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ORIGINAL RESEARCH

Organic manures: an efficient move towards maize grain biofortification

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Abstract

Purpose In a novel approach, certain organic wastes byproducts of agro industries were assessed for their ability to support maize growth and Zn bioavailability in maize grain.

Methods In a field experiment, maize (*Zea mays*) was supplemented with farm yard manure (FYM), press mud (PM), fisheries manure (FM), and slaughter house waste (SHW) in combination with Zn soil application (ZnS) and Zn foliar spray (ZnF) with recommended doses of N:P:K (140:100:60 kg ha^{-1}), respectively. Besides assessing the maize growth, grain, and straw yield, Zn bioavailability in maize grain was also studied.

Results Organic materials combined with ZnS and ZnF significantly increased the maize yield and Zn bioavailability. PM + ZnS increased the grain yield by 69.71%, while FM + ZnF and FYM + ZnF increased the grain Zn concentration by 86.37 and 86.16%, respectively. Moreover, grain Zn content was greatly influenced by PM + ZnS and PM + ZnF resulted an average increase by 160%. Phytate concentration and phytae:Zn molar ratio in grain were decreased by 30.34 and 66.92%, respectively by FYM + ZnF. Estimated Zn bioavailability ranged from 0.92 to 2.04 mg Zn/300 g in maize grain, and was maximum by PM and FYM combined with ZnF.

Conclusion Organic manures influence the nutrient uptake from soil, increase the product quality, and act as a good organic fertilizer. The current study revealed that organic manures can enhance crop growth and Zn uptake in grain in sustainable manner. It would be an eco-friendly approach by utilizing organic wastes annually generated by agro industries.

Keywords Biofortification · Maize · Organic manures · Yield · Zinc application

Introduction

Maize (*Zea mays* L.) is grown throughout the world with annual production of 875.22 million tons (FAO 2012). In Pakistan, it adds about ≥ 10% of the entire agricultural production and 15% services (FAO 2014). Among the major crops (wheat, cotton, and rice) in Pakistan, it is fourth leading crop cultivated on one million hectares, producing 3.5 million metric tons annually (FAO 2014; PARC 2015).

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It is a rich source of dietary fiber (72%), proteins (10%), and energy (365 kcal/100 g) with low fat (4%). It can be processed in a number of food ingredients such as oil, alcohol, and starch sweeteners (Ranum et al. 2014). High yielding cultivars require maximum fertilizers which led to the decline in soil fertility, nutrient use efficiency, plant available micronutrient and hampered the farming systems, and food availability in developing countries (Cakmak 2008; Jones and Healey 2010).

Zinc (Zn), a micronutrient, plays critical role in ≥ 300 eukaryotic enzymes. In plants, it maintains structural veracity of proteins, and regulates auxin production, photosynthesis, nitrogen metabolism, respiration, and cell wall formation (White and Broadley 2009). In human beings, severe deficiency of Zn causes serious complications like growth retardation, immunity disturbance, and mental problems, specifically for children and pregnant women (Gibson 2006).

It is stated that > 25% world's population is facing shortage of Zn, which is an alarming situation for human being and food crops (Maret and Sandstead 2006; Chasapis et al. 2012). In East Asia especially Pakistan and India, about 50–70% population is Zn deficient, especially, in children and women (Shivay and Prasad 2012).

Maize crop is very susceptible to Zn scarcity and its insufficiency is ubiquitous in semi-arid areas (Singh et al. 2005). The major causes disturbing the Zn phytoavailability are redox potential (Eh), low Zn contents, high calcite, pH, sodium (Na), calcium (Ca), magnesium (Mg), bicarbonate, concentration of all ligands which have ability to form organo-Zn complexes, biological indices in the rhizosphere, concentration of other trace metals, and availability of micro–macro specifically phosphate (P) in soil solution (Alloway 2009; Imran et al. 2016b). Indeed, mobility of Zn^{2+} in soils is dependent on proton actions; therefore, its mobility decreases in higher pH due to greater uptake ability of mineral surfaces, hydrolyzed Zn forms, Fe-oxide co-precipitation, and chemisorption on calcite. High pH is due to high concentration of calcium carbonate ($CaCO_3$), heavy liming, high concentration of salts, reduced conditions and content of pedogenic origin (Alloway 1995). In Pakistan (Punjab), arable land pH is about 9.2 (Muhammad et al. 2008) which ultimately decreases the availability of nutrients for plant uptake.

Potentially available solution to overcome the nutrient deficiency is the reuse of organic wastes which have potential to sustain organic matter. It is well known to bring improvements in soil microbiota functions, soil aeration, moisture retention, and availability of nutrients (Girmay et al. 2008). Many types of manures (e.g., green crop residues, mulch, industrial wastes, animal dung, and domestic wastes) have been efficiently applied to crops and resulted higher availability of Zn to plants by microbial actions, straight donation, or chemical conversion reactions (Maliwal et al. 2007; Quilty and Cattle 2011).

Zinc fertilizers have been widely used to enhance the crop yield and to increase Zn concentration in grains by various (broadcasting, foliar spray, banding, and in combinations) methods (Rehim et al. 2014; Imran et al. 2015; Sarwar et al. 2015; Imran and Rehim 2017). Foliar spray of Zn improved grain yield and increased Zn and starch contents (Foti et al. 2008; Imran et al. 2016a).

It is evident from the previous studies that organic matter addition in combination with soil and foliar Zn fertilization enhanced macro and micronutrients and contribute to increase the crop yield and nutrient uptake. However, comparisons of organic manures with regard to Zn bioavailability in maize grain have not been reported.

Keeping in view the above scenario, a study was planned using different organic manures and single source of Zn to attain best organic manure and Zn application method which optimize crop growth, yield, and Zn concentration in grain.

Experimental methods

Growth conditions

A field experiment was performed in 2015 at the research field of Faculty of Agricultural Sciences and Technology (FAST), Bahauddin Zakariya University, Multan. Soil samples were randomly collected at the depth of 0–15 cm prior to crop sowing for physicochemical analysis. The crop was sown on calcareous loam soil with low phytoavailable Zn

Table 1 Physical and chemical properties of soil used in the experiment

Soil property	Unit	Value	Method
Textural class	–	Loam	USDA classification method
Sand	%	45.1	Hydrometer method (Gee and Bauder 1986)
Silt	%	36.8	
Clay	%	18.1	
pH_s	–	7.92	pH of saturated soil paste
EC_e	$dS\ m^{-1}$	0.541	Electric conductivity of saturated soil paste extract
$CaCO_3$	%	0.45	Acid dissolution (Allison and Moodie 1965)
OM	%	0.51	Walkley–Black method (Nelson and Sommers 1982)
AB-DTPA Zn	$mg\ kg^{-1}$	0.63	Extracted with AB-DTPA (Soltanpour 1985)

(AB-DTPA 0.63 mg Zn kg^{-1}soil; Table 1; Black 1965; Keeney and Nelson 1982; Whittig et al. 1986).

The study consisted on 11 treatments; Ck (without Zn and manures), FYM +ZnS (farm yard manure + Zn soil application @ 16 kg ha^{-1}), FYM + ZnF (farm yard manure + Zn foliar spray 0.5% w/v of Zn solution), PM + ZnS (press mud + Zn soil application @ 16 kg ha^{-1}), PM + ZnF (press mud + Zn foliar spray 0.5% w/v of Zn solution), FM + ZnS (fisheries manure + Zn soil application @ 16 kg ha^{-1}), FM + ZnF (fisheries manure + Zn foliar spray 0.5% w/v of Zn solution), SHW + ZnS (slaughter house waste + Zn soil application @ 16 kg ha^{-1}), SHW + ZnF (slaughter house waste + Zn foliar spray 0.5% w/v of Zn solution), ZnS (Zn soil application @ 16 kg ha^{-1}), and ZnF (Zn foliar spray of 0.5% w/v of Zn solution). Nitrogen (N), phosphorous (P), and potassium (K) were applied by recommended doses for maize crop (140:100:60 kg ha^{-1}) as Urea, DAP, and K_2SO_4, respectively. Nitrogen was applied in two splits: first at the time of sowing and second after 30 days of sowing of the crop. The suggested doses of manures (10 ton ha^{-1} FYM, 8 ton ha^{-1} PM, 2 ton ha^{-1} SHW and 1 ton ha^{-1} FM) were applied in soil at the time of seedbed preparation. All manures were mixed thoroughly ploughing soil through rotavator. Source of Zn was $ZnSO_4 \cdot 7H_2O$.

The experiment was laid out in randomized complete design (RCBD) with three replications. All plots had an area of 3 m × 5 m and firm hills around to prevent intermixing of manures. Maize cv. Hybrid-6585 seed (30 kg ha^{-1}) was applied having plant-to-plant distance 22.5 cm and row-to-row distance 75 cm. With the interval of 10 days, crop was irrigated with tube well water. Weeds were manually removed by hoeing and pesticide.

Crop harvesting and chemical analysis

Harvesting was performed at maturity and manually threshed to determine grain and stover yield. After collection of cobs and stover sub samples, each sample was washed with distilled water and dried prior to oven dry at 65 °C for 72 h. Wet digestion of ground samples was done in di-acid mixture of HNO_3:$HClO_4$ with ratio of 2:1. Zinc concentration of digested samples was determined with atomic absorption spectrometer (PerkinElmer, analyst 100, Waltham, USA. Phytate extraction was made with 10 ml of 0.2 N HCl and continuously shaking the mixture for 2 h at 25 °C. Phytate concentration in extract was determined by indirect method (Haug and Lantzsch 1983) using a spectrophotometer (Shimadzu, UV-1201 Kyoto, Japan) at 519 nm wavelength.

Estimated Zn bioavailability in grain

Zn bioavailability from dietary intake depends on Zn and phytate; therefore, qualitatively estimated bioavailability was described in rice grain as ([phytate]:[Zn] ratio) (Brown et al. 2001; Weaver and Kannan 2002). While quantitative estimated bioavailability was determined by Trivariate Zn absorption model (Miller et al. 2007):

$$\mathrm{TAZ} = 0.5\,(A_{\mathrm{MAX}} + \mathrm{TDZ} + K_{\mathrm{R}} \cdot (1 + \mathrm{TDP}/K_{\mathrm{P}}) - \sqrt{(A_{\mathrm{MAX}} + \mathrm{TDZ} + K_{\mathrm{R}} \cdot (1 + \mathrm{TDP}/K_{\mathrm{P}})) - 4 \cdot A_{\mathrm{MAX+TDZ}}}),$$

where TAZ = total daily absorbed Zn mg day^{-1}, TDZ = total daily dietary Zn mmol Zn day^{-1}, A_{MAX} = maximum Zn absorption = 0.091, K_R = equilibrium dissociation constant of zinc-receptor-binding reaction = 0.680, K_P = equilibrium dissociation constant of Zn-phytate binding reaction = 0.033, and TDP = mmol phytate per day

Key maize consuming countries are Mexico, Zambia, and Zimbabwe; and their normal per capita maize usage is about 300 g per day (FAO 2013). Therefore, total daily absorbed (TAZ) was counted for 300 g maize flour and said "estimated Zn bioavailability". In addition, estimated bioavailability of Zn results is declared on the basis of adult's consumption of 300 g maize flour as daily intake.

Statistical analysis

All the data were statistically analyzed using "SPSS 17.0 American" software. To compare the means of all the treatments, a general linear model and analysis of the gathered data was performed by (ANOVA). Significant differences were measured by Tukey's test and graphs were made using Sigma plot version 13.00®.

Results

Growth parameters

Addition of different organic manures in combination with Zn soil and foliar fertilization resulted in significantly ($P \leq 0.05$) increased plant height, number of rows per cob, number of grains per cob, and cob length compared to control (Table 2). Plant height was maximum (234.3 cm) at PM + ZnS followed by FM + ZnF (230 cm), PM + ZnF (227 cm), and FYM + ZnS (226 cm), respectively, and all other treatments showed higher plant height than control (172.60 cm) (Table 3). In comparison with soil and foliar application, PM + ZnS showed (3.22%) higher influence than PM + ZnF and FYM + ZnS was (2.26%) higher in plant height as compared with FYM + ZnF, while PM + ZnS was 12.11 and 10.52% greater than ZnF and ZnS.

Number of rows per cob ranged (8–15.67) and number of grains per cob ranged (17.66–32.00). The maximum rows and grains per cob was noticed by PM + ZnS and PM + ZnF, while all other treatments were at par with each other and higher in comparison with control (Table 2). Cob length was significantly higher in all treatments in comparison

Table 2 Effect of organic manures and Zn fertilization on maize plant growth attributes

Treatments	Plant height (cm)	No. of rows per cob	No. of grains per cob	Cob length (cm)
Control	172.60 ± 1.52 g	08.00 ± 1.00 f	17.66 ± 66 h	21.20 ± 2.30 h
FYM + ZnS	226.00 ± 1.00 c	13.66 ± 0.57 a–c	28.33 ± 1.15 bc	31.76 ± 1.43 ab
FYM + ZnF	221.00 ± 2.00 d	14.00 ± 1.00 ab	27.00 ± 1.00 cd	28.56 ± 0.58 b–d
PM + ZnS	234.30 ± 0.57 a	15.33 ± 0.57 a	32.00 ± 1.00 a	33.67 ± 0.57 a
PM + ZnF	227.00 ± 2.00 bc	15.67 ± 0.57 a	30.67 ± 0.57 ab	30.16 ± 1.25 a–c
FM + ZnS	221.00 ± 2.00 d	11.00 ± 1.00 cd	25.00 ± 1.00 de	27.16 ± 0.61 c–e
FM + ZnF	230.67 ± 1.52 ab	12.33 ± 1.15 b–d	24.00 ± 1.00 ef	27.06 ± 0.50 c–e
SHW + ZnS	217.00 ± 1.00 de	12.00 ± 1.00 b–d	22.00 ± 1.00 fg	23.30 ± 0.98 e–g
SHW + ZnF	220.6 ± 2.08 d	12.00 ± 1.00 b–d	22.67 ± 0.57 e–g	22.50 ± 1.32 fg
ZnS	212.60 ± 1.52 ef	10.67 ± 1.52 de	20.33 ± 1.52 gh	25.90 ± 1.85 d–f
ZnF	209.00 ± 1.00 f	10.67 ± 0.57 de	18.67 ± 0.57 h	21.50 ± 2.29 g

Different letters in the same column indicate significant differences by LSD at $P \leq 0.05$ and ± indicate standard error ($n = 3$)

Table 3 Effect of organic manures and Zn fertilization on maize plant yield attributes

Treatments	Grain yield (ton ha^{-1})	Straw yield (ton ha^{-1})	1000-grain weight (g)
Control	3.83 ± 0.03 g	7.74 ± 0.36 h	177.00 ± 0.00 g
FYM + ZnS	5.94 ± 0.05 c	11.77 ± 0.10 c	257.66 ± 3.00 c
FYM + ZnF	5.76 ± 0.02 c	11.43 ± 0.11 d	247.33 ± 2.00 d
PM + ZnS	6.50 ± 0.10 a	12.82 ± 0.14 a	265.00 ± 2.51 b
PM + ZnF	6.18 ± 0.06 b	12.34 ± 0.15 b	274.33 ± 1.52 a
FM + ZnS	5.21 ± 0.11 d	10.91 ± 0.06 e	217.33 ± 2.00 e
FM + ZnF	5.24 ± 0.07 d	10.65 ± 0.11 e	220.67 ± 1.52 c
SHW + ZnS	4.22 ± 0.11 e	10.29 ± 0.12 f	205.00 ± 2.51 f
SHW + ZnF	4.09 ± 0.06 e	10.16 ± 0.04 f	202.33 ± 2.08 f
ZnS	4.05 ± 0.06 ef	9.81 ± 0.04 g	200.00 ± 2.64 f
ZnF	4.19 ± 0.11 e	9.74 ± 0.09 g	202.33 ± 2.08 f

Different letters in the same column indicate significant differences by LSD at $P \leq 0.05$ and ± indicate standard error ($n = 3$)

to control treatment (Table 3). Maximum cob length was recorded in PM + ZnS (33.67 cm), FYM + ZnS (31.76 cm), PM + ZnF (30.16 cm), and FYM + ZnF (28.56 cm), respectively (Table 2).

Yield attributes

Fertilization of Zn and addition of organic manures significantly ($P \leq 0.05$) produced high grain and stover yield and thousand grain weight. Grain yield by PM + ZnS, PM + ZnF, FYM + ZnS, and FYM + ZnF was 69.71, 61.79, 55.09, and 50.39%, respectively, higher than control (Table 3). While, among the treatments, PM + ZnS was 6.09, 9.43, and 50% higher than PM + ZnF, FYM + ZnS, and ZnS, respectively (Table 3).

Stover yield ranged 7.740–12.82 ton ha^{-1}. It was maximum in PM + ZnS (12.82 ton ha^{-1}), followed by PM + ZnF (12.34 ton ha^{-1}), FYM + ZnS (11.77 ton ha^{-1}), FYM + ZnF (11.43 ton ha^{-1}), and SHW + ZnS (10.91 ton ha^{-1}).Various organic manures and Zn fertilization methods showed significant difference in 1000-grain weight. It ranged 177–274 g (Table 3). It was mainly influenced by PM + ZnF and FYM + ZnS, while all other treatments had greater 1000-grain weight as compared with control. In contrast to the Zn soil and foliar application, Zn soil application had more 1000-grain weight as compared with foliar application (Table 3).

Zinc concentration in grain and stover

Various organic amendments and Zn appliance significantly ($P \leq 0.05$) enhanced Zn concentration in grains and stover (Table 4). Zinc concentration in grains ranged (19.26–36.06 mg kg^{-1}) among the treatments. Zinc concentration was 86.37, 86.16, 80.28, and 74.6% higher in FM + ZnF, FYM + ZnF, PM + ZnF, and PM + ZnS, respectively, as compared to control, while between the treatments FM + ZnF was 10% higher than FYM + ZnS and 6.6% higher

Table 4 Effect of organic manures and Zn fertilization on Zn conc. in grains, stover, and Zn contents in grains and accumulation in shoot

Treatments	Zn concentration in grain (mg kg^{-1})	Zn concentration in stover (mg kg^{-1})	Zn content in grain (μg $seed^{-1}$)	Zn accumulation in shoot (g ha^{-1})
Control	19.37 ± 1.68 c	16.55 ± 1.97 b	3.42 ± 0.25 d	202.32 ± 11.51 f
FYM + ZnS	32.66 ± 2.57 ab	32.97 ± 1.72 a	8.41 ± 0.61 a	582.10 ± 2.90 b
FYM + ZnF	36.06 ± 3.04 a	34.79 ± 3.66 a	8.92 ± 0.08 a	605.72 ± 27.91 ab
PM + ZnS	33.82 ± 4.47 a	34.20 ± 2.82 a	8.96 ± 1.21 a	658.33 ± 23.68 a
PM + ZnF	34.92 ± 1.65 a	33.68 ± 2.49 a	9.57 ± 1.77 a	631.95 ± 8.96 ab
FM + ZnS	26.83 ± 2.79 abc	19.56 ± 2.06 b	5.82 ± 0.55 bc	353.44 ± 27.31 cd
FM + ZnF	36.10 ± 1.34 a	20.58 ± 2.23 b	7.96 ± 0.34 ab	408.80 ± 16.07 c
SHW + ZnS	21.90 ± 2.54 c	21.03 ± 1.46 b	4.49 ± 0.53 cd	308.77 ± 11.81 de
SHW + ZnF	19.26 ± 1.97 c	22.14 ± 2.46 b	3.89 ± 0.35 cd	303.84 ± 31.07 de
ZnS	23.85 ± 1.85 bc	19.62 ± 0.58 b	4.77 ± 0.40 cd	289.31 ± 10.63 e
ZnF	21.50 ± 2.58 c	17.80 ± 2.07 b	4.35 ± 0.50 cd	261.86 ± 20.61 e

Different letters in the same column indicate significant differences by LSD at $P \leq 0.05$ and ± indicate standard error ($n = 3$)

than PM + ZnS (Table 4). In stover, maximum Zn concentration was recorded in FYM + ZnF (34.79 mg kg^{-1}), followed by FYM + ZnF (34.79 mg kg^{-1}), PM + ZnS (34.20 mg kg^{-1}), and PM + ZnF (33.68 mg kg−1), and minimum in control (16.55 mg kg^{-1}). Zinc concentration in stover was less than in grains. Maximum increase in Zn content of maize grains was (179.82%) by PM + ZnF followed by, 161, 160.82, 145, and 132.75% by PM + ZnS, FYM + ZnF, FYM + ZnS, and FM + ZnF, respectively, as compared with control.

Zinc accumulation in shoot was also significant ($P \leq 0.05$) than control in all treatments (Table 4) ranging from 202.32 to 658.33 g ha^{-1}. In contrast to Zn soil and foliar application in combination with organic manures, Zn soil application showed more Zn accumulation in shoot 658.33 g ha^{-1}.

Phytate concentration in grain

Phytate concentration in grain varied among all the treatments. It was significantly ($P \leq 0.05$) higher in control in comparison with other treatments (Fig. 1a). Maximum decrease in phytate concentration was recorded in FYM + ZnF (30.34%) and PM + ZnS (26.83%). In all other treatments, phytate concentration was less as compared to control (13.68 mg g^{-1}) (Fig. 1a). Phytate content in grains significantly differed among all the treatments (Fig. 1b). It ranged from 2.15 to 2.65 mg $seed^{-1}$. Maximum phytate content was in PM + ZnS, while minimum in SHW + ZnF (Fig. 1b) as compared with control. Phytate content in grain (kg ha^{-1}) was significantly different for each treatment. Press mud combined with Zn soil application (PM + ZnS) has maximum phytate content increase percentage (24%) followed by FYM + ZnS (15.74%) and all other treatments have higher phytate content in grains as compared with control (Fig. 1c).

Various organic amendments and Zn appliance significantly ($P \leq 0.05$) decreased grain [phytate]: [Zn] molar ratio (Fig. 2a). Maximum decrease in phytate: Zn molar ratio was recorded in FYM + ZnF (66.92%), PM + ZnS (65.56%), PM + ZnS (64.73%), and in FYM + ZnS (62.77%) as compared with control.

Estimated Zn bioavailability

Different organic manures and soil fertilization and foliar spray of Zn significantly influenced ($P \leq 0.05$) the predictable Zn bioavailability in maize grains (Fig. 2b). Maximum estimated bioavailability of Zn was 2.04 mg for 300 g maize grain at FYM + ZnF followed by PM + ZnF (1.99 mg/300 g) and PM + ZnS (1.97 mg/300 g), and minimum at control (0.92 mg/300 g).

Relative yield

Organic amendments with Zn application significantly ($P \leq 0.05$) influenced relative yield (%). Maximum relative yield was recorded by PM + ZnS (100%) followed by PM + ZnF (95%), FYM + ZnS (91%), FYM + ZnF (89%), and FM + ZnF (81%) as compared with control (59%). All other treatments' relative yield was higher than control (Fig. 3).

Discussion

Most of the Pakistani arable soils are Zn deficient (Imran et al. 2016a; b) the same is the case with this experimental soil (≤ 1 mg AB-DTPA extractable Zn per kg of soil; Table 1). The major factors contributing to low bioavailability of Zn might be parent material, low Zn content in

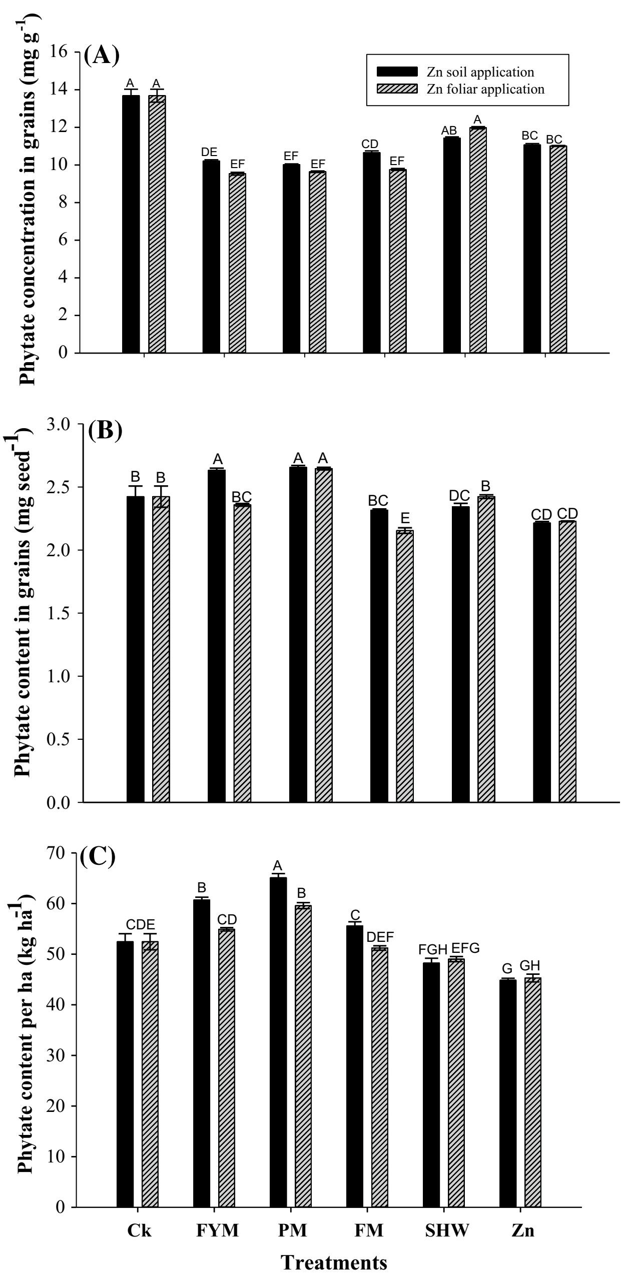

Fig. 1 Effect of organic manures and Zn fertilization on phytate concentration (**a**), phytate content (**b**), and phytate content per ha (**c**). Different letters indicate significant differences by LSD at $P \leq 0.05$ and error bars indicate ± standard error ($n = 3$)

soil, high pH, low organic matter, highly weathered, soil erosion, and coarse textured soils (Singh et al. 2005; Ryan et al. 2013). Organic manures are the potential source of micro–macro nutrients, increase microbial activities, modify the soil physical behaviour, and influence the availability of applied nutrients (Pandey et al. 2007). Combined use of organic manures and Zn make readily availability of Zn, healthy growth of roots, and maintain the adequate uptake of Zn (Patil et al. 2017).

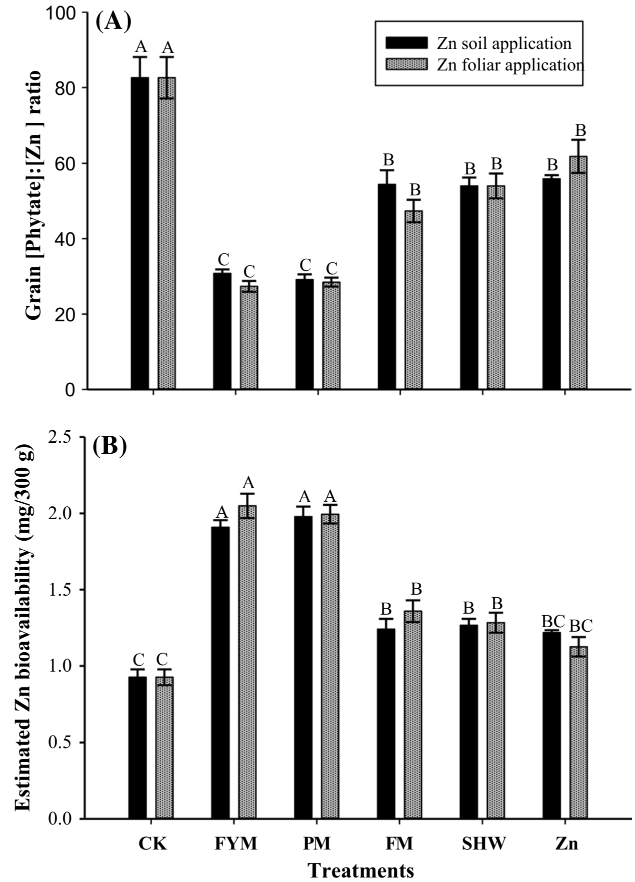

Fig. 2 Effect of organic manures and Zn fertilization on grain phytate Zn molar ratio (**a**) and estimated Zn bioavailability (**b**). Different letters indicate significant differences by LSD at $P \leq 0.05$ and error bars indicate ± standard error ($n = 3$)

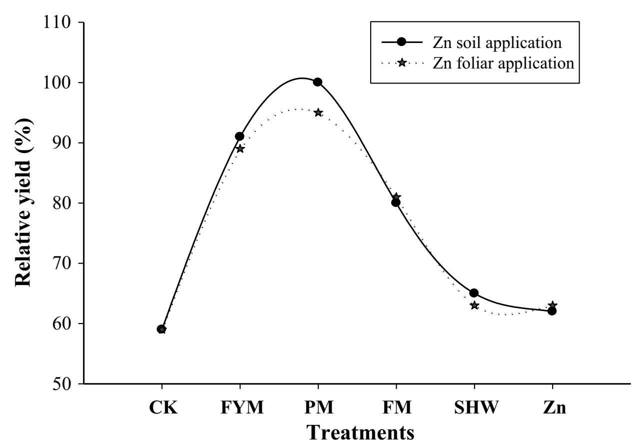

Fig. 3 Effect of organic manures and Zn fertilization on relative yield (%) of maize crop

Improvement in plant growth was unexpected as Zn scarcity in soil (0.63 mg kg^{-1} soil; Table 2). Organic amendments and Zn application significantly ($P \leq 0.05$) enhanced the crop growth and yield (Table 2). Application of organic manures improved the soil physicochemical properties such as change in soil pH and organic complex formation and make readily availability of Zn for plant uptake (Rehman et al. 2012). Application of Zn (soil and foliar) with press mud addition enhanced crop production (khan et al. 2015). In this study, improved crop productivity is due to the supply of macro (NPK) and micronutrient (Zn, Fe, Cu, and Mn) through nutrient-enriched press mud having potential to activate the microbial activities in soil rhizosphere making the readily availability of nutrients to rhizospheric microbes which ultimately increase the soil enzymatic activity and increase the phytoavailability of required nutrients to the crop and increase the crop growth (Bangar et al. 2000; Rakkiyappan et al. 2001). Second reason for the more growth and yield of maize is the application of Zn with press mud, because, for plants, Zn is necessary for auxin synthesis which elongates the plant cell and enhances the cell growth (Imran and Rehim 2017). Several other studies have reported that addition of organic manures (farm manure, press mud, green manure, and crop residue) can significantly enhance the cereal crop growth and yield providing essential macro as well as micronutrients (Agbede et al. 2008; Wang et al. 2012). These all studies make stronger our results that addition of organic manures with Zn fertilization can promote plant growth and enhance the crop yields.

Bioavailability of Zn in maize grains and stover was significantly ($P \leq 0.05$) increased by addition of organic manures and Zn fertilization (Table 4). This increase in Zn grain concentration, Zn stover concentration, Zn content, and Zn accumulation in shoots indicates that all the manures have potential to increase the phytoavailability of Zn to maize crop. It might be due to application of Zn-enriched manures with Zn fertilization, because organic manures in soil influence the microbial population which can enhance Zn content in rhizosphere by changing soil chemistry and release at time for plant uptake (Tejada et al. 2006; Zhang et al. 2013; Patil et al. 2017). Foliar spray of Zn (1840 g ha^{-1}) and (1500 g ha^{-1}) resulted in increase of 28–68% and 61%, respectively, Zn in wheat (Zhang et al. 2010; Zhao et al. 2014). Therefore, organic manures specifically, farm yard manure, fisheries manure, and press mud along with Zn foliar and soil fertilization can influence the availability of Zn to shoot and grains of maize crop.

Phytic acid (hexakisphosphoric acid) accumulates mainly in seeds and grains in the form of phosphate during ripening period, which has strong capacity to chelate the cations which adversely decrease the bioavailability of Zn to mammalians (Lonnerdal 2002; Fredlund et al. 2006). Our results stated that phytate concentration in grains and phytate content were significantly ($P \leq 0.05$) decreased (Fig. 1a–c) when organic manures were applied with Zn soil and foliar method. This decrease in phytate concentration is strongly supported by findings of (Imran et al. 2015; Imran and Rehim 2017).

Organic amendments and Zn application significantly ($P \leq 0.05$) reduced the [phytate]:[Zn] molar ratio (Fig. 2a). These results indicate that addition of organic manures with Zn fertilization has potential to decrease grain phytate zinc molar ratio and increase the bioavailable Zn in maize grains. It might be due to the increase in grain yield and fertilization of Zn (Imran and Rehim 2017).

Application of various organic manures and Zn soil and foliar application methods increased the estimated bioavailability up to (2.04 mg/300 g maize grain) using trivariate model (Miller et al. 2007; Fig. 2b).Therefore, it can be stated that biofortification of maize by Zn soil and foliar fertilization along with organic amendments could meet the recommended dietary intake of Zn for human beings (3 mg per day; Institute of Medicine 2001).

There was a significant ($P \leq 0.05$) role of organic manures and Zn application on relative yield (%) of maize crop (Fig. 3). PM + ZnS showed (100%) increase in relative yield followed by PM + ZnF (95%) and all other treatments had greater yield as compared with control. This clearly demonstrated that organic manures' addition and Zn soil and foliar application have pronounced effects on grain yield of maize crop.

Conclusion

Addition of organic manures with Zn fertilization methods (soil and foliar) seems an effective approach for biofortification of maize crop. Maximum grain yield was increased PM + ZnS and maximum Zn concentration was increased by FM + ZnF. Estimated bioavailability was also greatly influenced by the FYM + ZnF. Among the organic manures and Zn application methods, FYM and foliar spray are more effective to upsurge Zn bioavailability and Zn density in maize grain. Conclusively, soil and foliar Zn fertilization of maize in combination with organic manures would be an adorable way to get the desired yield and Zn concentration in maize grains.

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