

# Micronutrients (Fe, Mn, Zn and Cu) balance under long-term application of fertilizer and manure in a tropical rice-rice system

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## Abstract

**Purpose** The balance of micronutrients in soils is important in nutrient use efficiency, environmental protection and the sustainability of agro-ecological systems. The deficiency or excess of micronutrients in the plough layer may decrease crop yield and/or quality. Therefore, it is essential to maintain appropriate levels of micronutrients in soil, not only for satisfying plant needs in order to sustain agricultural production but also for preventing any potential build-up of certain nutrients. **Materials and methods** A long-term fertilizer experiment started in 1969 at Central Rice Research Institute, Cuttack, Odisha, India. Using this experiment, a study was conducted to analyze the balance of micronutrients and their interrelationship. The experiment was composed of ten nutrient management treatments viz. control; nitrogen (N); N + phosphorus (NP); N + potassium (NK); nitrogen, phosphorus and potassium (NPK); farmyard manure (FYM); N + FYM; NP + FYM; NK + FYM; and NPK + FYM with three replications. Micronutrients in soil (total and available), added fertilizers and organic manures and in rice plant were analyzed. Besides, atmospheric deposition of the micronutrients to the experimental site was also calculated. A micronutrient balance sheet was prepared by the difference between output and input of total micronutrients.

**Results and discussion** Application of FYM alone or in combination with chemical fertilizer increased the

diethylenetriamine pentaacetate (DTPA)-extractable Fe, Mn and Zn over the control treatment. The treatment with NPK + FYM had the highest soil DTPA-extractable Fe, Mn, Zn and Cu after 41 years of cropping and fertilization. Application of chemical fertilizers without P decreased the DTPA-extractable Zn over the control while the inclusion of P in the fertilizer treatments maintained it on a par with the control. The application of P fertilizer and FYM either alone or in combination significantly increased the contents of total Fe, Mn, Zn and Cu in soil mainly due to their micronutrient content and atmospheric depositions. A negative balance of Zn was observed in the N, NP, NK and NPK treatments, while a positive balance observed in the remaining treatments. The balance of Mn was negative in all the treatments, due to higher uptake by the rice crop than its addition.

**Conclusions** Long-term application of chemical fertilizers together with FYM maintained the availability of micronutrients in soil and, thus, their uptake by rice crop.

**Keywords** Atmospheric deposition · Farm yard manure · Micronutrient balance · Micronutrient uptake

## 1 Introduction

Iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn) are micronutrients which are essential in small quantities to microorganisms, plants and animal organisms, including humans. Through their involvement in various enzymes and other physiologically active molecules, they play critical roles in the biological processes of organisms. They are required in very small quantities for normal growth and development of the plants. Deficiency of any of these micronutrients hampers normal plant growth, and plant may exhibit deficiency symptoms resulting in reduction in yield and quality of crops. On

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the other hand, presence of these elements in toxic concentrations may also adversely affect the growth of plants. Therefore, it is essential to maintain soil micronutrients at appropriate levels, not only for satisfying plant needs but also for preventing any potential build-up in order to sustain agricultural production and maintain environmental quality.

The addition of micronutrients to arable land mainly comes from chemical fertilizers, organic manures, sewage sludge and atmospheric depositions (Sharma et al. 2008; Li et al. 2010). The balance of micronutrients in soils is important in nutrient use efficiency, environment quality protection and the sustainability of agro-ecological system (Wang et al. 2007; Fanguero et al. 2008). Smalling et al. (1997) identified ten variables required for the construction of a nutrient budget of which eight are relevant to the micronutrients. These include inputs (fertilizers, organic inputs, atmospheric depositions and sedimentation) and outputs (harvested products, crop residue removal, solute leaching, runoff and erosion). Usually, rock phosphorus fertilizers (e.g. superphosphate) containing Cu, Zn, Fe, Mn, Cd, Pb, As and Hg may increase concentrations of micronutrients or heavy metals in soil after long-term application (Nziguheba and Smolders 2008). Livestock manures also contain micronutrients, and remarkable increase in soil micronutrients was reported after livestock manure application to arable land (Dach and Starmans 2005). Concentrations of micronutrients in commercial K and N (urea) fertilizers are not well documented, and little attention has been given to their application compared to the applications of superphosphate and organic manures in terms of the availability of micronutrients. More recent researches have indicated a rising trend in atmospheric deposition of nutrients and toxic metals in different parts of the world, including the Indian sub-continent (Patel et al. 2001; Azimi et al. 2004; Singh and Agrawal 2005). Keller et al. (2001) pointed out the relative importance of atmospheric deposition for heavy metal input in arable ecosystems. Atmospheric deposition of metals affects soil physical and chemical properties, microbial interactions and human health through dietary intake.

Soil properties, such as pH, organic matter contents and available forms of macronutrients, are significantly affected by the use of long-term mineral fertilizers and organic manures which determine availability of micronutrients to plants (Rutkowska et al. 2014). Use of mineral fertilizers, especially nitrogenous fertilizers, decrease soil pH which in turn enhances mobility of Fe, Mn, Zn and Cu (Upreti et al. 2009). Several studies showed that use of phosphorus fertilizers limits Zn availability to plants (Mann et al. 2006; Fageria et al. 2011). Long-term application of farmyard manure increases the organic matter content in soil which enhances Zn availability (Rehman et al. 2012). Availability of micronutrients in soil is directly linked with their uptake by plants and content in staple foods, which not only directly affect food quality but also are closely related to human health.

Attempts have been made to study the micronutrients in response to fertilization (Phattarakul et al. 2012); however, little information is available on the balance of micronutrients due to long-term effect of intensive rice-rice cultivation with the application of fertilizers and manure. This study aimed to study the following: (1) the balance of soil micronutrients due to long-term intensive rice-rice cultivation under different fertilization treatments and (2) the changes in uptake of micronutrients by rice as affected by fertilization treatments as compared to control.

## 2 Materials and methods

### 2.1 Study site and soil chemical properties

This study was conducted in a long-term field experiment which had been carried out from 1969 at the research farm of the ICAR-Central Rice Research Institute, Cuttack, Odisha, India (20° 25' N, 85° 55' E; 24 m above mean sea level). Climate of the study site is sub-humid tropical with mean annual precipitation of 1500 mm, of which 75–80 % is received during June to September. Mean annual temperature is 27.6 °C, and the mean temperatures of wet and dry seasons are 28.0 and 27.1 °C, respectively. The soil is derived from the deltaic alluvium of river Mahanadi and classified as Aeric Endoaquept (Soil Survey Staff 2010). Initial soil at the beginning of the long-term experiment had sandy clay loam texture (31 % clay, 17 % silt and 52 % sand), bulk density 1.40 Mg m<sup>-3</sup>, percolation rate 10 mm day<sup>-1</sup>, cation exchange capacity (CEC) 15.2 cmol (p<sup>+</sup>)kg<sup>-1</sup>, pH 6.6 (using 1:2.5, soil/water suspension), organic carbon 6.6 g kg<sup>-1</sup>, total nitrogen 0.8 g kg<sup>-1</sup>, exchangeable K 0.26 cmol (p<sup>+</sup>)kg<sup>-1</sup> and available P 13.0 mg kg<sup>-1</sup>.

### 2.2 Field experiment

Ten treatments, including control (no fertilizer or manure application); nitrogen alone (N); nitrogen and phosphorus (NP); nitrogen and potassium (NK); nitrogen, phosphorus and potassium (NPK); farm yard manure alone (FYM); nitrogen with manure (N + FYM); nitrogen and phosphorus with manure (NP + FYM); nitrogen and potassium with manure (NK + FYM); and nitrogen, phosphorus and potassium with manure (NPK + FYM), were arranged in randomized block design with three replications. All the plots were under rice-rice cultivation system where rice was grown as mono crop twice in a year, in wet season (June to October) followed by dry season (December to May). The doses of fertilizers were 60:40:40, N/P<sub>2</sub>O<sub>5</sub>/K<sub>2</sub>O kilogram per hectare in wet season and 80:40:40 N/P<sub>2</sub>O<sub>5</sub>/K<sub>2</sub>O kilogram per hectare in dry season through urea, superphosphate and potassium chloride,

respectively. Phosphorous and potassium were applied as basal, and nitrogen was applied in three equal splits in respective treatments. The wastes from the Institute's dairy farm were used to prepare the FYM which contained 171–189 g total C kg<sup>-1</sup> and 4–16 g total N kg<sup>-1</sup>. Every year, FYM (5 Mg ha<sup>-1</sup>) was applied uniformly in all the treatments receiving FYM during last week of May. The average Cu, Zn, Fe and Mn concentrations in the organic manure, urea, superphosphate and K fertilizer are shown in Table 1.

### 2.3 Sampling and measurements

Rice grain and straw were harvested and quantified treatment wise, both in wet and dry seasons each year. Grain and straw samples from each treatment in both the seasons were collected each year and were powdered before digestion with H<sub>2</sub>SO<sub>4</sub> for determination of N and tri-acid mixture (HNO<sub>3</sub>/HClO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>) for determination of P, K and micronutrients (Jackson 1964). Topsoil samples (0–15 cm) were collected in December 2010 following the harvest of wet season rice crop. Three random soil cores were taken from each plot to form a composite sample. The samples were air-dried and ground with a wooden pestle and mortar to pass through a 2-mm sieve for determination of soil pH, plant available macronutrients and micronutrients and total micronutrients. Soil pH was measured with a pH electrode at a soil to water ratio of 1:2.5 (Jackson 1964). Soil organic carbon (SOC) was analyzed with an elemental analyzer (Flash 2000; Thermo Scientific); available N by Subbiah and Asija (1956); available P by Bray and Kurtz (1945); available K by Piper (1966); and diethylenetriamine pentaacetate (DTPA)-Fe, DTPA-Mn, DTPA-Zn and DTPA-Cu by Lindsay and Norvell (1978) methods. Total Fe, Mn, Zn and Cu in soil were determined by tri-acid digestion method (Agemian and Chau 1976). Organic manure and fertilizer materials were ground and digested with HClO<sub>4</sub>-HNO<sub>3</sub> (Amacher 1996; Nziguheba and Smolders 2008). Available and total Fe, Mn, Zn and Cu were analyzed using atomic absorption spectrophotometer (SpectrAA 55B, Varian).

### 2.4 Soil micronutrient balances

The fertilizers and organic manure samples were collected prior to application, and the average micronutrient contents were quantified for the last 5 years (Table 1). The input of micronutrients was computed by multiplying total amounts of fertilizers and organic manures applied over the 41 years with their average micronutrient contents. Micronutrients from atmospheric deposition were estimated as outlined in Thakur et al. (2004) and Tiwari et al. (2008). The estimation was assumed to be equal to the amount of micronutrients from atmospheric deposition in the region with comparable climate (Thakur et al. 2004; Tiwari et al. 2008) and economic development, located in the vicinity of the study region. Crop harvest was the primary way of micronutrient outputs in the region. Grain and straw yields of each treatment were measured during the wet and dry seasons every year. At physiological maturity, grain yields (adjusted to 14 % moisture content) were measured in a 10-m<sup>2</sup> harvest area centred within each plot, and concentrations of Fe, Mn, Zn and Cu in grain and straw were determined separately from a five-hill sample. Plant samples were dried to constant weight at 70 °C and ground, and concentrations of the micronutrients in plant tissue were determined using atomic absorption spectrophotometer. The micronutrient field balance was calculated as the difference between element inputs and output.

### 2.5 Quality control

Analysis of micronutrients in the samples (soil, plant, fertilizer and manure) was done with the help of an atomic absorption spectrophotometer (SpectrAA 55B, Varian). The limits of detection (LODs) of various micronutrients (Fe, Zn, Mn and Cu) were in the range of 0.01 to 0.05 mg L<sup>-1</sup>. All laboratory glasswares for the analysis of micronutrients were pre-soaked in 50 mg L<sup>-1</sup> detergent solution for 8 h, then washed in tap water and thereafter soaked in 150 mL L<sup>-1</sup> HNO<sub>3</sub> solution over night, and finally rinsed by de-ionized water. Individual standards of micronutrients (Fe, Zn, Cu and Mn) were obtained from Merck (Germany) and were used for calibration and quality assurance. In order to check the precision of the

**Table 1** Average micronutrient concentrations in different kinds of fertilizers applied during 1969–2010

Micronutrients	Organic fertilizer mg kg <sup>-1</sup>	Superphosphate	Potassium chloride	Urea
Fe	3882	5550	454	1.0
Mn	299	488	nd	nd
Zn	84.8	68.2	nd	nd
Cu	16.2	8.5	nd	nd

nd not detected

instrument, calibration checks were performed after analysis of 50 samples and samples with known concentration of elements were run after the analysis of every set of 50 samples.

## 2.6 Statistical analysis

Data on soil properties, concentration and content of micronutrients in crops were analyzed using one-way ANOVA with SAS software package version 9.2 (SAS 2008). Significance among the data values was determined at 5 % probability ( $P < 0.05$ ). Differences between the treatments were compared using the Duncan's multiple range test (DMRT) at the 0.05 level with the SAS software package version 9.2 (SAS 2008).

## 3 Results and discussion

### 3.1 Basic soil properties after 41 years of fertilizers and manure application

Effects of long-term application of fertilizers and manure on soil pH, organic carbon, available N, available P and available K are shown in Table 2. The pH of the treated plots declined from an initial value of 6.6 in 1969 to a lowest value of 5.6 and a highest value of 6.2 recorded in NP and FYM treatments, respectively. Continuous application of chemical fertilizers alone or in combination with FYM declined the soil pH which may be attributed to the continuous cropping and use of urea N, which, owing to its acid forming reactions in the soils, would have decreased the pH. This is in accordance with the results of Li et al. (2010) who found that long-term application of fertilizer N through urea resulted into significant decrease of pH. In the control treatment also, the soil pH was lower than the initial value, which indicated that the continuous intensive cultivation results into the acidification (Dawe et al. 2000). The magnitude of decline in combined application of inorganic fertilizers and FYM was comparatively less due to the buffering action of the FYM which resisted the drastic reduction in soil pH. Dong et al. (2012) suggested that organic manure could alleviate soil acidification to some extent.

As compared with the initial value, SOC content in the control decreased slightly after 41 years of continuous cropping. Maintenance of the SOC in the control even after 41 years can be explained by the reduced decomposition of both added and native SOC due to anaerobic conditions which prevail throughout the year in a rice-rice system (Guo and Lin 2001). Significantly higher levels of SOC were recorded in the treatments receiving both chemical fertilizers and FYM (N + FYM, NP + FYM, NK + FYM and NPK + FYM) as compared to the control, N, NP, NK, NPK and FYM (Table 2). This was expected since organic matter was continually being added externally to the soil through FYM and also through

**Table 2** Soil properties in the treatments after 41 years of cropping and fertilization

Treatments	pH	Organic carbon g kg <sup>-1</sup>	Available N kg ha <sup>-1</sup>	Available P	Available K	DTPA-Fe mg kg <sup>-1</sup>	DTPA-Zn	DTPA-Mn	DTPA-Cu	Total Fe	Total Zn	Total Mn	Total Cu
Control	6.01	6.30	154	9.9	117	39.1	0.86	13.1	3.7	26,903	52.6	421	22.0
N	5.87	7.05	218	11.1	117	37.9	0.75	11.2	3.9	26,912	53.2	438	23.0
NP	5.59	7.50	227	18.3	108	37.2	0.89	12.1	3.5	28,512	63.0	563	24.6
NK	5.94	6.98	227	9.9	136	35.4	0.74	12.0	4.4	26,675	54.0	444	24.4
NPK	5.75	7.88	225	22.7	125	33.6	0.81	11.5	3.7	28,828	62.1	561	24.4
FYM	6.21	7.28	206	18.8	128	40.6	1.26	14.4	4.9	29,025	72.1	632	27.1
N + FYM	6.03	8.78	237	18.8	134	42.1	1.02	13.8	4.1	28,097	67.6	612	28.5
NP + FYM	5.91	9.25	246	33.7	126	41.7	1.19	13.2	4.3	30,700	69.0	624	26.1
NK + FYM	6.11	9.20	251	19.9	154	42.4	0.92	14.2	4.5	27,750	60.0	591	26.3
NPK + FYM	6.08	9.30	245	33.2	147	45.8	1.12	14.1	4.4	32,387	66.6	589	26.1
LSD ( $p < 0.05$ )	0.37	1.10	17.2	2.1	10.2	3.9	0.08	1.4	0.5	1615	6.3	39.0	1.8



plant roots (Mandal et al. 2007). Some researchers have also found that long-term manure application can increase soil organic matter content (Gami et al. 2001; Mandal et al. 2007; Majumder et al. 2007; Gulde et al. 2008). The low build-up of SOC in the treatment applied with FYM alone is a result of low input of organic matter through plant roots consequent to lower biomass production under this treatment. A significant increase in SOC under NPK treatment over the control can be attributed to the increased biomass production and more addition of root biomass to the soil (Mandal et al. 2007).

Soil available N, P and K contents were significantly affected by different fertilization treatments (Table 2). Long-term manure application along with chemical fertilizers led to significantly higher values of soil available N compared to the other fertilization treatments. It has also been reported by many authors (Mann et al. 2006; Linquist et al. 2007; Shahid et al. 2013) that the manure application leads to increase in soil available N and available P. However, higher levels of these soil nutrients were maintained when these nutrients were applied on long-term basis with the manure (Motavalli and Miles 2002). Unlike available N and available P, available K was the highest in NK + FYM treatment, followed by the NPK + FYM treatment, demonstrating the role of chemical fertilizers and organic manure in the supplementation of K in the soil. Previous studies have shown that application of rice straw significantly increased available K besides increasing organic matter contents (Sharma et al. 2000). Similarly, the available K in NK treatment was higher than NPK in our study. The evident increase of available K in treatments getting K supplement through either chemical fertilizer or manure over time suggests that continuous addition of K would dramatically improve the soil available K supply. Continuous exclusion of K in fertilizer schedules resulted in a decline in soil K under an intensive rice-rice system (Masto et al. 2007).

### 3.2 Concentrations of total micronutrients in soil after 41 years of fertilizers and manure application

Total soil Fe concentration of all the treatments ranged from 26,903 mg kg<sup>-1</sup> in control to 32,387 mg kg<sup>-1</sup> in NPK + FYM treatment (Table 2). In general, the application of chemical fertilizers (except urea) and organic manure resulted in the build-up of total iron in the soil. It is evident (Table 1) that the SSP, MOP and FYM contain high amount of iron that, upon application, helps in the build-up of this element over the years. It is likely that the contents of soil Fe are very high; therefore, inputs by application of the fertilizers or outputs by crop removal had little effects on the total soil Fe contents. Similarly, the total soil Mn concentration of all the treatments ranged from 421 mg kg<sup>-1</sup> in control to 632 mg kg<sup>-1</sup> in FYM treatment (Table 2). Soil total Zn concentration was highest in the FYM treatment and lowest in the control treatment.

Similar trend was also observed for total soil Mn and Cu. The treatments with superphosphate and manure application had higher total Mn, Zn and Cu than the control, N and NK treatments which suggested that the application of P fertilizer and manure increased soil total Mn, Zn and Cu concentrations. Total soil Mn and Zn values were distinctly lower in treatments that did not receive either P fertilizer or manure because a great deal of soil Mn and Zn was taken up and removed by rice crop during both the dry and wet seasons every year with very little addition of these elements through atmospheric deposition. However, applications of P fertilizer and organic manure alone or in combination significantly increased soil total Mn, Zn and Cu due to the presence of these elements in phosphatic fertilizer and manure (Table 1), demonstrating the role that P fertilizer and manure played in affecting total soil Mn, Zn and Cu concentrations. These results are in agreement with the earlier reports wherein it was observed that application of P fertilizer and organic manure with incorporation of straw resulted in significant increases in soil total Cu, Zn, Fe and Mn (Li et al. 2010).

### 3.3 Concentration of available micronutrients in soil after 41 years of fertilizers and manure application

There was a significant difference for DTPA-Fe in the treatments which received FYM and one which did not receive the FYM. The lowest DTPA-Fe concentration was recorded in the NPK treatment which was even significantly lower than the control, N, FYM, N + FYM, NP + FYM, NK + FYM and NPK + FYM and was at par with NK and NP treatments (Table 2). It is mainly due to the continuous removal of iron by the crops in large quantities. Setia and Sharma (2004) also reported that increasing chemical fertilizer (N and K) amounts to accelerated depletion of DTPA-Fe from soils. Moreover, the treatment that received NPK + FYM had the highest concentration of DTPA-Fe, which may be attributed to the contribution of high amount of Fe from the manure (Table 1). Similarly, lower DTPA-Mn concentrations were observed in those treatments that did not receive FYM. However, DTPA-Mn varied from 11.2 to 14.4 mg kg<sup>-1</sup> in all the treatments, indicating that Mn deficiency was not likely to occur, if proper superphosphate and animal manure were applied, as 2.0–5.0 mg kg<sup>-1</sup> was regarded as Mn deficiency level (Sillanappa 1982). DTPA-Mn tends to increase after long-term application of chemical fertilizers in alkaline soils (Wei et al. 2006), but in acid soils, there was significant reduction in DTPA-Mn (Malhi et al. 1998). In addition, application of organic fertilizer to alkaline soils increases available Mn concentration, but the reverse is true for an acid soil (Li et al. 2009). Clearly, various fertilization treatments

caused remarkable changes of available Mn. The increase might be due to decrease in soil pH and enhanced dissolution of Mn compounds.

Application of chemical fertilizers with P omission reduced the DTPA-Zn over the control; however, inclusion of P in the fertilizer schedule maintained it at par with the control because Zn present in the superphosphate fertilizer offsets its loss due to the crop harvest from the plots. Application of FYM alone or in combination with chemical fertilizers increased the DTPA-Zn over the control treatment (Table 2). Furthermore, available Zn levels in all the treatments including unfertilized one were more than  $0.50 \text{ mg kg}^{-1}$  (DTPA extractable Zn), the critical value for Zn deficiency that has been adopted by Sillanappa (1982) for this area. One interesting observation was that in the NP treatment, available Zn was lower compared to the control treatment. One possible explanation for this could be that NP fertilizer promoted more crop growth than control treatment, resulting in an increase in plant uptake and subsequent removal of Zn at harvest from the NP-fertilized plots. In this study, average rice yield was about 50 % higher in the NP treatment compared to control. Manure not only supplies large amounts of Zn to the soil, but also promotes biological and chemical reactions that result in the dissolution of non-available Zn. Consequently, available Zn in the FYM-applied treatments was significantly higher than in the plots applied with fertilizer alone.

Soil DTPA-extractable Cu in the treatments ranged from 3.5 to  $4.9 \text{ mg kg}^{-1}$  (Table 2). The increase in DTPA-Cu in the FYM treatments was ascribed to high Cu concentration in the organic manure and lesser removal because of lower yield under this treatment. Fertilization with chemical fertilizers alone did not have a significant effect on available Cu, whereas fertilization with FYM alone or in combination with chemical fertilizers had a significant effect on available Cu. The reason for low availability may be due to the fact that fertilizers used in this experiment contained very little Cu (Table 1). The increased availability of Cu in FYM-applied plots may be attributed to the production of compounds of low molecular weight during decay of manure. Low-molecular-weight compounds liberated during decay of plant and animal residues as well as those applied with sewage sludge may greatly increase the availability of Cu to plants (Alina 2011). In addition, contents of DTPA-Cu were still higher than the  $0.2 \text{ mg kg}^{-1}$ , the critical level of DTPA-Cu (Viets and Lindsay 1973; Lindsay and Norvell 1978), after 41 years of cropping and fertilization.

The differential trends in total and available micronutrients in these treatments can be explained by the facts that total

nutrient content was affected mainly by crop uptake, and therefore, the magnitude of the decrease depended on crop type and uptake intensity. However, changes in available nutrient content were governed by root uptake and the release of non-available forms into soil solution. The impact of fertilization on available nutrients was the result of equilibrium between the two processes.

### 3.4 Balance of micronutrients after 41 years of fertilizers and manure application

The inputs, outputs and balances of micronutrients were estimated to analyze the potential future effects of fertilization on the concentration of micronutrients.

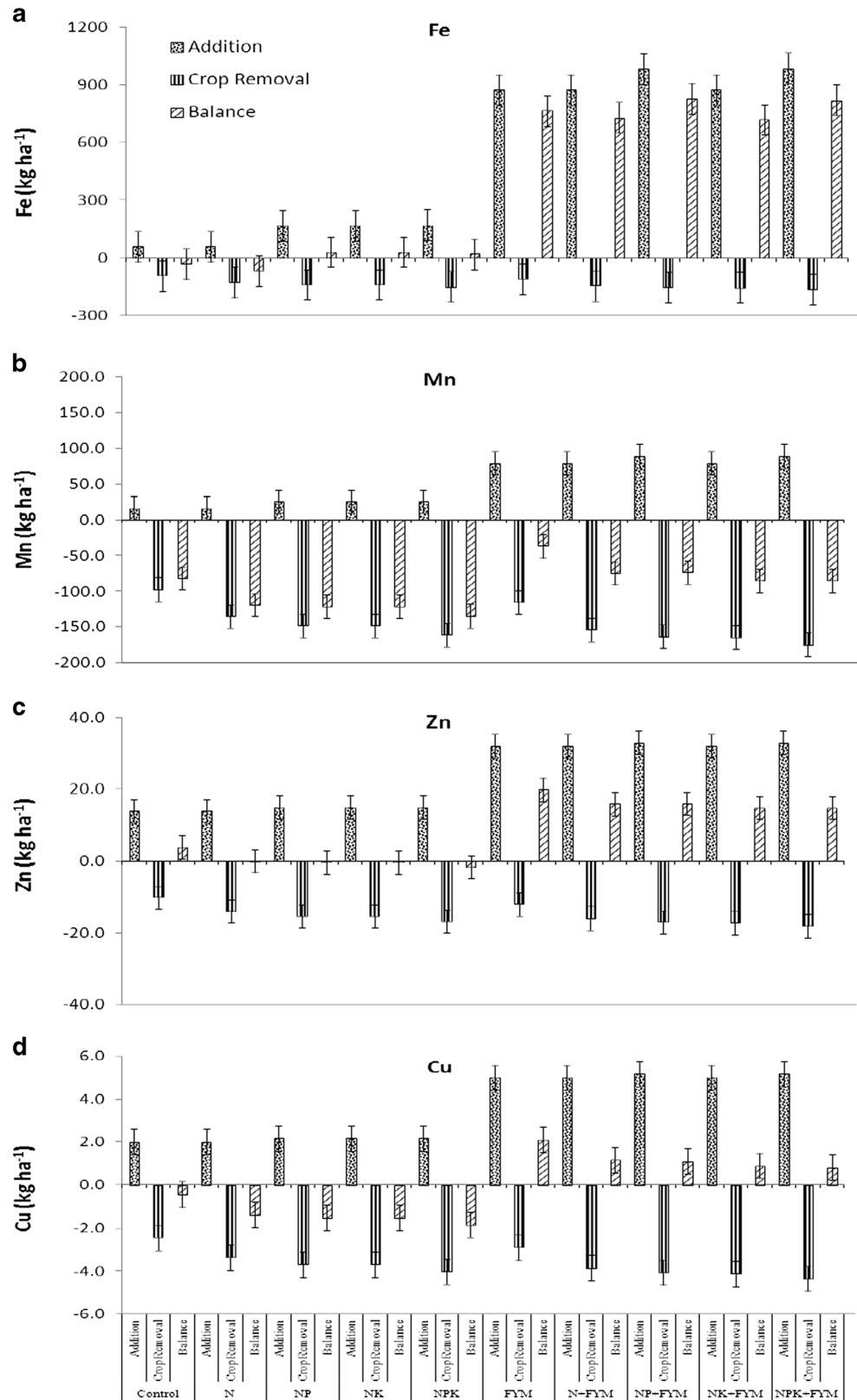
#### 3.4.1 Inputs of micronutrients

The input of micronutrients to the soil primarily consists of mineral fertilizers, FYM and atmospheric deposition (Fig. 1). The concentrations of micronutrients particularly Mn, Zn and Cu in N and K fertilizers were too low to detect. As a result, inputs by mineral fertilizers were only reported for P fertilizer, and for Fe, a little contribution from K fertilizer was noticed. The NPK + FYM treatment received the highest inputs, since they were treated with both manure and mineral fertilizers. Inputs of micronutrients in the FYM treatment were higher than those of NPK treatment, as micronutrient contents were higher in the manure than in the mineral fertilizers. Atmospheric deposition fluxes of micronutrients in the study region were significantly higher than those from mineral fertilizers, except for P fertilizer. Moreover, FYM is the most important source of micronutrients. Inputs of micronutrients by mineral fertilizers were primarily from the P fertilizer, which were lower than those treated with manure. We concluded that there was little risk of pollution to the soil at such a dose of P fertilizer ( $40 \text{ kg ha}^{-1}$  during wet and dry season), which confirmed the conclusion made by McBride and Spiers (2001). Li et al. (2010) suggested that applications of P and organic manure are the major sources of micronutrients in soil which resulted in significant increases in soil total Cu, Zn, Fe and Mn. The region where study area is located is not much industrialized and is away from the heavy industrial establishments; hence, the contribution of atmospheric deposition is low as compared to the manure application.

#### 3.4.2 Outputs of micronutrients

We used outputs of micronutrients only from crops. Different amounts of outputs of each element from 1969 to 2010 were observed (Fig. 1). Highest output level was observed for Mn compared to the other elements, which decreased in the following order:  $\text{Fe} > \text{Zn} > \text{Cu}$ . The control treatment displayed the lowest yield for each element, while the output in the FYM

**Fig. 1** Total inputs of **a** Fe, **b** Mn, **c** Zn and **d** Cu via fertilizers, manure and atmospheric deposition; total outputs of micronutrients by crop harvest; and micronutrient balance in different treatments during 41 years of cropping and fertilization. *Error bar* shows the standard error of mean



treatment was significantly lower than those of the NPK and NPK + FYM treatments for each element. The highest amounts of micronutrients removed from soil were always

observed in the NPK + FYM treatment, where the highest crop yield was also recorded. Outputs increased with the increase in yield. We observed small changes in the

concentrations of micronutrients in crops under various treatments. The differences in removal of micronutrients by crop uptake and harvest were primarily affected by the variation in crop biomass yield among various treatments (Li et al. 2007). Due to the higher yield and uptake of micronutrients, the application of FYM significantly affected the budgets of soil micronutrients. In addition, the leaching losses of micronutrients can also affect the output; however, as reported by Nicholson et al. (2006), leaching of micronutrients could be ignored compared to the amounts that may have entered the soil.

### 3.4.3 Balances of micronutrients

Balances of micronutrients were calculated by the difference of inputs and outputs from 1969 to 2010 (Fig. 1). In the treatments where P fertilizer or manure was not applied, the balances of micronutrients in soil were negative. Amendment of soil micronutrients with manure and mineral fertilizers results into positive balance for Fe, Zn and Cu; however, the balance for Mn remains negative under all the treatments. Inputs from manure were much higher than those of the mineral fertilizers and the atmospheric deposition. P fertilizer contributed significantly mainly for Fe and helps in making a positive balance for this element. The positive balance of Zn in control and N treatment is due to the lower crop output and compensation from the atmospheric deposition. These results indicated that nutrient cycling had an obvious effect on the balances of micronutrients. The NPK treatment had a lower input of micronutrients by mineral fertilizers and a higher output due to increased yield. This indicated that the need of micronutrient supplementation in the NPK treatment was largest when compared to the other treatments. During the 41 years, the highest positive balance was for Fe in the NPK + FYM

treatment. Its concentration was  $822.8 \text{ kg ha}^{-1}$ , equivalent to  $374 \text{ mg kg}^{-1}$  in arable soil (the density of soil is  $1.4 \text{ g cm}^{-3}$ ). Compared with the background of the Fe concentration ( $350,000 \text{ mg kg}^{-1}$ ; Alina 2011), the increase in total Fe level was small but had important influences on available Fe. Balances of Mn were negative in all the treatments, while for Cu, application of manure amounts for positive balance. In case of Fe, application of FYM and P fertilizer either alone or in combination results into the positive balance; however, the amounts of excesses were small compared to the total Fe in soil. As for Zn, negative balances were observed in NP, NK and NPK treatments, and for rest other treatments, there were positive balances. In NP and NPK treatments, except for Fe, balances for Mn, Zn and Cu were negative, suggesting the need for supplementation of these micronutrients for sustainable crop production. In this study, the input of micronutrients from the atmospheric deposition was low as compared to organic manure input; however, previous studies have shown that deposition was an important source for the agroecosystem and accounted for 20–80 % of the total input (Azimi et al. 2004; Ali-Khodja et al. 2008). The results of our study showed that the balances of micronutrients were negative without fertilizer and manure applications. P fertilizer contributed significantly towards compensating loss of Fe and, to a lesser extent, for Zn, whereas manure application increased the concentration of all the studied micronutrients in the soil.

### 3.5 Uptake of micronutrients by rice

The uptake of Fe in the rice varied from 765 to  $1200 \text{ g ha}^{-1}$  (Table 3). Highest uptake of Fe was recorded in NP + FYM treatment which was significantly higher than the uptake of Fe in the control, N and NK treatments and was at par with NPK

**Table 3** Grain yield, straw yield and micronutrient uptake of rice during 2010–2011 under different fertilizer treatments

Treatments	Grain yield t ha <sup>-1</sup>	Straw yield	Micronutrient uptake			
			Fe g ha <sup>-1</sup>	Zn	Mn	Cu
Control	3.00	3.64	765	198	1082	18.3
N	4.30	5.49	929	303	1555	26.8
NP	4.90	5.95	1125	281	1764	25.8
NK	4.80	5.62	985	314	1601	25.7
NPK	5.40	5.84	1058	283	1620	30.9
FYM	4.30	5.18	1038	288	1316	28.5
N + FYM	5.10	6.13	1174	296	1746	33.8
NP + FYM	5.30	6.56	1200	290	1822	32.5
NK + FYM	5.20	6.29	1111	330	1695	30.3
NPK + FYM	6.00	6.10	1109	304	1782	34.7
LSD ( $p < 0.05$ )	0.86	0.97	208	38	171	2.7



+ FYM, NK + FYM, N + FYM, FYM, NPK and NP treatments, suggesting that the application of FYM and single super phosphate either alone or in combination added significant amount of Fe in soil that was taken up by the rice plant. There was no significant difference between control, N and NK, indicating that application of urea or urea combined with fertilizer K did not increase the Fe uptake. Earlier studies have shown that FYM and single super phosphate contain considerable amount of Fe, which, when applied to the soil, results in higher availability of this micronutrient (Walia et al. 2010), and thus, the crop uptake of this micronutrient significantly increases (Mann et al. 2006).

The treatments NK + FYM, NK, NPK + FYM, N and N + FYM had significantly higher uptake of Zn than the control treatment (Table 3). It suggests that application of fertilizers and manure either alone or in combination promoted the uptake of Zn by rice. It was reported that proper levels of N and K could enhance the uptake of Zn by rice; our results were in agreement with earlier reports (Li et al. 2007; Dash et al. 2010; Rutkowska et al. 2014; Xue et al. 2014). However, wherever phosphatic fertilizers have been applied, the corresponding increase in the Zn uptake over the control was less as compared to the treatments where phosphatic fertilizer was not used. Some of the earlier authors have reported that under phosphorus fertilization, the mobility of Zn decreases because of precipitation of  $Zn_3(PO_4)_2$  in the soil solution (Fan et al. 2011; Rutkowska et al. 2014). An exception to this was observed in NPK + FYM treatment, where along with the P fertilization, Zn uptake increased. It may be due to the higher biomass yield under this treatment that would have resulted in higher uptake; besides, manure application also increases the Zn availability. Behera et al. (2011) reported that during the decomposition of organic matter, Zn forms labile organic mineral complexes which resulted in the increase in Zn content of soil.

Data on uptake of Mn by rice due to various treatments are presented in Table 3, which show significant variations on Mn uptake under these treatments over the control with the application of chemical fertilizers and organic manure either alone or in combination. Application of super phosphate and FYM resulted into the increased uptake of Mn due to addition of Mn by their use. The increased uptake of the Mn in N and NK treatments was largely due to the increased biomass production under these treatments as compared to the control. Some of the earlier findings have reported that application of fertilizer N increased the Mn uptake by rice crop over control (Duhan and Singh 2002). Application of urea enhances the uptake of Mn by the plant, and the interaction between Mn and N was found to be positive (Das 2000).

The uptake of Cu by rice ranges from 18.3 to 34.7 g ha<sup>-1</sup> in control and NPK + FYM treatments, respectively (Table 3). Higher uptake of Cu was observed in the manure-treated plots. Among the chemical fertilizer-applied plots, significantly higher uptake of Cu was observed in the NPK treatment. The uptake of Cu in N, NP and NK treatments was at par and significantly higher than the control. Application of chemical fertilizers although increased the Cu uptake, but the balanced fertilization (NPK) resulted in higher uptake. Earlier authors have reported that balanced fertilization not only increases grain yield and maintains soil nutrient balance, but also accelerates rice nutrient uptake (Mann et al. 2006; Li et al. 2007; Xue et al. 2014). Similar findings were reported by Aulakh and Malhi (2005) who enumerated that the interaction of other soil macronutrients and micronutrients also affected micronutrient uptake by crops.

#### 4 Conclusions

Long-term experiments are the valuable resources for studying the nutrient dynamics and overall assessment of the impacts of fertilization. After 41 years of various fertilizers and manure treatments, concentrations of DTPA-extractable Fe, Zn and Cu were significantly higher in NPK + FYM treatment as compared to control, while available soil Mn did not differ significantly. The application of phosphate fertilizer and organic manure contributed most towards the addition of micronutrients, and a little addition was also made through atmospheric deposition. The results of our study show that the balances of micronutrients were negative without fertilizer and manure applications. P fertilizer contributed significantly towards compensating loss of Fe and, to a lesser extent, for Zn, whereas manure application increased the concentrations of all the studied micronutrients in soil and hence maintained a positive balance for Fe, Zn and Cu. The balance of Mn was negative in all the treatments, because of its less addition and higher uptake by the rice crop. Long-term fertilization affects the amounts of Fe, Zn, Mn and Cu in soil through their effects on physical and chemical soil properties which in turn regulates the uptake of micronutrients by rice crop.

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