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Copper and Zinc Fractions in Soils Growing Capsicum under Protected Conditions in Shivalik Region of Himachal Pradesh

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ABSTRACT

Micronutrients plays significant role in crop nutrition as they form integral part of essential nutrients required by plants. They are playing role in photosynthesis, enzymatic activities, flowering, auxin synthesis, rooting, seed and fruit development, sugar transport. The eight essential micronutrients required by plants are iron, manganese, copper, zinc, boron, molybdenum, nickel and chlorine. The available pool of micronutrients in soil is small portion of total nutrient content in soil. DTPA extractable micronutrients are considered as available pool. Micronutrients exists in different fractions such as residual, Iron/Aluminium oxide bound, organic matter bound, carbonate bound, Easily reducible Mn, exchangeable and water soluble forms. The study was conducted in randomly selected 56 polyhouse soils growing capsicum in four districts (14 Soil samples from each) of Himachal Pradesh with aim to work out different fractions of zinc and copper in soil and their relationship with different soil physico-chemical properties. The sequential extraction procedure as outlined by Ma and Uren (1995) was used for the study with minor modifications. The DTPA extractable copper and zinc ranged from 0.51 to 14.32 mg kg^{-1} and 0.83 to 4.18 mg kg^{-1}, respectively. Residual fraction in soil constituted 65.21 and 74.20% of the total Cu and Zn contents, respectively. pH showed significant negative correlation with different fractions of Cu and Zn in soil, organic matter bound fractions of Cu and Zn were observed to be highly correlated with the soil organic carbon content. Carbonate bound fraction was positively correlated with the $CaCO_3$ content in soil. The different fractions showed different degree of correlation among themselves. Exchangeable fractions showed highly positive correlation with the OM bound and water soluble fractions in both the nutrients. Hence it may be concluded from the results that these soils are having large pool of Zn and Cu contents which are present in different forms and are influenced to a significant degree by different soil physico-chemical properties.

Keywords Copper and zinc fraction, Soil growing, Capsicum, Protected conditions, Fruit development.

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INTRODUCTION

Vegetable production under polyhouse conditions offers a congenial environment for the crop growth to express yield to their fullest potential as it overcomes the barrier of biotic and abiotic stress, provided soil have adequate and balanced supply of nutrients. Off-season vegetable cultivation have become possible with the introduction of this technology in state like Himachal Pradesh where growing season is limited. But the concern arises that if we are fetching higher returns from higher production, surely it is associated with exhaustion of soil nutrients and therefore the soil after 5 to 7 years of cultivation becomes nutrient exhausted. We need to have proper knowledge of balanced nutrition and supplementing soil with required quantity of nutrients what we are harvesting out with the crop. Zinc and copper are two of those 8 essential micronutrients which plays important role in crop nutrition and their life cycle. Till now, studies were focused only on DTPA extractable micronutrients, which do not provide us adequate information about total and other non extractable fractions of these nutrients in soil, but they have their significance as those forms gets converted to available forms when soil conditions changes. The present study was conducted to investigate the different fractions of these two micronutrients in soil and work out how these different fractions are correlated to soil physico-chemical properties and also workout how these fractions are correlated.

MATERIALS AND METHODS

A preliminary survey of the study area was conducted in order to collect basic information on the soil, water, nutrient management, cropping pattern and other cultural practices being followed in the polyhouses and on the basis of that the representative 56 polyhouses growing capsicum were selected. The fourteen random polyhouses growing capsicum from each of four districts (Shimla, Sirmaur, Solan and Bilaspur) of Himachal Pradesh were selected. The elevation of the studied polyhouses ranged from 710 m to 2190 m amsl. The size of polyhouses ranged from 250 to 2560 m^2. The sample was taken from 0 – 15 cm soil depth. pH and EC was measured in 1:2 soil : Water suspension (Jackson 1973). SOC was estimated by method as outlined by Walkley and Black 1934. $CaCO_3$ was determined by Rapid titration method (Puri 1943). HCO_3- was determined by Rapid Titration method (Reitemeier 1943). CEC was determined by Sodium and Ammonium Acetate Centrifuge method (Bower *et al.* 1952). Clay content was determined by Hydrometer Method (Bouyoucos 1927). DTPA extractable Fe, Mn, Cu and Zn was estimated by method as outlined by Lindsey and Norvell (1978). The fractionation study to evaluate the different fractions of iron, manganese, copper and zinc was carried out by sequential extraction procedure as outlined by Ma and Uren (1995) with minor modifications. The soil samples were fractionated into various micronutrient fractions viz., water soluble, sorbed (exchangeable), easily reducible Mn, carbonate bound, organic matter bound, iron and aluminum oxides and residual fractions. Extraction was done with various reagents, prepared in double distilled water, using 1 : 10 Soil –solution ratio, except for water soluble, which had 1 : 5 ratio of soil and water. The soil solution was centrifuged after required shaking period, supernatant was filtered and soil was again treated with successive extractant. The total concentration of these nutrients was determined after digestion of soil with aqua-regia (HCL and HNO_3 in 3:1 ratio). 1 g of soil was digested with 25 ml of aqua regia over hot plate for 3 h). Residual fraction was obtained by subtracting the sum of total of different fractions from total content of micronutrients. The constituents in all the extracts were determined on Atomic Absorption Spectrophotometer. The flow sheet of complete procedure adopted is as follows:

Flow sheet of sequential extraction of different micronutrient fractions

Dry soil (5 g)
↓
Distilled water, 1:5, shaking 2 h → Water soluble
↓
1% NaCa HEDTA in 1M NH_4 oAc, pH 8.3, 1:10, shaking 2 h → Sorbed (Exchangeable)
↓
0.2% quinol in 1M NHCoAc, 7. 0, 1:10, shaking 2 h → Easily Reducible Mn
0.5M Na/HoAc, pH 4.74, 1:10, soaking 15 h, shaking 3 h → Carbonate Bound
5 mL 30% H_2O_2, pH 4.74, digested twice at 85 °C, and extracted by

0.5 M Na/HoAc for 1 h → Organic Matter Bound
↓
0.175M $(NH_4)_2C_2O_4$
–0.100 M $H_2C_2O_4$, pH 3.25, 1:10,
soaking 15 h, shaking 2 h. → Iron and aluminum oxides
↓
Total minus extractable amounts → Residual

RESULTS AND DISCUSSION

Fractionation of copper in polyhouse soils

Data on chemical fractions of Cu in polyhouse soils of Himachal Pradesh is presented in Table 1. Water soluble and exchangeable Cu in these soils ranged from 0.43 – 14.37 and 2.64 – 36.50 mg kg^{-1}, with mean values of 4.39 and 12.07 mg kg^{-1}, contributing 3.77 and 10.38%, respectively, to the total Cu in these soils.

The easily reducible manganese and carbonate bound fraction ranged from 1.06 – 5.38 and 3.83 – 8.95 mg kg^{-1}, with an average content of 3.60 and 6.27 mg kg^{-1}, thus contributing 3.10 and 5.39 per cent, respectively, to the total Cu in these soils.

The organic matter and Iron oxide bound fraction ranged from 4.50 – 17.62 and 2.27 – 8.72 mg kg^{-1}, with mean values of 9.20 and 5.02 mg kg^{-1}, which were 7.91 and 4.31%, respectively, of the total Cu in these soils.

The residual Cu fraction ranged between 2.55 and 1149.05 mg kg^{-1}, with a mean value of 75.84 mg kg^{-1}. The mean contribution of residual fraction is 65.21% towards total Cu.

Total Cu content in the studied polyhouse soils varied between 31.30 and 1210 mg kg^{-1}, with an average value of 116.30 mg kg^{-1}. DTPA extractable Cu in the polyhouse soils varied from 0.51 – 14.32 mg kg^{-1}, with an average value of 3.27 mg kg-^{1}. The relative Abundance of various Cu fractions was found to be in order of: ER-Mn < W.S. < Fe-Ox bound < Carbonate bound < O. M. bound < Exch. < Residual, with the exception of Shimla district, where easily reducible fraction was greater than water soluble fraction. The DTPA extractable Cu is just 2.81 % of the total Zn content of the soil, suggesting wide scope of sufficient Zn availability for long term cultivation without need of any external inputs.

Fractionation of zinc in polyhouse soils

Data on chemical fractions of Zn in polyhouse soils of Himachal Pradesh is presented in Table 2. Water soluble and exchangeable Zn in these soils ranged from 0.01 – 1.57 and 4.94 – 10.02 mg kg^{-1}, with mean values of 0.25 and 8.53 mg kg^{-1}, contributing 0.26 and 8.63% respectively, to the total Zn content in these soils.

The easily reducible manganese and carbonate bound fractions ranged from 0.52 – 11.19 and 0.99 – 4.48 mg kg^{-1}, with mean values of 6.17 and 2.45 mg kg^{-1}, which were 6.25 and 2.48%, respectively, of the total Zn in these soils.

The organic matter and Iron oxide bound fraction ranged from 1.42 – 6.49 and 1.17 – 8.42 mg kg^{-1}, with mean values of 3.23 and 4.86 mg kg^{-1}, forming

Table 1. Copper fractions of soils under polyhouse conditions.

District (Mean)	Copper fractions in polyhouse soils (mg kg^{-1}) W.S.	Exch.	ER-Mn	Carbonate	OM.	Fe-Ox	Residual	Total content	DTPA extract-able
Shimla	3.47	9.05	4.50	5.96	8.78	6.10	142.07	179.59	2.36
Sirmaur	3.83	10.43	3.78	6.30	7.69	5.31	12.36	49.71	2.74
Solan	7.18	19.34	3.17	6.25	10.76	4.44	109.18	160.32	4.80
Bilaspur	3.07	9.47	2.96	6.57	9.56	4.21	39.75	75.57	3.20
Overall mean	4.39	12.07	3.60	6.27	9.20	5.02	75.84	116.30	3.27
Overall range	0.43-14.37	2.64 – 36.50	1.06-5.38	3.83- 8.95	4.50-17.62	2.27-8.72	2.55 – 1149.05	31.30- 1210.00	0.51- 14.32
% of Total Cu	3.77	10.38	3.10	5.39	7.91	4.31	65.21		

Table 2. Zinc fractions of soils under polyhouse conditions.

District	Zinc fractions in polyhouse soils (mg kg^{-1}) WS	Exch.	ER-Mn	Carbonate	OM	Fe Ox	Residual	Total content	DTPA extractable
Shimla	0.53	9.25	7.04	2.80	3.80	5.79	77.93	107.14	2.52
Sirmaur	0.31	8.51	6.17	2.51	3.57	4.84	70.45	96.34	2.77
Solan	0.09	8.26	7.53	2.13	3.16	5.02	72.72	98.92	3.03
Bilaspur	0.08	8.11	3.96	2.36	2.41	3.77	72.27	92.96	2.76
Overall mean	0.25	8.53	6.17	2.45	3.23	4.86	73.34	98.84	2.77
Overall range	0.01-1.57	4.94-10.02	0.52-11.19	0.99-4.48	1.42-6.49	1.17-8.42	39.94-135.82	55.10-158.80	0.83-4.18
% of Total Zn	0.26	8.63	6.25	2.48	3.27	4.91	74.20		

3.27 and 4.91%, respectively, of the total Zn content in these soils.

The residual Zn fraction ranged between 39.94 and 135.82 mg kg^{-1}, with a mean value of 73.34 mg kg^{-1}. The mean contribution of residual fraction towards total Zn was 74.20%.

Total Zn content in the studied polyhouse soils varied between 55.10 and 158.80 mg kg^{-1}, with an average value of 98.84 mg kg^{-1}. DTPA extractable Zn in the polyhouse soils varied from 0.83 – 4.18 mg kg^{-1}, with an average value of 2.77 mg kg^{-1}. Abundance of various Zn fractions was found to be in order of: W.S. < Carbonate bound < O. M. bound < Fe-Ox bound < ER-Mn < Exch. < Residual. DTPA extractable Zn is just 2.80% of the total Zn content of the soil, which tells us the scope of native Zn in soil and their transformation possibilities.

Correlation Studies

Simple correlation between chemical fractions of Cu and Zn and with soil physico-chemical properties were worked out.

Relationships of copper fractions among themselves and with soil physico-chemical properties

The data presented in Table 3 reveals that water solu-

Table 3. Relationships (r-values) of copper fractions among themselves and with soil properties.

Cu	pH	EC	OC	$CaCO_3$	HCO_3-	CEC	Clay	DTPA
WS	-0.04	0.34*	0.52**	-0.10	0.21	0.30*	0.37**	0.15
Exch	0.02	0.42**	0.55**	0.17	0.17	0.39**	0.38**	0.47**
ER-Mn	-0.46**	-0.26	-0.16	0.03	-0.15	-0.42**	-0.20	-0.03
Carbonate	0.49**	-0.34*	-0.26	0.45**	0.06	0.09	-0.10	0.16
OM.	-0.10	0.54**	0.77**	-0.07	0.38**	0.38**	0.18	0.53**
FeOx	-0.34*	-0.17	-0.08	-0.10	-0.16	-0.28*	-0.12	0.06
Residual	-0.11	0.08	0.28*	-0.14	0.03	-0.28*	0.04	-0.05
Total content	-0.12	0.10	0.31*	-0.13	0.05	-0.25	0.06	-0.02

Table 3. Continued.

Cu	WS	Exch	ER-Mn	Carbonate	OM	Fe-Ox	Residual
WS							
Exch	0.51**						
ER-Mn	-0.05	-0.06					
Carbonate	-0.33*	-0.01	-0.09				
OM	0.44**	0.56**	-0.01	-0.23			
Fe-Ox	-0.20	0.03	0.64**	-0.02	0.10		
Residual	0.16	0.17	-0.06	-0.12	0.27*	-0.06	
Total content	0.19	0.22	-0.05	-0.13	0.31*	-0.05	0.99**

** Significant at the 0.01 level, * Significant at the 0.05 level.

Table 4. Relationships (r-values) of Zinc fractions among themselves and with soil properties.

Zn	pH	EC	OC	$CaCO_3$	HCO_3-	CEC	Clay	DTPA
WS	-0.27*	-0.23	-0.38**	-0.09	-0.14	-0.48**	-0.19	-0.22
Exch	-0.28*	-0.12	0.01	0.03	-0.08	-0.39**	-0.27*	0.14
ER-Mn	-0.15	0.24	0.43**	-0.07	0.31*	0.02	0.05	0.52**
Carbonate	0.28*	-0.43**	-0.39**	0.25	0.01	-0.32*	-0.25	-0.07
OM	-0.35**	0.21	0.52**	-0.13	0.02	-0.25	-0.27*	0.22
FeOx	-0.33*	0.05	0.13	-0.19	0.03	-0.11	-0.14	0.34**
Residual	-0.09	0.13	0.11	-0.19	-0.02	-0.19	-0.07	0.25
Total content	-0.16	0.14	0.17	-0.20	0.01	-0.24	-0.11	0.34*

Table 4. Continued.

Zn	WS	Exch	ER-Mn	Carbonate	OM	Fe-Ox	Residual
WS							
Exch	0.43**						
ER-Mn	0.20	0.26					
Carbonate	0.38**	0.40**	0.17				
OM	0.25	0.42**	0.47**	0.10			
FeOx	0.29*	0.34**	0.43**	0.16	0.43**		
Residual	0.15	-0.02	0.18	-0.06	0.13	0.11	
Total content	0.25	0.13	0.36**	0.04	0.30*	0.28*	0.97**

** Significant at the 0.01 level, * Significant at the 0.05 level.

ble fraction of copper was positively and significantly correlated to EC (r=0.34*), OC (r=0.52**), CEC (r=0.30*) and clay content (r=0.37**).

The exchangeable fraction was also found to be positively and significantly correlated with EC (r=0.42**), OC (r=0.55**), CEC (r=0.39**), clay content (r=0.38**), DTPA Cu (r=0.47**) and water soluble fraction (r=0.51**). The easily reducible manganese fraction, however, was found to be negatively and significantly correlated with soil pH (r= -0.46**) and CEC (r= -0.42**).

The carbonate bound fraction was found to be positively and significantly correlated with soil pH (r=0.49**) and $CaCO_3$ content (r=0.45**), but negatively correlated with EC (r= -0.34*) and water soluble fraction (r= -0.33*).

The organic matter bound fraction had a positive and significant correlation with EC (r=0.54**), OC (r=0.77**), HCO_3- (r=0.38**), CEC (r=0.38**), DTPA Cu (r=0.53**), water soluble fraction (r=0.44**) and exchangeable fraction (r=0.56**). But, the Iron oxide bound fraction was found to be negatively and significantly correlated with pH (r= -0.34*) and CEC (r= -0.28*), but positively correlated with easily reducible manganese fraction (r=0.64**).

The residual fraction of copper was found to be positively correlated with OC (r=0.28*) and organic matter bound fraction (r=0.27*), but had a significantly negative relationship with CEC (r= -0.28*). The total Cu content, however, was found to be positively correlated with OC (r=0.31*), organic matter bound fraction (r=0.31*), and a very high correlation with residual fraction (r=0.99**).

The pH was found to be negatively and significantly correlated with easily reducible manganese fraction and Iron oxide bound fraction, which suggests an inverse relationship between pH and solubility or availability of these fractions. The carbonate bound fraction was found to be positively correlated with soil pH (r= 0.49**). Organic carbon was positively correlated with water soluble, exchangeable, organic matter bound and Iron oxide bound fraction of Cu, which may be due to higher contents of organic matter in these soils. The $CaCO_3$ content of the soil was positively correlated with the carbonate bound fraction. The CEC was found to be positively correlated with water soluble, exchangeable and organic matter bound fractions, which shows that the CEC, contributes significantly to plant available forms of copper. Water soluble fraction was positively correlated with exchangeable and organic matter bound fraction indicating that a dynamic equilibrium exists between these forms. The residual and total content were found to be highly correlated (r=0.99**) which indicate that the solubility of copper between these forms is small. The results are in accordance with the findings of Behera *et al.* (2009) and Fathi *et al.* (2014)

Relationships of zinc fractions among themselves and with soil physico-chemical properties

The data in Table 4 reveals that water soluble fraction of zinc was negatively and significantly correlated to pH (r= -0.27*), OC (r= -0.38**) and CEC (r= -0.48**). The exchangeable fraction was found to be negatively and significantly correlated with pH (r= -0.28*), CEC (r= -0.39**), clay content (r= -0.27*) and positively correlated with water soluble fraction (r=0.43**).

The easily reducible manganese fraction was found to be positively and significantly correlated with soil OC (r=0.43**), HCO_3- (r=0.31**) and DTPA Zn (r= 0.52**). The carbonate bound fraction was found to be positively and significantly correlated with soil pH (r=0.28*), water soluble fraction (r=0.38**) and exchangeable fractions (r=0.40**), but negatively correlated with EC (r= -0.43*), OC (r= -0.39**) and CEC (r= -0.32*).

The organic matter bound fraction was found to be negatively correlated with soil pH (r= -0.35**) and clay content (-0.27*), but positively and significantly correlated with OC (r=0.52**), exchangeable fraction (r=0.42**) and easily reducible manganese fraction (r=0.47**)

The Iron oxide bound fraction of zinc was found to be negatively and significantly correlated with pH (r= -0.33*), but had a significantly positive relationship with DTPA Zn (r=0.34**), water soluble fraction (r=0.29*), exchangeable fraction (0.34**), easily reducible manganese fraction (r=0.43**) and organic matter bound (r=0.43**).

The residual fraction showed highly significant correlation only with total zinc content (r=0.97**). However, the total Zn content of the soil was found to be positively correlated with DTPA Zn (r=0.34*), easily reducible manganese fraction (r=0.36**), organic matter bound fraction (r=0.30*) and iron oxide bound fractions (r=0.28*).

The pH was found to be negatively and significantly correlated with water soluble, exchangeable, organic matter bound fraction and iron oxide bound fraction, which suggests the increase in solubility and availability of these Zn fractions as the pH decreases. The carbonate bound fraction was found to be positively correlated with soil pH, as with other micronutrients. The organic carbon was positively correlated with easily reducible manganese and organic matter bound fraction of Zinc, showing that the organic carbon has a profound influence on these fractions. $CaCO_3$ content showed negative correlation with Iron oxide bound fraction and total Fe content, which suggests the lower availability of Fe in $CaCO_3$ rich soils. The CEC was found to be negatively correlated with water soluble, exchangeable and carbonate bound fractions. Water soluble fraction was positively correlated with exchangeable fraction showing the dynamic equilibrium exists between these two forms. The relationship between residual and total content was found to be highly significant (r=0.97**) which indicates that the mobility of Zinc is low between residual and plant available fractions. The results are in accordance with the findings of Behera *et al.* (2009), Wijebandara *et al.* (2011) and Fathi *et al.* (2014).

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