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Effect of zinc and boron application on fractions of zinc and boron in soils of paddy-cowpea cropping sequence

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Abstract
A field experiment was conducted during *Kharif* and *Rabi* season of 2019-20 in paddy - cowpea cropping system at Bhairapura village, Hassan district, Karnataka to study the effect of zinc and boron application on fractions of zinc and boron in soil of paddy-cowpea cropping sequence. Paddy was the test crop to study the direct effect and cowpea crop was raised to study the residual effect. The experiments were laid out in Randomized Complete Block Design with thirteen treatments and replicated thrice. At harvest of paddy and cowpea crops, T_7 treatment (NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax) recorded significantly higher water soluble and exchangeable, organically complexed, amorphous and crystalline sesquioxide bound, manganese oxide bound and residual zinc and it was at par with T_5 (NPK + FYM + $ZnSO_4$ @ 25 kg ha^{-1} + Borax @ 5 kg ha^{-1}). Among the fraction, the residual zinc recorded highest zinc fraction and water soluble zinc recorded lowest zinc fraction. Significantly higher readily soluble, specifically adsorbed, oxide bound, organic matter bound, residual and total boron was observed in T_7 treatment (NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax) compared to other treatments at harvest of both crops. Residual boron has highest contribution to total boron as compared to other fractions.

Keywords: Zinc, boron, fractions of zinc and boron

Introduction
During the last few decades, agricultural production has increased due to use of high yielding varieties and enhanced consumption of chemical fertilizers. Imbalanced use of chemical fertilizers by farmers has deteriorated soil health and declined soil organic carbon content. This has caused deficiencies in nutrients and micronutrients like Zn along with B resulting in major problem in achieving higher yield targets of rice. It is essential to adopt a strategy of using chemical fertilizers with organic manures. Organic manures enhances the soil fertility and yield of crops by rendering unviable sources of elemental nitrogen bound, phosphate and decomposed plant residues into available form in order to facilitate the plant to absorb the nutrients (Jagadish Timsina, 2019) [4]. FYM is being used as major source of organic manure in field crops, which influence physical, chemical and biological properties of soil.
Zinc and boron are essential micronutrient elements required by plants in small quantities for their successful growth and development. Zinc is involved in many enzymes activities, but it is not known whether it acts as functional, structural or regulatory co-factor. However, zinc is required for synthesis of tryptophan and production of growth hormones (auxins) such as indole acetic acid. Boron is a non metallic element and the only non-metal of the group 13 of the periodic table and is an essential micronutrient for crops. More than 90 per cent of the B in plants is found in cell walls and it's most important role is associated with cell wall formation. Zinc exists in five distinct pools in soils. These pools differ in strength (or reversibility) and therefore in their susceptibility to plant uptake, leaching and extractability. Zinc in soluble organic complexes and exchange positions are of major importance in maintaining of zinc level sufficient for wetland rice (Murthy, 1982) [12]. Boron exists in the soil in five fractions. Zerrari *et al.* (1999) [22] reported that these fractions are readily soluble, specific adsorbed, oxide bound, organic matter bound and residual (these are in silicate minerals, and cannot be used by plants).

Material and Methods
Fractionation of zinc in soils
Zinc in soils was fractionated into different forms designated as water soluble + exchangeable (WSEX-Zn), organically complexed (OM- Zn), crystalline sesquioxide bound (CRYOX-Zn), amorphous sesquioxide bound (AMOX-Zn), manganese oxide bound (MnOX-Zn) and

Residual (RES) zinc. Each fraction is operationally defined as given below Murthy (1982) [12] modified by Mandal and Mandal (1986) [8].

Extractant	Step	Fraction	Conditions Solution Soil (g): Solution (ml)
1M $(NH_4)OAc$ (pH 7.0)	1	Water soluble + Exchangeable (WSEX-Zn)	5: 20; shake for 1 hour
0.05 M $Cu(OAc)_2$	2	Organically complexed (OM- Zn)	5: 20; shake for 1 hour
0.3 M Sodium citrate + 1.0 M $NaHCO_3$ + 1 g $Na_2S_2O_4$ [Citrate-Bicarbonate- Dithionite (CBD)]	3	Crystalline sesquioxide bound (CRYOX-Zn)	Boiling water bath, 10 min, stir occasionally, keep on water bath (70 – 80°C), 15 min, stir occasionally
0.2 M $(NH_4)_2C_2O_4.H_2O$ + 0.2 M $H_2C_2O_4$ (pH 3.0)	4	Amorphous sesquioxide bound (AMOX-Zn)	5: 20 shake 1 hour
0.1 M NH2OH.HCl (pH 2.0)	5	Manganese oxide bound (MnOX- Zn)	Shake 30min
HCl+ HNO_3 conc	6	Residual (RES) zinc	1: 08 Aqua regia

The extractions were taken in 50 ml polypropylene centrifuge tubes with suitable weight of soil. Between each successive extraction, the supernatant was obtained by centrifuging for 15 min (3000 rpm) and filtering. The concentration of zinc in the centrifugate was determined by Atomic Absorption Spectrophotometer (Page *et al*., 1982) [14].

Fractionation of boron in soils

A separate analysis was done to determine all the fractions of boron in different soil and land use systems. Methods and procedures for separate extraction of soil boron fractions were based on the sequential fractionation procedures of Datta *et al*. (2002) [1]. The soil boron was divided into readily soluble boron, specifically adsorbed boron, oxide bound boron, organically bound boron and residual fraction. The extraction methods are summarized below. Boron concentrations in the extracted solutions were determined by spectrophotometer.

Fractionation procedure and colorimetric estimation of boron

Readily soluble boron

Ten gram of soil in duplicate was weighed into 50 ml polyethylene centrifuge tubes to which 20 ml of 0.01 M $CaCl_2$ was added and shaken for 16 h (Hou *et al*., 1994). After centrifuging at 10,000 rpm for 30 minutes the supernatant solution was filtered through Whatman no 42 filter paper. Boron was determined in clear extracts using azomethine-H reagent (Datta *et al*., 2002) [1].

Specifically adsorbed boron

The residue from the above step was then extracted with 20 ml of 0.05 M KH_2PO_4 by shaking for 1 h (Hou *et al*., 1994). After centrifugation at 10,000 rpm for 30 minutes the supernatant solution was filtered through whatman no 42 filter paper. Boron was determined in clear extract using azomethine-H (Datta *et al*., 2002) [1].

Oxide bound boron

The residue from the previous step was extracted with 40 ml of 0.175 M NH4- oxalate, pH 3.25 (Hou *et al*., 1994, 1996; Jin *et al*., 1987; McLaren and Crawford, 1973) [9] by shaking for 4 hr) most of these extracts had a yellow to slight reddish colour due to slight dissolution of organic matter.

To remove the colour, a 14 ml portion of the extract was taken into 50 ml Teflon beaker and the weight of the beaker plus aliquot was noted. The content was then warmed on a hot plate and 2 ml of 5 N NaOH solution was added to completely precipitate the dissolved Fe as $Fe(OH)_3$. The beaker with the aliquot was weighed again and the loss in weight was made up by adding distilled water. While doing so, the weight of the 2 ml 5 N NaOH was also taken into account. The suspension was filtered through Whatman No. 42 filter paper and thus Fe was separated. Nine ml aliquot of the filtrate was taken into a 50 ml Teflon beaker and 4 ml concentrated H_2SO_4 and 1 ml of $HClO_4$ (60%) were added and heated on hot plate at 135±5 ^OC to destroy the organic matter. When the volume was reduced to about 6 ml, $HClO_4$ was added in an increment of 0.5 ml until the solution became colourless and the volume reduced to 4 to 5 ml. The content was then transferred to a 15 ml graduated polyethylene tube and the final volume was made up to 6 ml. After centrifuging at 10,000 rpm for 15 min, boron in the clear extracts was determined by using carmine reagent (Datta *et al*., 2002) [1].

Organically bound boron

The residue from the NH_4-oxalate extraction was treated with 40 ml of 0.5 M NaOH by shaking for 24 hrs followed by filtration through whatman No. 42 filter paper. The extracts of all samples except sandy soils were dark in colour due to the dissolution of organic matter. Therefore 14 ml of aliquot was taken in a Teflon beaker to destroy the organic matter a 9 ml aliquot of the filtrate was taken into a 50 ml Teflon beaker and 4 ml of concentrated H_2SO_4 and 1ml $HClO_4$ (60%) were added and heated on hot plate at 135±5 ^oC to destroy the organic matter. When the volume was reduced to about 6 ml, $HClO_4$ was added in an increment of 0.5 ml until the solution became colourless and the volume reduced to 4 to 5 ml. The content was then transferred to a 15 ml graduated polyethylene tube and the final volume was made up to 7 ml. After centrifuging at 10,000 rpm for 15 min, boron in the clear extracts was determined by using carmine reagent (Datta *et al*., 2002) [1].

Residual fraction

The residue from the previous step was dried and ground. A 1 gm subsample was taken into a 50 ml Teflon beaker and few drops of concentrated H_2SO_4, 5 ml of HF (40%), and 0.5 ml $HClO_4$ (60%) were added (Lim and Jackson, 1982). The beaker was placed on a hot plate at 135±5 ^oC and the volume was reduced to about 3 ml. Then, 5 ml of concentrated H_2SO_4 and 5 ml of HF (40%) were added and heating continued. Further HF was added in increment to complete digestion of the soil. After digestion, 3 to 5 ml of $HClO_4$ (60%) was added depending upon the intensity of colour in the extract to get a clear extract. Finally, the volume was reduced to 3 to 4 ml by heating to drive off HF and $HClO_4$ completely. The content

was then transferred to a polyethylene centrifuge tube and the volume was made up to 25 ml. After centrifuging at 10,000 rpm, boron in the clear supernatant was determined spectrometrically with carmine reagent.

Result and discussion

Distribution of zinc fractions in soil at harvest of paddy crop are presented in Table 1. The zinc fractions differed significantly due to zinc and boron application through their varied levels. T_7 treatment (NPK + FYM + 25 kg ha^{-1} $ZnSO_4$ + 10 kg ha^{-1} Borax) recorded significantly higher water soluble + exchangeable zinc (0.92 mg kg^{-1}), organically complexed zinc fraction (2.36 mg kg^{-1}), amorphous sesquioxide bound zinc (3.24 mg kg^{-1}), crystalline sesquioxide bound zinc fraction (3.42 mg kg^{-1}) and Manganese oxide bound zinc and it was on par with T_5 followed by T_6 and T_4 and was found superior over all other treatments.

This might be due to high zinc buffering capacity of soils which resulted in low amount of water soluble + exchangeable zinc (WSEX- Zn) (Deb, 1997). The WSEX was found to be least among Zn fractions as Zn in this form is mobile and readily available for biological uptake in the environment. Similar results were found by Ramzan *et al*. (2014) [17], Soltani *et al*. (2015) [20], Spalbar *et al*. (2017) [21] and Nisab and Ghosh (2019). It is known to play a significant role in Zn nutrition of lowland rice and water logging causes an increase in the OCx forms of native soil Zn with a constant decrease in other forms, suggesting equilibrium of this form in soil (Mandal and Mandal, 1986) [8]. Similar values of organically complexed Zn have been reported by Prasad and Shukla (1996) [15]. The OCx fraction of Zn varied directly with the organic carbon content of the soils (Mandal and Mandal, 1986) [8]. These results are in line with findings of Ramzan *et al*. (2014) [17] and Kandali *et al*. (2016) [6].

Higher value of amorphous sesquioxide zinc attributed to greater ability of amorphous sesquioxide to adsorb Zn because of their high specific surface area (Devis and Leckie, 1978). Water logging may cause an increase in the Amor forms of native soil (Mandal and Mandal, 1986) [8]. Similar results were observed by Soltani *et al*. (2015) [20] and Spalbar *et al*. (2017) [21]. Higher crystalline sesquioxide bound zinc could be owing to chemical affinity or particular adsorption, as well as the high concentration of crystalline iron oxide. Similar results obtained by Pal *et al*. (1997). This fraction of the soil is more stable, especially in upland conditions. Zn^{2+} is incorporated into defect structures in crystalline oxide to compensate for changes in values, and Zn^{2+} is bound or adsorbed as a result Schwertmann *et al*. (1985).

Lower water soluble + exchangeable zinc (0.38 mg kg^{-1}), organically complexed zinc fraction (0.88 mg kg^{-1}), amorphous sesquioxide bound zinc (1.46 mg kg^{-1}), crystalline sesquioxide bound zinc (2.30 mg kg^{-1}) and manganese oxide bound zinc (3.18 mg kg^{-1}) were recorded in control (T_1) and package of practice (T_2).

Residual zinc was significantly superior over all other treatments. Significantly higher values (214.89 mg kg^{-1}) were recorded in T_7 treatment (NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax) and followed by T_5 (206.38 mg kg^{-1}) compare to other treatments. Residual zinc contributed to total zinc pool was 93.63 to 94.45 per cent. Lower residual zinc was recorded in T_1 (Control) and package of practice (T_2). However, the residual zinc showed the highest zinc fraction and water soluble zinc showed less zinc fraction in field experiment compared to other fractions.

The above findings indicated that the residual Zn was the dominant fraction among all the Zn fractions studied and is in agreement with the findings of Raja and Iyengar (1986) [16] and Mishra, (2009) [10]. The residual form of Zn is associated with mineral fraction of soil. The submergence cause marked increase in residual Zn content of soil. The results showed that water logging resulted in marked increase in the residual Zn in soil, which indicates considerable mobilization of zinc to residual fraction. Comparable results were also observed by Mandal (1996). Many researchers reported that large portion of Zn was in the residual fraction, with very little effect on the extraction plant uptake (Zang *et al*., 2014, Kandali *et al*., 2016, Wijebandara *et al*., 2011) [6].

All these fractions of zinc (water soluble and exchangeable, organically complexed, amorphous and crystalline sesquioxide bound, manganese oxide bound and residual zinc) increased with increase in levels of zinc and boron and also with increase in levels of combination along with NPK + FYM. Among these fractions in treated plots, the least fraction was water soluble and exchangeable fraction and highest fraction was residual zinc.

Effect of graded levels of zinc and boron on distribution of Zinc fractions in soil at harvest of cowpea

Distribution of zinc fractions in soil at harvest of cowpea crop is presented in Table 2. Zinc levels is having a significant effect on the distribution of distinct zinc fractions in soil, which are observed in the following order: RES >>MnOX > Cry > AmOX > OC > WSEX Zn. Zinc fractions such as WSEX, OC, AMOX, CRY and MnOX in soil at harvest of cowpea increased with increasing levels of $ZnSO_4$ and distribution of zinc fractions decreased compared to paddy post-harvest soils. Whereas, in RES Zn in soil at harvest of cowpea increased compared to paddy post-harvest soils. T_7 treatment (NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax) noticed significantly higher water soluble + exchangeable zinc, organically complexed, amorphous sesquioxide bound, crystalline sesquioxide bound, manganese oxide bound and residual zinc and it is on par with T_5. Lower values are recorded in control (T_1) and package of practice (T_2). The distribution of zinc fractions in post-harvest soils of cowpea followed the similar trend as that of zinc fractions in post-harvest soils of paddy. These results were in accordance with Kumar and Qureshi (2012) [7].

Effect of graded levels of zinc and boron on distribution of boron fractions in soil at harvest of paddy

Distribution of boron fractions in soil at harvest of paddy crop are presented in Table 3. The boron fractions differed significantly due to zinc and boron application through their varied levels. T_7 treatment (NPK + FYM + 25 kg ha^{-1} $ZnSO_4$ + 10 kg ha^{-1} Borax) had significantly higher readily soluble boron (1.82 mg kg^{-1}), specifically adsorbed boron fraction (1.98 mg kg^{-1}), oxide bound boron (4.08 mg kg^{-1}), organically bound boron fraction (3.93 mg kg^{-1}) and residual boron (82.21 mg kg^{-1}) and it was on par with T_6 followed by T_{12} and T_{13} and found superior over all other treatments. Lower readily soluble boron, specifically adsorbed boron fraction, oxide bound boron, organically bound boron fraction and residual boron were recorded in control (T_1) and package of practice (T_2).

Readily soluble fraction includes both hot water soluble boron

and non-specifically adsorbed boron. Readily soluble boron content due to various B levels was found to be more than the control and significant increase from the control was observed due to different treatments. Readily soluble boron is the boron fraction present in the soil solution and adsorbed weekly by various soil particles. This form is mostly available to plant uptake. These findings are supported by findings of Saviour Naveen *et al*. (2014) [18]. The second most available form is specifically adsorbed boron **(**SP B), it may be adsorbed onto clay surfaces or associated with organic matter in soil. These result in accordance with Padbhushan and Kumar, 2017 [13]. The specifically adsorbed B status in soil after the harvest of paddy crop significantly differed with rate of B application. The remaining fractions oxide bound, organically bound and residual boron are unavailable for plant uptake (Padbhushan and Kumar, 2017 [13] and Jegadeeswari and Muthumanickam, 2017). It includes boron tightly bound at the mineral surfaces and boron replaced by Al and Fe ions. Manganese (Mn) forms a part of the structure through isomorphous substitution (McLaren and Crawford 1973) [9]. It is a less labile fraction of B, which sorbs B into unavailable forms. Diana (2006) [2] reported that boron concentrations in soil vary from 2 to 200 mg B kg^{-1}, but generally less than 5-10% is available to plants. Besides aluminium and iron oxides, calcium carbonate and organic matter, clay minerals are considered to be amongst the primary B adsorbing surfaces in soils (Goldberg, 1997) [3].

Residual B is associated with primary and secondary minerals within the crystal structure and constitutes a substantial portion of Total B that is unlikely to be released in the mid and long-term under the conditions normally found in native soils (McLaren and Crawford 1973) [9]. The residual fraction is a non-labile form of B. This pool constitutes about 87·4–99·7% of total B.

Effect of graded levels of zinc and boron on distribution of boron fractions in soil at harvest of cowpea

Distribution of boron fractions in soil at harvest of cowpea crop are presented in Table 4. Boron levels had a significant effect on the distribution of distinct boron fractions in soil, which were observed in the following order: RES >> Oxide> Org > SA> RS B. Boron fractions such as RS, SA, Org and Oxide bound boron in post-harvest cowpea soils reduced compared to paddy post-harvest soils. Whereas, in RES B in post-harvest cowpea soils increased compared to paddy post-harvest soils. The treatment T_7 (NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax) had significantly higher water soluble + exchangeable zinc, organically complexed, amorphous sesquioxide bound, crystalline sesquioxide bound and residual zinc. Lower values were recorded in control (T_1) and package of practice (T_2). The distribution of boron fractions in soil at harvest of cowpea followed the same pattern as that of boron fractions in post-harvest soils of paddy. This result was in line with Mohamed (2014) [11].

Table 1: Effect of graded levels of zinc and boron on distribution of zinc fractions (mg kg^{-1}) in soil at harvest of paddy

Treatment	WSEX Zn	OC Zn	CRYOX Zn	AMOX Zn	MN Zn	RES Zn
	mg kg^{-1}					
T_1: Control	0.38	0.88	2.30	1.46	3.18	139.41
T_2: Package of practice (NPK + FYM + 20 kg ha^{-1} $ZnSO_4$)	0.62	1.59	2.74	2.21	3.45	165.88
T_3: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$	0.68	1.70	2.79	2.39	3.53	170.38
T_4: NPK + FYM + 20 kg ha^{-1} $ZnSO_4$ + 5 kg ha^{-1} Borax	0.76	2.18	3.14	2.90	3.86	188.69
T_5: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 5 kg ha^{-1} Borax	0.88	2.33	3.28	3.17	4.17	206.38
T_6: NPK + FYM + 20 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.79	2.24	3.20	2.99	3.75	193.92
T_7: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.92	2.36	3.42	3.24	3.98	214.89
T_8: NPK + 20 kg ha^{-1} $ZnSO_4$	0.48	1.47	2.64	1.95	3.30	154.33
T_9: NPK + 25 kg ha^{-1} $ZnSO_4$	0.52	1.58	2.69	2.14	3.43	159.84
T_{10}: NPK + 20 kg ha^{-1} $ZnSO_4$ + 5 kg ha^{-1} Borax	0.62	1.72	2.74	2.42	3.67	166.50
T_{11}: NPK + 25 kg ha^{-1} $ZnSO_4$+ 5 kg ha^{-1} Borax	0.71	1.88	2.86	2.63	3.83	176.99
T_{12}: NPK + 20 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.67	1.77	2.80	2.47	3.60	172.74
T_{13}: NPK + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.75	1.93	2.93	2.68	3.78	181.96
S.Em±	0.03	0.04	0.03	0.04	0.04	2.96
C.D. at 5%	0.09	0.10	0.14	0.15	0.13	8.65
Initial	0.35	0.85	0.27	1.41	3.12	138.55

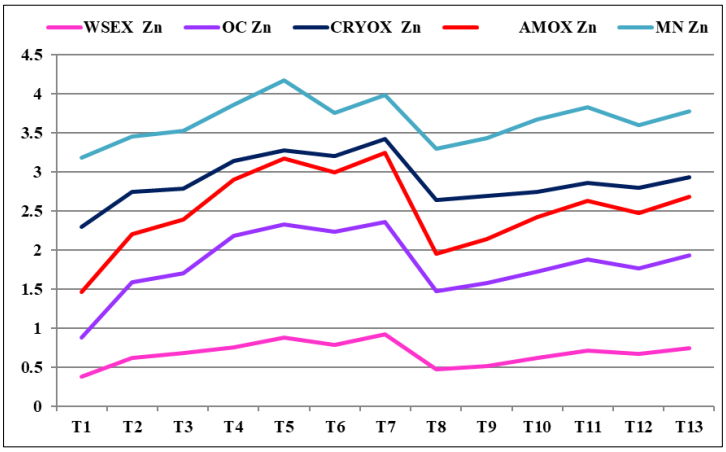

Fig 1: Effect of graded levels of zinc and boron on distribution of zinc fractions (mg kg^{-1}) in soil at harvest of paddy

Table 2: Effect of graded levels of zinc and boron on distribution of zinc fractions (mg kg^{-1}) in soil at harvest of cowpea

Treatment	WSEX Zn	OC Zn	CRYOX Zn	AMOX Zn	MN Zn	RES Zn
	mg kg^{-1}					
T_1: Control	0.26	0.82	2.16	1.22	2.91	141.88
T_2: Package of practice (NPK + FYM + 20 kg ha^{-1} $ZnSO_4$)	0.46	1.51	2.63	2.01	3.28	168.50
T_3: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$	0.50	1.63	2.72	2.23	3.36	172.74
T_4: NPK + FYM + 20 kg ha^{-1} $ZnSO_4$ + 5 kg ha^{-1} Borax	0.65	2.14	3.07	2.74	3.68	189.36
T_5: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 5 kg ha^{-1} Borax	0.73	2.27	3.27	3.06	3.86	208.21
T_6: NPK + FYM + 20 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.69	2.18	3.15	2.79	3.60	195.08
T_7: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.78	2.31	3.35	3.13	3.77	215.49
T_8: NPK + 20 kg ha^{-1} $ZnSO_4$	0.41	1.40	2.45	1.78	3.16	155.67
T_9: NPK + 25 kg ha^{-1} $ZnSO_4$	0.43	1.51	2.59	1.92	3.23	161.54
T_{10}: NPK + 20 kg ha^{-1} $ZnSO_4$ + 5 kg ha^{-1} Borax	0.48	1.68	2.67	2.26	3.44	169.72
T_{11}: NPK + 25 kg ha^{-1} $ZnSO_4$+ 5 kg ha^{-1} Borax	0.52	1.82	2.78	2.48	3.63	178.33
T_{12}: NPK + 20 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.56	1.70	2.71	2.34	3.35	174.70
T_{13}: NPK + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.59	1.86	2.83	2.51	3.58	183.85
S.Em±	0.02	0.04	0.04	0.05	0.03	2.47
C.D. at 5%	0.05	0.11	0.12	0.14	0.10	7.22

Table 3: Effect of graded levels of zinc and boron on distribution of boron fractions (mg kg^{-1}) in soil at harvest of paddy

Treatment	RS B	SA B	Oxide B	Org B	Res B
	mg kg^{-1}				
T_1: Control	0.74	1.07	3.02	3.05	51.22
T_2: Package of practice (NPK + FYM + 20 kg ha^{-1} $ZnSO_4$)	0.91	1.19	3.16	3.12	59.11
T_3: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$	0.95	1.22	3.21	3.18	61.38
T_4: NPK + FYM + 20 kg ha^{-1} $ZnSO_4$ + 5 kg ha^{-1} Borax	1.38	1.52	3.64	3.66	70.55
T_5: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 5 kg ha^{-1} Borax	1.49	1.63	3.78	3.71	73.91
T_6: NPK + FYM + 20 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	1.75	1.85	3.97	3.85	78.96
T_7: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	1.82	1.98	4.08	3.93	82.21
T_8: NPK + 20 kg ha^{-1} $ZnSO_4$	0.79	1.15	3.14	3.09	56.05
T_9: NPK + 25 kg ha^{-1} $ZnSO_4$	0.81	1.18	3.19	3.14	58.20
T_{10}: NPK + 20 kg ha^{-1} $ZnSO_4$ + 5 kg ha^{-1} Borax	1.19	1.39	3.54	3.60	64.11
T_{11}: NPK + 25 kg ha^{-1} $ZnSO_4$+ 5 kg ha^{-1} Borax	1.28	1.46	3.66	3.69	66.22
T_{12}: NPK + 20 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	1.53	1.55	3.73	3.74	69.38
T_{13}: NPK + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	1.65	1.62	3.87	3.78	72.01
S.Em±	0.03	0.05	0.04	0.03	1.87
C.D at 5%	0.10	0.21	0.16	0.16	7.39
Initial	0.69	1.03	2.95	2.98	51.05

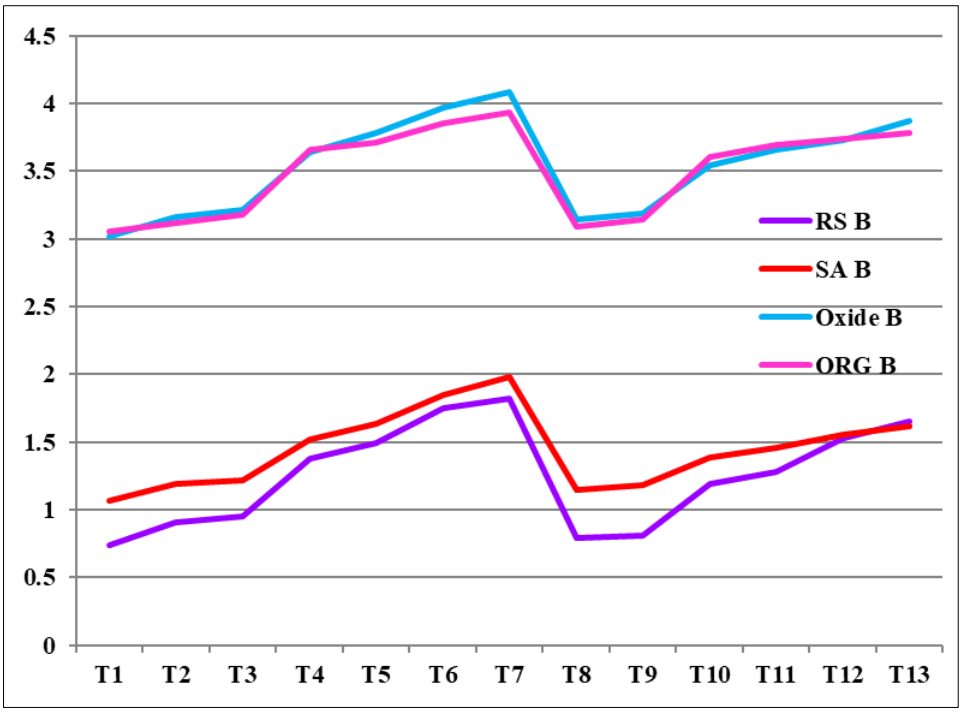

Fig 2: Effect of graded levels of zinc and boron on distribution of boron fractions (mg kg^{-1}) in soil at harvest of paddy

Table 4: Effect of graded levels of zinc and boron on distribution of boron fractions (mg kg^{-1}) in soil at harvest of cowpea

Treatment	RS B	SA B	Oxide B	Org B	Res B
	mg kg^{-1}				
T_1: Control	0.43	0.87	2.39	1.59	55.55
T_2: Package of practice (NPK + FYM + 20 kg ha^{-1} $ZnSO_4$)	0.47	1.07	2.58	1.76	61.60
T_3: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$	0.50	1.12	2.64	1.80	63.55
T_4: NPK + FYM + 20 kg ha^{-1} $ZnSO_4$ + 5 kg ha^{-1} Borax	0.67	1.28	2.96	2.14	76.52
T_5: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 5 kg ha^{-1} Borax	0.71	1.35	3.07	2.20	78.91
T_6: NPK + FYM + 20 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.83	1.46	3.21	2.36	84.72
T_7: NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.88	1.54	3.28	2.45	89.09
T_8: NPK + 20 kg ha^{-1} $ZnSO_4$	0.46	0.93	2.43	1.63	57.42
T_9: NPK + 25 kg ha^{-1} $ZnSO_4$	0.48	0.98	2.48	1.66	59.12
T_{10}: NPK + 20 kg ha^{-1} $ZnSO_4$ + 5 kg ha^{-1} Borax	0.63	1.18	2.84	1.92	72.11
T_{11}: NPK + 25 kg ha^{-1} $ZnSO_4$+ 5 kg ha^{-1} Borax	0.66	1.23	2.89	1.96	74.33
T_{12}: NPK + 20 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.73	1.31	3.04	2.05	75.38
T_{13}: NPK + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax	0.77	1.39	3.09	2.09	77.01
S.Em±	0.02	0.03	0.04	0.03	1.87
C.D at 5%	0.05	0.10	0.11	0.10	7.39

Conclusion

At harvest of paddy and cowpea crops, T_7 treatment (NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax) recorded significantly higher water soluble and exchangeable, organically complexed, amorphous and crystalline sesquioxide bound, manganese oxide bound and residual zinc and it was at par with T_5 (NPK + FYM + $ZnSO_4$ @ 25 kg ha^{-1} + Borax @ 5 kg ha^{-1}). Among the fraction, the residual zinc recorded highest zinc fraction and water soluble zinc recorded lowest zinc fraction. Significantly higher readily soluble, specifically adsorbed, oxide bound, organic matter bound, residual and total boron was observed in T_7 treatment (NPK + FYM + 25 kg ha^{-1} $ZnSO_4$+ 10 kg ha^{-1} Borax) compared to other treatments at harvest of both crops. Residual boron has highest contribution to total boron as compared to other fractions.

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