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Sandeep Sharma[a], Girish Chander[b] & T. S. Verma[c]
[a] Department of Soils, Punjab Agricultural University, Punjab, India
[b] Resilient Dryland Systems, International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru, India
[c] Department of Soil Science, HP Agricultural University, Palampur, India

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COPPER DYNAMICS IN A TYPIC HAPLUDALF UNDER RICE-WHEAT CROPPING SYSTEM AFTER TWELVE YEARS OF ANNUAL *LANTANA CAMARA* L. RESIDUE INCORPORATION

Sandeep Sharma,[1] Girish Chander,[2] and T. S. Verma[3]
[1]*Department of Soils, Punjab Agricultural University, Punjab, India*
[2]*Resilient Dryland Systems, International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru, India*
[3]*Department of Soil Science, HP Agricultural University, Palampur, India*

□ *Long term effects of lantana (*Lantana camera *L.) residue and fertilizer application were studied on copper (Cu) fractions in a Typic Hapludalf under rice-wheat cropping at Palampur, India (32° 6′N, 76° 3′E). A partitioning of soil Cu revealed residual Cu and organically bound Cu as the most dominant fractions followed by Cu occluded by free oxides, specifically exchangeable Cu and soil solution and exchangeable Cu. Continuous incorporation of lantana after 12 years resulted in redistribution of Cu from non-available forms to readily and potentially available forms in soil. All the Cu fractions were positively interrelated amongst themselves and with grain yield and Cu uptake in rice and wheat crops. Specifically exchangeable Cu followed by organically bound Cu were the most important Cu fraction contributing towards grain yield and Cu uptake in rice and wheat crops.*

Keywords: copper fractions, copper uptake, lantana, fertilizers, integrated nutrient management, rice-wheat

INTRODUCTION

Copper (Cu) is associated with various soil components in different factions, such as water soluble, exchangeable, chelated, and complexed forms associated with organic matter, occluded in the sesquioxides and as part of the lattice structure of primary and secondary-minerals. It has high affinity towards both inorganic and organic constituents and therefore readily transforms into different forms.

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Address correspondence to Girish Chander, Soil Science, RP1: Resilient Dryland Systems, Building 300, International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru-502324, Andhra Pradesh, India. E-mail: g.chander@cgiar.org

The rice and wheat grown in annual rotation which is the predominant cropping system in India, leads to alternate flooding and upland conditions, which result in creating different chemical environment in soils during the rice and wheat growing periods. Under submerged conditions that prevail during the rice growing, a series of electrochemical, biochemical and microbiological changes occur in the soil (Ponnamperuma, 1972), but when wheat is grown, these changes are reversed owing to the upland conditions (Manchanda et al., 2003). The rice-wheat system in fact, is now showing signs of fatigue and is no longer exhibiting increased production with increases in nitrogen (N), phosphorus (P), and potassium (K) input use apparently due to neglected micronutrients. Organic amendments that are being looked to be integrated with chemical fertilizers are known to improve soil productivity under rice-wheat cropping (Timsina and Connor, 2001) apparently due to in general soil health improvement, including addition of micronutrients and redistribution of their fractions. The continuous cycle of reduced and oxidized soil conditions and organic amendments have a bearing on the transformation of micronutrients in soil (Han and Banin, 2000; Hoang et. al., 2009; Rupa et al., 2001; Saha and Mandal, 2000).

The alternative uses of crop residues/straw for cattle feed in Indian conditions and small quantities of organic materials available as soil amendment necessitates looking for alternate sources of organic sources. Lantana (*Lantana camara* L.) is a fast growing abnoxious weed in India. Because of its fast growth, lantana has turned into a serious weed, with a danger of encroaching on cultivated lands. It has no value as cattle feed because it contains toxins such as 'lantidine', which causes tymphany disease if eaten by cattle. Its growth and foliage are maximum during wet season (June-September) when rice is cultivated. Keeping in view its abundance and limited alternate use, a long-term field experiment with rice-wheat cropping system was initiated to study its utility as an alternate organic source of nutrients and evaluating its effect on soil Cu transformation.

MATERIALS AND METHODS

Study Site

A long term field experiment was started in 1988 in a silty clay loam soil (Typic Hapludalf) at the experimental farm of the Himachal Pradesh Agricultural University, Palampur, India (32°6′N, 76°3′E,1300 m above mean sea level). The experimental soil had 300 g kg^{-1} clay, 540 g kg^{-1} silt, 160 g kg^{-1} sand, 5.6 pH, 0.88% organic carbon, 12 cmol kg^{-1} cation exchanage capacity, 0.12 g kg^{-1} available N [potassium permanganate ($KMnO_4$-oxidizing fraction)], 8.0 mg kg^{-1} Olsen's P, and 0.08 g kg^{-1} ammonium acetate (NH_4OAc)-extracted K. The site lies in the Palam valley of Kangra District at foothills of Dhauladhar ranges and represents the mid-hill wet-temperate zone of the

North-West Himalayas. The mean annual rainfall in Palampur is about 2,312 ± 618 mm, with the wettest months being June to September.

Experimental Detail

A long term field experiment was started during kharif/rainy season (mid-June to mid-September) 1988 to study the effect of four levels of lantana incorporation (0, 10, 20, and 30 Mg ha^{-1} on fresh weight basis) and three tillage practices (no puddling, puddling, and soil compaction) for rice. It was laid out in a completely randomized block design with 12 treatments, replicated thrice (plot size 10 m^2). The residual effect of lantana incorporation and tillage practices were evaluated on the succeeding wheat crop every year up to rabi/post-rainy season (November-April) 1992–1993. During kharif/rainy season 1993, however, the experiment was modified and the tillage practices were replaced with three levels of N (50, 75, and 100% of the recommended 90 kg N ha^{-1}) for rice. Nitrogen levels for wheat were 100, 75, and 50% of the recommended 120 kg N ha^{-1}. These treatments were maintained until rabi 1996–1997. From kharif 1997, the fertilizer levels were further modified to 33, 66, and 100% of the recommended N and K (40 kg ha^{-1}) to rice. Phosphorus application was skipped. N, P, and K application to wheat was also modified as 66% of the recommended levels (120, 90, and 30 kg N, P, and K ha^{-1}, respectively). Regarding method of application in rice, entire K was applied at transplanting, 50% N 10 days after transplanting, and the remaining 50% N in two splits (20 and 40 days after transplanting). For wheat, all P and K, and 50% N were applied at sowing, and the remaining 50% N top dressed in two equal splits at crown root initiation and flowering stages.

The fertilizers used were urea, single super phosphate, and muriate of potash for N, P, and K, respectively. Lantana biomass from wastelands was collected and incorporated 10 to 15 days before transplanting rice. Lantana twigs were chopped into small pieces (4 to 5 cm), spread uniformly over the entire plot, and incorporated in the surface soil (0 to 0.15 m) using spades. Each plot was then irrigated and left as such for 10 to 15 days, dug again, and mixed up manually. Tender twigs of Lantana contained on a dry weight basis 403 g kg^{-1} carbon (C), 22.3 g kg^{-1} N, 2.0 g kg^{-1} P, 14g kg^{-1} K with a C/N ratio of 21.

Soil Sampling and Analysis

Soil samples were collected from the 0–0.15 m layer (treatment-wise) after 12 cycles of rice-wheat cropping (i.e., after the wheat harvest in 2001–2002). The soil samples were mixed thoroughly, air dried in shade, crushed to pass through 2 mm sieve, and stored in sealed plastic jars for analysis. After processing, soil samples were analyzed for diethylenetriaminepenta acetic acid (DTPA)-Cu (Lindsay and Norvell, 1978) and five different fractions of Cu viz., soil solution and exchangeable Cu (Cu-CA), specifically adsorbed exchangeable Cu (Cu-AAC), organically bound Cu (Cu-PYR), copper occluded by free oxides (Cu-OX) and residual Cu (Res-Cu). The fractionation method proposed by McLaren and Crawford (1973) was used to determine different chemical pools of soil Cu.

Statistical Analysis

The data were subjected to standard analysis of variance (ANOVA) of completely randomized block design (Gomez and Gomez, 1984) and the means of the treatments were tested using least significant differences at 5% level probability by using the IRRISTAT data analysis package. Cu uptake computed in rice and wheat crop yields was correlated with different forms of Cu and the interdependency among different forms of Cu was also determined.

RESULTS AND DISCUSSION

Copper Fractions

A partitioning of soil Cu revealed residual Cu (Res-Cu) and organically bound Cu (Cu-PYR) as the most dominant fractions followed in decreasing order by Cu occluded by free oxides (Cu-OX), specifically exchangeable Cu (Cu-AAC) and soil solution and exchangeable Cu (Cu-CA) the least (Table 1). The Res-Cu and Cu-PYR fractions represent the Cu content associated with mineral forms and organic combinations, respectively (Iu et al., 1981; Raghupathi and Vasuki, 1992), and therefore their highest contents are on expected lines. The relative contribution of Cu-CA, Cu-AAC, Cu-PYR, Cu-OX, and Res-Cu towards total Cu was 0.16, 0.85, 42.7, 12.9 and 43.5%, respectively. The lower Cu value in soil solution and exchangeable form indicates the low affinity of soil cation exchange sites for Cu ions (Atanassova and Okazaki, 1997).

The application of fertilizers had no significant effect on Cu fractions except Cu-AAC. The Cu-AAC fraction increased by 2.3% with the application of fertilizers at 66% level and by 4.6% with 100% of fertilizers dose as compared with 33% dose. The increase in Cu-AAC might be due to enhanced specific sites in organic matter for Cu adsorption as a result of addition of higher left over residue as well as root biomass in the soil under treatments with higher fertilizer levels which recorded higher crop yields (Sharma et al., 2009). The incorporation of lantana from 10 to 30 Mg ha^{-1} significantly increased all fractions of Cu over no lantana treatment. The increase was more in Cu-CA followed by Cu-AAC and Cu-PYR and minimum in Res-Cu. The content of Cu-CA in soils depends mainly on organic carbon content and cation

TABLE 1 Effect of fertilizer and lantana application on different Cu fractions in soil

Lantana addition (Mg ha^{-1})	Fertilizers applications (% of the recommended dose)			
	33	66	100	Mean
	Soil solution and exchangeable Cu (Cu-CA) (mg kg^{-1})			
0	0.023	0.021	0.021	0.0216
10	0.036	0.033	0.028	0.0323
20	0.040	0.038	0.036	0.0380
30	0.046	0.045	0.043	0.0446
Mean	0.0362	0.0342	0.0320	
CD (P = 0.05)	F = NS	L = 0.006	L × F = NS	
	Specifically exchangeable Cu (Cu-AAC) (mg kg^{-1})			
0	0.154	0.155	0.155	0.154
10	0.166	0.170	0.175	0.171
20	0.178	0.182	0.190	0.183
30	0.200	0.204	0.210	0.205
Mean	0.174	0.178	0.182	
CD (P = 0.05)	F = 0.003	L = 0.004	L × F = 0.005	
	Organically bound Cu (Cu-PYR) (mg kg^{-1})			
0	9.087	9.088	9.088	9.088
10	9.150	9.153	9.163	9.155
20	9.289	9.295	9.305	9.296
30	9.347	9.350	9.358	9.351
Mean	9.218	9.221	9.228	
CD (P = 0.05)	F = NS	L = 0.026	L × F = NS	
	Cu occluded by free oxides (Cu-OX) (mg kg^{-1})			
0	2.754	2.754	2.755	2.755
10	2.768	2.772	2.780	2.773
20	2.785	2.790	2.794	2.790
30	2.800	2.806	2.812	2.806
Mean	2.777	2.780	2.784	
CD (P = 0.05)	F = NS	L = 0.006	L × F = NS	
	Residual Cu (Res-Cu) (mg kg^{-1})			
0	9.375	9.376	9.378	9.376
10	9.390	9.392	9.398	9.393
20	9.400	9.406	9.407	9.404
30	9.412	9.416	9.424	9.417
Mean	9.394	9.398	9.402	
CD (P = 0.05)	F = NS	L = 0.012	L × F = NS	

exchange capacity (CEC) of the soils. Lantana application has increased the organic carbon content (Sharma et al., 2010) and apparently the CEC, which contributed to increase in Cu-CA content. Similarly, the contents of Cu-AAC and Cu-PYR are the functions of soil organic matter, and so lantana has also resulted into the buildup of these two fractions in the soils. Copper has a natural affinity for organic matter to form inner sphere complexes with humic substances than any other micronutrient (Mathur and Levesque, 1983;

TABLE 2 Effect of fertilizer and lantana application on DTPA-Cu and total-Cu in soil

	Fertilizers applications (% of the recommended dose)			
Lantana addition (Mg ha^{-1})	33	66	100	Mean
	DTPA-Cu (mg kg^{-1})			
0	0.980	0.940	0.867	0.928
10	1.02	1.01	1.00	1.01
20	1.13	1.09	1.04	1.09
30	1.21	1.19	1.12	1.17
Mean	1.09	1.06	1.01	
CD (P = 0.05)	F = 0.056	L = 0.065	L × F = NS	
	Total-Cu (mg kg^{-1})			
0	21.391	21.394	21.397	21.394
10	21.510	21.520	21.544	21.525
20	21.692	21.711	21.732	21.712
30	21.805	21.821	21.847	21.824
Mean	21.600	21.821	21.630	
CD (P = 0.05)	F = NS	L = 0.03	L × F = NS	

McBride, 1994), therefore organic matter addition through lantana resulted into an increase in the contents of Cu fractions. Earlier studies (Agbenin and Felix-Henningsen, 2004; Bolan et al., 2003; Rupa et al., 2001) also found an increase in organically complexed copper with the application of organic manures. The Res-Cu represents mainly Cu-fractions present in mineral form and since addition of organic matter had no effect on mineralogical make up of soils and hence lantana incorporation had almost negligible effect on this particular fraction of Cu (Domingues and Vieira e Siliva, 1990). The interaction between fertilizer application and lantana incorporation had no significant effect on any of the Cu fraction except Cu-AAC. Fertilizer application at the rate of 100% of its recommended dose when applied in the presence of lantana additions (10 to 30 t ha^{-1}), increased Cu-AAC content significantly over its preceding dose (66% of recommended fertilizer dose). Cu-AAC depends entirely on organic matter content of soil. Since the application of fertilizer at the rate of 100 per cent of recommended dose has resulted into maximum increase in yield (Sharma et al., 2009) meaning thereby that maximum left over residue as well as root mass material remained in the soil. This extra addition of left over crop residues along with lantana incorporation might have increased organic matter content to a higher level, which, in turn, resulted in an increase in Cu-AAC.

DTPA-Cu and Total-Cu

The increasing levels of NPK fertilizers decreased DTPA-Cu content in soil apparently due to higher yield and uptake (Table 2). However, lantana

TABLE 3 Matrix of correlation coefficients showing relationship between different fractions of Cu in soil

	Cu-CA	Cu-AAC	Cu-PYR	Cu-OX	Res-Cu
Cu-CA	1.00				
Cu-AAC	0.90**	1.00			
Cu-PYR	0.76**	0.95**	1.00		
Cu-OX	0.95**	0.94**	0.99**	1.00	
Res-Cu	0.74**	0.94**	0.99**	0.99**	1.00

**Significant at 1%.

incorporation from 10 to 30 Mg ha^{-1} increased DTPA-Cu content significantly and consistently over the control. The increase was to the extent of 10, 18, and 28% at 10, 20, and 30 Mg ha^{-1}, respectively. This build-up in DTPA-Cu may be attributed to formation of Cu-humus complex of relatively high stability with humus, which, in turn decreased its susceptibility to fixation or precipitation in the soil in addition to Cu added through lantana biomass. Similarly, fertilizer application had no significant effect on total Cu content in the soil (Table 2). The total Cu is mainly governed by the type of parent material from which soils are formed (Eze et. al., 2010), however lantana application for long 12 years increased it over its no application (Table 2).

TABLE 4 Stepwise regression data showing interrelationship among different Cu fractions

	Stepwise variable on which y no. regressed	R^2	ΔR^2
Soil solution and exchangeable Cu (Cu-CA)	1. Cu-AAC	0.801	—
	2. Cu-AAC, Cu-PYR	**0.867	0.066
	3. Cu-AAC, Cu-PYR, Cu-Res	**0.885	0.018
	4. Cu-AAC, Cu-PYR, Cu-Res. Cu-OX	**0.8860**	0.001
Specifically adsorbed exchangeable Cu (Cu-AAC)	1.Cu-CA	0.873	—
	2. Cu-CA, Cu-PYR	**0.895	0.022
	3. Cu-CA, Cu-PYR,Cu-Res	**0.904	0.009
	4. Cu-CA, Cu-PYR, Res-Cu, Cu-OX	**0.904**	0.000
Organically bound Cu (Cu-PYR)	1. Cu-CA	0.964	—
	2. Cu-CA, Cu-AAC	**0.996	0.032
	3. Cu-CA, Cu-AAC, Cu-OX	**0.999	0.002
	4. Cu-CA, Cu-AAC, Cu-OX Res-Cu	**0.999**	0.000
Copper occluded by free oxides (Cu-OX)	1.Res-Cu	0.921	—
	2. Res-Cu,Cu-PYR	**0.929	0.006
	3. Res-Cu, Cu-PYR, Cu-AAC	**0.931	0.004
	4. Res-Cu, Cu-PYR, Cu-AAC, Cu-CA	**0.931**	0.000
Residual Cu (Res-Cu)	1.Cu-OX	0.906	—
	2. Cu-OX,Cu-PYR	**0.930	0.024
	3 Cu-OX,Cu-PYR, Cu-CA	**0.941	0.011
	4. Cu-OX,Cu-PYR, Cu-CA, Cu-AAC	**0.953**	0.012

**Significant at 1%.

TABLE 5 Effect of long term lantana and fertilizer application on total Cu uptake (kg ha^{-1}) by rice and wheat

Treatment	Rice		Wheat	
	After eleven years (Kharif, 2000)	After twelve years (Kharif, 2001)	After eleven years (Rabi, 2000–2001)	After twelve years (Rabi, 2001–2002)
Lantana application (Mg ha^{-1})				
0	24.90	30.23	10.46	13.20
10	29.06	36.59	13.07	20.62
20	34.12	41.17	15.96	23.73
30	37.88	41.80	17.96	25.12
Mean	31.49	37.45	14.36	20.67
LSD (0.05)	4.58	2.38	1.86	1.79
Fertilizer application (% of recommendation)				
33	27.92	33.67	10.62	15.06
66	32.10	38.24	15.97	23.74
100	34.65	40.44	16.28	24.96
Mean	31.56	37.45	14.29	21.25
LSD (0.05)	3.96	2.06	1.61	1.53

Interdependency Among Cu Fractions

All the Cu fractions were positively and significantly interrelated among themselves (Table 3). The linear stepwise regression data revealed that the most important variable contributing to the total variation in the regression of Cu-CA was Cu-AAC (Table 4). The R^2 value indicated that about 80% of the total variation in Cu-CA was explained by this fraction of Cu alone. Similarly, the most important variable contributing to the total variation in the regression of Cu-AAC and Cu-PYR was Cu-CA. About 87% of the total variation in Cu-AAC and 96% in Cu-PYR was explained only by Cu-CA alone. Similarly, the most important variable contributing to the total variation in the regression of CU-OX was Res-Cu (92%), and that contributing to the total variation in Res-Cu was Cu-OX (91%).

TABLE 6 Coefficient of correlation (r) between yield parameters and different Cu fractions

S. No.	Cu fractions	Wheat		Rice	
		Grain yield	Total Cu Uptake	Grain yield	Total Cu Uptake
1.	Cu-CA	0.95**	0.72**	0.88**	0.86**
2.	Cu-AAC	0.96**	0.85**	0.97**	0.96**
3.	Cu-PYR	0.92**	0.73**	0.89**	0.89**
4.	Cu-OX	0.90**	0.72**	0.87**	0.89**
5.	Res-Cu	0.91**	0.71**	0.86**	0.88**

**Significant at 1%.

TABLE 7 Stepwise regression data showing relationship between plant growth parameters 'Y' and soil Cu fractions

Step No.	Variable on which 'Y' is regressed	R^2	ΔR^2
Rice grain yield			
1.	Cu-AAC	0.866**	—
2.	Cu-AAC, Cu-PYR	0.966**	0.095
3.	Cu-AAC, Cu-PYR, Cu-CA	0.974**	0.009
4.	Cu-AAC, Cu-PYR, Cu-CA, Cu-OX	0.986**	0.012
5.	Cu-AAC, Cu-PYR, Cu-CA, Cu-OX, Res-Cu	0.988**	0.002
Cu uptake by rice			
1.	Cu-AAC	0.938**	—
2.	Cu-AAC, Cu-PYR	0.951**	0.013
3.	Cu-AAC, Cu-PYR, Cu-CA	0.959**	0.008
4.	Cu-AAC, Cu-PYR, Cu-CA, Cu-OX	0.959**	0.004
5.	Cu-AAC, Cu-PYR, Cu-CA, Cu-OX, Res-Cu	0.959**	0.000
Wheat grain yield			
1.	Cu-AAC	0.886**	—
2.	Cu-AAC, Cu-PYR	0.926**	0.040
3.	Cu-AAC, Cu-PYR, Cu-CA	0.940**	0.014
4.	Cu-AAC, Cu-PYR, Cu-CA,Cu-OX	0.940**	0.002
5.	Cu-AAC, Cu-PYR, Cu-CA,Cu-OX, Res-Cu	0.940**	0.000
Cu uptake by Wheat			
1.	Cu-AAC	0.875**	—
2.	Cu-AAC, Cu-PYR	0.918**	0.043
3.	Cu-AAC, Cu-PYR, Cu-CA	0.920**	0.003
4.	Cu-AAC, Cu-PYR, Cu-CA,Cu-OX	0.923**	0.003
5.	Cu-AAC, Cu-PYR, Cu-CA,Cu-OX, Res-Cu	0.923**	0.005

**Significant at 1%.

Copper Uptake

Like rice and wheat yields which are given elsewhere (Sharma et al., 2009), the uptake of Cu also increased significantly after twelve years of regular additions of lantana and fertilizer applications (Table 5). The lantana application from 10 to 30 Mg ha^{-1} increased Cu uptake in rice by 17 to 52% during Season-1 (kharif/rainy 2000) and 21 to 38% during Season-2 (kharif/rainy 2001). The corresponding values in Cu uptake by wheat were 25 to 70% during Season-1 (rabi/post-rainy 2000–2001) and 56 to 90% during Season-2 (rabi/post-rainy 2001–2002). Such increase in Cu uptake by rice and wheat due to the incorporation of lantana may be attributed to increase in their availability in the soil. Besides this, better proliferation of roots under the influence of lantana incorporation might have resulted in the increased absorption of water and nutrients from larger areas and greater depths (Sharma et al., 2009). Similarly, fertilizer application at 66 and 100% of recommended dose increased Cu uptake in rice by 15–24% during season-1 and 14–20% during season-2 when compared with 33% recommended fertilizer dose. In wheat, the Cu uptake increased by 50–53% during season-1 and 58–66% during season-2 under higher fertilizer levels over 33% level. The increase in Cu uptake either with lantana addition or with fertilizer application was mainly because of increase in rice and wheat yields (Sharma et al., 2009) under these treatments.

Relationship of Cu Fractions with Crop Yield and Cu Uptake

From the values of coefficients of correlation 'r', grain yield and Cu uptake in wheat and rice correlated positively and significantly with all the fractions of Cu (Table 6). Among different Cu fractions, Cu-AAC appeared to be the most important Cu fraction contributing towards grain yield of wheat (0.96**) and rice (0.97**) as well as towards Cu uptake by wheat (0.85**) and rice (0.96**). The R^2 values indicates that about 87% of the total variation in grain yield and 94% of the total variation in Cu uptake in rice could be explained only on the basis of Cu-AAC in soils (Table 7). The corresponding values in wheat were 89 and 88%. The second most important Cu fraction from the point of view of Cu nutrition of wheat as well as rice resulting higher grain yield and Cu uptake was Cu-PYR. In the present investigation, Cu-AAC and Cu-PYR were observed to be very efficient fractions in supplying Cu to wheat and rice, which may explain as to why these two Cu fractions had higher coefficient of correlation with plant growth parameters.

CONCLUSIONS

Continuous incorporation of lantana after 12 years resulted in redistribution of Cu from non-available forms to readily available and potentially available forms in soil. Incorporation of lantana residues increased rice and wheat crop yields and Cu uptake while simultaneously improved Cu status of the soil. All the Cu fractions were positively interrelated amongst themselves and with grain yield and Cu uptake in rice and wheat crops. Specifically exchangeable Cu (Cu-AAC) followed by organically bound Cu (Cu-PYR) were the most important Cu fraction contributing towards grain yield and Cu uptake in rice and wheat crops.

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