Copper dynamics in coffee growing soils of South India

Copper (Cu), being an essential micronutrient has important role in enzyme activation and thereby plant growth and development. Chemical reactions that control Cu transformations in soil-plant systems are complex in nature. In soils a wide range of constituents are known to adsorb Cu and it can be found in both organic as well as inorganic fractions. The adsorption of Cu is one of the important factors governing its availability to plants. Further, adsorption of Cu is dependent on soil pH, calcium carbonate, organic matter, oxides of iron/manganese contents, which are spatial and temporal variables (Singh and Saha, 1995; McLean and Bledsoe, 1996).

Post green revolution era has witnessed rapid decline of organic carbon reserves and essential nutrients in general and micronutrients in particular. In contrast, heavy metal contamination through P fertilizers, city waste compost, ameliorates, fungicides etc, has worsened the situation. In coffee cultivation copper is used as a fungicide rather than a nutrient, where a mixture of copper sulphate and calcium oxide (Bordeaux mixture) is sprayed for control of coffee leaf rust (*Hemileia vastatrix*) disease. Use of these sprays may prevent copper deficiencies in some soils while repeated applications can also lead to build up of copper to potentially toxic concentrations. Similarly the soils continuously treated with municipal sewage sludge also can accumulate high quantities of Cu. Hitherto copper phyto-toxicity has not been noticed in coffee plants in India.

It is a known fact that Cu sprayed either as a fungicide or as a micronutrient to a plant, redistributes in downward direction and ultimately ends up in litter and soils (Mabett, 1984). Since Cu has a high affinity for complexation by organic compounds and mineral components in the soil, is the least mobile of the micronutrients (Robert *et al.*, 1995). Whether the element is in sufficient, adequate or toxic to plant growth depends on soil properties, total Cu present, form in which the element is bound to soil and plant tolerance. Thus, the need to study the capacity of coffee growing soils to retain and release the Cu arises to evolve a suitable nutrient management package for that soil. Hence, a study was conducted to characterize Cu sorption in coffee growing soils representing different agro-climatic zones and to understand its relationship with various soil physico-chemical properties.

Major coffee growing regions *viz.*, Karnataka, Kerala, Andhra Pradesh and Tamil Nadu were considered for the study and surface soil samples (0-20cm) were collected from the research farms of CCRI (Balehonnur), RCRS-Chundale (Kerala), RCRS-RV Nagar (Andhra Pradesh) and RCRS-Thandigudi (Tamil Nadu) as representatives of the four selected locations. Soil samples were air dried and ground to pass through 2mm stainless steel sieve for further analyses. The pH, electrical conductivity-EC (1:2.5 soil-water suspensions) and organic carbon (OC) contents of soil samples were determined by following the standard procedures (Jackson, 1958). The clay content was determined by particle size analysis as described by Piper (1966). The cation exchange capacity (CEC) was estimated by the method of Gillman (1979), exclusively suggested for acid soils. The free iron oxide content was determined using sodium-dithionate-citrate buffer (Mehra and Jackson, 1967). The hydrous manganese oxide content was estimated by hydroxylamine hydrochloride ($0.1M$ $NH_2OH.HCl$ in $0.01 M$ HNO_3) solution (Chao, 1972). The total copper content was determined by aquaregia digestion (ISO: 11466, 1995) while labile Cu content was estimated by DTPA extraction (Lindsay and Norvell, 1978).

Among the soils selected for study, a wide variation in the physico-chemical properties was observed (Table 1). The soil pH varied from 5.2 (strongly acidic) to 6.8 (near neutral), organic carbon 17 to 62 g kg^{-1}, and CEC 10.4 to 17.6 cmol. kg^{-1}. Similarly, striking differences were noticed in free iron oxide (32.5 to 52.4 mg g^{-1}) and

Table 1. Physico-chemical properties of the selected soils

Location	pH	EC	OC	CEC	Clay	MnO$_2$	Fe$_2$O$_3$	DTPA-Cu	Total Cu
		(dSm^{-1})	(g kg^{-1})	(cmol. kg^{-1})	(%)	(mg g^{-1})			
Balehonnur	5.6	0.042	17	10.4	15.6	172	33.8	1.1	23
Chundale	6.1	0.062	29	11.1	15.4	227	47.6	1.7	30
R V Nagar	6.8	0.091	26	17.6	20.2	2204	52.4	4.4	58
Thandigudi	5.2	0.179	62	12.3	24.4	378	32.5	2.1	36

*EC- Electric conductivity, OC- Organic carbon, CEC- Cation Exchange Capacity

hydrous manganese oxide (172 to 2,204 mg g^{-1}) contents. The variation in DTPA-Cu was from 1.1 to 4.4 mg g^{-1}, while the total Cu was in the range of 23 to 58 mg g^{-1}.

Preliminary experiments revealed that 24 h was sufficient for complete equilibration of the Cu concentrations with the selected soils. Further, soils passed through 100 meshes were found ideal to avoid likely discrepancies during sample preparation and equilibration. Fifty milliliters each of 100, 200, 300, 400, 500, 600, 700 and 1000 μM Cu as CuSO$_4$.5H$_2$O prepared in 0.05 M CaCl$_2$ was added to one g of soil in 100 ml polypropylene centrifuge tubes. For each concentration gradient treatment three replications were maintained. The soil samples treated with Cu were shaken for 24 h in an incubator shaker at 25°C for equilibration, centrifuged and the supernatant filtered through Whatman no.42. The filtrate was analyzed for Cu by atomic adsorption spectrophotometer (model, GBC 932A). The Cu adsorbed was calculated as the difference between that in the solution initially and that remaining after equilibrium. The data on copper adsorption were interpreted in terms of Langmuir and Freundlich equations (Table 2). The derivatives of Langmuir equation (Adsorption maxima and Bonding energy) as well as that of Freundlich's (Sorption capacity and Rate of sorption) were correlated with the soil properties.

The adsorption of Cu by the selected soils as a function of Cu concentration at equilibrium is depicted in Fig.1. A perusal of data revealed that Cu sorption was more influenced by soil pH, CEC, OC and free oxides (Fe and Mn). However, the sorption data fitted well into both Langmuir and Freundlich equations with statistically significant R^2 values and the derivatives from these equations rendered precise prediction of Cu transformations in soils.

In general, soils with higher pH adsorbed higher Cu, owing to enhanced pH-dependent sites on colloids, reduced competition from H$^+$ ions and may be due to changed hydrolysis state of Cu which is congenial for sorption (Maguire et al., 1981; Raghupathi and Vasuki, 1993). The adsorption maxima remained the highest (1000) in R V Nagar soils followed by Thandigudi (909.1), Chundale (714.3) and Balehonnur soils (454.5). This followed the suit of soil pH in all the cases except in Thandigudi soils. In case of Thandigudi soils, the adsorption maximum was next only to that of R V Nagar soils despite having the lowest pH. This can be attributed to the presence of higher organic matter and its relatively higher share to CEC compared to compatriot soils. The hydrous manganese oxide might have created additional sites for sorption and mitigated the impact of acidity (Veeresh et al., 2003). Moreover the organic matter was found to have positive relationship with sorption. Organic constituents hold Cu in a kinetically available but thermodynamically stable form unlike Cu adsorbed on oxides which were accessible to isotropic changes (McLaren and Crawford, 1973).

Obviously soils with higher CEC are bound to have higher sorption and this was evident in all the soils studied. However, earlier reported specific adsorption of

Table 2. Copper adsorption equations and derivatives

Location	Langmuir equation	R^2	Adsorption maxima	Bonding energy	Freundlich equation	R^2	Sorption capacity	Rate of sorption
Balehonnur	Y=0.0022 C+ 0.1417	0.86**	454.5	0.016	log Y =0.3650 log C+ 1.6488	0.95**	44.5	0.365
Chundale	Y= 0.0014 C+ 0.0252	0.97**	714.3	0.056	log Y= 0.3327 log C+ 2.0764	0.99**	119.2	0.333
R V Nagar	Y = 0.001 C+ 0.0073	0.96**	1000.0	0.137	logY = 0.4701 log C+ 2.1872	0.97**	153.9	0.470
Thandigudi	Y=0.0011 C+ 0.0146	0.94**	909.1	0.075	log Y = 0.4106 log C+ 2.1062	0.99**	127.7	0.411

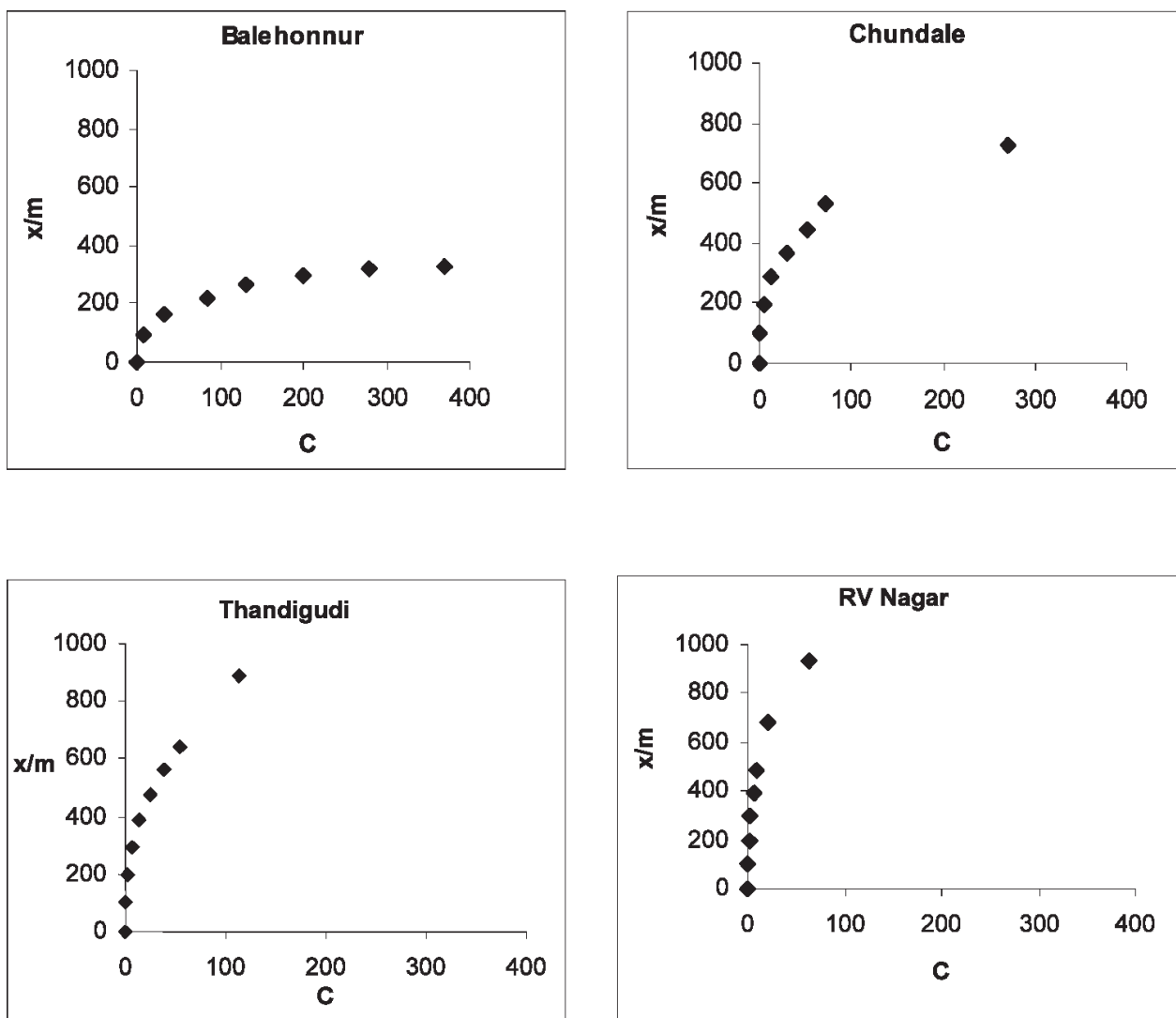Significance * P-0.05, ** P-0.01

Fig. 1. Copper adsorption, x/m (μM g⁻¹) as a function of equilibrium concentration, C (μM L⁻¹)

Cu by manganese oxide (Padmanabhan, 1983) can not be undermined in the present cases as positive correlations revealed its active role. The specific adsorption mechanisms include incorporation of Cu in to crystal lattice either by surface or interlayer sorption. Unlike manganese oxide, the iron oxide has no significant relationship with adsorption maxima. This may be attributed to the differences in charge carried by respective oxides in a given soil environment. The manganese oxide carries negative charge unlike iron oxide in near neutral environment and hence has high sorptive affinity for copper (McKenzie, 1980).

Large variation noticed in bonding energy among the soils may be related to differential composition of constituents responsible for sorption. In the present study R V Nagar soils recorded the highest (0.137) bonding energy followed by Thandigudi (0.075), Chundale (0.056) and Balehonnur soils (0.016). A significant positive

relationship of bonding energy with pH (0.99**) and CEC (0.96*) has highlighted the active components for sorption. Thus, soil pH has dominant role in deciding hydrolysis state of Cu, in turn bonding energy and subsequently strength of sorption. The statistically significant correlation coefficient values of bonding energy with CEC and manganese oxides confirmed the influence of these properties on Cu adsorption in the coffee growing soils. Strong affinity between Cu and calcium carbonate owing to higher bonding energy is proved in many soils (Raiky and Takkar, 1983). However, chances of occurrence of calcium carbonate in acid environment are remote and application through external sources was found to enhance sites for adsorption besides ameliorating soil acidity (Veeresh *et al.*, 2003).

Feasibility of Langmuir as well as Freundlich equations was verified by correlations amongst the derivatives from both the equations (Table 3). The

Table 3. Correlation of soil properties with adsorption derivatives

	pH	EC	OC	CEC	Fe_2O_3	MnO_2
A-Max	0.93	0.67	0.75	0.80	0.47	0.70
BE	0.99**	0.38	0.48	0.96*	0.68	0.91
SC	0.94	0.53	0.79	0.75	0.64	0.66
RS	0.79	0.43	0.16	0.91	0.30	0.88

* (0.96) significant at 5% and ** (0.99) significant at 1%

adsorption maxima had a positive correlation with sorption capacity (0.96*).

Among the four soils, RV Nagar soils retained more copper followed by Chundale, Thandigudi, and Balehonnur soils. Higher metal retention by the coffee growing soils invariably regulates the phytoavailable Cu and thereby the chances of Cu toxicity would be remote. Retention of Cu by these soils was found to be mainly dependent on soil pH, organic carbon, CEC and hydrous manganese oxide contents. Regular application of agricultural lime to the coffee growing soils is age old practices which regulates the soil pH and in turn the Cu retention. Hence, Cu toxicity has not observed in the coffee growing soils of south India.

References

Chao, T.T. 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Sci. Soc. Am. Proc.* **36**: 764-768.

Gillman, G.P. 1979. A proposed method for the measurement of exchange properties of highly weathered soils. *Aust. J. Soil Res.* **17**: 129-139.

ISO 11466, 1995. International standard soil quality extraction of trace quantities of cadmium in soils in aquaregia, 03-01.

Jackson, M. L. 1958. pp. 38-226. In: *Soil chemical analysis*. Prentice Hall, Bombay.

Lindsay, W.L. and Norvell, W. A. 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Am. J.* **42**: 421-428.

Mabett, T. 1984. Copper fungicides offer versatility and economy for the tropics. *World Crop* **36**(3): 86 – 103.

Maguire, M., Slavek, J., Vimpany, Z., Higgginson, F.R and Pickering, W.F. 1981. Influence of pH on copper and zinc uptake by soil clays. *Aust. J. Soil Res.* **19**:217-219.

McKenzie, R. M. 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. *Aust. J. Soil Res.* **18**: 61-73.

McLaren, R.G., and Crawford, D.V. 1973. Studies on soil copper II - The specific adsorption of copper by soils. *J. Soil Sci.* **24**: 443 -52.

McLean, J.E., and Bledsoe, B.E., 1996. pp. 19 – 56. Behavior of Metals in Soils. In: *EPA Environmental Assessment source book,* (Ed.) J. Russell Boulding, CRC Press.

Mehra, O.P., and Jackson, M.L. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* **7**: 317-327.

Padmanabhan, M.1983. Adsorption desorption behaviour of copper (II) at the goethite solution. *Aust. J. Soil Res.* **21**: 309.

Piper, C.S., 1966. pp. 47-79. In: *Soil and plant analysis*. Hans. Publishers, Bombay.

Raiky, N.P. and Takkar, P.N. 1983. Zinc and copper adsorption by a soil with and without removal of carbonates. *J. Ind. Soc. Soil Sci.* **31**: 611- 614.

Raghupathi, H.B., and Vasuki, N. 1993. Copper adsorption behaviour of some soils of North Karnataka. *J. Indian Soc. Soil Sci.* **41**: 70- 74.

Robert, L., Mikkelsen and James J. Camberato, 1995. pp 128. Potassium Sulfur, Lime and Micronutrient Fertilizers. In: *Soil Amendments and Environmental Quality*, (Ed) Jack E. Rechcigl, Lewis Boca Raton, FL.

Singh, M V. and Saha, J.K. 1995. Progress Report of All India Coordinated Research Project of micro and secondary nutrients and Pollutant Elements in Soils and Plants. IISS, Bhopal. 145 p.

Veeresh, H., Tripathy, S., Chaudhuri, D., Hart, B.R., and Powell, M. A. 2003. Competitive adsorption behaviour of selected heavy metals in three soil types of India amended with fly ash and sewage sludge. *Environ. Geol.* **44**: 363 – 370.

Central Coffee Research Institute, Coffee Research Station, Chikmagalur District - 577 117

Maria Violet D'Souza,
B.S. Sherigara,
S.M. Prasanna,
Hareesh B.S,
Jayarama