Indian Journal of Ecology (2023) 50(3): 608-614
DOI: https://doi.org/10.55362/IJE/2023/3940

Manuscript Number: 3940
NAAS Rating: 5.79

Uptake and Micronutrient Cations Transfer in Acid Alfisol as Influenced by Four Decadal Continuous Use of Amendments and Chemical Fertilizers in Maize-Wheat Cropping System

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Abstract: For a healthy human population and to improve maize quality, it is necessary to increase and maintain micronutrient content. A few studies have evaluated the long term impacts of nutrient management practices on micronutrient uptake and their translocation.The micronutrient uptake by maize, soil recovery (SRC) and transfer coefficients (TC) were determined in a 46-years-old long-term fertilizer experiment at Palampur (Himachal Pradesh) during *kharif* 2018. The study revealed improved micronutrients uptake by maize with balanced NPK application along with FYM or lime. Treatment 100% NPK+FYM and 100% NPK+lime witnessed higher level of micronutrients than other treatments. The SRC values of micronutrients followed the order: Zn>Cu>Fe>Mn. However, no significant difference in translocation coefficient was noted. Soil organic carbon was positively and significantly correlated with Cu , Fe , Mn and Zn uptake . Integrated use of inorganic fertilizers along with FYM or lime in acidic soils can regulate the micronutrient uptake in soil-plant systems, therefore eliminating the need to supply micronutrients from external sources and ultimately assisting in the production of crops with grater nutritional value.

Keywords: FYM, Lime, Micronutrients, Soil recovery coefficient, Transfer coefficient

Nearly 30% of India's cultivated land is covered with acid soils (Kumar et al 2014), suffering from low agricultural production because of hydrogen (H^+), iron (Fe), aluminum (Al) and manganese (Mn) toxicities and/or nitrogen (N), phosphorus (P), calcium (Ca), magnesium (Mg) and zinc (Zn) deficiencies (Andric et al 2012). Even the external addition of chemical fertilisers does not seem to help the situation because nutrient fixation results in low use efficiency. Numerous researchers have recommended various nutrient management practices to increase crop yields in acid soils, such as neutralization of soil acidity using limestone, dolomite or similar liming materials; application of organic manures alone or in combination with balanced chemical fertilisers etc. (Lelei et al 2006, Onwonga 2006, Gowda et al 2017, Dhiman et al 2019). Generally, acid soils have sufficient or even toxic levels of micronutrients (Kovačević and Rastija 2010, Castro and Crusciol 2015), but their plant availability and uptake are affected due to agricultural practices. Micronutrients play major structural and functional roles in a plant's physiological processes and are critical for increasing crop yields and nutritional quality, albeit required in a minimal amount (Ciampitti and Vyn 2013). Despite this, micronutrient deficiency is a worldwide problem leading to poor micronutrient uptake. As a result, the productivity of agriculture systems is declining, human and animal health is also affected due to low micronutrient contents in food grains (Saha et al 2019). Welch and Graham (2004) estimated that nearly 2 billion people in the world are deficient in Fe and Zn, most of which belong to developing and under-developed countries. The situation worsens due to the heavy use of macronutrient fertilisers, with little or no application of micronutrients. Being a costly strategy, soil and foliar application of micronutrients are not popular among farmers.

Dynamic processes of root uptake, transportation and translocation, and dry matter accumulation affect the micronutrient concentrations in a plant, besides their sufficient availability in the soil (Miner et al 2018). Integration of chemical NPK fertilisers with organic amendments such as FYM has been reported to correct the micronutrient deficiencies and regulate their supply to the plants (Shabnam and Sharma 2016, Khaliq et al 2017, Parmar et al 2022). Ma and Zheng (2018) ascribed this to the synergistic or antagonistic interactions between macro- and micronutrients that occur in soil and plants. Increased organic matter content increases the availability of micronutrients, facilitating the transfer of micronutrients from soil to plants (Moharana et al 2017). Therefore, it is essential to obtain an understanding of the interaction between nutrient management practice, soil properties and plant's micronutrient uptake in the long term. However, literature reports regarding the impact of continuous cropping, fertilizer and amendments on the uptake of micronutrients with respect to their soil availability and their translocation from vegetative to economic plant parts are very few. Therefore, present study was conducted to investigate the effect of continuous use of NPK fertilisers, FYM and lime for forty-six years on maize yield, micronutrients uptake, transfer and soil recovery and the relationship between soil organic carbon content and micronutrients uptake in an acid Alfisol. It is hypothesised that the application of fertilisers, FYM and liming would affect the uptake of micronutrients and transport.

MATERIAL AND METHODS

Location of the field experiment: The study was carried out in the ongoing long-term fertilizer experiment on maize-wheat cropping sequence, sited at the experimental farm of the Department of Soil Science, Chaudhary Sarwan Kumar Himachal Pradesh Agriculture University, in Palampur, India (31°6′ and 76°3′ E) (Fig. 1). The experiment was started in the year 1972, following a randomized block design on Typic Hapludalf of silt loam texture. The initial soil properties have been given in Table 1.

Treatment details: The study was carried out in maize-wheat system which included eleven treatments with three replications (Table 1) in plot size of 15 m^2. The 100% NPK represents the recommended doses of N (urea): 120, P_2O_5 (single super phosphate) - 60, and K_2O (muriate of potash) - 40 kg/ha. Since *kharif* 2011, 100% and 150% doses of P were reduced by 50% because of P build-up over the years, and farmyard manure (FYM) application was started in T_1 at the rate of 5 t/ha (dry weight). In T_9, S-free diammonium phosphate was used to supply P. Zinc sulfate (25 kg/ha) was applied every year in treatment T_5 until *rabi* 2010-11. Farmyard manure was applied in T_8 at the rate of 5 t/ha (dry weight) rate to the maize crop, corresponding to local practice. In T_{10}, lime at the rate of 900 kg/ha lime ($CaCO_3$) sifted through a 100-mesh sieve was applied.

Field experiment: A power tiller was used for field preparation, and the maize hybrid Kanchan Gold was sown after irrigation. Afterwards, the crop's water requirement was met through the monsoon rainfall received during the crop growth period (2605 mm). Active ingredients of atrazine (1.125 kg/ha) were applied before emergence for chemical weed control in all the treatments except in T_4, where weeds were removed manually and incorporated in the same plots. The standard package of practices was followed for raising the crop. The crop was harvested upon attaining physiological maturity, and grain and stover yield was recorded at harvesting.

Sample collection and processing: Grain and stover samples of maize were collected from each plot at harvesting time. The collected plant samples were washed under running tap water and then dried in a hot air oven at 60 ℃ for 48 hours till a constant weight was attained. The dried grain samples were ground to a fine powder using a stainless-steel grinder and stored in air-tight bags for further analysis. The dried stover samples were ground in a Wiley mill fitted with stainless-steel parts and stored in paper bags.

Analytical procedure: A finely ground plant sample (1 g) was taken in a 150 ml Erlenmeyer flask and digested in a di-acid mixture (HNO_3 and $HClO_4$ in a 9:4 ratio). The sample digest was diluted to 100 ml with double distilled water, followed by filtration of the aqueous extract through Whatman no. 42 filter paper. The filtrate's concentration of the micronutrient cations (Fe, Mn, Cu, and Zn) was directly measured in an atomic absorption spectrophotometer (Jackson 1973). Soil organic carbon content (SOC), DTPA-

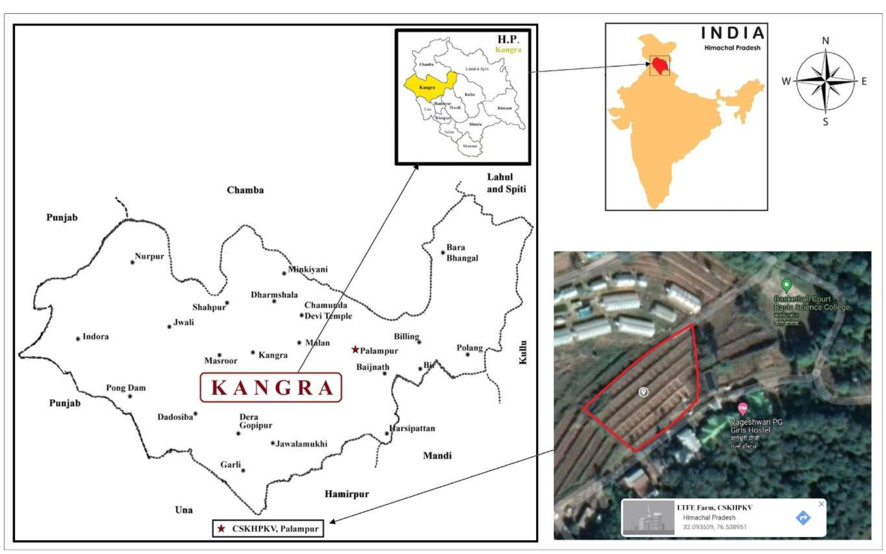

Fig. 1. Experimental location

extractable Fe, Mn, Cu, and Zn have been described by Thakur et al (2023).

Calculation of Nutrient Uptake, Transfer Coefficients, and Soil Recovery Coefficient

Nutrient uptake: The micronutrient uptake by maize was calculated following the formula below:

$$\text{Micronutrient uptake (g/ha)} = \frac{\text{Nutrient concentration (mg/kg)} \times \text{Dry matter yield (kg/ha)}}{100}$$

Soil recovery coefficient: The following formula calculated the soil recovery coefficient (SRC):

$$\text{Soil recovery coefficient} = \frac{\text{Nutrient uptake by plant (g/ha)}}{\text{Nutrient content in soil (g/ha)}}$$

Transfer coefficient: The transfer coefficient (TC) was of each micronutrient was worked out by using the following formula:

$$\text{Transfer coefficient} = \frac{\text{Concentration of the element in grain (mg/kg)}}{\text{Concentration of the element in stover (mg/kg)}}$$

Statistical analysis: Web Agri Stat Package 2.0 (WASP 2.0) was used for statistical analysis of the data and compared at a significance level of 0.05 using Duncan's multiple range test (DMRT). Graphs and tables were prepared using MS WORD 2019.

RESULTS AND DISCUSSION

Maize yield and micronutrient cations uptake: Maize yield in all the treatments, except 100% N, was significantly higher than the control (Fig. 2). In 100% N treatment, no grain and stover yield was recorded. Applying FYM or lime with a recommended dose of fertilisers significantly increased maize grain yield over sole application of fertilisers by almost 48 and 37 per cent, respectively. In T_4, maize grain yield recorded a nearly 16 per cent increase over T_2. In T_6 and T_9, a respective decline of almost 53 and 55 per cent was recorded in grain yield compared to T_2. With the application of Zn (T_5) or higher NPK doses (T_3), no significant improvement in grain yield over recommended NPK application (T_2) was recorded. Significant difference among treatments with respect to micronutrient uptake was observed due to the long-term application of fertilisers, FYM and lime (Table 2). Iron uptake by maize grain was recorded lowest in control (26.2 g/ha) and highest in 100% NPK + FYM (369.2 g/ha), followed by 100% NPK + lime (281.5 g/ha). The Fe uptake by maize stover recorded in FYM amended plots (T_8) was significantly higher than the rest of the treatments. The Mn uptake in 100% NPK + FYM by maize grain was nearly 65 per cent higher than in 100% NPK treatment, while the lowest Mn uptake by grain (18.0 g/ha) and stover (42.3 g/ha) was recorded in control, apart from zero uptakes in T_7. Zinc uptake by maize grain in 100% NPK + FYM (151.7 g/ha) was at par with 100% NPK + Zn (136.5 g/ha), followed by 124.4 g/ha in 100% NPK + lime. Similarly, Cu uptake by maize grain varied from 37.4-549.9 g/ha. In 100% NPK + FYM, Cu uptake by maize stover was highest and was statistically superior over the rest of the treatments.

The higher uptake of micronutrient cations (Fe, Mn, Zn, and Cu) in FYM treated plots was probably due to the release of micronutrients from FYM, reduced losses of micronutrients

Table 1. Soil properties (0-15 cm) before the sowing of maize (2018)

Treatment	pH*	Organic carbon (g/kg)	DTPA extractable micronutrients (mg/kg)			
			Fe	Mn	Zn	Cu
T_1 (50% NPK+FYM)	5.31	10.70	27.8	21.1	1.3	1.7
T_2 (100% NPK)	5.24	10.20	30.2	23.0	1.2	1.6
T_3 (150% NPK)	4.92	9.75	31.1	25.8	1.3	1.7
T_4 (100% NPK + hand weeding)	5.23	11.70	30.8	22.6	1.4	1.8
T_5 (100% NPK + Zn)	5.38	9.25	27.8	22.5	4.1	1.8
T_6 (100% NP)	5.14	9.70	28.4	23.2	1.3	1.6
T_7 (100% N)	4.40	8.10	32.5	22.9	1.4	1.5
T_8 (100% NPK + FYM)	5.54	13.40	37.3	37.7	2.4	2.3
T_9 (100% NPK (-S))	5.28	9.65	22.6	21.8	1.5	1.7
T_{10} (100% NPK + lime)	6.27	11.10	23.5	23.5	1.3	1.7
T_{11} (Control)	5.46	8.05	18.9	16.7	1.1	1.3
Initial (1973)	5.80	7.90	26.0	24.3	1.9	0.4

*(1:2.5, soil: water)

through chelation and proliferation of root growth, resulting in better nutrient uptake and higher crop yield. Li et al (2007) observed that incorporating organic manures significantly increased nutrient uptake by maize plants and facilitated the allocation and transfer of nutrient elements to the maize ears and grains. Furthermore, soil amendment with lime (T_{10}) improved soil health, increased nutrient uptake, and thereby higher productivity over NPK alone (T_2) (Lelei et al 2006). The omission of essential plant nutrients in T_6 and T_9 might have created nutrient imbalances in the soil, resulting in lesser micronutrient uptake and poor crop yield in these plots compared to the balanced fertilizer application (T_2). In the absence of the addition of nutrients from external sources and continuous removal of nutrients by crops, control recorded the least micronutrient cation uptake (Thangasamy et al 2017, Shambhavi et al 2018). In our study, zero yields recorded in T_7 indicated that continuous urea application had substantially declined the soil pH, which led to poor soil structure and reduced and imbalanced availability of essential plant nutrients (Ma and Zheng 2018). Application of Zn in T_5 improved the Zn uptake significantly over 100% NPK, as reported by Behera et al (2015).

Soil recovery coefficient: The soil recovery coefficient (SRC) is an indicator of micronutrient uptake by plants in relation to their availability in the soil. If the SRC value is less than one, the nutrient element is present in a sufficient amount in the soil to meet the nutritional needs of the plants. This study observed a significant effect of different fertilizer

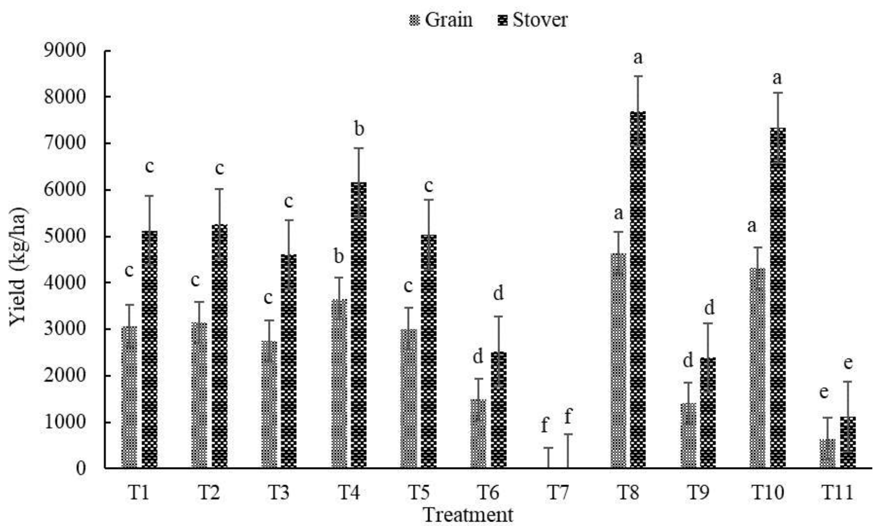

Fig. 2. Effect of continuous use of fertilizers and amendments on maize grain and stover yield. Values with the same letters are not significantly different at P ≤ 0.05. Bars represent standard error

Table 2. Effect of continuous use of fertilizers and amendments on Fe, Mn, Zn and Cu uptake by maize grain and stover

Treatment	Fe uptake (g ha^{-1})		Mn uptake (g ha^{-1})		Zn uptake (g ha^{-1})		Cu uptake (g ha^{-1})	
	Grain	Stover	Grain	Stover	Grain	Stover	Grain	Stover
T_1	193.3^{c}	717.8^{d}	136.7^{c}	338.2^{d}	74.9^{d}	196.0^{d}	67.6^{d}	170.1^{d}
T_2	210.2^{c}	758.1^{d}	144.6^{c}	355.5^{d}	85.6^{cd}	211.3^{d}	78.0^{d}	185.3^{d}
T_3	192.6^{c}	737.0^{d}	130.1^{c}	314.7^{d}	76.8^{d}	196.7^{d}	72.7^{d}	184.8^{d}
T_4	262.2^{b}	935.4^{c}	178.0^{b}	439.9^{c}	104.0^{c}	266.0^{c}	100.2^{c}	262.2^{c}
T_5	195.8^{c}	698.4^{d}	132.8^{c}	334.6^{d}	136.5^{ab}	339.7^{b}	71.9^{d}	161.1^{d}
T_6	79.8^{d}	317.8^{e}	57.4^{d}	147.1^{e}	31.0^{e}	82.7^{e}	32.7^{e}	73.4^{e}
T_7	0.0^{e}	0.0^{f}	0.0^{e}	0.0^{e}	0.0^{g}	0.0^{f}	0.0^{f}	0.0^{f}
T_8	369.2^{a}	1443.0^{a}	238.5^{a}	672.7^{a}	151.7^{a}	407.4^{a}	151.8^{a}	398.1^{a}
T_9	78.2^{d}	296.0^{e}	53.0^{d}	144.9^{e}	30.0^{ef}	87.3^{e}	29.6^{e}	66.9^{e}
T_{10}	281.5^{b}	1132.8^{b}	198.3^{b}	553.0^{b}	124.4^{b}	338.7^{b}	124.6^{b}	306.4^{b}
T_{11}	26.2^{e}	99.5^{f}	18.0^{e}	42.3^{e}	10.9^{fg}	26.4^{f}	9.3^{f}	28.0^{f}

Values with the same letters are not significantly different at P <0.05

treatments on SRC (Table 3). The SRC values were less than one in all the treatments but zero in T_7. Apart from zero in T_7, the lowest SRC value for all micronutrient cations was obtained in control. At the same time, significantly greater SRCs were recorded under balanced application of fertilisers alone (Fe-0.014, Mn-0.01, Cu-0.069, Zn-0.106) and in treatment integration with FYM (Fe-0.023, Mn-0.011, Cu-0.107, Zn-0.097) or lime (Fe-0.027, Mn-0.013, Cu-0.110, Zn-0.135). Hand-weeding treatment (T_4) also recorded significantly higher SRC values (Fe-0.017, Mn-0.012, Cu-0.090, Zn-0.121). The SRC values of micronutrients followed the order Zn (0.016-0.135) > Cu (0.110-0.013)> Fe (0.027-0.003) > Mn (0.013-0.002).

The SRC value of more than one indicates insufficiency of the element for plant nutritional needs (Rutkowska et al 2014). In study, the micronutrient amounts in the soil were sufficient to meet the nutritional needs of the plants, irrespective of the fertilisers and amendments applied as indicated by SRC values of less than one. The lowest SRC values under control could be due to exhausted nutrient reserves that declined the overall biomass production. In contrast, fertilisers and amendments markedly increased the phyto-availability of micronutrients, overall crop growth and biomass production. Previous studies have also reported similar improvements in soil micronutrient recovery due to fertilizer and organic manure in maize-wheat rotation (Li et al 2007), wheat-potato-lupines sequence (Rutkowska et al 2014) and rice-wheat system (Saha et al 2019). Weed biomass incorporation in T_4 improved the SOC content and created congenial conditions for nutrient recycling and crop growth.

Transfer coefficient: The TCs of micronutrients from maize stover to grain were computed and presented in Table 3. The TCs of Fe, Mn, Zn and Cu varied in the range of 0.42-0.47, 0.61-0.70, 0.58-0.71 and 0.58-0.77, respectively. Except T_7, all the treatments were statistically comparable, and no significant effect of fertilizer and amendment application was observed on the translocation of micronutrient cations from maize stover to grain. However, TCs of Fe were recorded lower as compared to TC values of Zn, Cu and Mn. TCs of micronutrient cations were not affected by the application of fertilisers and manures. Although the application of balanced fertilisers and amendments (T_2, T_4, T_8 and T_{10}) increased the micronutrient uptake as indicated by SRC values and it is speculated that starch dilution of micronutrients in grains as a result of increased dry matter production nullified the effects of increased uptake. The results differ from some studies that have reported an increase in the micronutrient TCs with fertilisers and organic manure application (Li et al 2007, Ma and Zheng 2018, Saha et al 2019), but our results corroborate with the findings of Behera et al (2015) and Miner et al (2018). We attributed the lower TC values of Fe, as compared to Zn, Cu and Mn, to their functional roles in the plants. Since Fe is involved in the lignin and suberin formation, its major portion remained in the vegetative parts. In contrast, comparatively higher amounts of Zn, Cu and Mn were transported to grains.

Relationship between nutrient uptake and soil organic carbon: Micronutrient cations' uptake by maize (grain and stover) was strongly associated with SOC content, and the correlation was significant at 1 and 5 per cent level of significance (Fig. 3). The Pearson's correlation coefficients between micronutrient uptake and SOC content followed the order of Cu > Fe > Mn > Zn (from high to low, r = 0.924-0.807). Iron, Mn, Zn and Cu play a critical role in numerous metabolic functions and structural build-up of plants. Their availability in

Table 3. Effect of continuous use of fertilizers and amendments on soil recovery coefficient and transfer coefficient

Treatment	Soil recovery coefficient				Transfer coefficient			
	Fe	Mn	Zn	Cu	Fe	Mn	Zn	Cu
T_1	0.015^{cd}	0.010^{cd}	0.093^{c}	0.062^{c}	0.45^{a}	0.67^{a}	0.64^{a}	0.67^{a}
T_2	0.014^{cd}	0.010^{bc}	0.106^{c}	0.069^{c}	0.47^{a}	0.68^{a}	0.68^{a}	0.70^{a}
T_3	0.013^{d}	0.008^{d}	0.097^{c}	0.069^{c}	0.44^{a}	0.69^{a}	0.65^{a}	0.66^{a}
T_4	0.017^{c}	0.012^{ab}	0.121^{b}	0.090^{b}	0.47^{a}	0.68^{a}	0.66^{a}	0.64^{a}
T_5	0.015^{cd}	0.010^{cd}	0.055^{d}	0.063^{c}	0.47^{a}	0.66^{a}	0.67^{a}	0.74^{a}
T_6	0.006^{e}	0.004^{e}	0.040^{e}	0.030^{d}	0.43^{a}	0.66^{a}	0.63^{a}	0.76^{a}
T_7	0.000^{g}	0.000^{f}	0.000^{g}	0.000^{f}	0.00^{b}	0.00^{b}	0.00^{b}	0.00^{b}
T_8	0.023^{b}	0.011^{bc}	0.097^{c}	0.107^{a}	0.42^{a}	0.61^{a}	0.62^{a}	0.63^{a}
T_9	0.007^{e}	0.004^{e}	0.044^{de}	0.026^{d}	0.45^{a}	0.62^{a}	0.58^{a}	0.77^{a}
T_{10}	0.027^{a}	0.013^{a}	0.135^{a}	0.110^{a}	0.42^{a}	0.61^{a}	0.63^{a}	0.69^{a}
T_{11}	0.003^{f}	0.002^{f}	0.016^{f}	0.013^{e}	0.46^{a}	0.70^{a}	0.71^{a}	0.58^{a}

Values with the same letters are not significantly different at $P < 0.05$

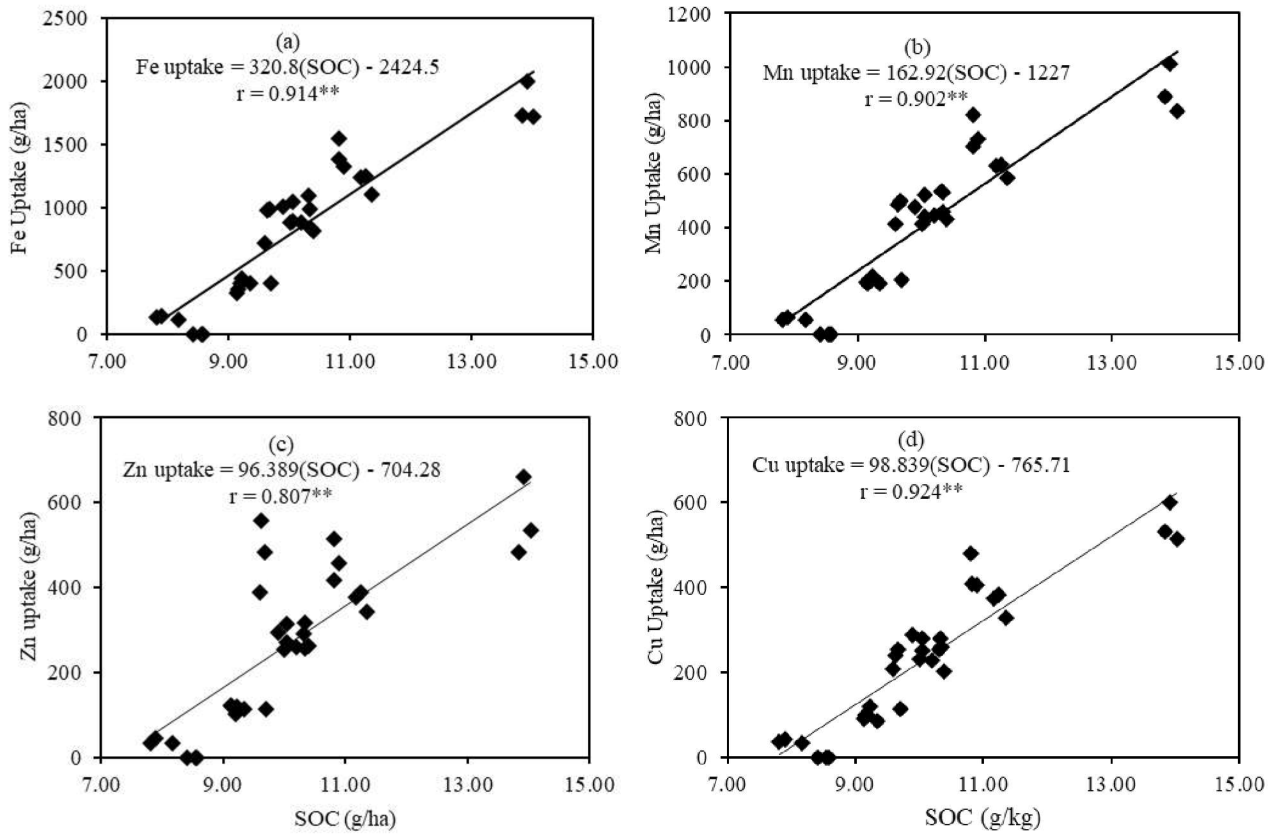

Fig. 3. Linear regression relationship of soil organic carbon (SOC) with a) Fe uptake, b) Mn uptake, c) Zn uptake and d) Cu uptake (n=33)as affected by continuous use of fertilizers and amendments. Note that the axes may not begin from zero

the soil predominantly affects their plant uptake (Li et al 2007). Therefore, factors affecting the availability of micronutrients in the soil can also affect their uptake by the crops. Soil organic matter is one of the most critical factors affecting the soil's micronutrient availability, directly impacts its uptake (Miner et al 2018).The study confirm that a strong correlation was observed between SOC content and uptake of Fe, Mn, Zn and Cu. This was ascribed to the formation of complexes between micronutrient cations and organic complexes that increased the availability of native micronutrients and eased their uptake by plants (Chaudhary and Narwal 2005).

CONCLUSIONS

The uptake of micronutrients and their soil recovery quantitatively varied depending on the fertilisers and amendments added to the soil during the last forty-six years. The results confirmed our hypothesis that integration of balanced fertilisation with FYM or liming led to a marked improvement in the uptake of micronutrients. The SRC values indicated a sufficient availability of micronutrients to the plants, but long-term integrated application of fertilisers with FYM or lime proved to be significantly superior in increasing the micronutrient uptake in relation to their availability in the soil. Regardless of the fertiliser or amendments applied, the translocation of micronutrients from stover to grain in the plants was not affected significantly. Hence maintaining or improving soil organic matter is necessary to increase the micronutrient uptake in the crops, which will ultimately result in crops of superior nutritional quality.

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Received 12 December, 2022; Accepted 15 April, 2023