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ON THE MECHANISM OF PHOSPHORUS-COPPER INTERACTION IN CORN AND FLOODED RICE ON A CALCAREOUS SOIL

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Abstract. Application of P to a calcareous soil depressed Cu uptake in corn but enhanced its uptake in submerged rice. Increased Cu uptake in rice occurred by two processes; by enhanced plant growth and by Mn stimulation of Cu absorption by rice roots. Phosphorus had markedly increased Mn concentration in soil percolate. Copper solubility decreased but its depressing effect on Cu contents in plants was overshadowed by relatively a greater Mn and plant growth stimulation of Cu uptake in rice. By contrast to their strong inhibition in upland crops, H, Zn, and Fe had no effect on Cu absorption by lowland rice.

Copper fertilizer did not influence P uptake in either corn or rice plants.

Copper deficiency occurs in lowland rice on many calcareous soils of Pakistan.[14] These soils also receive liberal application of phosphatic fertilizers. The literature on P-Cu interaction indicates P to strongly inhibit Cu uptake by plants[3,4,10,15] and to accentuate its severe deficiency in upland crops. Such studies have rarely been conducted on flooded rice. Rice, being physiologically different from upland crops responds differently to nutrient interaction. For example, Mn shows no effect on Zn absorption by upland plants[6,7] but strongly inhibits its uptake in lowland rice.[16] Similarly P depressed Zn contents in corn but enhanced its uptake in rice.[12] The nature of Fe-Cu and Mn-Fe interactions in flooded rice is similarly different from that in barley.[8] A preliminary study at Riso (India) on a calcareous soil shows that contrary to its effect in upland crops, P may have little effect on Cu uptake by flooded rice. The results, however, were not definitive and needed further information for proper evaluation. The present soil and solution culture studies were, therefore, conducted to investigate the effect of P on Cu uptake and to understand the mechanism of P-Cu interaction in submerged rice. The results were compared with those on corn.

Materials and Methods

Effect of P on Cu Uptake by Rice and Corn from Soil. A surface calcareous soil to a depth of 15 cm was collected from the Rice Research Institute, Kala Shah Kaku, (Punjab). It was air-dried, crushed in a wooden mortar, passed through a 2-mm plastic sieve and analysed for the various physicochemical properties. The soil (pH 8.3) was clayey in texture, contained 1.2% organic matter, 12.7 p.p.m. $NaHCO_3$-extractable P, 1.9% $CaCO_3$ and 3.8 p.p.m. DTPA (diethylenetriamine pentaacetic acid) extractable Cu.[18] Soil portions of 4.5 kg were filled in polythene lined plastic pots of 20-cm surface dia. and 23 cm height. The basal fertilizer dressing consisted of 75 p.p.m. N as urea. Treatments included were O, 2. 5, 5.0 p.p.m. Cu (as $CuSO_4$) and O, 16, 32 p.p.m. P (as KH_2PO_4) for rice and O, 5 p.p.m. Cu and 13, 16 p.p.m. P for corn experiments. The treatments in factorial combination were imposed in triplicate. All the fertilizers were thoroughly mixed with soil before planting. Six 20-day old nursery seedlings of Basmati-370 rice (*Oryza sativa* L.) were planted in each pot in August 1974 and the pots kept flooded with deionized water throughout plant growth. For corn (*Zea mays* L.) experiment, 10 seeds of J-1 maize hybrid were sown in each pot and the stand thinned to 5 healthy plants 10 days later. The soil in pots was brought to field capacity every day by addition of deionized water.

Rice and corn plants were harvested by cutting at ground level 35 days after sowing, rinsed thoroughly in two baths of deionized water, dried in paper sacs at 70°C and ground in a Wiley mill fitted with stainless steel blades and other interior parts of the cutting chamber. One g portion of the ground material was digested with 25 ml diacid mixture (redistilled HNO_3 and $HClO_4$ at 4:1). Copper in the diluted digest was determined by atomic absorption spectroscopy[1] and P by spectro colorimetry after developing metavanadate yellow colour.[13] Total Cu and P contents were calculated by multiplying their concentration with plant dry matter yields.

Effect of P on the Solubility of Cu and other Ions in Soil. The effect of P on the solubility kinetics of Cu and other ions in submerged soil was studied according to the method of Rahmatullah *et al.*[16] Soil portions of 4.5 kg were filled in plastic pots and treated with nil or 64 p.p.m. P (as KH_2PO_4) in triplicate. Pots were flooded with deinoized water and a 5-cm level of standing water was maintained for six weeks during the rice growing months of August and September in 1974. About 150 ml soil percolate was drawn out by gravity each week through side holes of pots in conical flasks previously filled with N_2 gas. The pH was immediately determined by drawing small portions of percolates in a specially designed oxygen-free cell. Six drops of concd H_2SO_4 were added to the remaining solutions to avoid oxidation. They were then analysed for Cu, Zn, Mn, Fe, Ca and Mg by

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atomic absorption spectroscopy[1] and for P by spectroclorimetry.[13]

Effect of Various Ions on Cu Absorption by Rice Roots from Solutions. The method of seedling growth and absorption studies has been described in detail elswehere.[14,16] Intact rice seedlings grown on a complete nutrient solution[14] for 10 days were allowed to absorb Cu for 2 hr from solutions of 10 μM $CuCl_2$ and 500 μM $CaCl_2$ containing various nutrient treatments (Table 4). The pH of absorbing solution was adjusted at 5.7 and temperature at 20 C. The solutions were continuously aerated during absorption period. The electrostatically adsorbed Cu on roots was eliminated by washing them for 30 min. in a solution of 500 μM $CaCl_{62}$ at 5°C. The roots before and after Cu absorption were digested in redistilled HNO_3-$HClO_4$ mixture and their Cu contents determined with an atomic absorption spectrophotometer.[1] Rates of Cu absorbtion was calculated from difference in their Cu contents.

Results and Discussion

Application of P increased concentration and total contents of P in corn plants (means significantly different at $P<0.05$ or 0.01, (Table 1). It strongly depressed Cu concentration in corn plants (P of means <0.01). The effect was purely antagonistic since total Cu contents also declined markedly (P of means <0.01) except in the presence of 5 p.p.m. Cu where depression was relatively small. The present results, thus, support the existing literature indicating P inhibition of Cu uptake in upland crops.[3,4,10,15] Precipitation of Cu as $Cu_3(PO_4)_2$, its inhibition of Cu absorption mechanism[6] or reduction in its translocation from roots to shoots 15 were reported to be responsible.

Phosphatic fertilizer increased P uptake in submerged rice (means significantly increased at $P<0.05$ or 0.01 (Table 2). It has no effect on Cu concentration (small differences were insignificant) but strongly increased total Cu-contents in all the treatments (P of means <0.05) except in 10 p.p.m. Cu where Cu stimulation did not occur. Thus the results support the only two earlier reports indicating P to have either little[2] or enhancing effect[9] on total Cu-contents in swamp rice. The nature of P-Cu interaction in these studies could not be evaluated since they did not report dry matter yield or Cu concentration in plants. Phosphorus seems to increase Cu uptake in rice atleast partly through higher root proliferation in soil from increased plant growth. Thus, in most of the treatments, it increased Cu contents in plants only when plant yield was also enhanced. A highly significant correlation ($r=0.85$, $P<0.01$, calculated from Table 2) existed between dry-matter yield and total Cu-contents in rice plants. In addition to yield effect, additional processes seem to be also involved in P-Cu interaction in Cu uptake by rice.

TABLE 1. EFFECT OF PHOSPHORUS AND COPPER APPLICATION ON DRY MATTER YIELD AND ON THEIR UPTAKE BY CORN FROM A CALCAREOUS SOIL.

Fertilizers applied (p.p.m.) Cu	P	Dry matter yield (g/pot)	Cu concn in plants (p.p.m.)	Total Cu contents in plants (Ug/pot)	P concn in plants (%)	Total P contents in plants (mg/pot)
0	13	3.89	9.76	38.2	0.12	4.77
	26	4.03	6.06	24.4	0.19	7.62
5	13	3.79	12.91	49.1	0.11	4.16
	26	5.57	8.03	45.2	0.14	8.26

TABLE 2. EFFECT OF PHOSPHORUS AND COPPER APPLICATION ON DRY MATTER YIELD AND THEIR UPTAKE BY FLOODED RICE CORN FROM A CALCAREOUS SOIL

Fertilizers applied (p.p.m.) Cu	P	Dry matter yield (g/pot)	Cu concn in plants (p.p.m.)	Total Cu contents in plants (Ug/pot)	P concn in plants (%)	Total P contents in plants (mg/pot)
0	0	6.2	11.7	72.7	0.21	12.8
	16	6.4	13.1	81.2	0.26	16.4
	32	8.8	11.2	97.9	0.26	22.4
	64	8.5	11.9	101.4	0.28	23.5
2.5	0	7.7	10.2	78.1	0.19	14.1
	16	9.6	11.7	111.3	0.19	18.1
	32	8.8	11.8	102.0	0.25	21.6
	64	8.5	12.2	103.1	0.28	23.3
5.0	0	6.9	11.9	80.7	0.21	13.8
	16	8.8	12.1	108.0	0.19	16.4
	32	8.7	14.3	123.9	0.24	20.1
	64	7.5	11.6	88.0	0.28	21.1
0.0	0	7.7	14.8	114.9	0.17	12.6
	16	7.7	15.2	116.5	0.19	14.6
	32	8.1	14.4	117.2	0.22	17.4
	64	7.0	13.3	93.1	0.24	16.2

TABLE 3. EFFECT OF PHOSPHORUS ON KINETICS OF WATER SOLUBLE COPPER AND OTHER IONS IN SUBMERGED CALCAREOUS SOIL.

Treatments	Weeks after submergence					
	I	II	III	IV	V	VI
Cu Concentration (p.p.m.)						
Control	0.05	0.05	0.03	0.03	0.02	0.02
64 p.p.m. P	0.03	0.03	0.02	0.02	0.02	0.01
(P Concentration (p.p.m.)						
Control	0.09	0.06	0.04	0.04	0.05	0.19
64 p.p.m P	0.17	0.28	0.24	0.19	0.13	0.36
pH						
Control	7.8	7.8	7.7	7.9	7.8	8.1
64 p.p.m. P	7.7	7.7	7.5	7.8	7.7	7.8
Zn Concentration (p.p.m.)						
Control	0.50	0.32	0.36	0.28	0.29	0.18
64 p.p.m. P	0.62	1.33	1.23	1.05	0.78	0.10
Mn Concentration (p.p.m.)						
Control	0.15	0.39	0.78	0.23	0.26	0.38
64 p.p.m. P	0.06	0.66	2.67	3.52	3.03	4.30
Fe Concentration (p.p.m.)						
Control	0.41	0.23	0.21	0.29	0.15	0.30
64 p.p.m. P	0.20	0.20	0.15	0.24	0.54	1.67
Ca Concentration (p.p.m.)						
Control	644	471	340	260	194	153
64 p.p.m. P	456	423	396	323	255	193
(Mg Concentration (p.p.m.)						
Control	111	95	81	72	62	50
64 p.p.m. P	62	90	91	86	77	72

Kinetic studies on Cu solubility indicated P to depress Cu concentration in soil solution at most of the intervals of soil incubation ($P<0.05$, Table 3). Its mechanism is not known but Cu precipitation as $Cu_3(PO_4)_2$ may have been involved. The pH effect was not important [3] as KH_2PO_4 used in these studies did not increase soil pH. Concentration of Ca and Mg did slightly increase but they do not interact with Cu on specific adsorption surfaces of soil. Zn., Mn and Fe strongly complete with Cu for adsorption sites [11,17] but their increased concentration in soil percolate (Table 3) could be expected to increase rather than depress Cu-contents in soil solution. Whatever the mechanism may be, the reduced Cu solubility with P application could be expected to severely decrease Cu uptake in plants.[6] This effect would have been quite evident in cases where plant yield did not increase Cu uptake in plants as in treatment of 10 p.p.m. applied Cu (Table 2). The expected decreased Cu uptake in plants from lower Cu solubility, however, appears to be strongly counteracted by a marked Mn stimulation of Cu absorption by rice roots ($P<0.01$, (Table 4). Phosphorous had increased Mn contents in soil solution many fold (Table 3) which enhanced rate of Cu absorption to almost double. Manganese is, therefore, at least partially responsible for P stimulation of Cu uptake in submerged rice. Thus, at least three simultaneous operating processes account for P-Cu interaction in Cu nutrition of flooded rice: depression in Cu solubility tends to decrease Cu uptake by plants which is completely overshadowed by relatively a higher stimulatory effect of Mn and plant yield resulting generally in a net increase in total Cu-contents in rice plants. Most surprisingly Zn, Fe and H which strongly depress Cu absorption by upland plants showed no effect on Cu uptake in flooded rice (Table 4).

TABLE 4. EFFECT OF VARIOUS IONS ON COPPER ABSORPTION BY BASMATI-370 RICE FROM SOLUTIONS CONTAINING 10 μM $CuCl_2$ AND 500 μM $CaCl_2$.

Treatments	pH of nutrient solution	Rate of Cu absorption (μg atom/g fresh root/hr)
Control	5.7	2.76
20 μM $ZnCl_2$	5.7	2.28
30 μM $FeCl_2$	5.7	2.44
50 μM $MnCl_2$	5.7	4.09
5 μM CaClw	5.7	2.36
500 μM $MgCl_2$	5.7	2.99
HCl	4.7	2.76

Application of Cu did not influence concentration and total contents of P (small differences were generally insignificant) either in corn (Table 1) or in flooded rice (Table 2).

Discussion

The present studies substantiate earlier reports indicating differential nature of nutrient interaction in swamp rice than in upland crops.[8] Thus P strongly depressed Cu uptake in corn but increased its uptake in rice. Similar discrepancy in P effect on Zn uptake by the two plant species was observed in our other studies.[12] Nutrient interaction of upland crops seem to have little implication in flooded rice and must be studied separately for rice.

Kausar *et al.*,[14] found Cu deficiency in submerged rice on many calcareous soils supporting normal growth of wheat and other upland crops. Since deficiency was highly correlated with the length of period of soil flooding during rice growth, they postulated increased contents of P, Zn, Mn, Fe and H in flooded soil[16] to be mainly responsible for Cu deficiency in rice since these ions have been reported to strongly inhibit Cu absorption by roots of upland crops.[6] The present studies do not support this hypothesis since Zn, Fe and H had little influence and Mn and P, by contrast, stimulated Cu absorption in flooded rice.

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