 1303 ppm at day 15. The addition of HAs associated with ammonium dihydrogen phosphate significantly increased the amount of H_2O-P in soils, especially at day 15, compared with the treatment without humic acid. Soil H_2O-P was maintained around 1600 ppm during the whole incubation period when HA1, HA2 and HA4 were added to the soil. After addition of ammonium dihydrogen phosphate with HA3, H_2O-P decreased from 1610 ppm at day 4 to 1370 ppm at day 15. Occluded P was markedly decreased by the addition of HAs. HAs inhibited Oc-P formation by 23–40% and 33–60% at days 4 and 15, respectively. The effects of HAs on Fe-P, Al-P and Ca-P was not as large as on water soluble P and occluded P. Soil total inorganic P was not affected by the addition of HAs.

Pot experiment

Fractionation of soil P during wheat growth is given in Table 3. Application of HAs supplied 5–7 ppm more water soluble P to the wheat, whereas the amounts of occluded P were 2–10 ppm less with HAs than without. The addition of HAs significantly decreased the amounts of Ca-P, from 315 ppm to 219–220 ppm at earing stage and from 295 ppm

Table 2. Fractionation of soil P from laboratory study at Days 4 and 15 (ppm)

Treatment	H_2O-P	Al-P	Fe-P	Oc-P	Ca-P	Total
Day 4						
HA1+P	1690	245	18	828	547	3328
HA2+P	1695	295	15	710	590	3305
HA3+P	1610	316	22	823	562	3333
HA4+P	1680	332	4	698	618	3332
P	1458	290	6	1007	697	3458
Control	106	55	3	237	439	840
L.S.D. (5%)	115	51	9	171	59	220
Day 15						
HA1+P	1690	239	23	873	587	3412
HA2+P	1620	381	14	795	663	3473
HA3+P	1370	228	39	963	679	3279
HA4+P	1650	334	15	695	656	3350
P	850	418	6	1303	657	3234
Control	101	59	3	291	467	921
L.S.D. (5%)	107	31	12	340	77	368

H_2O-P = water soluble phosphorus extracted by 1 N NH_4Cl.
Al-P = aluminium phosphate extracted by 0.5 N NH_4F.
Fe-P = iron phosphate extracted by 0.1 N NaOH.
Oc-P = occluded phosphate extracted by $Na_2S_2O_4$-citrate.
Ca-P = calcium phosphate extracted by 0.5 N H_2SO_4.

Table 3. Fractionation of soil P from the pot experiment at two stages of growth (ppm)

Treatment	H_2O-P	Al-P	Fe-P	Oc-P	Ca-P	Total P
At earing						
HA1+P	29	56	3	158	219	465
HA5+P	30	58	2	155	220	465
P	23	53	3	165	315	559
Control	15	50	3	130	225	423
L.S.D. (5%)	9	N.S.	N.S.	10	13	19
At harvest						
HA1+P	23	12	13	122	276	446
HA5+P	23	10	14	123	274	444
P	18	13	15	125	295	466
Control	13	9	16	121	232	391
L.S.D. (5%)	3	N.S.	N.S.	N.S.	10	11

N.S. = Not significantly different.
H_2O-P, Al-P, Fe-P, Oc-P and Ca-P are defined in Table 2.

to 274–276 ppm at harvest. Soil total inorganic P levels were 95 and 20–22 ppm less with HAs than without at earing stage and at harvest, respectively. Water soluble P, Al-P and occluded P decreased during the period of wheat growth in all of the treatments.

Results in Table 4 indicate that the addition of HAs greatly increased soil available P in the earlier stage, from 17 ppm with ammonium dihydrogen phosphate alone to 30 ppm with HA1-ammonium dihydrogen phosphate mixture. Concentrations of total P in the plant were not influenced by addition of ammonium dihydrogen phosphate or HAs in the early stage of wheat growth, but in later stages total P in the plant significantly increased from 0.091% to 0.123% with ammonium dihydrogen phosphate alone and to 0.149–0.159% with HA-ammonium dihydrogen phosphate mixtures. P uptake by plants during the period of wheat growth was increased by ammonium dihydrogen phosphate. The addition of HAs with ammonium dihydrogen phosphate further increased the amounts of P uptake by plants, especially in the later stages. HA1 performed better than HA5 in increasing soil available P, plant total P and P uptake. Addition of ammonium dihydrogen phosphate alone increased wheat yields by 147%. Statistical analysis indicated that the application of HAs with ammonium dihydrogen phosphate increased wheat yield significantly more than the application of ammonium dihydrogen phosphate alone. HA1 gave a greater yield than HA5, but the difference between them was not statistically significant.

Field experiment

In the field trial, wheat yield was increased by 8.6% by the addition of ammonium dihydrogen phosphate, by 25.4% by the addition of HA5, and by 31.8–36.5% by the addition of HAs with ammonium dihydrogen phosphate (Table 5). The yield with ammonium dihydrogen phosphate alone was not significantly different from that of the control treatment. However, the addition of HAs greatly increased yield. No significant differences were found between the treatments with different HAs, and there was no evidence of a synergistic effect when HAs were added with ammonium dihydrogen phosphate in the field experiment.

DISCUSSION

Total inorganic P in the alkaline soil decreased from 840–921 ppm without plants to 391 ppm after wheat growth where ammonium dihydrogen phosphate was not applied (Tables 2 and 3). The concentration of total inorganic P in the soil was greater during the period of wheat growth when ammonium dihydrogen phosphate was applied alone compared with the HA-ammonium dihydrogen phosphate mixtures. In contrast, the concentration of total P in the plant at harvest was less without HAs than with HAs. These results suggest that the addition of HAs to phosphorus fertilizer made more of the P available to plants, decreased phosphorus fixation in the soil, increased P uptake and increased the yield of wheat.

The field experiment showed that yield of wheat was increased simply by the addition of HA alone, although greater yields were obtained with HA plus ammonium dihydrogen phosphate. The effects of HAs in increasing yield could include microbiological stimulation (Petrovic *et al.*, 1982) and structural or pH amelioration of the alkaline soil (Li & Wang, 1988). Azam & Malik (1983) reported that soaking wheat seeds in a solution of HAs increased seedling growth, improved root development and enhanced uptake of water by the roots. Abadia (1984) stated that HAs have very small effects on extractability of microelements and P, and suggested that their effect in enhancing plant growth

Table 5. Wheat yields from the field trial (kg/plot)

Treatment		Mean	Increase
Control		29.9 a	
P	broadcast as powder	32.5 a	8.6%
HA5(300)†	broadcast as powder	37.5 b	25.4%
P-HA5(150)†	broadcast as pellets	39.4 b	31.8%
P-HA5(300)	broadcast as powder	40.4 b	35.1%
P-HA1(150)	broadcast as pellets	40.8 b	36.5%

Means followed by the same letter are not significantly different at the 5% level.
† The amounts of humic acid added were 300 or 150 g/plot.

Table 4. Soil available P, plant total P, P uptake and wheat yields from the pot experiment

	Earing stage			Harvest stage			
Treatment	Available P (ppm)	Total P (%)	P uptake (mg/pot)	Available P (ppm)	Total P (%)	P uptake (mg/pot)	Yield (g/pot)
HA1+P	30	0.195	2.90	17	0.159	5.53	3.48
HA5+P	29	0.164	2.02	16	0.149	4.75	3.19
P	17	0.152	1.93	11	0.123	2.79	2.27
Control	12	0.159	0.71	7	0.091	0.84	0.92
L.S.D. (5%)	11	N.S.	0.27	4	0.013	0.35	0.81

N.S. = Not significantly different.

may result from changes at the soil–root interface that make nutrients more available.

CONCLUSIONS

The availability of phosphorus in fertilizer added to alkaline soil can be increased by the application of humic acids. They decrease phosphorus fixation and provide more water soluble P for the plant. Wheat yield and P uptake were both increased by the presence of humic acids.

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