



RESEARCH ARTICLE

Investigation of inorganic fertilizers and manuring on copper fractions and their relationships with soybean-safflower yield and soil properties under long-term fertilizer experiment in vertisol

D M Zol¹, Bhagyasha R Gajbhiye¹, R N Khandare^{1*}, Snehal Shilewant¹, R H Wanjari², Anil Nagwanshi² & Sharad R Kadam¹

¹Department of Soil Science, College of Agriculture, Vasanttrao Naik Marathwada Krishi Vidyapeeth, Parbhani 431 402, Maharashtra, India
²ICAR- Indian Institute of Soil Science, Berasia Road, Navi Bagh 462038, Bhopal, Madhya Pradesh, India

*Correspondence email - ram.khandare11@gmail.com

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Abstract

The present study investigates the long-term effects of integrated nutrient management on copper (Cu) fractions and their interactions with soil properties and crop yield in Vertisols under a soybean-safflower cropping system. Soil samples were collected after the 18th crop cycle from a long-term fertiliser experiment initiated in 2006-07 at VNMKV, Parbhani, Maharashtra. Various treatments combining inorganic fertilisers (NPK) and organic manures (FYM) were assessed for their impact on different Cu fractions, DTPA-Cu, water-soluble Cu, exchangeable Cu, reducible Cu, residual Cu and total Cu using sequential extraction techniques. The results revealed that balanced fertilisation with 100 % NPK combined with FYM at 5 t ha⁻¹ significantly enhanced the concentrations of all Cu fractions, particularly residual and DTPA-extractable forms. This treatment also recorded the highest grain and straw yields for both soybean and safflower and the maximum Cu uptake. Positive and significant correlations were observed between all Cu fractions and key soil properties such as organic carbon, available N, P, K and S, whereas negative correlations were found with soil pH and CaCO₃ content. Notably, DTPA-Cu, residual Cu and total Cu exhibited strong associations with crop yields, highlighting their role in Cu bioavailability and plant nutrition. In this study, all fractions of copper showed a positive and significant relationship with grain and straw yield of soybean and safflower at 1 % and 5 % levels. The study underscores the importance of integrating organic and inorganic nutrient sources to maintain soil health, improve Cu dynamics and sustain long-term crop productivity in vertisols.

Keywords: copper fraction; copper uptake; long term experiment; safflower; soybean; yield

Introduction

Long-term fertilizer experiments offer a better platform to visualise the status of micronutrients in soil under intensive cropping systems and their contribution to sustaining the productivity of soybean and safflower at the end of the 18th crop cycle. Inorganic fertilisers play a crucial role in the production and productivity of food grains, but the imbalanced application of fertilisers onto long-duration crops adversely affects the soil health and reduces in productivity of crops (1). Although it is known, to fact that macro and micronutrients play a vital role in enhanced crop productivity, the micronutrients are yet to be a part of nutrient management under intensive cropping system (2). The importance of copper is an essential micronutrient for crop plants, vital for photosynthesis, respiration, nitrogen utilisation and protein production. It also acts as a cofactor for enzymes, supports lignin formation for structural integrity and is necessary for pollen variability and seed development. Copper

deficiencies lead to stunted growth, chlorosis (yellowing) of new leaves and increased susceptibility to diseases in crops. However, micronutrients are needed by crop plants in smaller quantities in comparison to primary elements and a high proportion of Cu is bound by the soil organic matter and is tightly held on exchangeable complex on clay particles by cationic forces. The nature of clay minerals and the presence of Fe and Al oxides are important in regulating the behaviour of Cu in soil. Despite the soil pH, CaCO₃, organic matter and clay content are also important for the transformation and bioavailability of copper for the growth of the crop plants (3). The water-soluble and exchangeable forms of copper are, assumed to be readily available, but other forms of copper, when sufficient in their activity, become important in the nutrition of crop plants (4). Copper in soils generally exists in several forms, including free ions in the soil solution, exchangeable, organic, precipitated and residual forms. Usually, most copper in soil exists in unavailable forms, with only a low concentration of Cu existing in

available forms, with the proportion of available and unavailable forms varies widely among soils within and between agro-ecological regions (5). The intensive cropping system of soybean-safflower exhausting the nitrogenous, phosphorous and potassium fertilisers for increasing the production of these crops has depleted the availability of copper in soils of Vertisol (6). However, many studies were carried out to find out the existence of Cu in soil; the information with respect to the current status of Cu forms in vertisols under long-term fertiliser experiment and their contribution to availability, uptake and relationship with soil properties is inadequate. Hence, the objective of this investigation was to assess the current status and distribution of Cu fractions in soil under long-term fertiliser use and to examine their contribution to Cu availability for crops, in Vertisols.

Materials and Methods

Experimental site

The experimental farm was situated within the Godavari catchment area in India between 17°35' to 26°40' N latitude and 74°40' to 78°15' E longitude with an altitude of 347 M above mean sea level (MSL). The Parbhani district lies under the semi-arid tropical climate on the Deccan plateau. The average annual rainfall of the district is 1697.6 mm. The maximum rainfall is recorded in September and October. The annual minimum temperature ranged between 9.0 °C to 25.4 °C and maximum from 27.9 °C and 37.5 °C during December and April, respectively, in the year 2021-2022. The relative humidity was minimum and maximum varied from 12% to 95%, respectively. The experimental soil is characterised by black colour dominated by montmorillonite clay with a high coefficient of expansion and shrinkage in summer, which leads to deep cracking. The experimental soils were formed from basaltic material. According to the 7th approximation, the soils are classified as *Typic Haplusterts* and are included in the Parbhani series (7).

Treatment details

The Long-term fertiliser experiments are being carried out on a fixed site having plot size 13.5 m² × 10 m² each since 2006-07 under All India Coordinated Research Project (AICRP) on Long-term fertiliser experiments with eleven treatments which are imposed in a randomised block design with four replications in soybean safflower cropping sequence. The experiment consists of eleven treatments of optimal, sub-optimal and super-optimal rates of fertiliser application including NPK, N or NP alone, NPK along with Zn or FYM and an unfertilized control plot. The fertilisers N, P, K and Zn were applied through urea, SSP, MOP and zinc sulfate respectively. The FYM in the

corporation was done in the soil before sowing to *kharif* crop every year. The experiment was laid out in randomized block design with twelve treatments in four replicate ions to minimise the impact of variability within the treatments (Table. 1). The treatments were T₁- 50 % NPK, T₂-100 % NPK, T₃- 150 % NPK, T₄- 100 % NPK + hand weeding, T₅- 100 % NPK + ZnSO₄ at 25 Kg/ha⁻¹, T₆- 100 % NP, T₇- 100 % N, T₈- 100 % NPK + FYM at 5 t ha⁻¹, T₉- 100 % NPK - Sulphur (P was applied through DAP), T₁₀- FYM at 10 t ha⁻¹, T₁₁- absolute control, T₁₂- Fallow (find out the soil properties only)

Methodology

The soil samples were collected from an ongoing experiment of long-term fertiliser during 2021-22 at Vasantrao Naik Marathwada Krishi Vidyapeeth, Parbhani, in Maharashtra, at the end of the 18th crop cycle of the soybean-safflower cropping system. The balanced application of 100 % NPK + FYM at 5 t ha⁻¹ gave higher content of different fractions of copper, i.e. available copper, water soluble copper, exchangeable copper, reducible copper, total copper and residual copper than to imbalanced use of inorganic fertilisers of 100 % N, 100 % NP, 50 % NPK and control. The suboptimal and above-optimal dose of NPK fertilisers is based on the optimal dose to determine the need for inorganic fertilisers. Crop plants, NPK and Zinc fertilizers are applied at the time of sowing and FYM is applied to the soil before sowing. Recommendations were given by the university.

Sampling and analysis of soil

Soil samples were collected at 0 cm-15 cm depth from eleven treatment plots before at harvest of the crop. The air-dried samples were carefully and gently ground with the wooden mortar and pestle to break the soil lumps (clods) and were passed through a sieve of 2 mm diameter. The sieved samples were used for the estimation of different fractions of copper in soil. The soil of the experimental field is alkaline in nature, prone to the availability of copper and different organic acids secreted by root exudates and FYM as organic nutrients provide a congenial environment and organic carbon, readily available food for microorganisms, which contributes total and available copper in soil. The sequential fractionation scheme was employed to determine different chemical pools of copper in soil as outlined below (11). Total Cu was estimated as one gram of soil was digested with 15 mL tri-acid mixture of HNO₃:HClO₄:H₂SO₄ (10:4:1) and the volume was made to 50 mL with double-distilled water. DTPA extractable copper was estimated as per standard procedure. Residual copper was calculated by deducting water soluble copper + exchangeable copper + DTPA available copper + reducible copper from the total

Table 1. Long-term effect of fertilizers and manuring on the yield of soybean and safflower at 18th crop cycle

Code	Treatment details.	Soybean yield (q ha ⁻¹)		Safflower yield (q ha ⁻¹)	
		Grain	Straw	Grain	Straw
T ₁	50 % NPK	9.20	27.24	9.91	25.63
T ₂	100 % NPK	10.68	30.35	12.57	28.71
T ₃	150 % NPK	11.18	31.08	13.05	30.55
T ₄	100 % NPK + hand weeding	10.21	29.39	12.23	28.25
T ₅	100 % NPK + zinc sulphate	10.93	30.49	12.83	29.21
T ₆	100 % NP	9.57	27.45	11.60	26.92
T ₇	100 % N	4.41	11.33	5.43	15.47
T ₈	100 % NPK + FYM at 5 t ha ⁻¹	11.24	32.06	13.42	34.41
T ₉	100 % NPK – sulphur	9.93	28.67	11.88	27.40
T ₁₀	Only FYM at 10 t ha ⁻¹	8.26	22.23	8.56	19.60
T ₁₁	Control	3.39	8.88	3.95	10.53
S.E. m ±		0.40	0.80	1.03	2.33
C.D. at 5 %		1.17	2.33	2.99	6.75

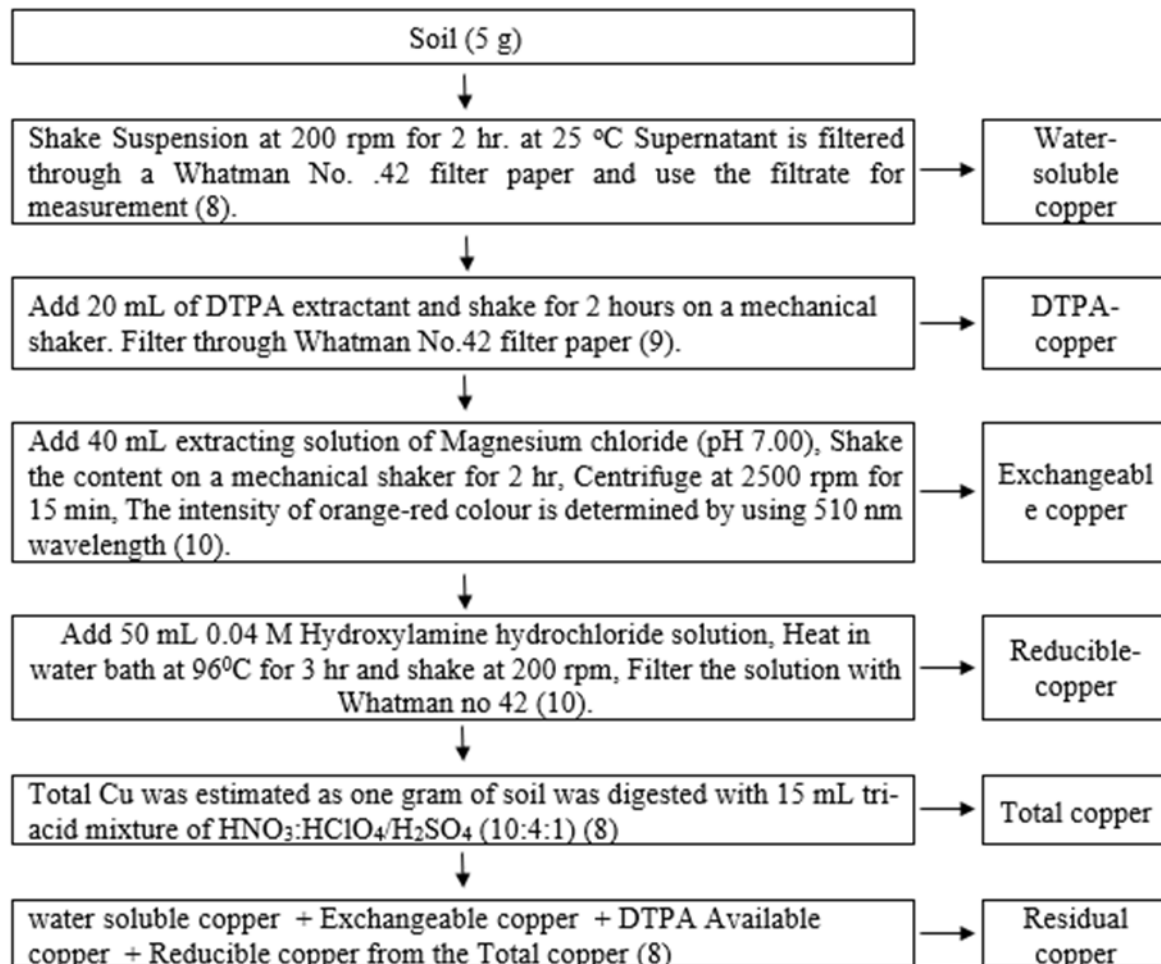


Fig. 1. Determination of Copper.

copper (8). All the Cu fractions were determined by using an atomic absorption spectrophotometer (Fig. 1).

At maturity after harvest of the crop, grain and straw yields were recorded for Cu uptake determination. Grain and straw samples were collected from each plot at the time of harvest of these crops. Soil samples were washed thoroughly and processed by following standard techniques of first air-drying and then oven-drying at 70 °C for 48 hours, before grinding. These samples were then digested in a triacid mixture of nitric acid (HNO₃), HClO₄ and H₂SO₄ and the Cu concentration in the digested sample was determined by AAS (8).

Statistical analysis

The data during the course of investigation were subjected to analysis of variance vis-à-vis correlation through the requisite statistical computations to predict the cause relationship of copper fractions and the relationship with soil properties by different treatments and productivity of the soybean-safflower cropping system (12). Appropriate standard error and critical differences were monitored at 5% level during the investigation of the experiment.

Results and Discussion

Grain and straw yield

The manuring and inorganic fertilizers enhanced the grain yield of soybean and safflower ranged from 3.39 ha¹ to 11.24 ha¹ and 3.95 ha¹ to 13.42 ha¹ respectively and 100% NPK with FYMat 5 t ha¹ recorded significantly highest grain yield and it was significantly at par with

150% NPK (11.18 q ha⁻¹ and 13.05 q ha⁻¹), 100% NPK (10.68 and 12.57 q ha⁻¹), 100% NPK + hand weeding (10.21 and 12.23 q ha⁻¹) and 100% NPK + Zn (10.93 q ha⁻¹ and 12.83 q ha⁻¹) in soybean and safflower crop, respectively. Yield enhancement in soybean and safflower might be due to stimulated soil microbes are valuable as they supply nutrients, but also, they enhance the synchrony of plant nutrient demand with soil (3, 13). The higher yields with the application of NPK + FYM could be attributed to enhanced population of stimulated nitrogen-fixing and phosphate-solubilising microorganisms and thus steadily increased availability of nutrients. However, copper uptake (Fig. 2) in soybean and safflower grain and straw was also enhanced due to manuring and inorganic treatments and significantly gave the highest uptake in 100% NPK + FYM than to sub-sub-optimal treatments. Similarly, better crop yields obtained as well as increased concentration of Cu in plants may be ascribed to the combined application of 100% NPK + FYM and such results are in agreement with the findings of Behera and others (6). With the increment in supply of essential elements through organic and inorganic sources, their availability, mobilisation, ion and influx into plant tissue and thus improving content and uptake in the crops. Research indicates that application of 100% NPK + FYM showed the highest uptake of Cu (18.62 g ha⁻¹) by soybean than the control in Vertisol. The imbalance application of inorganic fertilizers of 100% NP (9.57, 27.45 and 11.60, 26.92), 100% N (4.41, 11.33 and 5.43, 15.47), 100% NPK-Sulphur (9.93, 28.67 and 11.88, 27.40) only FYM at 10 t ha⁻¹ (8.26, 22.23 and 8.56, 19.60) and absolute control (3.39, 8.88 and 3.95, 10.53) gave lowest grain and straw yields of soybean and safflower than balanced application of inorganic fertilizers.

Forms of copper

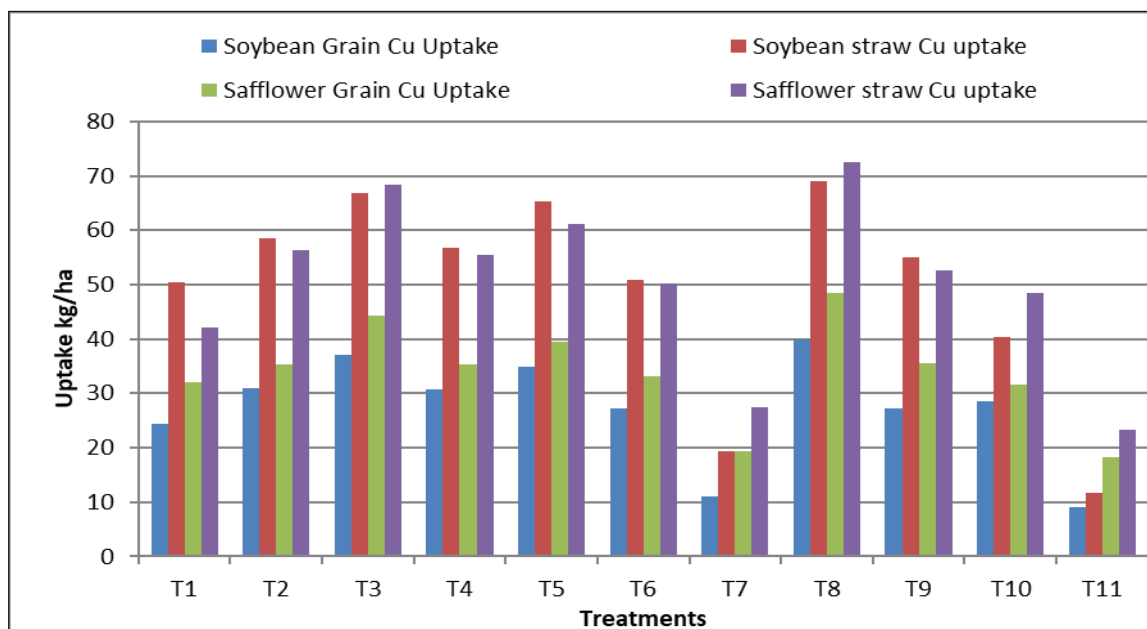


Fig. 2. Long-term effect of fertilizers and manuring on copper uptake by soybean and safflower at the 18th crop cycle. T₁: 50 % NPK; T₂: 100 % NPK; T₃: 150 % NPK; T₄: 100 % NPK + hand weeding; T₅: 100 % NPK + zinc sulphate; T₆: 100 % NP; T₇: 100 % N; T₈: 100 % NPK + FYM at 5 t ha⁻¹; T₉: 100 % NPK – sulphur; T₁₀: Only FYM at 10 t ha⁻¹; T₁₁: Control.

A perusal of the data revealed that several fractions of the copper were investigated from a 0 cm-15 cm layer of soil and resulted in the concentration of available copper, water-soluble copper, exchangeable copper, reducible copper, total copper and residual copper after harvest of the 18th crop cycle are obtainable in Table 2 and these fractions were revealed in the order of total copper > residual copper > available copper > exchangeable copper > water soluble copper > reducible copper under a long-term fertilizer experiment in the soybean-safflower cropping system in Tyic Haplustert

DTPA copper and water-soluble copper

It is evident from Table 2 that DTPA copper was significantly recorded as maximum with application 100 % NPK + FYM at 5 t ha⁻¹ (2.88 mg kg⁻¹), 150 % NPK (2.87 mg kg⁻¹) and 100 % NPK + Zn (2.77 mg kg⁻¹). Moreover, the copper fractions in 100 % NP, 100 % NPK + hand weeding, 100 % NPK, 100 % NPK-sulphur, 50 % NPK and only FYM at 10 t ha⁻¹ were 2.69, 2.67, 2.63, 2.64, 2.55 and 2.56 mg kg⁻¹ respectively, in surface soil. However, available copper increased over control when chemical fertilizers were applied in conjunction with organics and it declined over control with the application of chemical fertilizer alone in the last 18th years of the crop cycle. The application of 100 % NPK + FYM at 5 t ha⁻¹ gave the maximum available copper than to the other treatments due to DTPA-Cu may be attributed to the formation of Cu-humus complex of relatively high stability with humus, which, in turn, decreased its susceptibility to fixation or precipitation in the soil. Research indicates that the availability of Cu to the plants is higher in surface soil (0 cm–15 cm) than in sub-surface soil (6, 15). Similarly, water-soluble copper was also varied from 0.21 to 0.28 mg kg⁻¹ under different treatments and significantly found maximum in 100 % NPK + FYM 5 t ha⁻¹ (0.28 mg kg⁻¹), followed by 100 % NPK + Zn (0.27 mg kg⁻¹) and 150 % NPK (0.26 mg kg⁻¹), respectively, in surface soil. It was observed that (Table 2) the concentration of water-soluble copper was also found significantly highest with 100 % NPK, 100 % NPK + hand weeding and FYM at 10 t ha⁻¹ were 0.24, 0.25 and 0.20 mg kg⁻¹, respectively but the water-soluble copper was lowered with 50 % NPK (0.21 mg kg⁻¹), control (0.22 mg kg⁻¹) and 100 % N (0.20 mg kg⁻¹). The 100 % NPK + FYM at 5 t ha⁻¹ recorded maximum content of water-soluble copper

because farmyard manures gave significantly higher amounts of water-soluble copper than any other nutrient management strategies and this was attributed to metallic micronutrients present in water-soluble forms that exist in a state of dynamic equilibrium and constitute a labile pool from which plants absorb them (16).

Exchangeable copper and reducible copper

Exchangeable copper (Table 2) in surface soil ranged from 0.36 to 0.43 mg kg⁻¹ and it was noted maximum was obtained with 100 % NPK + FYM at 5 t ha⁻¹ (0.43 mg kg⁻¹), than by the application of 100 % NPK + Zn (0.42 mg kg⁻¹) and 150 % NPK (0.41 mg kg⁻¹). It was also observed that the concentration of exchangeable copper in 100 % NPK, 100 % NPK + HW and FYM at 10 t ha⁻¹ were 0.39, 0.39 and 0.40 mg kg⁻¹, respectively and significantly maximum than 50 % NPK (0.38 mg kg⁻¹) and control (0.36 mg kg⁻¹) and 100 % N (0.35 mg kg⁻¹) at harvest of safflower crop. The increase in exchangeable copper might be due to enhanced specific sites of inorganic matter for Cu adsorption as a result of the addition of higher left-over residue, as well as root biomass in the soil under treatments (17). Exchangeable copper was found to decrease with the increase in pH, which might be due to the precipitation of Cu as hydroxides and hydroxyl carbonates. It may also be due to increased specific adsorption of Cu by soil components (18). Similarly, reducible copper (Table 2) also, ranged from 0.15 mg kg⁻¹ to 0.24 mg kg⁻¹ and was significantly noted highest in 100 % NPK + FYM at 5 t ha⁻¹ (0.24 mg kg⁻¹) which was found to be at par with 100 % NPK + Zn (0.23 mg kg⁻¹), 150 % NPK (0.22 mg kg⁻¹) and only FYM at 10 t ha⁻¹ (0.21 mg kg⁻¹). Reducible copper concentration in 100 % NPK (0.19 mg kg⁻¹), 100 % NPK + hand weeding (0.20 mg kg⁻¹) and FYM at 10 t ha⁻¹ (0.21 mg kg⁻¹) were significantly maximum and the lowest reducible copper was noted with treatment by 100 % N (0.17 mg kg⁻¹) and control (0.15 mg kg⁻¹) at harvest. Residual copper was positively and significantly influenced by the application of inorganic fertilizers and manuring over control treatments. The reducible copper fraction differed significantly due to different treatments of inorganic fertilizers and manuring in long-term fertilization under Vertisol at harvest in the soybean-safflower cropping system. This might be attributed to the organic matter application retarded copper transformation from organic carbon into to reducible fraction (18). Research indicates that the highest

Table 2. Long-term effect of organic manures and inorganic fertilizers on different copper fractions in soybean-safflower cropping sequence under Vertisols

Code	Treatment details	DTPA-copper (mg kg ⁻¹)	Water-soluble copper (mg kg ⁻¹)	Exchangeable copper (mg kg ⁻¹)	Reducible copper (mg kg ⁻¹)	Residual copper (mg kg ⁻¹)	Total copper (mg kg ⁻¹)
T ₁	50 % NPK	2.55	0.21	0.38	0.17	23.91	27.22
T ₂	100 % NPK	2.63	0.24	0.39	0.19	24.03	27.48
T ₃	150 % NPK	2.87	0.26	0.41	0.22	24.38	28.14
T ₄	100 % NPK + hand weeding	2.67	0.25	0.39	0.20	24.19	27.69
T ₅	100 % NPK + zinc sulphate	2.77	0.27	0.42	0.23	24.28	27.97
T ₆	100 % NP	2.69	0.24	0.39	0.19	24.13	27.64
T ₇	100 % N	2.52	0.25	0.38	0.18	23.93	27.26
T ₈	100 % NPK + FYM at 5 t ha ⁻¹	2.88	0.28	0.43	0.24	24.42	28.25
T ₉	100 % NPK – sulphur	2.64	0.24	0.39	0.19	24.06	27.52
T ₁₀	Only FYM at 10 t ha ⁻¹	2.56	0.25	0.40	0.21	24.19	27.61
T ₁₁	Control	2.41	0.24	0.38	0.17	23.85	27.05
T ₁₂	Fallow	2.40	0.22	0.37	0.15	23.84	26.98
S.E m.±		0.06	0.007	0.006	0.009	0.127	0.27
C.D. at 5 %		0.18	0.02	0.02	0.03	0.367	0.764

value of reducible copper was recorded by application of 50 % NPK along with FYM at 10 in groundnut-wheat sequence (19). FYM act as a chelating agent due to chelation, the availability of copper is maximum with integrated nutrient management, i.e. 100 % NPK + FYM at 5 t ha⁻¹.

Residual copper and total copper

Residual copper (Table 2) in experimental soil of 0 cm-15 cm ranged from 23.84 mg kg⁻¹ to 24.42 mg kg⁻¹ and residual copper was noted significantly maximum in 100 % NPK + FYM at 5 t ha⁻¹ (24.42 mg kg⁻¹) than 150 % NPK (24.38 mg kg⁻¹) and 100 % NPK + Zn (24.28 mg kg⁻¹) respectively. The copper fraction in 100 % N, 100 % NP, 100 % NPK + hand weeding, 100 % NPK, 100 % NPK- sulphur and only FYM at 10 t ha⁻¹ were 23.93, 24.03, 24.19, 24.13, 24.06 and 24.19 mg kg⁻¹. While, minimum total copper was noted at 50 % NPK (23.91 mg kg⁻¹), followed by control (23.84 mg kg⁻¹). Similar findings are in close agreement with Research indicating that the residual copper content was higher under integrated use of organic and inorganic plots as compared to the only inorganically treated plots (20). A major part of the total-Cu content was present as residual, i.e. held within the silicate mineral structure. The dominance of residual-Cu accords with reports that oxides in soils and clays provide reactive sites for the almost irreversible chemisorption of Cu. Similarly, Research indicates that the highest value of residual copper was recorded in the application of FYM at 25 t ha⁻¹ to groundnut (19). In connection with these fractions the total copper (Table 2) in soil varied between 26.98 mg kg⁻¹ to 28.25 mg kg⁻¹ and fractions of total copper was significantly found maximum with application of 100 % NPK + FYM at 5 t ha⁻¹ 28.25 mg kg⁻¹ which was at par with application of 150 % NPK (28.14 mg kg⁻¹) and 100 % NPK + Zn (27.97 mg kg⁻¹). Moreover, total copper concentration in 100 % NPK, 100 % NPK + hand weeding and FYM at 10 t ha⁻¹ were 27.48, 27.69 and 27.61 mg kg⁻¹ respectively. Whereas, the minimum total copper was found with absolute control (27.05 mg kg⁻¹) and 50 % NPK (27.22 mg kg⁻¹) at harvest of the safflower crop. The organic material determines the natural concentration of total copper in soil. The type of bedrock and its mineral composition significantly dictate the copper concentrations in soil. Soils derived from copper-rich parent material inherently contain maximum total copper. The soil with high organic matter and clay content showed maximum total copper concentrations in the soil. The total copper fraction increased

significantly due to different inorganic fertilizers and manuring in long-term fertilization under Vertisol. Research indicates that the Vertisols are rich in total copper, with their content ranging from 200 mg kg⁻¹ to 250 mg kg⁻¹ (21). Soils having parent material derived from mafic rocks have relatively higher total Cu content. Total Cu is mainly governed by the type of parent material from which soils are formed (22). Research indicates that the high total Cu content in organically treated plots might be due to the build-up of organic matter under continuous manuring in soil (23). Similarly, as per our recommendations 5 t/ha along with inorganic fertilizers, research indicates that the highest value of total copper was recorded by application of FYM at 25 t ha⁻¹ to groundnut (T₉), followed by application of 50 % NPK in groundnut-wheat (19).

Relationship of different copper fractions with physico-chemical properties of soil

It is evident from the data table 3 all the forms of copper i.e. DTPA-copper, water soluble copper, exchangeable copper, reducible copper, residual copper and total copper were negatively correlated with soil pH ($r = -0.212, -0.425, -0.490, -0.485, -0.429$ and -0.365) but all the forms of copper i.e. DTPA-copper (-0.582^*), water soluble copper (-0.481^*), exchangeable copper (-0.583^*), reducible copper (-0.663^*), residual copper (-0.658^*) and total copper (-0.653^*) significantly but negatively correlated with CaCO₃ in soil. Soil pH of the experimental site is alkaline in nature, clay content is more, so at higher soil pH, copper ions form insoluble compounds and are strongly bound with organic matter and clay content and showed negative correlations with soil pH. However, the Calcium carbonate content was low and the clay content high, resulting in negative correlations with all fractions of copper in the experimental field. Whereas, EC of soil correlated non-significantly but positively with all forms of copper except DTPA-copper ($r = 0.608^*$). Organic carbon ($r = 0.769^{**}, 0.577^*, 0.785^{**}, 0.822^{**}, 0.817^{**}, 0.809^{**}$), available nitrogen ($r = 0.908^{**}, 0.716^{**}, 0.889^{**}, 0.898^{**}, 0.922^{**}, 0.930^{**}$), potassium ($0.753^{**}, 0.671^*, 0.843^{**}, 0.826^{**}, 0.857^{**}, 0.831^{**}$) and sulphur ($r = 0.811^{**}, 0.703^*, 0.879^{**}, 0.858^{**}, 0.908^{**}, 0.883^{**}$) were associated positively and significantly relationship with DTPA-copper, water soluble copper, exchangeable copper, reducible copper, residual copper and total copper, respectively. Water-soluble copper in soybean and safflower primarily binds with low molecular weight organic molecules and proteins within the plants. However, available

Table 3. Relationship of different copper fractions with physico-chemical properties of soil

Soil properties	DTPA-copper	Water soluble copper	Exchangeable Copper	Reducible copper	Residual copper	Total Copper
pH	-0.212	-0.425	-0.490	-0.485	-0.429	-0.365
EC	0.608*	0.422	0.363	0.431	0.426	0.505
OC	0.769**	0.577*	0.785**	0.822**	0.817**	0.809**
CaCO ₃	-0.582*	-0.481	-0.583*	-0.663*	-0.658*	-0.635*
Available N	0.908**	0.716**	0.889**	0.898**	0.922**	0.930**
Available P	0.754**	0.377	0.664*	0.658*	0.785**	0.762**
Available K	0.753**	0.671*	0.843**	0.826**	0.857**	0.831**
Available S	0.811**	0.703*	0.879**	0.858**	0.908**	0.883**

*Significance at 5 % level: 0.576, **Significance at 1 % level: 0.708.

phosphorus showed a significant and positive relationship with all forms of copper except water-soluble copper ($r = 0.377$) in Vertisol. The findings clearly revealed a positive correlation between organic carbon and various fractions of copper. This might be due to the formation of soluble Cu-organic complexes on the clay surface, but Cu was negatively correlated with pH, indicating increased availability of Cu at a lower pH range (24).

Correlations of copper fractions with yield

The results indicated that (Table 4) soybean grain yield showed positive and significant correlation with DTPA-copper, exchangeable copper, reducible copper, residual copper and total copper, which is evident by 'r' values 0.826**, 0.625*, 0.645**, 0.733* and 0.762*, respectively. However, it was associated ed positive and non-significant correlations with water-soluble copper, which was noticeable with $r = 0.292$. Similarly, soybean straw yield assembled a positive and significant correlation with DTPA-copper (0.801**), residual copper (0.691*) and total copper (0.724*). Further, safflower grain and straw yield also had positive and significant correlation with DTPA-copper (0.856** and 0.883**, exchangeable copper (0.627* and 0.655*), reducible copper ($r = 0.648*$ and 0.656*), residual copper ($r = 0.739**$ and 0.741**) and total copper (0.779** and 0.793**) respectively. While it showed positive but non-significant correlation with water-soluble copper ($r = 0.344$ and 0.358) by grain and straw yield of safflower, respectively. The positive and significant correlations with grain and straw yields of the crops were noticed (20, 25).

Conclusion

From the present study, it is concluded that significantly maximum grain yield of soybean and safflower was recorded with balanced application of 100 % NPK with FYM at 5 t ha⁻¹ and also, Cu uptake by the two crops was directly influenced by the organic and inorganic

fertilisers and observed significantly highest in NPK + FYM. The residual Cu fraction was the dominant fraction of total Cu in soil. While DTPA-copper, residual copper and total copper formed positive and significant relationships with soybean and safflower grain and straw. All the forms of copper formed positive and significant relationships with soil properties in Vertisol.

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Authors' contributions

DMZ contributed to the conceptualisation, methodology development, investigation and supervision of the study. BRG was involved in conceptualisation, investigation, formal analysis and supervision. RNK played a major role in conceptualisation, methodology development, resource management, data collection, investigation, formal analysis, writing of the original draft, visualisation and supervision. BRG contributed to conceptualisation, methodology development, resource management, data collection, investigation, formal analysis, visualisation and supervision. RHW assisted for analysis of copper fractions, their role in plant nutrition under long term fertilizer experiment, helped in writing of manuscript. AN played role in statistical analysis and computation of data in manuscript. SS was responsible for methodology development, resource provision, data collection and supervision. SRK assisted in data collection. All authors read and approved the final version of the manuscript.

Table 4. Correlation of different copper fractions with grain and straw yield of soybean and safflower in the soybean-safflower cropping sequence

	DTPA- copper	Water-soluble copper	Exchangeable copper	Reducible Copper	Residual Copper	Total Copper
Soybean grain yield	0.826**	0.292	0.625*	0.645*	0.733*	0.762**
Soybean straw yield	0.801**	0.236	0.583	0.596	0.691*	0.724*
Safflower grain yield	0.856**	0.344	0.627*	0.648*	0.739**	0.779**
Safflower straw yield	0.883**	0.358	0.655*	0.656*	0.741**	0.793**

*Significance at 5 % level: 0.602, **Significance at 1 % level: 0.735.

Compliance with ethical standards

Conflict of interest: The authors declare no conflicts of interest.

Ethical issues: None.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this manuscript, the authors used ChatGPT to correct grammatical mistakes and language editing. After using this tool/service, the authors reviewed and edited the content as needed and took full responsibility for the content of publication.

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