

# Effect of Different Fertilizers on Cu Uptake and Distribution in Paddy Plant

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**Abstract:** Pot experiments were conducted to study the effects of 8 fertilizers ( $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{KCl}$ ) on Cu uptake and distribution by paddy plant. The results indicated that nitrogen and potassium fertilizers had little effect on the biomass and yield of paddy, while the phosphate fertilizers significantly increased the biomass and yield of paddy. The total amount of Cu in rice were decreased by 13.5%~60.0% after fertilizers were applied(except  $\text{NH}_4\text{NO}_3$ ). Applying  $\text{NH}_4\text{NO}_3$  and  $\text{KH}_2\text{PO}_4$  all significantly increased the concentration of Cu in the shoot of paddy, whereas the rest 6 fertilizers decreased the concentrations of Cu in the shoot of paddy. The concentration of Cu in the grain under maturity stage were 13.926~30.148 mg/kg after fertilizer were applied, which increased by 2.85%~ 124.63%, and had significantly exceeded the national food heavy metal limits hygienic standard (10 mg/kg, GB15199-94). This study suggests that fertilizer application significantly increased the uptake of Cu of grain, and the effects of 8 fertilizers in the order:  $\text{KCl} > \text{NH}_4\text{Cl} > \text{K}_2\text{SO}_4 > \text{CO}(\text{NH}_2)_2 > \text{Ca}(\text{NO}_3)_2 > \text{Ca}(\text{H}_2\text{PO}_4)_2 > \text{NH}_4\text{NO}_3 > \text{KH}_2\text{PO}_4$ .

**Keywords:** paddy; uptake; distribution; Cu; fertilizers

## 1 Introduction

Since the 20th century, with the rapid development of mining industry, manufacturing, metallurgical industry and transportation, extensive use of agrochemicals and urban sewage discharge, heavy metal pollution to agricultural production and ecological environment became more and more serious. And it had definitely put great threaten to agricultural production in many areas. According to statistics, there is about 15000 t of Hg, 5 million t of Pb, 3.4 million t of Cu, 1 million t of Ni, 15 million t of Mn enter into environment every year over the world<sup>[1]</sup>, in which a large number of Cu into the soil, thus Cu become one of the major pollutants in the soil. Low concentration of Cu is necessary for plant growth, when lack of copper the plant will appear deficiency disease<sup>[2]</sup>. But excessive Cu will block the growth of crops and reduce yields, and it can uptake by plants and accumulate in the edible parts, which may pose a serious threat to human health<sup>[3]</sup>.

Commercial fertilizers play an important role in increasing food production, but they may also increase the uptake of heavy metals by plants through improvement in plant growth and in rooting intensity. Fertilizers can alter soil properties such as pH, surface charge, ionic constituents in solution and CEC or can directly react with heavy

metal ions<sup>[4-6]</sup>. All these effects would change the forms of heavy metals in soil and the uptake and distribution of heavy metal by plants. At present, large number of studies which concerned the impact of chemical fertilizer on heavy metals uptake by plants were carried out, but the related research reports mainly focused on Cd, Zn, Pb<sup>[7-10]</sup> and relatively few works involved in Cu. Therefore, it is extremely necessary to study the effect of different fertilizers on Cu uptake and distribution of plants in contaminated soil. This study was planned to investigate the effect of Cu uptake and distribution in rice after applying different fertilizers, and expected to give some advice for utilization of chemical fertilizers in metal-contaminated soil.

## 2 Materials and Methods

### 2.1 Materials

The soil used for pot experiment in this study was collected from a paddy field located in Guilin institute of agricultural sciences, China. The soil contained 25.3% clay, 32.7 g/kg total organic matter, 1.82 g/kg total N, 1.22 mg/kg total P, 46.64 mg/kg Cu and had a pH value (1:2.5 soil/water) of 7.74. Soil was sampled from 0 to 20 cm depth. The collected soil was air-dried and passed through 2-mm sieves. Then the screened soil was put into 45-cm diameter and 55-cm height plastic pots. The rice which named "II You No.838" were used for pot experiment, and it is broadly cultivated in the local fields.

### 2.2 Pot experimental

The amount of screened soil was 10 kg per pot and

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cow manure was the source of organic matter. Soil and organic matter mixture was allowed to react for two weeks in moist condition prior to transplanting rice seedlings. Cu solution was added to the pots as  $\text{CuSO}_4$  in 150 mg/kg level. Each pot received uniform basal application of 8 g/kg of complex manure, and the soil was mixed thoroughly. Prior to planting, the soil was flooded and allowed to equilibrate. After 10 days, 3 rice seedlings were transplanted into the pot soil submerged with a 2-3 cm layer of water. The pots were placed in an open-air networks indoors and the rice plants were kept flooded during the whole growing period.

The pot experiment including 8 fertilizers treatments and 1 non-fertilizer (control) were arranged. Each treatment was replicated three times. The fertilizers used in this study were  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{KCl}$ . During the whole growing period, nitrogen fertilizer was applied as 60 mg N/kg for additional fertilizer and 90 mg N/kg for earing fertilizer to each pot, respectively; phosphate fertilizer as basal fertilizer 140 mg P/kg to each pot; potash fertilizer as additional fertilizer 280 mg K/kg to each pot.

### 2.3 Sample Collection and Analysis

During the harvest time, plants were removed carefully and washed first with tap water followed by de-ionized water three times. Root, stem, leaf and grain were separated and then killed out. Then oven dried to a constant weight at 80°C. After drying, roots, stems and leaves were ground to powders using a Wiley Mill, and grain divided into grain and hull. All of the samples were treated with 4:1 concentrated  $\text{HNO}_3:\text{HClO}_4$ , and diluted to 25 cm<sup>3</sup> with 0.2%  $\text{HNO}_3$  solution. A quality control was implemented which included guaranteed reagent, reagent blank, one duplicate sample for every five samples, national reference material(GBW07604) and all required containers, glass wares etc. were previously soaked in 10%  $\text{HNO}_3$  and rinsed with deionized water. The concentration of Cu in the digested solution was measured by a flame atomic adsorption spectrophotometer (PE-AA700, Perkin Elmer, USA).

## 3 Results and Discussion

### 3.1 Effect of Different Fertilizers on Biomass and Yield of Paddy Plants

The effects of different fertilizers on biomass and yield of paddy plants are shown in Table 1. There was consistent effect of fertilizer type on the growth of paddy plants. Compared with the control, the yield of paddy was decreased after application of  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CO}(\text{NH}_2)_2$  and  $\text{K}_2\text{SO}_4$  with 9.2%, 17.6%, and 8.4%, respectively. While the application of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{KCl}$  and  $\text{KH}_2\text{PO}_4$  significantly increased the yield of

paddy by 23.0%, 11.0%, 61.7%, 16.4% and 69.8%, respectively. Moreover, the dry matter weight and 1000-grain weight by applying phosphate fertilizer were significantly higher than potassium, nitrogen and the control treatment. These results indicated that phosphate fertilizer application significantly promoted paddy to absorb nutrients and moisture from the soil, enhance its growth and development, increase in grains per spike, make grain full, raises the paddy yield.

**Table 1. Effect of different fertilizers application on growth and dry matter yield of paddy plants**

Fertilizers	Dry matter weight (g/pot)	Plant height (cm)	1000-grain Weight (g/pot)	Yield (g/pot)
Control	214.68	138.1	26.95	114.74
$\text{NH}_4\text{Cl}$	279.00	145.6	27.22	141.07
$\text{NH}_4\text{NO}_3$	243.96	142.4	27.13	127.38
$\text{Ca}(\text{NO}_3)_2$	215.82	138.7	27.35	104.24
$\text{CO}(\text{NH}_2)_2$	209.92	142.8	27.08	94.57
$\text{K}_2\text{SO}_4$	188.52	135.6	26.93	105.05
$\text{KCl}$	240.84	144.2	27.06	133.61
$\text{Ca}(\text{H}_2\text{PO}_4)_2$	306.82	146.4	28.39	185.55
$\text{KH}_2\text{PO}_4$	334.97	147.2	28.26	194.84

Note: These data are the mean value of three repeats, the followings are identical

### 3.2 Effect of Different Fertilizers on Cu Uptake and Distribution in Paddy Plant

The total amount of Cu in paddy were significantly decreased after fertilizers (except  $\text{NH}_4\text{NO}_3$ ) were applied (Figure 1 and Figure 2). Compared with control, the Cu concentration in the paddy increased by 6.9% after application of  $\text{NH}_4\text{NO}_3$ , but addition of  $\text{NH}_4\text{Cl}$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CO}(\text{NH}_2)_2$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{KCl}$  decreased the Cu concentration in the paddy by 34.8%, 50.8%, 50.9%, 62.0%, 27.9%, 41.9%, and 13.5%, respectively, and the most obvious effect of which was the application of  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ . This study suggests that fertilizer application can reduce the total amount of Cu which uptake by rice. AN et al<sup>[11]</sup> suggested that there might be attributed to two aspects of impact which could affect the uptake of heavy metals by plants after applying a large number of nutrition such as nitrogen, phosphorus and potassium fertilizer. On one hand, the availability of heavy metals in soil may be reduced due to a large number of application of nutrients, then the uptake and content of heavy metals in plants were decreased, thus reducing the damage caused by heavy metal stress; on the other hand, there may improve the energy metabolism of plants by nutrition elements application, thus enhanced the resistance of plants to heavy metals.

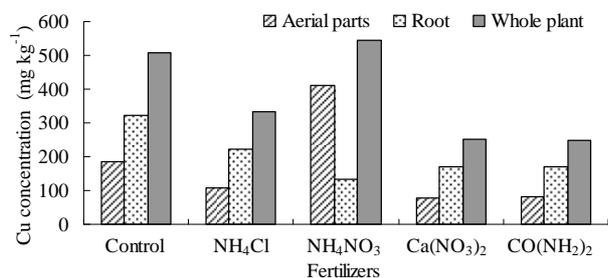


Figure 1. Effect of N fertilizer on Cu uptake by paddy

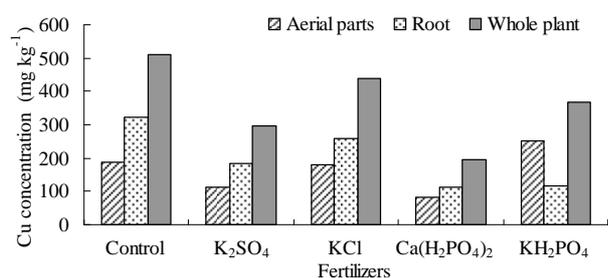


Figure 2. Effect of K or P fertilizer on Cu uptake by paddy

**Table 2. Cu distribution in the different tissues of paddy mg/kg**

Treatment	Root	Stem	Leaf	Grain	Chaff	Aerial part	Whole plant
Control	323.130	86.595	76.011	13.541	9.500	185.646	508.776
Nitrogen	174.466	38.003	107.294	18.785	5.219	169.302	343.768
Potassium	220.319	57.210	56.639	25.801	7.784	147.434	367.753
Phosphate	113.634	32.469	115.205	14.965	3.931	166.569	280.203
The mean	170.721	41.421	96.608	19.584	5.538	163.152	333.873

Note: The dates of nitrogen, potassium, phosphate line are the mean value of results by nitrogen, potassium, phosphate treatment, respectively. And the dates of last line are the mean value of results of all fertilizers treatment.

The distribution and transfer of Cu in paddy was significantly affected by fertilizer application. The addition of fertilizers significantly decreased the Cu concentrations in roots by 20.0% ~ 65.2%; and the Cu concentrations of aerial parts ranged from 78.014 mg/kg to 410.288 mg/kg, which the mean was 163.152 mg/kg, increased by 12.4% compared with the control (Table 2). However, the effect of different fertilizers on Cu distribution and transfer in paddy plants was different (Figure 3 and Figure 4). Compared to the control, the addition of NH<sub>4</sub>NO<sub>3</sub> increased the Cu concentrations in aerial parts by 121.0%, while applying NH<sub>4</sub>Cl, Ca(NO<sub>3</sub>)<sub>2</sub>, CO(NH<sub>2</sub>)<sub>2</sub> decreased the Cu concentrations in aerial parts by 41.6%, 58.0%, 56.6%, respectively. However, after application of 4 nitrogenous fertilizers, the Cu concentrations in grain were all higher than controls, but the rest parts of the content of Cu were significantly lower than control. Therefore, NH<sub>4</sub>NO<sub>3</sub> stimulated Cu transfer from the roots

to the aerial parts and a large number accumulate in leaf, while NH<sub>4</sub>Cl, Ca(NO<sub>3</sub>)<sub>2</sub> and CO(NH<sub>2</sub>)<sub>2</sub> were reduced the amount of Cu transfer from roots; but the 4 nitrogen are enhanced the Cu transfer and accumulation in grain. These indicated that the coexistence of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> may have the ability of enhancing Cu transfer from roots to the aerial parts in rice. Because of NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub> have the same cation, while NH<sub>4</sub>NO<sub>3</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> have the same anion, but the effect of them on Cu transfer from roots to the aerial parts in paddy was contrary.

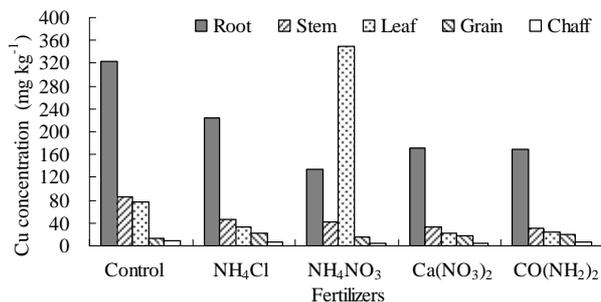


Figure 3. Effect of N fertilizer on Cu distribution in paddy

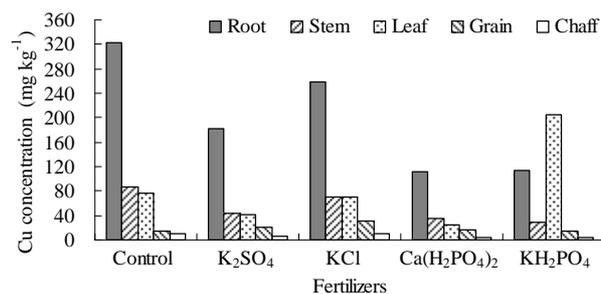


Figure 4. Effect of K or P fertilizer on Cu distribution in paddy

Compared with the control, application of K<sub>2</sub>SO<sub>4</sub>, KCl decreased the Cu concentrations in aerial parts by 38.9%, 2.3%, respectively. The Cu concentrations in grain which accounted for 7.2%, 6.9% of the total Cu of plants were increased by 56.4%, 124.6% to the control, respectively. Moreover, after application of KCl, the Cu concentrations in stems, leaves and hulls were slightly lower than control, while application of K<sub>2</sub>SO<sub>4</sub>, the Cu concentrations in roots, stems, leaves and hulls were significantly lower than control and KCl. This result shows that K<sub>2</sub>SO<sub>4</sub>, KCl were decreased the total amount of Cu that transfer from roots to aerial parts, but stimulated Cu accumulation in grain, and its impact were significantly higher than the 4 nitrogenous and 2 phosphate fertilizers. In addition, the effect of inhibition which on Cu transfer from roots to aerial parts in paddy was significantly higher by K<sub>2</sub>SO<sub>4</sub> than KCl, so, this result indicated that the coexistence of SO<sub>4</sub><sup>2-</sup> may have the ability of reducing Cu transfer from roots to aerial parts in paddy.

Compared with the control,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  supply led to a decrease in the Cu concentrations of aerial parts, roots, stems, leaves and hulls, with a decreasing percentage of 56.4%, 65.2%, 59.5%, 66.6% and 52.4%, respectively. However, application of  $\text{KH}_2\text{PO}_4$  caused an increase in the Cu concentrations by 35.8% for aerial parts, 169.8% for leaves, but reduced the Cu concentrations by 64.5% for roots, 65.5% for stems, 64.9% for hulls. Moreover, the Cu concentrations in grain which accounted for 8.3%, 3.8% of the total Cu of plants were increased by 18.2%, 2.8% to control, respectively. This reflects that  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  reduced the amount of Cu which transferred from roots to the above ground, while  $\text{KH}_2\text{PO}_4$  significantly stimulated transfer of Cu from roots to aerial parts in paddy, but they also have contributed to the transfer and accumulation of Cu for grain. These findings imply that the coexistence of  $\text{Ca}^{2+}$  may have the ability of reducing Cu transfer from roots to aerial parts in paddy.

The distribution of Cu in paddy was in the order of roots > stems > leaves > grain > chaff by the control, however, the order became to roots > leaves > stems > grain > chaff after fertilizers application. The application of different fertilizers significantly affected the uptake and distribution of Cu by paddy, although there were some differences among them. It should pay more attention to that the addition of 8 fertilizers all have contributed to Cu transfer from roots, stems and leaves to grain, and lead to the concentrations of Cu in grain were increased by 2.85% ~ 124.63% compared to the control. This indicated that 8 fertilizers could increase the Cu concentration of the edible part of paddy plants and thus the trend of ecological health risks of Cu in paddy plant maybe increased by fertilization. Kashem<sup>[12]</sup> observed that fertilizer cations increased the uptake of metals by improving growth conditions of plants. Therefore, the increase of Cu which transferred from other parts to grain may be due to the growth conditions of paddy was improved by fertilization. Compared with the control, the effects of 8 fertilizers on Cu uptake by grain was in the order of  $\text{KCl} > \text{NH}_4\text{Cl} > \text{K}_2\text{SO}_4 > \text{CO}(\text{NH}_2)_2 > \text{Ca}(\text{NO}_3)_2 > \text{Ca}(\text{H}_2\text{PO}_4)_2 > \text{NH}_4\text{NO}_3 > \text{KH}_2\text{PO}_4$ .

#### 4 Conclusions

The study showed that nitrogen and potassium fertilizers had no significantly in biomass, while the phosphate fertilizers significantly increased biomass. Application of  $\text{K}_2\text{SO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CO}(\text{NH}_2)_2$  led to paddy yield decreased by 8.4% ~ 17.6%, while the rest 5 fertilizers made paddy yield increased by 11.0% ~ 69.8%.

Compared with the control, the total amount of Cu in paddy were decreased by 13.5% ~ 62.0% after fertilizers (except  $\text{NH}_4\text{NO}_3$ ) were applied, it is due to the Cu concentration in roots significantly decreased. The Cu concentrations in aerial parts of paddy obviously in-

creased after application of  $\text{NH}_4\text{NO}_3$  and  $\text{KH}_2\text{PO}_4$ , while  $\text{NH}_4\text{Cl}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CO}(\text{NH}_2)_2$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  significantly decreased the Cu concentrations in aerial parts of paddy. But it had little effect on KCl.

The Cu concentration in grain under maturity stage were 13.926 ~ 30.418 mg/kg after 8 fertilizers were applied, which increased by 2.85% ~ 124.63%, and had significantly exceeded the national food heavy metal limits hygienic standard. This shows that fertilizer application significantly increased the uptake of Cu in grain, and the effects of 8 fertilizers was in the order of  $\text{KCl} > \text{NH}_4\text{Cl} > \text{K}_2\text{SO}_4 > \text{CO}(\text{NH}_2)_2 > \text{Ca}(\text{NO}_3)_2 > \text{Ca}(\text{H}_2\text{PO}_4)_2 > \text{NH}_4\text{NO}_3 > \text{KH}_2\text{PO}_4$ . In Cu contaminated soils, therefore, application of NPK fertilizers could give priority to  $\text{NH}_4\text{NO}_3$  and  $\text{KH}_2\text{PO}_4$ .

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