



## Soil copper and manganese availability to wheat (*Triticum aestivum*) as affected by long-term fertilization in an Inceptisol

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### ABSTRACT

Copper (Cu) and manganese (Mn) are two most important micronutrients, essential to living organisms through their involvement in different enzymes and other biologically active molecules. An experiment was conducted at the research farm of ICAR-Indian Agricultural Research Institute, New Delhi to investigate the impact of various fertilizers and manurial treatments on DTPA-extractable Cu and Mn in soil and their concentration in grain and straw of wheat (*Triticum aestivum* L.) after 46 years of continuous cropping. The soil and plants samples were collected at wheat harvest during April, 2018 and April, 2019 following fertilizers and manurial treatments: control, N alone, NP, NPK, 150% NPK, NPK+Zn and NPK+FYM. Results revealed that DTPA-extractable Cu did not show any significant variation among the various treatments except control but DTPA-Mn was highest under FYM treated plot. In addition, nutrient management options such as 150% NPK, NPK+FYM and NPK+Zn were equally effective in enhancing the yield of wheat. The concentration of Cu and Mn in grain varied from 5.25–7.63 and 28.5–36.4 mg/kg, respectively under different nutrient management options. Highest uptake of Cu and Mn was obtained under NPK+FYM treatment while control showed the lowest, indicating importance of organic manures for improving the nutritional quality of food grains. Transfer coefficient (indicating transfer nutrients from vegetative tissue to grain) of Cu did not change by fertilization and manuring to a significant level whereas balance and integrated use of fertilizers and manure significantly increased the transfer of Mn from straw to grains.

**Keywords:** Copper, Manganese transfer coefficient, Uptake, Yield

Copper (Cu) and Manganese (Mn) are two most important micronutrients which are essential to all living organisms including humans because of their role in regulating various biological functions of organisms (Shahid *et al.* 2016, Narender *et al.* 2018). In India, Cu and Mn deficiency were accounted for 5.4% and 5.5% of the country's cultivated land respectively, which are mostly reported in Punjab and Haryana (Shukla *et al.* 2014). Cultivation of the high-yielding and nutrient exhaustive cereals with excess use of NPK fertilizers since last 4–5 decades with little or no supplement of Cu and Mn from external sources caused depletion of native reserves of Cu and Mn in soils of Indo-Gangetic plain (IGP) (Shukla *et al.* 2020). The Cu and Mn in harvested grains of cereals grown in deficient soil are generally low, adversely affecting human health. According to the report published by Welch and Graham (2004), around 50% population of developing countries are suffering from micronutrients malnutrition due to excessive dependence on cereals (generally low in micronutrient) based diet for calorific requirements. In this

context, long-term fields experiments based on a different combination of fertilizers and manures are considered as a more meaningful tool to investigate the long-term sustainability of modern intensive cropping compared to the single-season fields trials (Behera and Singh 2009, Das *et al.* 2021). In India, more importance has been given to studying Zn compared to other cationic micronutrients (Behera *et al.* 2008). However, very little attention has been given to studying the uptake of Cu and Mn by wheat (*Triticum aestivum* L.) and their transfer from straw to grain in response to long-term fertilization practices. Therefore, present study was carried out with the objective to study the changes of Cu and Mn concentration in wheat grain and straw as affected by long-term application of fertilizer and manures, and also to investigate the plant uptake of Cu and Mn and their consecutive transfer from vegetative tissues to grain as affected by long-term fertilization and manuring.

### MATERIALS AND METHODS

*Experimental site:* To fulfill the objectives, soil samples were taken from an ongoing field trial under the aegis of All India Co-ordinated Research Project on Long-term Fertilizer Experiment (initiated in 1971), at the research farm of ICAR-Indian Agricultural Research Institute (28°37'–28°39'N,

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77°9'–77°11'E at an altitude of 217 m amsl), New Delhi during 2017–18 and 2018–19. The climate of the site is categorized as semi-arid, sub-tropical with cold winter and dry hot summer. At the starting of the experiment (1971), the soil was characterized as non-saline (EC ~ 0.45 dS/m), alkaline (pH ~ 8.3), contained 0.44% Walkley-Black C, 16 kg/ha Olsen's extractable P, 155 kg/ha ammonium acetate extractable K, 20 and 1.35 mg/kg of DTPA extractable Mn and Cu, respectively.

**Experimental details:** The field experiment was conducted on an undisturbed layout since 1971 with 10 different fertilizers and manurial treatments having 4 replications under randomized block design. Initially, the experiment was started with a pearl millet-wheat-cowpea cropping sequence, which was changed to maize-wheat-cowpea from 1982. Since 2002, the experiment has been continued as a maize-wheat cropping system. However, for the present investigation, 7 treatments with 4 replication were chosen, i.e. control, N (recommended dose of N), NP (recommended dose of N and P to both crops), NPK (recommended dose of N, P and K to both crops), 150% NPK (1.5 times to recommended dose of N, P and K to both crops), NPK+Zn (recommended dose of N, P and K to both crops and 5 kg Zn/ha to wheat crops) and NPK+FYM (recommended dose of N, P and K to both crops and FYM@ 5 t/ha to *kharif* crops). The recommended rate of N, P and K were 120 kg N/ha, 60 kg P<sub>2</sub>O<sub>5</sub>/ha and 40 kg K<sub>2</sub>O/ha, respectively which remained unchanged since starting of the experiment. N, P, K and Zn were applied through urea, diammonium phosphate, muriate of potash and zinc sulfate, respectively.

**Soil sampling and measurements:** Soil samples from each treatment were collected at wheat harvest of 2017–18 and 2018–19 from 0–15 cm depth with the help of a tube auger. Samples were then air-dried at room temperature and ground in a mortar and pestle to pass through a 2 mm sieve for analysis of DTPA-extractable of Cu and Mn. Air-dried soil weighing 10 g was continuously shaken with 20 ml of 0.005 M diethylene triamine penta acetic acid (DTPA), 0.01 M calcium chloride (CaCl<sub>2</sub>) and 0.1 M tri-ethanol amine (TEA) solution for 2 h at 25°C, which was then filtered through Whatman No. 42 filter paper (Lindsay and Norvel 1978). The Cu and Mn content in extract were measured using an atomic absorption spectrophotometer.

**Plant sampling and measurement:** At maturity, grain and straw yield of wheat for each plot was recorded and representative plant samples (both grain and straw) were collected from individual plots followed by washing with distilled water. Plant samples were then dried at 60°C for 48 h in a hot air oven followed by grinding in stainless steel Wiley mill. Straw and grain samples were then digested with a diacid mixture of nitric and perchloric acid (HNO<sub>3</sub>:HClO<sub>4</sub> = 4:1). The Cu and Mn content in digested extract was determined using the atomic absorption spectrophotometer. Total uptake was calculated as:

$$\text{Total uptake} = (\text{grain concentration} \times \text{grain yield}) + (\text{straw concentration} \times \text{straw yield})$$

**Statistical analysis:** Data generated in this investigation were processed for the 'F' test as applicable to randomized block design to identify significant differences among the treatment means with the help of SPSS statistical software. The same latter in each column in the tables or graphs represented no significant difference among the treatment means at 5% level of significance.

## RESULTS AND DISCUSSION

**DTPA-extractable Cu and Mn in soil:** Available Cu varied from 1.21–1.59 mg/kg among treatments after 4 decades of cultivation (Table 1). The DTPA-extractable Cu was significantly higher under all treatments receiving fertilizer and manure applications compared to control, though different treatments with varying rates of fertilizer and manure application reported similar values. Thangasamy *et al.* (2017) also found that application of chemical as well organic fertilizers did not show any significant effect on available Cu. Results of the present study also revealed that DTPA-Cu in soil is still higher than critical limit (0.2 mg Cu/kg of soil), even after 46 years of continuous cultivation.

Available Mn content varied from 6.35–11.02 mg/kg among different treatments, with the highest and lowest being observed in NPK+FYM and control, respectively in both the years, 2017–18 and 2018–19 (Table 1). The treatment receiving FYM had significantly higher DTPA-Mn compared to all other treatments, values being 70% higher over the control. This increase might be related to addition of Mn through organic manure. Besides, Ben-Yin *et al.* (2010) reported that application of organic manure reduced the soil pH through production of different organic and inorganic acids during decomposition that increased the dissolution of insoluble minerals bound Mn. The DTPA-Mn was statistically similar under NPK, 150% NPK and NPK+Zn. Results indicated that continuous cultivation with different combinations of fertilizers over 46 years led to an increase in available Mn over the control. Thangasamy *et al.* (2017) reported that continuous cropping over some time leads to changes in soil micro-environment that accelerated the release of plant-available Mn (Narender *et al.* 2018).

**Grain and straw yield of wheat:** Results showed that application of chemical fertilizers with or without FYM significantly influenced the yields over the years (Fig 1). The

Table 1 Available copper and manganese (mg/kg) different nutrient management options

Treatment	Available Cu		Available Mn	
	2017–18	2018–19	2017–18	2018–19
Control	1.21c	1.22c	6.39d	6.35d
N	1.49b	1.47b	7.01d	6.97d
NP	1.54ab	1.53ab	7.51cd	7.65cd
NPK	1.55ab	1.52ab	9.34b	9.3b
150% NPK	1.55ab	1.57a	9.51b	9.4b
NPK+Zn	1.57a	1.59a	8.56c	8.45c
NPK+FYM	1.46b	1.44b	11.02a	10.8a

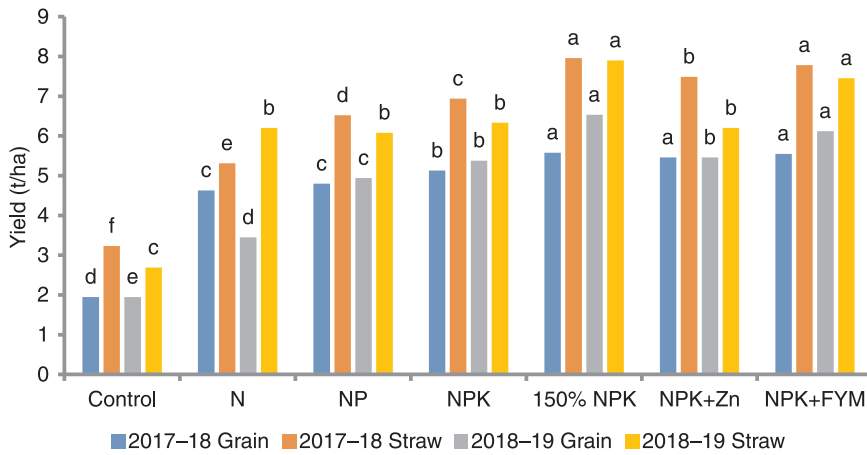


Fig 1 Grain and straw yield of wheat during 2017–18 and 2018–19 under different nutrient management options of long-term fertilizer experiment.

highest grain as well as straw yields of wheat was obtained under 150% NPK treatment that was at par with NPK+FYM and lowest in control. This increase in yield under 150% NPK might be related to application of super optimal doses of N, P and K that accelerated biomass production. In addition, yield advantage on application of FYM mainly related to supply of both macro and micronutrients from a single source along with improvement of different physical (pore space, water holding capacity and structure etc.) as well as biological properties (microbial activity, enzymatic activity etc.) (Chaudhary *et al.* 2019).

**Cu uptake by wheat:** Concentrations of Cu in wheat grain varied from 6.5–7.33 mg/kg in control and N alone treatments, respectively which were significantly higher than NP, NPK and 150% NPK treatments (5.25–5.75 mg/kg), suggesting absence of phosphorus fertilization in treatments resulted in higher grain concentration of Cu. Ben-Yin *et al.* (2010) reported that phosphatic fertilizer has negative impact on Cu content in wheat due to formation of insoluble  $Cu_3(PO_4)_2$ . The grain, straw and total uptake of Cu ranged from 12.7–46.7, 24.4–80.1 and 42.6–124.8 g/ha, respectively among the various treatments (Table 2). The highest and lowest uptake of Cu was found in NPK+FYM and control, respectively across the years. This result is in agreement with the finding of Behera *et al.* (2009). This remarkable increase in uptake in FYM treated plots is due to an increase in biomass production and promotion of chemical and biological reactions in soil by added organic matters (Chaudhary *et al.* 2019). Results also highlighted that N, NP, NPK, 150% NPK and NPK+Zn treatments did not show any significant change in total uptake of Cu but were significantly higher than control, indicating that total Cu uptake was directly related to soil DTPA extractable Cu (Table 1).

This is mainly because of increase in biomass production of wheat in response to application of chemical fertilizers over the control.

**Mn content and uptake by wheat:**

The average concentration of Mn in wheat grain varied between 29.4 mg/kg for N alone to 35.5 mg/kg for NPK+FYM treatment while the values ranged from 44.3–53.2 mg/kg in case of wheat straw with highest and lowest amount of Mn found in FYM treated plot and control, respectively. Results also pointed out that NP, NPK, 150% NPK and NPK+Zn treatments were at par concerning grain and straw Mn content. Higher Mn content in plant

samples under integrated nutrient management options was due to higher availability of Mn in soil because FYM act as source of Mn and continuous use of such manure over long periods might increase its availability through mineralization (Chaudhary *et al.* 2019). In addition, added organic matter on decomposition also accelerates the release of different forms of soil Mn through a variety of mechanisms (Wang

Table 2 Copper uptake (g/ha) by wheat during 2017–18 and 2018–19 under different nutrient management options of long-term fertilizer experiment

Treatment	2017–18			2018–19		
	Grain	Straw	Total	Grain	Straw	Total
Control	12.7c	29.9d	42.6c	13.8d	25.2d	39.0d
N	33.9b	55.2c	89.2b	25.0bc	63.9b	88.9bc
NP	27.6b	61.9bc	89.5b	29.7b	57.2bc	86.9bc
NPK	26.9b	56.6bc	83.5b	29.1b	52.8c	81.9c
150% NPK	31.4b	67.7b	99.0b	36.6b	66.4ab	103.0ab
NPK+Zn	32.8b	63.7bc	96.4b	33.4b	55.2c	88.6bc
NPK+FYM	42.3a	80.1a	122.4a	46.7a	73.0a	119.7a

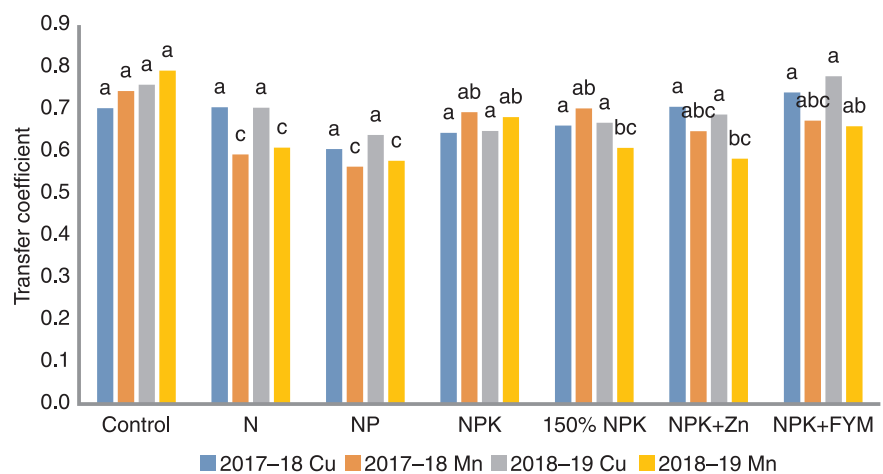


Fig 2 Impact of continuous cropping and fertilization on transfer coefficient of copper (Cu) and manganese (Mn) in wheat.

Table 3 Manganese uptake (g/ha) by wheat during 2017–18 and 2018–19 under different nutrient management options of long-term fertilizer experiment

Treatment	2017–18			2018–19		
	Grain	Straw	Total	Grain	Straw	Total
Control	64.4d	143.4e	207.8e	68.3d	118.9d	187.1d
N	132.0c	255.4d	387.4d	104.2c	307.5bc	411.7c
NP	140.6c	338.7bc	479.7c	154.6b	329.5bc	484.2b
NPK	163.1b	318.5c	481.7c	172.7b	298.1c	470.8b
150% NPK	180.2b	366.2bc	546.4b	192.6a	383.2a	575.8a
NPK+Zn	175.8b	372.6ab	548.1b	160b	311.9b	471.8b
NPK+FYM	202.0a	420.9a	622.9a	211.1a	389.6a	600.8a

*et al.* 2012). The impact of different nutrient management options on Mn uptake is presented in Table 3, which shows significant increase in Mn uptake either in all treatments receiving chemical fertilizers alone or in combination with FYM over the control. Integrated use of Zn with NPK did not enhance Mn uptake by wheat grain while straw Mn uptake was significantly higher under Zn treated plot over NPK treatment. Continuous application of FYM over last 46 years resulted in maximum uptake of Mn by both grain and straw of wheat under integrated application of NPK and FYM.

#### Transfer of Cu and Mn from vegetative tissue to grain:

Transfer coefficient (TC) of Cu and Mn was calculated as concentration of Cu/Mn in grain to straw (Fig 2). Transfer of Cu and Mn from wheat straw to grain is slow process and varied with soil Cu and Mn levels, respectively. The results also emphasized that concentration of both Cu and Mn was higher in straw as compared to grain. It is mainly related to the lower mobility of the micronutrients in plants. The TC of Cu did not show any significant difference with long-term fertilization and manuring. The TC (average of two years) value ranged from 0.62 for NP treatment to 0.76 for FYM treated plots (Fig 2). This result is consistent with some previous reports (Behera *et al.* 2015). But in case of Mn, treatments which received balanced application of fertilizers (like NPK, NPK+Zn, etc.) and integrated use of fertilizers and manure (NPK+FYM) resulted in significantly higher value of TC than treatments receiving imbalanced fertilization (like N and NP). The TC of Mn ranged from 0.57–0.77 (Fig 2). Higher TC in control might be related to lower biomass productions. Balance and integrated fertilization increased the soil organic carbon contents that resulted in higher TC of Mn (Thangasamy *et al.* 2017) while inadequate fertilization resulted in lower transfer coefficients (Li *et al.* 2007).

The present study concludes that continuous fertilization and cropping over last 46 years significantly impacted the availability of Cu and Mn in soil and their uptake by wheat depending on types and combinations of applied nutrients inputs. Different fertilizer and manure treatments did not have any significant impact on DTPA-extractable Cu except control while available Mn was significantly higher under

integrated nutrient management option compared to all other treatments. Balanced and integrated use of nutrients is very important because of plant nutrition as it enhanced the uptake of Cu and Mn from soil and accelerated the transfer of Cu and Mn from wheat straw to grains.

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