International Journal of Environment and Climate Change

Volume 12, Issue 12, Page 1761-1770, 2022; Article no.IJECC.96272
ISSN: 2581-8627
(Past name: British Journal of Environment & Climate Change, Past ISSN: 2231–4784)

Dynamics of Zinc Fractions in Soil as Affected by Zinc Fertilization in a Maize-maize Cropping Sequence in Upper Brahmaputra Valley Zone of Assam, India

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IJECC/2022/v12i121623

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/96272

Original Research Article

Received: 24/10/2022
Accepted: 30/12/2022
Published: 31/12/2022

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ABSTRACT

Zinc is considered as an important micronutrient for maize which is a promising emerging cash crop for the state of Assam, India. A field experiment was conducted at the experimental farm of Krishi Vigyan Kendra, Jorhat, Assam Agricultural University during 2018-19 and 2019-20 to study the dynamics of zinc fractions in soil in a maize-maize cropping sequence as affected by zinc fertilization. The experiment was laid down in a randomized block design (RBD) with twelve treatments combinations of basal and foliar application of zinc through zinc sulphate and zinc oxide nanoparticles (ZnO NPs). The results revealed that zinc fertilization significantlyinfluenced the studied zinc fractions in soil during both the years under investigation. The distribution of different zinc fractions in soils at harvest was found in the following order: water soluble plus exchangeable-Zn < complexed-Zn < crystalline sesquioxide bound-Zn < amorphous sesquioxide bound-Zn < residual-Zn. Among the zinc treatment combinations, soil application of Zn @ 3.75 kg ha^{-1} in combination with foliar application of 500 ppm ZnO NPs exhibited the highest concentration of water soluble plus exchangeable-Zn content (1.10 ppm) in soil. The highest concentration of complexed-Zn (2.95 ppm), amorphous sesquioxide-bound-Zn (4.11 mg kg^{-1}), crystalline sesquioxide-bound-Zn (3.76 ppm), residual-Zn (125.65 ppm) and total-Zn (137.33 ppm) were recorded in the treatment receiving soil application of Zn @ 7.5 kg ha^{-1}. Among the zinc fractions studied, the concentration and percent contribution of water soluble plus exchangeable-Zn to total-Zn was the lowest while residual-Zn fraction contributed the highest to the total soil zinc pool. Furthermore, path coefficient analysis revealed that the water soluble plus exchangeable-Zn had the highest contribution towards the plant available DTPA extractable-Zn in soil. Moreover, all the fractions of zinc were found to be significantly and positively correlated with each other indicating existence of dynamic equilibrium of zinc in soil.

Keywords: Zinc fractions; cropping sequence; zinc oxide nanoparticles; zinc fertilization; foliar application.

1. INTRODUCTION

Zinc (Zn) is considered as the fourth most important yield limiting nutrient after nitrogen, phosphorus and potassium. The plant available DTPA (diethylenetriaminepentaacetic acid) extractable zinc in Indian soils is less than 1% of total zinc [1]. Availability of zinc is reported to be associated with the transformation of zinc in soils and plant continuum through various mechanisms like adsorption by clay surfaces, hydrous oxide minerals, organic matter etc which affect Zn uptake by crops. Also, the availability of zinc to plants has been reported to be associated with the distribution of different zinc fractions in soil. Therefore, understanding the distribution of various zinc fractions in soils help to characterize the dynamics of Zn in soils as well as possible contribution of individual zinc fractions towards plant availability.

The distribution of Zn among various chemical forms may vary significantly in response to changing soil properties [2]. For a better perceptive, total Zn in soil can be broadly divided into five mechanistic fractions viz., water soluble plus exchangeable zinc (WSEx-Zn), complexed zinc (Comp-Zn), amorphous sesquioxide bound zinc (ASB-Zn), crystalline sesquioxide bound zinc (CSB-Zn), residual zinc (Res-Zn)which can be quantified using sequential fractionation schemes [3]. These fractions provides a detailed information on the geological, biological and chemical processes occurring in the soil system and give a detailed account of the available Zn for plants uptake. Oxide bound and residual Zn are known to be more stable while water soluble and exchangeable fractions are more soluble [4]. The dynamic equilibrium between these fractions is influenced by soil properties such as soil texture, pH and soil organic matter status [5].

Maize-maize cropping sequence is the most promising but exhaustive cropping sequence followed in upper Brahmaputra valley zone of Assam, India. The sequence is very much sensitive to fertilization and often shows deficiency of macro as well as micronutrients [6]. Furthermore, micronutrients deficiency primarily of zinc is often prevalent in upper Brahmaputra valley zone of Assam. However, systematic information on the dynamics of different zinc fractions in soil in maize-maize cropping sequence and their relationship with soil properties in the acidic soils of Assam is very limited. Therefore, the present study was aimed at obtaining a more detailed information and understanding of the dynamics of different zinc fractions, their relationship with soil properties in a maize-maize cropping sequence in Upper Brahmaputra Valley Zone of Assam.

2. MATERIALS AND METHODS

The field experiment was conducted at the experimental farm of Krishi Vigyan Kendra, Jorhat, Assam Agricultural University, India during 2018-19 and 2019-20 in both *rabi* as well as *kharif* season. The experimental site is situated in the Upper Brahmaputra Valley Zone (UBVZ) of Assam at latitude 26.8308^0 N and longitude 94.4565^0 E at an altitude of 112 m above mean sea level. The experiment was laid out in Randomized Block Design (RBD) with 12 treatments and 3 replications. The detail of the treatments with corresponding notations are presented in Chart 1.

The recommended dose of nitrogen (N), phosphorus (P) and potassium (K) were applied as urea, Single Super Phosphate (SSP) and Muriate of Potash (MOP), respectively. Soil samples from 0-15 cm depth from each plot were drawn before sowing and after harvest of crop and analysed for zinc fractions. Initial soil properties are given in Table 1.

2.1 Chemical Fractionation of Zinc

Different zinc fractions in soils were sequentially extracted following the procedure of Murthy, [3] as shown in Table 2.

2.2 Total Zinc (Total-Zn)

For analysis of total zinc, 0.1 g of each soil was digested with few drops of H_2SO_4 and 5 ml of HF + 0.5 ml of $HClO_4$ in a 30 ml capacity platinum crucible [7]. When the residue completely dissolved in 6 N HCl, the content of the crucible was transferred to 50 ml volumetric flask and volume made up. Digests were analyzed for zinc using ICP OES (Inductively coupled plasma-optical emission spectrometry) (Model: Agilent 5110). Results were expressed as…….

2.3 Residual zinc (Res-Zn)

Res-Zn was calculated as the difference between total zinc and sum of the zinc fractions *viz.,*WSEx-Zn, Comp-Zn, ASB-Zn and CSB-Zn.

2.4 Statistical Analysis

Fisher's method of analysis of variance was resorted to determine the statistical significance among the data recorded from various treatments in randomized block design. The respective F values as well as least significant differences were calculated at 5% probability level to determine the statistical significance among the variances of the different treatments. Moreover, path analysis was carried out in IBM SPSS to understand the contribution of different Zn fractions to plant available pool.

3. RESULTS AND DISCUSSION

3.1 Influence of Zinc Fertilization on Zinc Fractions in Soil

The fractions of zinc in soil studied in the present investigation are presented below-

3.2 Water Soluble and Exchangeable Zinc Fractions (WSEX-Zn)

WSEx-Zn content (pooled for two year) of the soil ranged from 0.30 to 1.10 ppm (Table 3). Among the treatments, highest concentration of WSEx-Zn (1.10 ppm) was recorded in the treatment receiving foliar application of 500 ppm ZnO NPs in combination with soil application of Zn @ 3.75 kg ha^{-1} and the lowest value was recorded (0.30 mg kg^{-1}) in the control which might be due to higher contribution of applied Zn towards this fraction due to foliar application of ZnO NPs as well as soil application of zinc. Moreover, contribution of WSEx-Zn to total zinc (0.86%) was also the highest in the same treatment. Similar results were also reported by Bala et al. [8] that foliar application of ZnONPs significantly influenced Zn content in soil and recorded the highest Zn content in soil with foliar spray treatment with 5.0 gL^{-1} ZnO NPs. Analogous results were also reported by Verma et al. [9] and Ghoneim [10]. The lowest value of WSEx-Zn fractions in soil in the control treatment might be attributed to continuous uptake by the crop with no external application of zinc fertilizer in these plots.

3.3 Complexed-Zn (Comp-Zn)

Perusal of data in Table 3 indicated significant increase in the Comp-Zn in soil with increase in the rate of zinc application. Soil application of Zn @ 7.5 kg ha^{-1} recorded significantly highest value of Comp-Zn (2.95 mg kg^{-1}) while; the lowest content (1.77 mg kg^{-1}) was recorded in the control. However, no significant difference in Comp-Zn in soil was observed among the foliar treatments. The percent contribution of Comp-Zn to Total-Zn (2.16%) was highest in the treatment receiving soil application of Zn @ 7.5 kg ha^{-1}. Results further revealed that increasing rate of soil application of zinc in combination with foliar application either with Zn (T_7 to T_9) or with ZnO NPs (T_{10} to T_{12}) had recorded an increase in Comp-Zn content in soil (Table 3).

Soil organic matter is an important soil constituent that influence availability of nutrients in soil. It consists of a range of organic compounds such as humic substances, organic acids of low and high molecular weight, carbohydrates, proteins, peptides, amino acids, lipids, waxes, polycyclic aromatic hydrocarbons and lignin fragments [11]. Many of these components of soil organic matter have a strong affinity to bind Zn [12,13]. The most stable organic substances *viz*., humic and fulvic acids contain a large number of functional groups (OH, COOH, SH, C=O) that have a great affinity for Zn [14]. The amount of zinc in organically bound form showed an increasing trend with increase in the rate of zinc application. Such increase might probably be due to release of applied zinc to available form and subsequent chelation by organic compounds. This increase in Comp-Zn fraction might also be attributed to the mechanism of chemisorption and complexation by organic ligands [15].

Chart 1. The detail of the treatments with corresponding notations

Sl. No.	Treatments	Notation
1	Control	T_1
2	Soil application of Zn @ 2.5 kg ha^{-1}	T_2
3	Soil application of Zn @ 5.0 kg ha^{-1}	T_3
4	Soil application of Zn @ 7.5 kg ha^{-1}	T_4
5	Foliar application of 0.5% Zn in three sprays (knee high, tasseling and silking stage)	T_5
6	Foliar application of 500 ppm ZnO NPs in three sprays (knee high, tasseling and silking stage)	T_6
7	T_5 + Soil application of Zn @ 1.25 kg ha^{-1}	T_7
8	T_5 + Soil application of Zn @ 2.5 kg ha^{-1}	T_8
9	T_5 + Soil application of Zn @ 3.75 kg ha^{-1}	T_9
10	T_6 + Soil application of Zn @ 1.25 kg ha^{-1}	T_{10}
11	T_6 + Soil application of Zn @ 2.5 kg ha^{-1}	T_{11}
12	T_6 + Soil application of Zn @ 3.75 kg ha^{-1}	T_{12}

Table 1. Initial physico-chemical properties of the experimental site

Soil characteristics		Value
A.	**Textural class**	Sandy loam
B.	**Chemical properties**	
i)	Soil reaction (pH)	5.29
ii)	Organic carbon (%)	0.58
iii)	Available N (kg ha^{-1})	188.00
iv)	Available P_2O_5 (kg ha^{-1})	25.89
v)	Available K_2O (kg ha^{-1})	151.34
xii)	Water soluble plus exchangeable-Zn (mg kg^{-1})	0.33
xiii)	Complexed-Zn (mg kg^{-1})	1.80
xiv)	Amorphous sesquioxide bound-Zn (mg kg^{-1})	2.82
xv)	Crystalline sesquioxide bound-Zn (mg kg^{-1})	2.42
xvi)	Residual-Zn (mg kg^{-1})	106.63
xvii)	Total-Zn (mg kg^{-1})	113.86

Table 2. Zinc sequential fractionation procedures

Fractions	Solution (mL)	Soil (g): solution (mL)	Conditions
(1) Water soluble + exchangeable-Zn (WSEx-Zn)	1 M(Ammonium acetate) NH_4OAc at pH 7.2	5:20	Shaken for 1 h, Centrifuge
(2) Complexed-Zn (Comp-Zn)	20 ml 0.5 M (Cupric acetate) Cu $(OAc)_2$	5:20	Shaken for 1 h, Centrifuge
(3) Amorphous sesquioxide bound-Zn (ASB-Zn)	0.2 M acidified NH_4 $(OX)_2$ (pH 3.0)	5:20	Shaken for 1 h, Centrifuge
(4) Crystalline sesquioxide bound-Zn (CSB-Zn)	40 ml 0.3 M Sodium Citrate + 5 ml 0.1M (Sodium bicarbonate) $NaHCO_3$ + 1 g $Na_2S_2O_4$ (Sodium dithionite) Kept on the water bath (70-80°C)	5:20	Stirred and kept on the water bath at a temperature of 70-80°C for 10 min For 15 min with occasional stirring Centrifuge after cooling

Table 3. Effect of zinc fertilization on WSEx-Zn and comp-Zn (mg kg^{-1}) in soil

Treatments	WSEx-Zn			Comp-Zn		
	Mean value (*Kharif* 2018-19 and 2019-20)	Mean value (*Rabi* 2018-19 and 2019-20)	Pooled Sequence	Mean value (*Kharif* 2018-19 and 2019-20)	Mean value (*Rabi* 2018-19 and 2019-20)	Pooled Sequence
T_1	0.31^{e}	0.30^{g}	0.30^{g}	1.76^{d}	1.75^{d}	1.77^{d}
T_2	0.49^{cd}	0.50^{ef}	0.49^{ef}	2.34^{bc}	2.34^{abcd}	2.36^{c}
T_3	0.57^{cd}	0.57^{de}	0.56^{de}	2.52^{b}	2.57^{ab}	2.58^{ab}
T_4	0.84^{b}	0.81^{c}	0.82^{c}	2.96^{a}	2.90^{a}	2.95^{a}
T_5	0.35^{e}	0.35^{g}	0.35^{g}	1.84^{d}	1.83^{cd}	1.86^{d}
T_6	0.55^{de}	0.54^{f}	0.55^{de}	1.85^{d}	1.86^{cd}	1.87^{d}
T_7	0.40^{e}	0.41^{g}	0.41^{g}	2.04^{cd}	2.03^{bcd}	2.00^{cd}
T_8	0.57^{c}	0.56^{de}	0.56^{de}	2.37^{b}	2.40^{abc}	2.40^{bc}
T_9	0.62^{c}	0.65^{d}	0.64^{d}	2.52^{b}	2.50^{ab}	2.53^{ab}
T_{10}	0.78^{b}	0.78^{bc}	0.78^{c}	2.05^{cd}	2.09^{bcd}	2.03^{cd}
T_{11}	0.94^{b}	0.93^{b}	0.94^{b}	2.39^{b}	2.41^{abc}	2.41^{bc}
T_{12}	1.11^{a}	1.11^{a}	1.10^{a}	2.48^{b}	2.47^{ab}	2.49^{b}
LSD (p≤0.05)	0.13	0.13	0.12	0.32	0.59	0.38
CV (%)	12.92	12.87	11.73	8.36	15.61	9.98

Mean values in each column followed by similar letters in superscript are not significantly different at 5% probability level

3.4 Amorphous Sesquioxide Bound-Zn (ASB-Zn)

Significantly higher content of ASB-Zn (4.11 ppm) was recorded in the treatment receiving soil application of Zn @ 7.5 kg ha^{-1} and the lowest (2.69 mg kg^{-1}) in the control (Table 4). Soil application of Zn @ 7.5 kg ha^{-1} recorded the highest percent contribution of ASB-Zn (3.00%) to total zinc (Table 6). The increase in ASB-Zn fraction with increase in the rate of zinc application could be attributed to addition of zinc fertilizer and subsequent transformation to this fraction due to presence of amorphous sesquioxide in the soil. These findings were in agreement with Wijibandara [16], Veeranagappa et al. [17] and Talukdar et al. [18]. Higher content of ASB-Zn fraction as compared to CSB-Zn as well as WSEx-Zn and Comp-Zn might be attributed to the greater ability of amorphous sesquioxides to adsorb zinc because of their high specific surface area [19,20] and [21]. Also, due to the acidic environment which favoured formation of amorphous sesquioxide bound-Zn in soil.

3.5 Crystalline Sesquioxide Bound-Zn (CSB-Zn)

Crystalline sesquioxide bound fraction of zinc (CSB-Zn) in soil is the predominant fraction due to presence of crystalline iron oxide in the soil. Among the treatments, soil application of Zn @ 7.5 kg ha^{-1} recorded significantly higher content of CSB-Zn (3.76 mg kg^{-1}) and the lowest (2.35 mg kg^{-1}) was recorded in the control in after harvest. The percent contribution of CSB-Zn (2.77%) to Total-Zn was also highest in the treatment receiving soil application of Zn @ 7.5 kg ha^{-1} (Table 4). The increase in CSB-Zn with increase in the rate of zinc application might be due to chemical affinity or specific adsorption and also due to predominance of crystalline iron oxide content in soil [22]. Zinc is said to be specifically adsorbed because the ion is sorbed by surfaces of synthetic oxides of iron (Fe) and aluminium (Al)(goethite, gibbsite) that have a net positive charge, so despite electrostatic repulsion, Zn is still adsorbed in significant amounts [23,24]. The higher contribution of sesquioxide bound-Zn might be attributed to higher amount of Zn adsorption on the surface of these oxides because of the higher concentrations of these ions in the soil [20].

3.6 Residual-Zn (Res-Zn)

Residual-Zn was the dominant fraction and considered as zinc reservoir in soil. The percent contribution of this fraction to total zinc was the highest among all other fractions studied (Table 5). The effect of zinc fertilization on residual-Zn in soil was found to be significant for both the years under investigation. The highest concentration of residual-Zn (125.65 mg kg^{-1}) was found in the treatment receiving Zn @ 7.5 kg ha^{-1} as soil application followed by the treatment receiving soil application of Zn @ 5.0 kg ha^{-1} (120.31 mg kg^{-1}) while, the lowest concentration residual-Zn (106.25 mg kg^{-1}) was recorded in the control. Residual-Zn fraction consistingof large proportion of total zincwas also reported by Singh [24] and Priyanka et al. [25] which might be due to conversion of labile zinc to non-labile form.

3.7 Total Zinc (Total-Zn)

The values of total-Zn content enable better depiction of Zn accumulation in the soil. The total-Zn content of soils depends on the parent material from which the soils have been developed. It is considered to be poor indicator of the zinc supplying capacity of soils for long term management of cropping system. The total-Zn content was found to be the highest among all the fractions and maximum content of total-Zn (137.33 mg kg^{-1}) was observed in the treatment receiving soil application of Zn @ 7.5 kg $ha^{-1}$and the lowest concentration (113.45 mg kg^{-1}) was recorded in the control. Effect of graded application of zinc fertilizer on different zinc fractions (Table 5) indicated that out of Total-Zn, majority of zinc was distributed in the Res-Zn fraction followed by ASB-Zn, CSB-Zn and Comp-Zn while WSEx-Zn occupied a very small portion (< 1%) of the total-Zn pool in soil. Behera et al. [26] observed that among different zinc fractions in soil, Res-Zn was the dominant fraction of the total-Zn under maize-wheat cropping system. Jyothi et al. [27] reported that the contribution of Res-Zn was the maximum followed by CSB-Zn and ASB-Zn fractions, while, the contribution of WSEx-Zn fraction was only 1-2 per cent.

Data presented in Tables 3, 4 and 5 divulged that application of zinc @ 7.5 kg ha^{-1}recorded significantly higher values of different fractions of zinc as compared to the control. Continuous addition of zinc at higher rates in this treatment and conversion of the added zinc resulted in transformation of zinc into these fractions. Vishvakarma [28] also reported an increase in the concentration of WSEx-Zn, organically bound-Zn and complexed-Zn fractions in soil with increase in the zinc levels. The control plots recorded lower values of these fractions probably due to non-application of zinc fertilizer externally and continuous uptake by the crop.

Thus, it is evident that zinc fertilization significantly influenced the distribution of different zinc fractions in soil. At harvest, different zinc fractions were found in the order: water soluble plus exchangeable-Zn (WSEx-Zn) < complexed-Zn (Comp-Zn) < crystalline sesquioxide bound-Zn (CSB-Zn) < amorphous sesquioxide bound-Zn (ASB-Zn) < residual-Zn (Res-Zn) fractions. These results were in accordance with the findings of Preetha and Stalin [29], Solanti et al. [30] and Spelbar et al. [21].

Correlation among the different zinc fractions (Table 7) revealed that all the fractions of zinc were significantly and positively correlated with each other. Results showed significant positive correlation among WSEx-Zn, Comp-Zn, CSB-Zn, ASB-Zn, Res-Zn and Total-Zn fractions indicating existence of dynamic equilibrium of zinc in soil.

Table 4. Effect of zinc fertilization on ASB-Zn and CSB-Zn (mg kg^{-1}) in soil

Treatments	ASB-Zn			CSB-Zn		
	Mean value (*Kharif* 2018-19 and 2019-20)	Mean value (*Rabi* 2018-19 and 2019-20)	Pooled Sequence	Mean value (*Kharif* 2018-19 and 2019-20)	Mean value (*Rabi* 2018-19 and 2019-20)	Pooled Sequence
T_1	2.75^{d}	2.74^{d}	2.69^{d}	2.40^{c}	2.39^{e}	2.35^{c}
T_2	3.24^{bcd}	3.26^{bcd}	3.25^{bcd}	3.05^{abc}	3.03^{bcd}	3.09^{b}
T_3	3.73^{ab}	3.74^{ab}	3.71^{ab}	3.43^{ab}	3.40^{ab}	$3.38a^{b}$
T_4	4.10^{a}	4.13^{a}	4.11^{a}	3.80^{a}	3.82^{a}	3.76^{a}
T_5	2.87^{d}	2.88^{cd}	2.82^{d}	2.45^{c}	2.44^{de}	2.41^{c}
T_6	2.75^{d}	2.76^{d}	2.73^{d}	2.47^{c}	2.49^{cde}	2.48^{c}
T_7	3.14^{cd}	3.12^{bcd}	3.13^{cd}	2.92^{bc}	2.89^{bcde}	2.85^{bc}
T_8	3.45^{bc}	3.48^{abc}	3.45^{bc}	3.11^{abc}	3.08^{bc}	3.15^{b}
T_9	3.55^{abc}	3.56^{abc}	3.48^{bc}	3.32^{ab}	3.41^{ab}	3.33^{ab}
T_{10}	3.14^{cd}	3.14^{bcd}	3.13^{cd}	2.89^{bc}	2.91^{bcde}	2.84^{bc}
T_{11}	3.46^{bc}	3.49^{abc}	3.46^{bc}	3.14^{abc}	3.13^{b}	3.13^{b}
T_{12}	3.53^{abc}	3.55^{abc}	3.49^{bc}	3.37^{ab}	3.39^{ab}	3.36^{ab}
LSD ($p\leq0.05$)	0.58	0.69	0.61	0.75	0.61	0.65
CV (%)	10.26	12.16	10.84	14.64	11.95	12.80

Mean values in each column followed by similar letters in superscript are not significantly different at 5% probability level

Table 5. Effect of zinc fertilization on Res-Zn and total-Zn (mg kg^{-1}) in soil

Treatments	Res-Zn			Total-Zn		
	Mean value (*Kharif* 2018-19 and 2019-20)	Mean value (*Rabi* 2018-19 and 2019-20)	Pooled Sequence	Mean value (*Kharif* 2018-19 and 2019-20)	Mean value (*Rabi* 2018-19 and 2019-20)	Pooled Sequence
T_1	106.42^{g}	106.09^{g}	106.25^{g}	113.63^{h}	113.27^{h}	113.45^{j}
T_2	115.74^{cd}	115.90^{cd}	115.82^{de}	124.85^{ef}	125.02^{de}	124.93^{fg}
T_3	120.55^{b}	120.06^{b}	120.31^{b}	130.80^{b}	130.34^{b}	130.57^{b}
T_4	125.39^{a}	126.91^{a}	125.65^{a}	137.09^{a}	137.57^{a}	137.33^{a}
T_5	110.48^{fg}	109.68^{f}	109.58^{f}	116.98^{g}	117.17^{g}	117.08^{i}
T_6	110.36^{f}	110.61^{f}	110.48^{f}	117.89^{g}	118.15^{fg}	118.02^{i}
T_7	111.12^{ef}	111.87^{ef}	111.49^{f}	119.61^{g}	120.33^{f}	119.97^{h}
T_8	116.22^{cd}	116.13^{cd}	116.17^{de}	125.73^{de}	125.68^{de}	125.71^{ef}
T_9	118.85^{bc}	118.93^{bc}	118.89^{bc}	128.86^{bc}	129.06^{bc}	128.96^{bc}
T_{10}	114.04^{de}	114.45^{de}	114.24^{e}	122.85^{f}	123.38^{e}	123.11^{g}
T_{11}	116.57^{cd}	117.51^{bc}	117.04^{cd}	126.51^{cde}	127.48^{cd}	126.10^{de}
T_{12}	117.34^{c}	118.14^{bc}	117.74^{cd}	127.82^{cd}	128.66^{bc}	128.24^{cd}
LSD ($p\leq0.05$)	3.89	3.09	2.44	2.75	2.47	1.83
CV (%)	12.22	13.23	12.66	13.24	9.85	10.38

Mean values in each column followed by similar letters in superscript are not significantly different at 5% probability level

3.8 Path Analysis

A path analysis was carried out to understand the contributions of different zinc fractions towards the plant available form of Zn in soil i.e., DTPA-Zn (Fig. 1). The direct effects of the studied Zn fractions towards DTPA-Zn were 0.783 (WSEx-Zn), 0.661 (Comp-Zn), 0.003 (ASB-Zn), 0.802 (CSB-Zn), 4.145 (Res-Zn) and 5.244 (Total-Zn). However, the indirect effect of the studied Zn fractions followed an opposite trend, where, the contribution towards DTPA-Zn were 0.052, -0.554, -0.010, -0.901, -4.386 and -4.974 for WSEx-Zn, Comp-Zn, ASB-Zn, CSB-Zn, Res-Zn and Total-Zn, respectively. Likewise, the combined direct and indirect effect of WSEx-Zn (0.834) was the highest towards DTPA-Zn followed by Total-Zn (0.269) and Comp-Zn (0.106). This indicated that the WSEx-Zn had the highest contribution towards the plant available fraction of Zn in soil.

Table 6. Percent (%) contribution of different Zn fractions to total-Zn in soil

Treatments	WSEx-Zn	Comp-Zn	ASB-Zn	CSB-Zn	Res-Zn
T_1	0.26	1.75	2.82	2.51	92.66
T_2	0.40	1.87	2.60	2.43	92.70
T_3	0.44	1.93	2.86	2.61	92.14
T_4	0.60	2.16	3.00	2.77	91.49
T_5	0.29	1.57	2.46	2.09	93.59
T_6	0.38	1.57	2.34	2.10	93.61
T_7	0.33	1.70	2.61	2.42	92.93
T_8	0.46	1.89	2.76	2.46	92.42
T_9	0.50	1.95	2.76	2.61	92.19
T_{10}	0.64	1.66	2.53	2.36	92.79
T_{11}	0.74	1.88	2.74	2.47	92.16
T_{12}	0.86	1.92	2.76	2.64	91.81

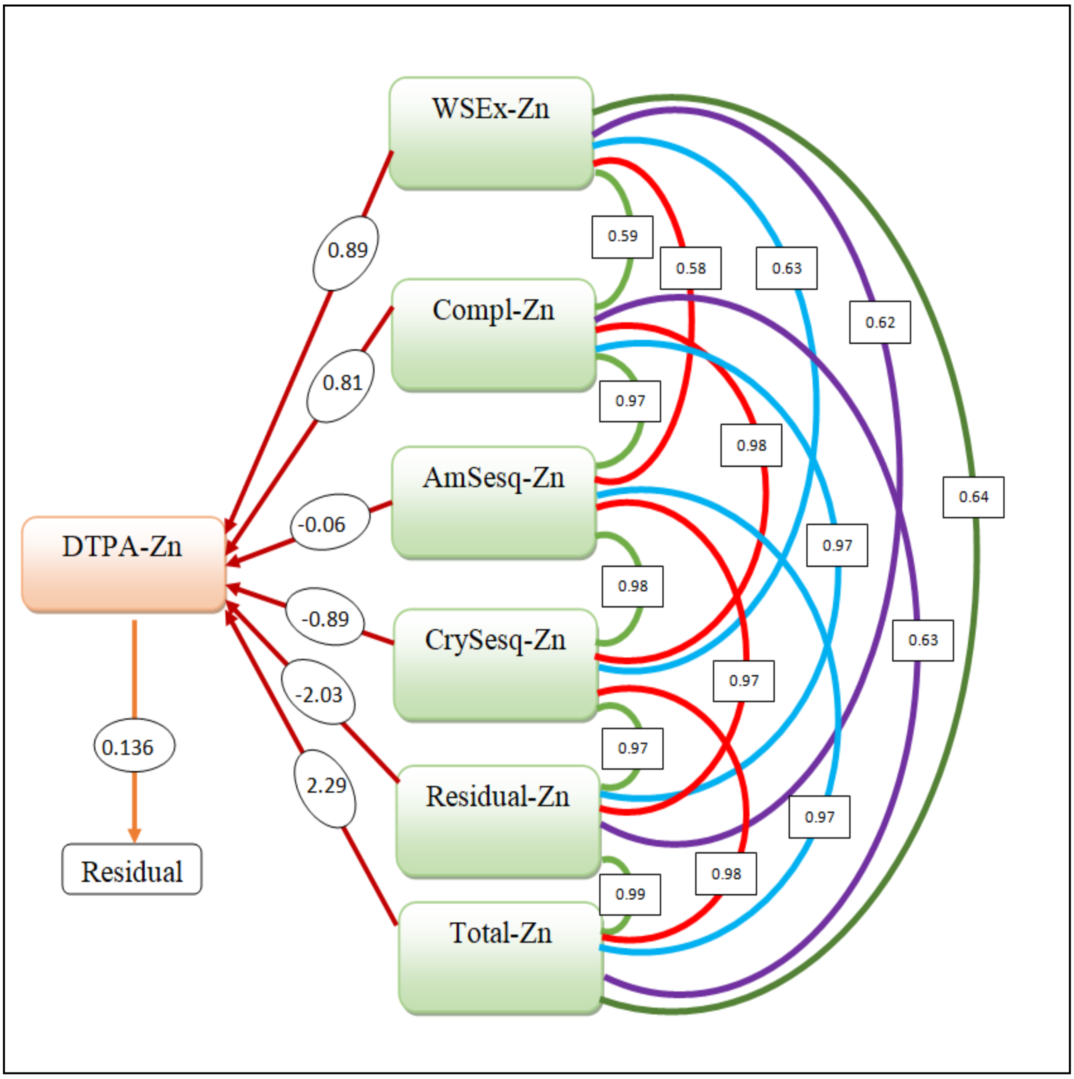

Fig. 1. A path analysis diagram and coefficient factors affecting DTPA-Zn

Table 7. Correlation coefficient (r) among zinc fractions and DTPA-Zn

	WSEx-Zn	Comp-Zn	ASB-Zn	CSB-Zn	Res-Zn	Total-Zn
Complex-Zn	0.594*					
ASB-Zn	0.587*	0.977**				
CSB-Zn	0.634*	0.982**	0.980**			
Residual-Zn	0.627*	0.979**	0.975**	0.973**		
Total-Zn	0.635*	0.982**	0.979**	0.981**	0.997**	
DTPA-Zn	0.942**	0.656*	0.634*	0.672*	0.673*	0.680*

** Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed)*

4. CONCLUSIONS

The dynamics of the studied zinc fractions in maize - maize cropping sequence was significantly influenced by the treatment combination of basal and foliar application of zinc during both the years under investigation. The distribution of different zinc fractions in soils at harvest was found in the following order: water soluble plus exchangeable-Zn < complexed-Zn < crystalline sesquioxide bound-Zn < amorphous sesquioxide bound-Zn < residual-Zn.WSEx-Zn fraction least contributed to total-Zn however, had the highest contribution towards the plant available DTPA extractable-Zn in soil as divulged by path analysis. Foliar application with zinc nanoparticles significantly increasedWSEx-Zn in soil. Furthermore, all the fractions of zinc were found to be significantly and positively correlated with each other indicating existence of dynamic equilibrium of zinc in soil.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/96272