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Long-term effect of residual zinc and crop residue on zinc fractionation with different path

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Abstract

The long term effect of crop residue and residual zinc on Zn fractions in soil and their contribution to Zn uptake in rice-wheat system was studied in calciorthents of the Rajendra Agricultural University, Pusa, Samastipur, (Bihar), India, during 2010-11 and 2011-12. Application of zinc and crop residue increased the water soluble + exchangeable, complexed, organically bound, carbonate and amorphous oxide, crystalline oxide, residual and total Zn in the soil. The order of dominance of different fractions in soil was total Zn (164.35 mgkg^{-1}) > residual – Zn (156.41 mgkg^{-1}) > Zn bound to crystalline oxide (3.06 mgkg^{-1}) > complexed Zn (2.27 mgkg^{-1}) > organically bound Zn (1.14 mg kg^{-1}) > water soluble plus exchangeable Zn (0.84 mgkg^{-1}) and Zn bound carbonate and amorphous oxide (0.73 mg kg^{-1}). All the soil Zn fractions were significantly correlated among themselves indicating existence of a dynamic equilibrium with each other. Zinc uptake by rice-wheat was improved with zinc along with crop residue. Among different Zn fractions, Zn bound to crystalline oxide, followed by Zn bound to carbonate and amorphous oxide play a key role in explaining the variation in yield and nutrient uptake by rice and wheat. The highest zinc uptake by rice and wheat was reported with the conjoint use of 100 % crop residue and 10 kg Zn ha^{-1}.

Keywords: yield, Zn uptake, rice, wheat, crop residue

1. Introduction

Zinc, an essential element in plant growth and metabolism, exists in soil in different forms such as primary and secondary minerals, insoluble inorganic and organic precipitates, soluble organic complexes and exchangeable and adsorbed forms and as soil solution zinc. These forms are in a state of dynamic equilibrium. The amount and rate of transformation of these forms of zinc solution determine the size of the labile Zn pool. There are many reports on study of different micro-nutrient fractions of soils (Viets, 1962; Smith and Shoukry, 1968) [21], but only few studies have been carried out with the application of organic and inorganic fertilizers under rice-wheat cropping system in calcareous soils (Kamali *et al*., 2010, 2011; Pandey, 2012; Prasad *et al*., 2010) [6, 13, 15].

The calcareous soil of Bihar occupying a sizeable area is deficient of zinc to the extent of 80-90 % of the tested soil samples and symptoms of zinc deficiency are frequently observed on many crops (Sakal *et al*., 1996) [16]. Widespread occurrence of zinc deficiency in soil suggests that both native and applied forms of Zn react with the inorganic and organic phase in soil and thereby affect its availability. Zinc diffusion, which is one of the most limiting steps in calcareous soil, is affected by the application of organic materials. Availability of Zn to plants is influenced by amount of Zn present in different chemical pools which could be affected by organic matter incorporation. Zinc is known to exist in soil in different chemical pools and its solubility and availability to plant is a function of physical and chemical properties of the soil. Organic amendments such as FYM, compost, crop residue, etc. have marked effect on the solubility and availability of different forms of Zn because of their bio-degradation in soil (Dhaliwal *et al*., 2010, 2012; Mishra et al., 2009; Singh *et al*., 2003) [4, 3, 12, 19].

The wide scale adoption of rice-wheat system has ushered in an increase in agricultural production, but this intensive system over a period of time and nature of the crops has set declining yield trends as well as deterioration in soil productivity even with optimum use of fertilizers. Hence, for restoration of soil productivity, there is an urgent need to look forward to other options of supplying plant nutrient like crop residues incorporation. The adverse effect of incorporation of rice and wheat straw can be counteracted by integrating organic amendments with crop residues (Singh *et al*., 2004) [5]. The continuous recycling of crop residue restores the organic matter content and also increases microbial population in the soil (Prasad, 2005) [14].

Therefore, for sustained agricultural productivity on a long term basis, proper appraisal of different forms of zinc and their relationships with soil characteristics and Zn uptake by crops

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is essential. Hence, the present investigation was carried out to study the effect of organic and inorganic fertilizers on zinc fractions in calciorthents and their influence on zinc uptake.

2. Materials and methods

A field experiment was conducted during 1993-94 in light textured highly calcareous soil deficient in available zinc (0.56 mgkg^{-1}) at Research Farm, R.A.U., Pusa (Bihar). To begin with, the straw of wheat crop (Nov., 1993 – April, 1994) was incorporated in soil. The first crop of this long-term experiment on rice-wheat cropping system, i.e., paddy was transplanted in July, 1994 and harvested in Nov., 1994, followed by second crop of wheat (Nov., 1994 – April, 1995). The experimental soil (0-15 cm) had pH (1:2) 8.5, EC 0.36 dSm^{-1}, organic carbon 0.62 g kg^{-1}, available N 236.1 kg ha^{-1}, available P 19.7 kg ha^{-1}, available K 100.0 kg ha^{-1} and available Zn 0.56 mg kg^{-1}. Four levels of crop residues, viz. no crop residue (CR$_0$), 25% of straw produced (CR$_{25}$), 50% of straw produced (CR$_{50}$) and 100% of straw produced (CR$_{100}$) were applied as treatment in the main plots. The treatments were given to each crop every year. The main plot was divided into 4 sub-plots in which treatments, viz. no Zn (Zn$_0$), 2.5 kg Znha^{-1} (Zn$_{2.5}$), 5.0 kg Zn ha^{-1} (Zn$_{5.0}$) and 10.0 kg Zn ha^{-1} (Zn$_{10.0}$) were super imposed over crop residue levels. These four levels of Zn were applied only to first crop as a starter dose. The experiment was laid out in a split plot design with three replications and plot size were 5.0 x 2.0 m^2. The recommended doses of NPK (120:60:40) were applied to each crop of rice and wheat as urea, single superphosphate and muriate of potash. Half of nitrogen and entire doses of P and K were applied at the time of transplanting of rice and sowing of wheat and remaining N fertilizer was applied in the equal splits at tillering and flower initiation stage. Rice and wheat crops were grown continuously under rice-wheat cropping system. The present experiment comprised 33rd crop of rice (July, 2010 – Nov., 2010), 34th crop of wheat (Nov., 2010 – April, 2011) and next year, 35th crop of rice (July, 2011- Nov., 2011) and 36th crop of wheat (Nov., 2011 – April, 2012). Rajshree and HD 2733 were used as the test varieties of rice and wheat, respectively.

The grain and straw samples were taken at the harvest of rice and wheat crops, and washed sequentially in detergent solution (0.2% liquid), 0.01 N HCl solution and deionized water and dried in oven at 70ºC. Finely grinded samples were digested in a di-acid mixture (HNO_3:$HClO_4$ 3:1 v/v) and diluted. Digested samples were analyzed for micronutrients using atomic absorption spectrophotometer. The total uptake of micronutrients by grain and straw was computed. Surface soil samples (0-15 cm) from each plot of the field experiment were collected at the harvest of wheat crop as 36th crop in rice-wheat rotation. Soil samples were air-dried and pulverized to pass through 2.0 mm sieve and various pools of Zn were determined using different extractants according to the scheme described by Raja and Iyenger (1986).

3. Result

3.1 Crop yields

3.1.1 Rice

The grain and straw yields of 35th crop of rice as influenced by zinc and continuous application of crop residue at four levels varied from 3.63 - 4.71 t ha^{-1} and 5.07 - 6.60 t ha^{-1}, respectively. The effect of zinc significantly enhanced the mean grain and straw yields of rice from 3.90 - 4.37 t ha^{-1} and 5.47 - 6.13 t ha^{-1}, respectively, even after 18 years of application (Table 1). The mean grain and straw yields of rice increased continuously from 3.89 - 4.45 t ha^{-1} and 5.45 - 6.25 t ha^{-1} with increasing crop residue levels. The highest grain yield (4.71 t ha^{-1}) was recorded at 100 % crop residue level and 10 kg Znha^{-1}.

3.1.2 Wheat

The grain and straw yields of 36th crop of wheat as influenced by residual effect of zinc and crop residue levels ranged from 3.12 - 4.13 t ha^{-1} and 4.87 - 6.44 t ha^{-1}, respectively (Table 1). The residual effects of zinc and crop residue levels were similar to those observed in 35th crop of rice. The grain and straw yields of wheat increased from 3.39 - 3.66 and 5.29 - 5.70 t ha^{-1}, respectively, with increasing levels of Zn. Similarly, the grain and straw yields of wheat increase from 3.22 - 3.92 and 5.02 - 6.11 tha^{-1}, respectively, with increasing levels of crop residue.

Table 1: Long-term influence of crop residue and residual Zn on grain and straw yield under rice-wheat cropping system in calcareous soil**.**

Zn level (kg Znha^{-1})	Grain yield (tha^{-1})					Straw yield (tha^{-1})				
	Crop residue level (% of yield produced)					Crop residue level (% of straw produced)				
	0	25	50	100	Mean	0	25	50	100	Mean
Rice (35th crop)										
0	3.63^{d}	3.83^{d}	4.05^{c}	4.10^{d}	39.03^{c}	5.07^{d}	5.38^{d}	5.67^{d}	5.78^{d}	5.47^{d}
2.5	3.90^{c}	3.97^{c}	4.23^{b}	4.43^{c}	41.33^{b}	5.45^{c}	5.57^{c}	5.93^{c}	6.23^{c}	5.79^{c}
5.0	3.93^{b}	4.07^{b}	4.35^{ab}	4.56^{bc}	42.28^{bc}	5.57^{b}	5.77^{b}	6.12^{b}	6.40^{b}	5.96^{b}
10.0	4.08^{a}	4.23^{a}	4.43^{a}	4.71^{a}	43.68^{a}	5.75^{a}	5.97^{a}	6.22^{a}	6.60^{a}	6.13^{a}
Mean	3.89	4.03	4.27	4.45	--	5.45	5.67	5.98	6.25	--
CD(P=0.05)	CR – 0.29; Zn –0. 18; CR x Zn – NS					CR – 0. 31; Zn –0. 20; CR x Zn – NS				
Wheat (36th crop)										
0	3.12^{b}	3.22^{c}	3.46^{bc}	3.76^{d}	3.39^{c}	4.87^{b}	5.03^{c}	5.40^{d}	5.87^{d}	5.29^{d}
2.5	3.26^{a}	3.40^{b}	3.50^{b}	3.85^{c}	3.50^{bc}	5.08^{a}	5.31^{b}	5.47^{c}	6.00^{c}	5.46^{c}
5.0	3.24^{ab}	3.54^{ab}	3.59^{ab}	3.92^{b}	3.57^{b}	5.06^{ab}	5.52^{ab}	5.60^{b}	6.12^{b}	5.57^{b}
10.0	3.26^{a}	3.57^{a}	3.67^{a}	4.13^{a}	3.66^{a}	5.08^{a}	5.56^{a}	5.73^{a}	6.44^{a}	5.70^{a}
Mean	3.22	3.43	3.56	3.92	--	5.02	5.36	5.55	6.11	--
CD(P=0.05)	CR –0. 29; Zn –0. 11; CR x Zn – NS					CR – 0.40; Zn – 0.25; CR x Zn – NS				

3.2 Zinc uptake

The increase in Zn uptake by rice and wheat from 210 - 289 g ha^{-1} and 178 - 245 g ha^{-1}, respectively, with residual effect of zinc was mainly due to increase in yields of rice and wheat with Zn application. Crop residue application increased Zn uptake by rice and wheat from 191 - 306 g ha^{-1} and 167 - 264 gha^{-1}, respectively (Table 2).

Table 2: Effect of residual zinc and crop residue (CR) on Zn uptake (gha^{-1}) by rice and wheat under rice-wheat cropping system.

Zinc level (kgha^{-1})	**Zn uptake by rice**					**Zn uptake by wheat**				
	Crop residue level (% of straw produce)					**Crop residue level (% of straw produce)**				
	0	25	50	100	Mean	0	25	50	100	Mean
0	153^d	205^d	227^d	256^d	210^d	150^d	160^d	186^d	215^d	178^d
2.5	182^c	217^c	247^c	288^c	234^c	164^c	186^c	212^c	249^c	203^c
5.0	206^b	250^b	254^b	315^b	256^b	173^b	207^b	235^b	272^b	222^b
10.0	224^a	268^a	296^a	367^a	289^a	181^a	224^a	255^a	321^a	245^a
Mean	191	235	256	306	--	167	194	222	264	--
CD (P=0.05)		CR = 27; Zn = 17; CR x Zn = NS				CR = 18; Zn = 9; CR x Zn = NS				

3.3 Distribution of zinc into different fractions in soil

The data on soil zinc factions like water soluble plus exchangeable (WSE-Zn), inorganically complexed (COM-Zn), organically bound (ORG-Zn), amorphous sesquioxide bound (AMO-Zn), crystalline sesquioxide bound (CRY-Zn), residual (RES-Zn) and total zinc (Total Zn) depicted in Figures 1 a, b, c, d, e, f & g revealed that content of these fractions in different treatments varied from 0.53 to 1.13, 2.06 to 2.52, 0.87 to 1.58, 0.68 to 0.91, 2.55 to 3.78, 150.98 to 160.75 and 157.67 to 170.67 mg kg^{-1}, respectively. The amount of different fraction of Zn in soil followed the order: AMO-Zn (0.73 mg kg^{-1}) < WSE-Zn (0.84 mg kg^{-1}) < ORG-Zn (1.14 mg kg^{-1}) < COM-Zn (2.27 mg kg^{-1}) CRY-Zn < (3.06 mg kg^{-1}) < RES-Zn (156.41 mg kg^{-1}) < TOTAL-Zn (164.35 mg kg^{-1}). It is clear from the diagram in Figure 1 that most of the total zinc was present in residual form and only a small fraction was present in easily available forms. i.e., WSE form.

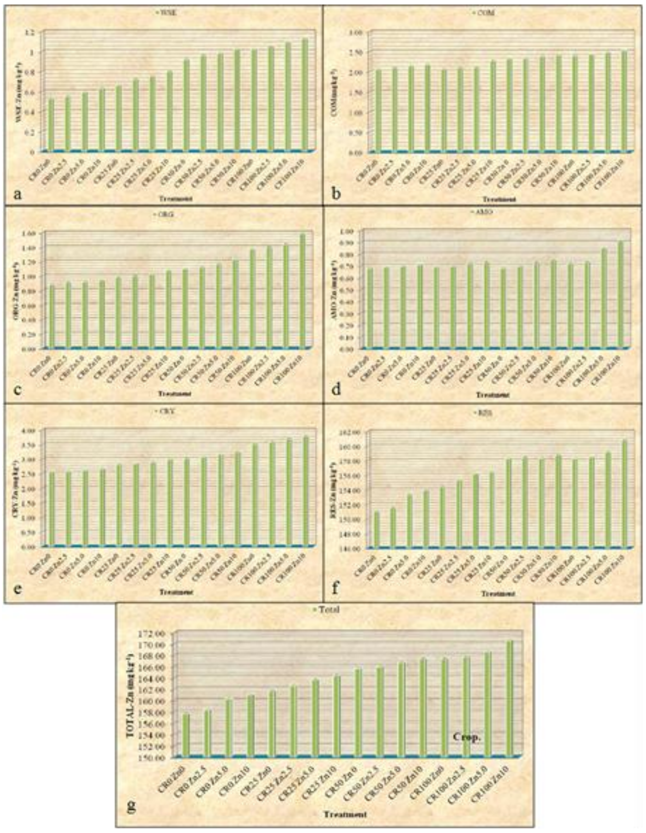

Fig 1: Distribution of zn in different fraction (mg kg^{-1}) in post harvest soil of wheat (36th crop) as influenced by crop residue and residual starter zinc. (a) Water soluble +Exchangeable Zn (WSE-Zn) content in PHS of wheat 36th crop; (b) inorganically complexed (COM-Zn) in PHS of wheat 36th crop; (c) organically bound (ORG-Zn) in PHS of wheat 36th crop; (d) amorphous sesquioxide bound (AMO-Zn)) in PHS of wheat 36th crop; (e) crystalline sesquioxide bound (CRY-Zn) in PHS of wheat 36th crop; (f) residual (RES-Zn) in PHS of wheat 36th crop and (g) total zinc (Total Zn) in PHS of wheat 36th crop

3.4 Correlation analysis among different fraction of zinc

The data on correlation coefficient value among different Zn fractions (Table 3) revealed that dynamic equilibrium of zinc existed between water soluble plus exchangeable, organic complexed, crystalline sesquioxide bound residual and total Zn formed as positive and highly significant among these fractions as shown in their correlation coefficient values.

Table 3: Correlation coefficients among soil different zinc fractions.

Soil Zinc Fraction	**COM Zn**	**ORG Zn**	**AMO Zn**	**CRY Zn**	**RES Zn**	**total Zn**
WSE Zn	0.958**	0.930**	0.655**	0.948**	0.974**	0.986**
COM Zn	--	0.925**	0.710**	0.923**	0.909**	0.935**
ORG Zn	--	--	0.806**	0.993**	0.888**	0.928**
AMO Zn	--	--	--	0.770**	0.659**	0.701**
CRY Zn	--	--	--	--	0.909**	0.944**
RES Zn	--	--	--	--	--	0.995**

**Significant at P = 0.01 level

3.5 Correlation studies of different fractions of zinc with plant parameter

The correlation studies were also carried out with plant parameters like grain yield of rice, grain yield of wheat, total Zn uptake by rice and total Zn uptake by wheat based in Pooled of 33rd and 35th rice crop and pooled of 34th and 36th wheat crop with different Zn fractions and the correlation coefficient value (r) are presented in Table 4. It was noticed that all fractions of Zn viz. water soluble + exchangeable zinc, complexed zinc, organically bound Zn, Zinc bound by Amorphous oxide, crystalline sesquioxide bound Zn, Residual and Total Zn were positively and significantly correlation with all the plant parameters tested, showing thereby importance of these fractions in Zn utilization by crops.

Table 4: Correlation coefficients among different fractions of zn in soil vs. plant parameters.

Different fractions of Zn in soil	**Plant Parameter**			
	GYR	**GYW**	**Zn UR**	**Zn UW**
WSE Zn	0.921**	0.936**	0.884**	0.912**
COM Zn	0.919**	0.901**	0.882**	0.909**
ORG Zn	0.903**	0.922**	0.896**	0.931**
AMO Zn	0.807**	0.797**	0.827**	0.872**
CRY Zn	0.909**	0.931**	0.898**	0.926**
RES Zn	0.920**	0.942**	0.907**	0.912**
TOTAL Zn	0.930**	0.956**	0.922**	0.934**

**Significant at P = 0.01 level

3.6 Direct and indirect effect of different zinc fractions on crop yield and zn uptake through path analysis

The quantity and direction of contribution of Zn fractions towards pooled grain yield of rice (33rd and 35th crop), pooled grain yield of wheat (34th and 36th crop), total Zn uptake by rice and total Zn uptake by wheat was studied through path analysis. The path coefficients obtained are given in Tables 5, 6, 7 and 8.

3.6.1 Path coefficient analysis for grain yield of rice

The path coefficient analysis for grain yield of rice (RGY) revealed that the direct effect of total Zn, followed by Zn bound to carbonates and amorphous oxides, Zn bound by crystalline oxides, complexed Zn and water soluble + exchangeable Zn on rice grain yield was higher and positive (Table 5). Although the direct effects of residual Zn (RES Zn) and organically bound Zn (ORG Zn) on RGY were negative, yet they showed highly significant and positive association with RGY mainly due to the indirect effects via total Zn. Residual Zn and organically bound Zn consistently showed highly negative indirect effects on RGY. The indirect effects of all the soil parameters via total Zn were very high and positive. The negative direct and indirect effects of residual Zn and organically bound Zn were counter balanced mainly by the positively indirect effects via total Zn. The path coefficient study revealed that the parameters such as total Zn, Zn bound to carbonates and amorphous oxides (AMO Zn), Zn bound by crystalline oxides (CRY Zn) and complexed zinc (COM Zn) are very important for their contribution to RGY.

Table 5: Direct (diagonal) and indirect effects of various fractions of zn on grain yield of rice.

Soil Zn fraction	WSE Zn	COM Zn	ORG Zn	AMO Zn	CRY Zn	RES Zn	TOTAL Zn	GYR
WSE Zn	0.0799	0.2428	-1.3370	0.3642	0.3766	-1.7507	2.9455	0.9212**
COM Zn	0.0765	0.2534	-1.3307	0.3948	0.3688	-1.6338	2.7918	0.9189**
ORG Zn	0.0742	0.2344	-1.4384	0.4480	0.3947	-1.5963	2.7864	0.9030**
AMO Zn	0.0523	0.1800	-1.1595	0.5557	0.3059	-1.1846	2.0571	0.8071**
CRY Zn	0.0757	0.2339	-1.4283	0.4277	0.3975	-1.6328	2.8349	0.9085**
RES Zn	0.0778	0.2304	-1.2780	0.3664	0.3612	-1.7967	2.9591	0.9203**
TOTAL Zn	0.0788	0.2370	-1.3428	0.3830	0.3775	-1.7813	2.9847	0.9369**

** Significant at P = 0.01 level
Residual effect = 0.1997

3.6.2 Path coefficient analysis for grain yield of wheat

The path coefficient analysis for grain yield of wheat (WGY) revealed that the direct effect of total Zn, followed by water soluble + exchangeable Zinc (WSE Zn), Zn bound by crystalline oxides (CRY Zn) and Zinc bound to carbonates and amorphous oxides (AMO Zn) on wheat grain yield was higher and positive (Table 6). The direct effect of organically bound zinc, residual zinc (RES Zn) and complexed zinc (COM Zn) was higher and negative on wheat grain yield resulting in realization of lower wheat grain yield. Although the direct effects of organically bound zinc, Residual zinc and complexed zinc on wheat grain yield were negative, yet they showed highly significant and positive association with WGY mainly due to the positive and direct effects via Total Zn. The indirect effects of all the Zinc fractions/parameters via total Zn were very high and positive.

Table 6: Direct (diagonal) and indirect effects of various fractions of zn on grain yield of wheat.

Soil Zn fraction	WSE Zn	COM Zn	ORG Zn	AMO Zn	CRYZn	RES Zn	TOTAL Zn	GYW
WSE Zn	0.3678	-0.1414	-0.6764	0. 2767	0. 3124	-0.6586	1.4558	0.9363**
COM Zn	0.3524	-0.1476	-0.6732	0. 3000	0. 3043	-0.6146	1.3798	0. 9011**
ORG Zn	0.3419	-0.1366	-0.7277	0. 3404	0. 3274	-0.6005	1.3772	0. 9221**
AMO Zn	0.2410	-0.1049	-0.5866	0. 4223	0. 2537	-0.4456	1.0167	0. 7967**
CRY Zn	0.3485	-0.1362	-0.7226	0. 3250	0. 3297	-0.6142	1.4011	0. 9313**
RES Zn	0.3584	-0.1342	-0.6465	0. 2784	0. 2996	-0.6759	1.4625	0. 9423**
TOTAL Zn	0.3630	-0.1381	-0.6793	0. 2910	0. 3131	-0.6701	1.4752	0. 9548**

** Significant at P=0.01 level
Residual effect = 0.2108

3.6.3 Path coefficient analysis for zinc uptake by rice

The path coefficient analysis revealed that the direct effect of total Zn, followed by Zn bound by crystalline oxides (CRY Zn), complexed zinc (COM Zn) and Zinc bound to carbonates and amorphous oxides (AMO Zn) on Zn uptake by rice was higher and positive (Table 7). The direct effect of water soluble + exchangeable Zinc, followed by organically bound zinc and residual zinc was higher and negative on Zn uptake by rice, resulting in realization of lower Zn uptake by rice. Although the direct effects of water soluble + exchangeable Zinc (WSE Zn), organically bound zinc (ORG Zn) and residual zinc (RES Zn) on Zn uptake by rice were negative, yet they showed highly significantly and positive association with Zn uptake by rice mainly due to the positive indirect effects via total Zn. The indirect effects of all the soil Zn fractions via total Zn were very high and positive. The negative direct effects of water soluble + exchangeable Zinc, organically bound zinc and residual zinc were counter balanced mainly by the positive indirect effects via total Zn.

Table 7: Direct (diagonal) and indirect effects of various fractions of zn with zn uptake by rice.

Soil Zn fraction	WSE Zn	COM Zn	ORG Zn	AMO Zn	CRY Zn	RES Zn	TOTAL Zn	ZnUR
WSE Zn	-1. 1592	0. 3986	-1. 1034	0. 2903	0. 5906	-0. 9857	2. 8531	0. 8843**
COM Zn	-1. 1105	0. 4161	-1. 0982	0. 3147	0. 5751	-0. 9199	2. 7042	0. 8815**
ORG Zn	-1. 0775	0. 3849	-1. 1871	0. 3570	0. 6189	-0. 8988	2. 6990	0. 8965**
AMO Zn	-1. 7596	0. 2956	-1. 9569	0. 4429	0. 4797	-0. 6670	2. 9926	0. 8274**
CRY Zn	-1. 0948	0. 3840	-1. 1787	0. 3409	0. 6232	-0. 9193	2. 7460	0. 8976**
RES Zn	-1. 1295	0. 3784	-1. 0547	0. 2920	0. 5664	-0. 0116	2. 8663	0. 9073**
TOTAL Zn	-1. 1439	0. 3892	-1. 1082	0. 3053	0. 5920	-0. 0030	2. 8911	0. 9224**

****** Significant at P=0.01 level
Residual effect = 0. 2181

3.6.4 Path coefficient analysis for zinc uptake by wheat

The path coefficient analysis of different soil Zn fractions and Zn uptake by wheat revealed that the direct effect of total Zn, followed by Zinc bound to carbonates and amorphous oxides (AMO Zn) and water soluble + exchangeable Zn (WSE Zn) on Zn uptake by wheat was higher and positive (Table 8). The direct effect of residual Zn (RES Zn), followed by organically bound Zn (ORG Zn), Zn bound by crystalline oxides (CRY Zn) and Complexed Zn (COM Zn) was higher and negative on Zn uptake by wheat, resulting in realization of lower Zn uptake by wheat. Although the direct effects of residual Zn, organically bound Zn, Zn bound by crystalline oxides and complexed Zn on Zn uptake by wheat were negative, yet they showed highly significant and positive association with Zn uptake by wheat mainly due to the positive indirect effects via total Zn. The indirect effects of all the soil Zn fractions *via* total Zn were very high and positive. The negative direct and indirect effects of residual Zn, organically bound Zn, Zn bound by crystalline oxides and complexed Zn were counter balanced mainly by the positive indirect effects via total Zn. The path coefficient study revealed that total Zn, followed by Zn bound to carbonates and amorphous oxides and water soluble + exchangeable Zn are very important soil Zn fractions contributing to Zn uptake by wheat.

Table 8: Direct (diagonal) and indirect effects of various chemical fractions of zinc with zn uptake by wheat.

Soil Zn fraction	WSE Zn	COM Zn	ORG Zn	AMO Zn	CRY Zn	RES Zn	TOTAL Zn	ZnUW
WSE Zn	0. 3918	-0. 0656	-0. 3672	0. 3924	-0. 3252	-1. 3442	2. 2297	0. 9117**
COM Zn	0. 3754	-0. 0685	-0. 3655	0. 4254	-0. 3168	-1. 2544	2. 1134	0. 9090**
ORG Zn	0. 3642	-0. 0634	-0. 3951	0. 4827	-0. 3408	-1. 2256	2. 1093	0. 9313**
AMO Zn	0. 2568	-0. 0487	-0. 3185	0. 5988	-0. 2642	-1. 9095	2. 5573	0. 8720**
CRY Zn	0. 3713	-0. 0632	-0. 3923	0. 4609	-0. 3432	-1. 2536	2. 1460	0. 9258**
RES Zn	0. 3818	-0. 0623	-0. 3510	0. 3948	-0. 3119	-1. 3795	2. 2401	0. 9119**
TOTAL Zn	0. 3867	-0. 0641	-0. 3688	0. 4127	-0. 3260	-1. 3677	2. 2594	0. 9322**

** Significant at P = 0.01 level
Residual effect = 0.1427

4. Discussion

The effect of crop residue and Zn on rice yield was statistically significant. This may probably be due to two reasons; firstly, because of decrease in available zinc levels in soil under no Zn treatment and secondly, due to solubilisation of native as well as applied zinc at higher levels by different crop residues which produce complexing agents and nutrients after microbial decay of crop residue (Singh *et al*., 2003) [19]. There was marked increases in yield due to increasing levels of crop residues at all levels of zinc (Prasad, 2005; Prasad *et al*., 2010) [14. 15].. The grain and straw yields of rice at 50 % crop residue level along with starter dose of 10 kg Zn ha^{-1} were at par with yields obtained at 100 % crop residue incorporation alone. Improvement in organic carbon and microbial population might be the reason for augmenting the rice productivity (Pandey, 2012) [12]. The yield of wheat during initial few years was adversely affected at higher level of crop residue incorporation due to probably immobilization of nitrogen and micronutrients by decomposing microflora. The yield of wheat increased with increasing levels of crop residue (Kumar *et al*., 2012). It results in built-up of organic carbon, nitrogen levels and micronutrients which accelerated faster rate of decomposition of crop residue. Heterotrophic microorganisms used crop residue as a source of organic carbon, nutrient and energy, and degraded crop residue in soil. The extent of nutrient availability depends not only on type of organic additives but also on the built-up of autochthonous microorganism. The effects of crop residue and residual Zn levels affected wheat yield significantly but their interaction effect was non-significant (Singh and Singh, 2012) [3].

Crop residue on decay produced a variety of biochemical substances (organic acids, polyphenols, amino acids and polysachharides) which stimulated the solubility, transport and availability of Zn. Similar results have also been reported by Prasad *et al.* (2010) [15] and Pandey (2012) [12] in calcareous soil under rice-wheat system. It was observed that crop residue incorporation and residual starter Zn application significantly increased the content of different fraction however increase was very meager in amorphous fraction. It was also clear from the data that most of the Zn recycled through crop residue either alone or along with applied Zn got accumulated in residual and crystallize fraction followed by organic fraction. It was also noticed that more than 95 per cent of the total native zinc existed in residual fraction. Application of Zn either through inorganic fertilizer or recycled through crop residue, there was an increase in the quantity of this fraction. The increase was more pronounced when Zn was applied along with 100 per cent crop residue levels. Crop residue addition increased the water soluble plus exchangeable fraction of Zn (WSE Zn) from 0.34 to 0.66 per cent. The distribution of other Zn fractions in native to applied Zn with or without crop residues varied from 1.31 to 1.48 per cent (complexed form COM-Zn), 0.55 to 0.93 per cent (Organically bound form ORG-Zn), 0.43 to 0.53 per cent (amorphous form AMO-Zn) and 1.62 to 2.21 per cent in crystalline form (CRY-Zn) of Total Zn. The distribution of native and applied Zn held by amorphous iron and aluminum oxide (0.73 mg kg^{-1}) was much less than that held by crystalline Fe and Al oxide (3.06 mg kg^{-1}). Although, the per cent of total Zn in inorganically complexed form (1.46) was found next to crystalline Fe and Al oxide bound form (2.16) but the transformation of applied Zn was meager. The distribution of total Zn into residual fraction was also reported to be more than 90 per cent (Mandal and Mandal, 1986, Dhaliwal *et al*., 2010, and Dhaliwal *et al.* 2012) [11, 4, 3].

These results are in accordance with the findings of Mandal and Mandal, (1986) [11] also reported that a small fraction viz. 0.26, 0.74, 1.58 and 0.71 per cent of the Total zinc occurred as water soluble + exchangeable Zn, organic complexed, amorphous sesquioxide and crystalline sesquioxide bound Zn forms respectively. Low content of Zn as inorganic fraction in the present investigation might be due to high organic carbon content (0.69 to 1.11%) as well as calcareous nature of soil (32.23 to 33.43% free $CaCO_3$). So far impact of treatments on the different fractions of Zn were concern, the levels of crop residues incorporations, levels of applied residual Zn and their interactions were found statistically significant. Increasing levels of crop residues incorporation or residual applied Zn significantly increased the different pools of Zn. The maximum amount of different pools of Zn was obtained in the treatment having 100% crop residue incorporation along with Zn @10 kg ha^{-1}. Dhaliwal *et al*., (2012) [3] presented their views on fractionation of zinc with the combination of organic in the same trend. Existence of dynamic equilibrium among all these fractions have been reported by many workers like Hazara *et al* (1987), Chowdhary *et al* (1997) and Sharad and Verma (2001) [17] . This suggested that Mutual transformation of water soluble plus exchangeable-Zn (WSE-Zn), complexed Zn (COM-Zn) organically bound Zn (ORG-Zn), amorphous Zn (AMO-Zn), crystalline sesquioxide bound Zn (CRY-Zn), residual and total Zn seems to be dominant for maintaining Zn-equilibria in soil. The importance of these fractions with respect to different plant parameters has also been demonstrated by Kumari 2003 [10], Kumar 2006 [8], Pandey 2012 [12]. High positive direct effect of total Zn, Zn bound to carbonates and amorphous oxides, Zn bound by crystalline oxides, complexed Zn and water soluble + exchangeable Zn on rice grain yield has also been reported earlier by Kumari (2003) [10] and Kumar (2006) [8]. The direct of residual Zn (RES Zn), followed by organically bound Zn (ORG Zn) was higher and negative on rice grain yield resulting in realization of lower RGY.

The negative direct and indirect effects of organically bound zinc, residual Zinc and complexed Zinc were counter balanced mainly by the positive indirect effects via total Zn. The path coefficient study revealed that the parameters such as total Zn, water soluble + exchangeable Zinc, Zn bound by crystalline oxides and Zinc bound to carbonates and amorphous oxides are very important for their contribution to WGY. Kumari (2003) [10] and Kumar (2006) [8] also reported negative direct effects of organically bound Zinc, residual Zinc and complexed Zinc on WGY. Organically bound Zinc, residual Zinc and complexed Zinc consistently showed highly negative indirect effects on WGY. The path coefficient study revealed that the parameters such as total Zn, Zn bound by crystalline oxides, complexed zinc and Zinc bound to carbonates and amorphous oxides are very important for their contribution to Zn uptake by rice. High positive effect of total Zn, Zn bound by crystalline oxides, complexed zinc and Zinc bound to carbonates and amorphous oxides on Zn uptake by rice has been reported earlier (Kumari, 2003; Kumar, 2006; Kumari, 2010) [8, 10, 9]. Kumari (2003) [8] and Kumar (2006) [10] also reported negative direct effects of water soluble + exchangeable Zinc, organically bound zinc and residual zinc on Zn uptake by rice. High positive direct effect of Total Zn, Zn bound to carbonates and amorphous oxides and water soluble + exchangeable Zn on Zn uptake by wheat has been reported earlier (Kumari, 2003; Kumar, 2006; Kumari, 2010) [8, 10, 9]. Kumari (2003) [8], Kumar (2006) [10] and Kumari (2010) [9] also reported negative direct effects of residual Zn, organically bound Zn, Zn bound by crystalline oxides and complexed Zn on Zn uptake by wheat. Residual Zn, organically bound Zn, Zn bound by crystalline oxides and complexed Zn consistently showed high and negative indirect effects on Zn uptake by wheat. The path coefficient study as described above confirmed the importance of water soluble + exchangeable and crystalline sesquioxide bound Zn. Similarly, Das (1998) [2], Kumar *et al.* (2004) [7] and Kumari (2010) [9] have also reported the importance of crystalline sesquioxide bound Zn on Zn uptake by crop.

4. Conclusion

The different fractions of soil Zn are in dynamic equilibrium with each other and their availability to growing crop depends on their intensities and soil condition. This implies that depleted levels of readily available Zn in soil could be replenished by other pools of soil Zn. All the soil Zn fractions were significantly correlated among themselves indicating existence of a dynamic equilibrium with each other. Zinc uptake by rice-wheat was improved with zinc along with crop residue. Among different Zn fractions, Zn bound to crystalline oxide, followed by Zn bound to carbonate and amorphous oxide play a key role in explaining the variation in yield and nutrient uptake by rice and wheat.

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6. References

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