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DYNAMICS OF COPPER FRACTIONS IN CALCAREOUS VERTIC USTOCHREPTS UNDER AICRP-LTFE SOILS

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ABSTRACT

The investigation was carried out under the ongoing AICRP-LTFE with groundnut-wheat cropping sequence at Junagadh Agricultural University, Junagadh, during the year 1999(Initial soil), 2002-03(4th year) , 2006-07(8th year) after completion of crop cycle. The spectrum of different forms of copper revealed that they did not differ significantly only in water soluble and percentage available form of Cu. Even in long run different form differed significantly. There was slight decrease in overall DTPA available Cu content after 4 year (1.289 ppm) and also after 8 year (1.178 ppm). DTPA-Cu showed significantly higher values in T_9 (1.569 ppm) followed by T_8 (1.453 ppm) and T_{11} (1.360 ppm) as compared to other chemical fertilizer treatment in long run but the later values were quite high than the critical values and therefore addition Cu has not been prescribed. There were some inter-conversion hence the DTPA-Cu showed an increasing trend in treatment T_9 and T_8. The DTPA available Cu followed by residual and per cent available. There were inter-conversions from DTPA available as well as total form to the reducible forms in a long run.

KEY WORDS
LTFE's soil, Cu fraction, water soluble-Cu, exchangeable-Cu, DTPA available- Cu, Total-Cu, per cent available- Cu)

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INTRODUCTION

Micronutrient deficiencies in crop plants are widespread in all over the world because of increased micronutrient demands from intensive cropping practices and adaptation of high-yielding cultivars having higher micronutrient demand. Moreover, enhanced production of crops on marginal soils that contain low levels of essential nutrients, increased use of high analysis fertilizers with low amounts of micronutrient contamination, decreased use of animal manures, composts and crop residues, use of soils that are inherently low in micronutrient reserves and involvement of natural and anthropogenic factors that limit adequate plant availability add to the cause (Fageria *et al.,* 2002). In India, intensive cropping with nutrient exhaustive high-yielding varieties coupled with the use of high analysis fertilizers for enhancing food grain production have catalyzed the rapid depletion of available micronutrients in soil in general (Singh, 2009). Herencia *et al.* (2008) reported that with the addition of organic and mineral fertilization, OM-bound fractions of micronutrients increased their availability and uptake in the soil. To understand the chemical reactions and bioavailability of soil zinc, it is essential to investigate its release behaviour of various fractions in soils Saviour and Stalin (2014). Dhaliwal and Walia (2008) reported that incorporation of manures increased the availability of the micronutrients like Zn, Cu, Fe and Mn. Long-term experiments (LTE) offer a better platform to visualize the status of micronutrients in soil under intensive cropping and their contribution to sustained production. Copper is tightly held on the soil exchangeable complex. The major factors which are important in transformation of Cu are soil pH, $CaCO_3$, organic matter and clay content. Even the nature of clay minerals and presence of oxides of Fe and Al are important in regulating the behavior of Cu in soil. The Cu is held in soil by other than the usual cationic forces. Even extremely insoluble compounds show some availability of Cu. The water soluble and exchangeable forms are of course, assumed to be readily available, but other forms of micronutrients when sufficient in their activity becomes important in the nutrition of crop plants (Tandon, 1991). Therefore, there is a need to study the dynamics of different forms of Cu in intensive agriculture on long run basis present investigation was carried out.

MATERIALS AND METHODS

Surface soil samples (0-15 cm) were collected from the AICRP-LTFE soils conducted on groundnut-wheat sequence in RBD, replicated four times, at Instructional Farm Junagadh Agricultural University, Junagadh during the year 1999 (Initial), 2002-03 (4th year, after wheat) and 2006-07 (8th year, after wheat).

Treatment Detail

T_1 - 50 % NPK of recommended doses in G'nut-Wheat sequence,

T_2 - 100 % N P K of recommended doses in G'nut -Wheat sequence,

T_3 - 150 % N P K of recommended doses in G'nut -Wheat sequence,

T_4 - 100 % N P K of recommended doses in G'nut -Wheat sequence + $ZnSO_4$ @ 50 kg ha^{-1} once in three year to G'nut only (*i.e.* '99, 02, 05 etc),

T_5 - N P K as per Soil Test,

T_6 - 100 % N P of recommended doses in G'nut -Wheat sequence,

T_7 - 100 % N of recommended doses in G'nut -Wheat sequence,

T_8 - 50 % N P K of recommended doses + FYM @ 10 t ha^{-1} to G'nut and 100 % N P K to Wheat,

T_9 - Only FYM @ 25 t ha^{-1} to G'nut only,

T_{10} - 50 % N P K of recommended doses + Rhizobium + PSM to G'nut and 100 % N P K to Wheat,

T_{11} - 100 % N P K of recommended doses in G'nut -Wheat sequence (P as SSP) and

T_{12} - Control.

Copper fractionation method

The sequential extraction technique employed to separate the various forms of copper was Tessier's procedure by Jackson (1973) and Viets (1962) as water soluble, exchangeable, DTPA available, and reducible form. Total Cu status was determined by digesting the soil using HF: $HClO_4$ (5:1). These extracts were analyzed for their Cu content on Atomic Absorption Spectrophotometer. Residual form of Cu was calculated by deducting water soluble + exchangeable + DTPA available + reducible (*i.e.* available total) from the total Cu status of the soil. The per cent available Cu status was calculated as available total of the total Cu status of the soil.

RESULTS AND DISCUSSION

Cu - water soluble

The water soluble copper showed non significant difference among treatment when pooled over years and only significant result were observed in 8th year (Table 1). Overall water soluble copper declined overtime. In pooled, the highest value of Cu-

Table 1: Status of different forms of available copper in soils of LTFE experiment in 1st, 4th and 8th year

Treat.	Copper water soluble from in soil (ppm)				Copper exchangeable form in soil (ppm)			
	1st year	4th year	8th year	pooled	1st year	4th year	8th year	pooled
T1	0.185	0.207	0.075	0.155	0.251	0.254	0.179	0.228
T2	0.215	0.176	0.086	0.159	0.227	0.285	0.229	0.247
T3	0.161	0.158	0.069	0.129	0.283	0.297	0.246	0.275
T4	0.211	0.177	0.063	0.150	0.233	0.258	0.216	0.235
T5	0.183	0.144	0.075	0.134	0.255	0.300	0.195	0.250
T6	0.211	0.153	0.071	0.145	0.285	0.335	0.242	0.287
T7	0.184	0.149	0.068	0.134	0.252	0.346	0.238	0.278
T8	0.214	0.170	0.069	0.151	0.236	0.271	0.188	0.232
T9	0.209	0.179	0.082	0.157	0.212	0.245	0.158	0.205
T10	0.179	0.203	0.084	0.155	0.288	0.332	0.210	0.277
T11	0.188	0.167	0.082	0.146	0.235	0.329	0.253	0.272
T12	0.170	0.155	0.075	0.134	0.247	0.322	0.209	0.259
SEm±	0.018	0.021	0.005	0.009	0.018	0.034	0.026	0.015
CD at 5%	NS	NS	0.014	NS	NS	NS	NS	0.043
C.V.%	18.3	25.06	13.26	22.24	14.19	22.55	24.22	20.89
Mean	0.192	0.170	0.075	0.146	0.250	0.298	0.213	0.254
Y * T	S.Em.±	0.016205	C.D. at 5 %	NS	S.Em.±	0.027	C.D. at 5 %	NS

Treat.	Copper DTPA available form in soil (ppm)				Copper reducible form in soil (ppm)			
	1st year	4th year	8th year	pooled	1st year	4th year	8th year	pooled
T1	1.410	1.231	1.006	1.216	0.207	0.190	0.174	0.190
T2	1.471	1.356	1.298	1.375	0.173	0.232	0.151	0.185
T3	1.334	1.133	1.038	1.168	0.185	0.177	0.169	0.177
T4	1.418	1.283	1.024	1.242	0.203	0.197	0.181	0.194
T5	1.224	1.171	1.214	1.203	0.175	0.241	0.124	0.180
T6	1.471	1.205	0.998	1.224	0.174	0.155	0.185	0.171
T7	1.327	1.243	1.224	1.264	0.178	0.232	0.147	0.186
T8	1.412	1.650	1.298	1.453	0.192	0.263	0.231	0.229
T9	1.471	1.786	1.451	1.569	0.198	0.248	0.236	0.227
T10	1.275	1.126	1.340	1.247	0.206	0.202	0.155	0.187
T11	1.417	1.372	1.293	1.360	0.215	0.221	0.183	0.206
T12	1.413	0.913	0.950	1.092	0.189	0.123	0.124	0.145
SEm±	0.069	0.097	0.090	0.078	0.013	0.020	0.022	0.016
CD at 5%	NS	0.278	0.258	0.229	NS	0.056	0.064	0.048
C.V.%	9.89	14.98	15.23	13.35	14.04	18.86	25.76	19.7
Mean	1.387	1.289	1.178	1.285	0.191	0.207	0.172	0.190
Y * T	S.Em.±	0.086	C.D. at 5 %	0.241	S.Em.±	0.019	C.D. at 5 %	0.053

Table 2: Status of total, residual, per cent available and available total form of copper in 1st, 4th and 8th year in the LTFE soils

Treat.	Copper total form in soil (ppm)				Copper residual form in soil (ppm)			
	1st year	4th year	8th year	pooled	1st year	4th year	8th year	pooled
T1	13.17	12.32	10.56	12.02	11.12	10.44	9.63	10.40
T2	14.08	13.34	12.98	13.47	11.99	11.30	11.22	11.50
T3	13.74	12.16	9.83	11.91	11.78	10.39	8.31	10.16
T4	14.66	12.41	8.48	11.85	12.59	10.49	6.99	10.03
T5	13.81	12.25	9.78	11.95	11.97	10.39	8.18	10.18
T6	14.66	12.74	10.31	12.57	12.52	10.90	8.81	10.74
T7	14.01	12.35	9.41	11.92	12.07	10.38	7.73	10.06
T8	14.83	15.99	11.66	14.16	12.78	13.63	10.42	12.28
T9	14.44	17.94	15.56	15.98	12.35	15.48	13.64	13.82
T10	15.39	10.51	10.93	12.28	13.45	14.50	9.92	12.62
T11	14.66	12.01	12.86	13.18	12.61	9.92	11.05	11.19
T12	14.14	9.68	9.76	11.19	12.12	8.17	8.40	9.56
SEm ±	0.47	0.84	0.93	0.81	0.49	0.88	0.80	0.74
CD at 5%	NS	2.41	2.68	2.36	NS	2.55	2.30	2.16
C.V.%	6.52	13.09	16.93	12.15	7.92	15.60	16.77	13.45
Mean	14.30	12.81	11.01	12.71	12.28	11.33	9.52	11.05
Y * T	S.Em. ±	0.77	C.D. at 5 %	2.17	S.Em. ±	0.74	C.D. at 5 %	2.09

Treat.	Percentage available of Copper in soil				Total available forms of Copper in soil (ppm)			
	1st year	4th year	8th year	pooled	1st year	4th year	8th year	pooled
T1	15.59	15.31	13.01	14.64	2.05	1.88	1.43	1.79
T2	14.81	15.64	13.65	14.70	2.09	2.05	1.76	1.97
T3	14.32	14.66	15.68	14.89	1.96	1.76	1.52	1.75
T4	14.11	15.55	17.83	15.83	2.06	1.91	1.48	1.82
T5	13.40	15.78	16.39	15.19	1.84	1.86	1.61	1.77
T6	14.62	14.46	15.07	14.72	2.14	1.85	1.50	1.83
T7	13.85	16.00	18.36	16.07	1.94	1.97	1.68	1.86
T8	13.88	14.83	14.73	14.48	2.05	2.35	1.79	2.06
T9	14.75	13.77	12.51	13.68	2.09	2.46	1.93	2.16
T10	12.68	11.52	15.42	13.21	1.95	1.86	1.79	1.87
T11	14.06	17.46	14.08	15.20	2.05	2.09	1.81	1.98
T12	14.32	15.64	13.89	14.62	2.02	1.51	1.36	1.63
SEm ±	0.77	1.09	1.15	0.82	0.07	0.10	0.09	0.08
CD at 5%	NS	NS	3.32	NS	NS	0.28	0.27	0.24
C.V.%	10.88	14.43	15.33	13.78	7.40	10.07	11.50	9.59
Mean	14.20	15.05	15.05	14.77	2.02	1.96	1.64	1.87
Y * T	S.Em. ±	1.02	C.D. at 5 %	2.86	S.Em. ±	0.09	C.D. at 5 %	0.25

water soluble was observed under application of 100 % NPK in groundnut-wheat sequence(T_2). Komisarek *et al.* (1991) stated that increasing lime rates decreased water soluble Cu.

Cu - exchangeable

The exchangeable copper showed significant difference in pooled result and it was recorded higher under application of 100 % NPK in groundnut-wheat sequence(T_2) followed by T_7, T_{10}, T_3, T_{11}, T_{12} and T_2 (Table 1). In long term, there seems to be a slight increase in 4th year but it was declined again at 8th year of experimentation. Komisarek *et al.* (1991) stated that increasing lime rates decreased exchangeable Cu.

Cu - DTPA available

The DTPA available Cu showed significant difference due to treatments when pooled over year and also in Y x T interactions. Highest value was recorded by application of FYM @ 25 t ha^{-1} to groundnut (T_9) followed by T_8, T_2 and T_{11}. In long run, there was a slight decrease in overall DTPA copper (Table 1). The results are supported by earlier works of Prasad and Singh (1980) who also showed the increase in available Cu in a long run by application of either organic or inorganic fertilizers in LTFE soils. However Lal and Mathur (1989) reported an increase in available Cu even without application of any type of nutrients in different crops.

Cu - reducible

Pooled over the year and interactions were significant in reducible copper. Highest value was recorded by application of 50 % NPK in groundnut-wheat sequence + FYM @ 10 t ha^{-1} to groundnut (T_8) followed by T_9, T_{11}, T_4, T_1, T_{10}, T_7 and T_2. In long run term, there seems to be slight declined in overall reducible of copper form (Table 1). Organic matter application retarded Cu transformation from OC into residual fraction (Saha *et al.*, 2000).

Cu - total

The total copper showed significant difference among treatment, when pooled over the years. The highest value was recorded by application of FYM @ 25 t ha^{-1} to groundnut (T_9) followed by application of 50 % NPK in groundnut-wheat sequence + FYM @ 10 t ha^{-1} to groundnut and 100 % N P K to wheat (T_8) (Table 2). In long term, was decline in overall total copper due to long term changes in the soil chemistry.

Nevertheless there was distinct numerical reduction in total content over the years and the possibilities of mobilization from total to some of the available forms such as DTPA available and reducible copper can not be denied. The total copper content averaged 9.88 ppm with a range of 2.18 to 36.38 ppm (Tagwira, 1994).

Cu residual

This form also showed significant differences due to treatment as well as due to long term changes (Table 2). Highest value was recorded in application of FYM @ 25 t ha^{-1} to groundnut (T_9) followed by T_{10} and T_8. Most of the treatments recorded numerical reduction after 4 and 8 year as compared to initial year which also gave indication that the total form was mobilized not as the residual form but as the available form.

Cu - percentage availability

In the 8th year, highest value recorded in T_7 followed by T_4, T_5, T_3, T_{10} and T_6, while in initial year and 4th year the differences among treatments were not significant (Table 2). Though overall pooled differences were not significant but Y x T interaction was significant.

Cu available total

The available total copper showed significant differences among treatments when pooled over year and also Y x T interaction were significant. Highest value was recorded in application of FYM @ 25 t ha^{-1} to groundnut (T_9) followed by application of 100 % N P K of recommended doses in Groundnut -Wheat sequence (P as S S P) and 100 % N P K of recommended doses in G'nut -Wheat sequence. In long term, there seems to be a slight decrease after 8th year in available total content of copper (Table 2).

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