Journal of Applied Science and Agriculture, 9(3) March 2014, Pages: 942-947

AENSI Journals

Journal of Applied Science and Agriculture

ISSN 1816-9112

Journal home page: www.aensiweb.com/jasa/index.html

Effect of Applying Plant Residues and Zinc Sulfate on Chemical Forms of Zinc in Rhizosphere and Bulk Soil and Its Relationship to Wheat Grain

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ARTICLE INFO

Article history:
Received 8 January 2014
Received in revised form 20 February 2014
Accepted 23 February 2014
Available online 28 March 2014

Key words:
Wheat, Zinc, plant residues, Rhizosphere, Zinc chemical forms

ABSTRACT

Background: Zinc deficiency is considered as one of the major nutritional problems of people across the world, especially in areas where people's lives depend on cereal as a basic food. Several approaches have been proposed to deal with Zinc deficiency, of which the most common is the utilization of chemical fertilizers containing zinc. However, in calcareous soils which forms the majority of lands in Iran, most of these fertilizers will change shortly into non-absorbable form. A new strategy to deal with the shortage of micronutrient is bioenrichment of crops (crop enrichment). **Objective:** The purpose of this study is to investigate the effect of plant residues on chemical forms of zinc in the solid phase of the soil in rhizosphere and bulk soil and its correlation with the amount of zinc in wheat grain. **Result:** The results showed that the application of plant residues to the chemical forms of zinc resulted in the increase in organic and carbonated forms of zinc in the soil. But, all forms of zinc particularly its oxidized and residual forms were increased by applying the zinc sulfate. The correlation between the wheat grain and the chemical forms of zinc in soil showed that there was a significant positive correlation between the concentration of zinc in wheat grain and the zinc forms (Exchangeable, Organic and Carbonated) in the rhizosphere and bulk Soil. **Conclusion:** Conducting this study, we can conclude that the plant can absorb zinc in exchangeable, organic and carbonated forms. The main part of the zinc added to the soil is converted to a non-available form for the plant by zinc sulfate. But the application of plant residues can increase the unavailable added zinc to the soil into the available forms of zinc for the plants through decreasing pH and increasing the dissolved organic carbon.

To Cite This Article: Amir Kadkhodaie, Mahmoud Kalbasi, Mahmoud Solhi, Habiballah Nadian, Ali Gholami., Effect of Applying Plant Residues and Zinc Sulfate on Chemical Forms of Zinc in Rhizosphere and Bulk Soil and Its Relationship to Wheat Grain. ***J. Appl. Sci. & Agric.**, 9(3): 942-947, 2014*

INTRODUCTION

More than 80% of the cultivable lands suffer from zinc deficiency in various degrees and plants grown in these grounds may be zinc deficient, resulting in their reduced yield (Malakouti, 2005). Of the reasons for zinc deficiency in soils, it can be addressed to high pH, being calcareous soil, excessive utilization of phosphate fertilizers, high concentrations of bicarbonate in irrigation waters, all of which result in zinc deposit in the soil and thus its unavailability for plant to uptake. Therefore, it is necessary to add this element to the soil leading to high accumulation of the element in non-available form. Several strategies have been proposed to deal with the zinc deficiency in the soil such as crop rotation, adding sewage sludge to the land, and applying the plant residues to the soil. However, the application of plant residues to the soil is considered as a better method with fewer side-effects. Any element in the soil is found in different chemical forms which vary considerably in different soils. These differences lead to changes in the availability of elements for plant in different soils (Emst, 1996). Zinc is found in soluble and exchangeable forms, in bond with organic materials, carbonates, iron and aluminum oxides and as well as residues. But of all these forms, only the soluble and exchangeable forms, and in bond with organic materials are consumed by crops and they constitute only a minute percentage of the total zinc found in soil (Alloway, 2008). Khadivi (2003) studied the cumulative effects and the effect of compost residues, sewage sludge and manure on chemical forms and mobility factor of Pb, Ni, Cd, Zn, Cu and Fe in the soil. The results showed that the soluble, exchangeable, and carbonated forms, iron and aluminum oxides, and organic materials increased and the residues decreased by increasing the amount and frequency of fertilization. Nyamangara (1998) reported that application of sewage sludge and mineral salts increased the amount of Zinc

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in exchangeable part, while the major part of zinc was observed in the residual in the control treatment. Rhizosphere is the superficial layer of soil subject to the influence of plant roots and their associated microorganisms (Chen *et al*., 2006). Zinc forms such as deposited form by carbonates and phosphates, complex form with organic matter, iron oxides, and manganese oxides can be active and inactive depending on physical, chemical and biological properties of soil (Sposito, 1989). Change in the chemical form of metal and its bioavailability in the rhizosphere is the resultant of the biogeochemical concentration gradients of metal, pH, pCO2, pO2, the concentration of organic ligand, and microbial biomass (Hinsinger *et al*., 2009, Kidd *et al*., 2009). Wang & *et al* (2002) reported that the zinc bonded with iron and manganese oxides was decreased in wheat rhizosphere. They stated the reduction of iron and manganese oxides as the reason for the reduced zinc form in rhizosphere. In recent years, many researchers have based on adding different amounts of chemical fertilizers containing zinc and manure to the soil and not paid more attention to applying different plant residues in the soil and measuring the chemical forms of zinc in solid phase, as well as the correlation between these forms and the amount of zinc in wheat grain. This study will attempt to examine this issue in more accurate details.

Methodology:

This experiment was conducted in the form of a randomized complete block design with eight treatments (control, zinc sulfate, plant residues of alfalfa, bean and wheat and alfalfa plant residues, bean and wheat with zinc sulfate), in 3 replications in an Iranian farm at an altitude of 2059 m. of sea level, longitude of 51 degrees 39 minutes, and latitude of 31 degrees 56 minutes. At first, the studied land was plowed to a depth of 30 cm and after analyzing the soil (Table 1), it was added a required amount of macronutrients and micronutrients to all treatments, and to considered treatments zinc sulfate by 60 kg/ha and plant residues by 10 t/ha (ton per hectare) based on the mean of yield index of these plants (Malakooti & Nafissi, 1994). About two weeks after preparation of treatments, it was planted 350 kg/ha of wheat seeds in each treatment. During the growing season, the irrigation of crop was done based on plot, and the necessary agricultural cares such as eradicating weeds both mechanically and chemically. The soil was sampled in several locations at 0 to 30 cm depth from both the bulk soil and rhizosphere, and it was used the sequential extraction procedure to determine the various chemical forms of zinc in solid phase of soil. In this method, it was specified for each element 5 components, and the method was described in details in Table (2) (Tessier & *et al*, 1979). It was done the needed statistical calculations of the data by the software SAS, and the means of treatments were compared by Duncan test.

Table 1: Some physicochemical properties of the tested soil

pH	EC	OC	$CaCO_3$	Texture	P	K	Zn
---	dS/m	%	%	---	mg/kg	mg/kg	mg/kg
7.5	1.1	0.62	35	Clay Loam	9	270	0.3

Table 2: Measurement of Zinc Chemical forms to Tessier

chemical form of Zn	*Extraction*	*pH*	*Method*
Exchangeable	*20 ml 1 M NH_4OAc*	*7*	*30 min shaking and centrifuged*
Bound to Carbonates	*20 ml 1 M NaOAc*	*5*	*5 hours shaking and centrifuged*
Bound to Iron and Manganese Oxides	*20 ml 0.04 M $NH_2OH.HCl$ in 25% w/v HOAc*	*2*	*6 hours shaking on a 96 ^0C and centrifuged*
Bound to Organic Matter	*H2O2 30% 5 ml 0.1 M HNO3 / 10 ml+15 ml NH_4OAc 3.2 M*	*-*	*30 hours shking on a 85^0C*
Residual	*$HNO_3+HClO_4+H_2SO_4$*	*-*	*30 min shaking and centrifuged*

Results:

Application of plant residues and zinc sulfate to zinc chemical forms in rhizosphere region and bulk soil:

Applying plant residues in the soil increased significantly the organic and carbonated forms of zinc in rhizosphere region and bulk soil, but no change was observed in exchangeable, oxidized, and residual forms of zinc, compared to the control. Among the plant residues, alfalfa residues increased more the exchangeable and organic forms because of greater degradation (less C/N) and more chelating effect. The application of zinc sulfate to the soil causes a significant increase in all zinc forms in the rhizosphere and bulk soil. Also, in treatments to which was added the plant residues along with zinc sulfate, all zinc forms increased. But they had two differences compared to the treatment with zinc sulfate alone, that is, the organic form of zinc increased while the zinc residues decreased. It can be stated that the plant residues can prevent available zinc forms from converting into the zinc residues (Table 3).

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Table 3: Application of plant residues and zinc sulfate to zinc chemical forms

Treatments	Exchangeable	Organic	Carbonate	Oxide	Residual
bulk soil (mg/kg)					
Control	0.10 b	0.74 e	1.32 d	7.60c	66.98 c
Zinc Solfate	0.22 a	1.42b	2.02ab	11.66b	138.33 a
Wheat residue	0.11b	1.03d	1.63c	7.66c	101.00 c
Bean residue	0.12 b	0.91 c	1.60 c	7.56 c	100.33 c
Alfalfa residue	0.11 b	1.26 c	1.83 b	7.46 c	99.33 c
Wheat residue + Zinc Solfate	0.20 a	1.76 a	2.10 a	3.36 a	124.66 ab
Bean residue + Zinc Solfate	0.19 a	1.46 b	2.03 ab	11.90 b	131.66 ab
Alfalfa residue + Zinc Solfate	0.19 a	1.55 b	2.16 a	11.46 b	121.66 b
Rhizosphere(mg/kg)					
Control	0.14 b	1.13 d	2.45 d	6.93 b	95.67 b
Zinc Solfate	0.24 a	1.92 bc	3.46 b	9.46 a	132.33 a
Wheat residue	0.15 b	1.63 c	2.83 c	6.72 b	97.10 b
Bean residue	0.14 b	1.83 ab	3.00 c	6.53 b	94.67 b
Alfalfa residue	0.14 b	1.80 bc	2.9 c	5.46 b	99.33 b
Wheat residue + Zinc Solfa	0.27 a	2.41 a	4.00 a	11.66 a	116.33 a
Bean residue + Zinc Solfate	0.27 a	2.26 a	3.90 a	10.40 a	120.00 a
Alfalfa residue + Zinc Solfat	0.27 a	2.26 a	3.86 a	10.23a	120.00a

Means with the same letter are not significantly different at 5% level.

Correlation between some soil properties and available zinc and chemical forms of zinc:

Table (4) shows the correlation coefficients between some soil properties in rhizosphere and bulk soil and zinc forms. The results in Table (4) showed that there was a significant negative correlation between pH in bulk soil and zinc in available, exchangeable, carbonate and organic forms. But in the rhizosphere region, it was not observed a significant correlation between pH and chemical forms of zinc. A significant positive correlation was found between dissolved organic carbons in soil and the available zinc in rhizosphere and bulk soil. Based on other results, it can be addressed to the significant positive correlation between the available zinc and the exchangeable, organic, and carbonated zinc forms. But there was no significant correlation between the available zinc and oxidized and residual zinc forms.

Table 4: Correlation between soil properties and chemical forms of zinc

Soil properties	Available	Exchangeable	Organic	Crbonate		Oxide	Residual
Bulk soil (mg/kg)							
pH	-0.6 *	-0.2	-0.3	-0.4		0.23	0.1
EC	0.3	0.1	0.4	0.4		0.3	0.06
Soil organic carbon	-0.1	-0.1	-0.03	-0.08		-0.01	-0.09
Dissolved organic carbon	0.6*	0.2	0.4	0.5		0.07	0.2
Available zinc	1	0.7*	0.9**	0.9**	0.6	0.6	
Zinc amount in grain	0.9**	0.7*	0.9**	0.9**	0.6	0.6	
Rhizosphere (mg/kg)							
pH	- 0.5	-0. 3	-0. 2	-0.3	-0. 1	-0.1	
EC	0.09	-0.4	-0.2	-0.3	-0.6	-0.2	
Soil organic carbon	0.4	0.2	0.3	0.3	0.05	0.1	
Dissolved organic carbon	0.6*	0.1	0.4	0.3	0.01	0.08	
Available zinc	1	0.8**	0.9**	0.9 **	0.6	0.7	
Zinc amount in grain	0.9 **	0.8**	0.9**	0.9 **	0.6	0.6	

Concentration of zinc in wheat grain:

As seen in Fig (1), the application of plant residues to the soil led to the increase in zinc concentration in the wheat grain, compared to the control (no residue). This increase varied in treatments of different plant residues, and the most increase in the zinc concentration in wheat grain was found in the treatment of alfalfa plant residues. Also, the application of zinc sulfate to the soil resulted in the increase of zinc concentration in the grains and its impact was greater than the application of plant residues to the soil. Habibi (2010) reported in a greenhouse experiment that the addition of plant residues to the soil increases the organic carbons dissolved in the soil and consequently increases the absorption of zinc by the wheat grain.

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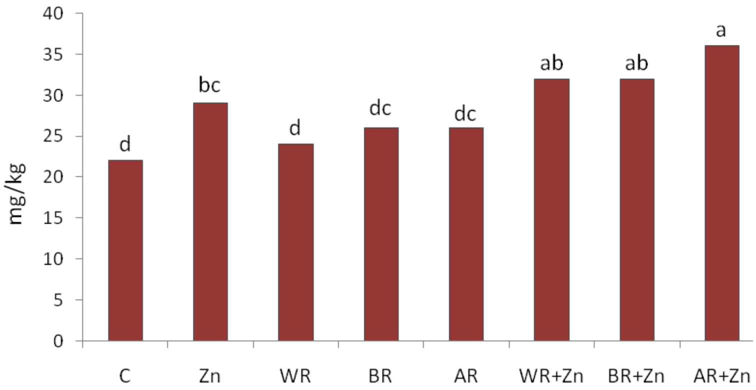

Fig. 1: Application of plant residues and zinc sulfate to zinc concentration of wheat grain Means with the same letter are not significantly different at 5% level.

Correlation between zinc concentration in wheat grain and chemical forms of zinc:

The correlation between the wheat grain and the chemical forms of zinc in rhizosphere and bulk soil is shown in Table (4). The results showed that there was a significant positive correlation between the concentration zinc in the wheat grain and the exchangeable, organic, and carbonated forms of zinc in the rhizosphere and bulk soil, but no significant correlation was observed between it and the oxidized and residual forms of zinc. It seems that these two forms play no role in zinc absorbed by the plant. It can be expressed that the plant absorbs zinc in exchangeable, organic and carbonated forms. The correlation between the available zinc and its carbonated form indicates that zinc in carbonated form doesn't affect only the availability of zinc negatively, but can serve also as potential source for zinc available to plants in calcareous soil.

Discussion:

As stated in the results, the application of plant residues to the soil increases the organic and carbonated forms of zinc in rhizosphere and bulk soil. Khadivi (2003) studied the cumulative effects and the effect of compost residues, sewage sludge and cow manure on chemical forms and mobility factor of Pb, Ni, Cd, Zn, Cu and Fe in the soil. The results showed that the soluble, exchangeable, and carbonated forms, iron and aluminum oxides, and organic form increased and the residual form decreased by increasing the amount and frequency of fertilization. The comparison between rhizosphere and bulk soil showed that the exchangeable, organic, and carbonated forms are more in the rhizosphere than that in the bulk soil. It could be because of lower pH, root exudates, and microbial activities in the rhizosphere region. A study by Golestanifar (2012) showed that the soluble and exchangeable zinc increased in the rhizosphere soil of oilseed rape and maize, compared to the bulk soil. It may indicate the effective role of rhizosphere processes in the increased bioavailability of zinc. Also Cattani & *et al* (2006) has reported that the more dissolved organic carbon is found in the rhizosphere than the bulk soil, and this enhanced the organic form of zinc in the rhizosphere. Wang & *et al* (2009) reported that the zinc bonded with iron and manganese oxides was decreased in wheat rhizosphere. They expressed the reduction of iron and manganese oxides as the reason for the reduced zinc form in rhizosphere. The results of correlation coefficients shows that there was a significant negative correlation between pH and available zinc in bulk soil. As a significant positive correlation was found between dissolved organic carbons in soil and the available zinc in rhizosphere and bulk soil. Iyengar & *et al*. (1981) reported that there was a significant negative correlation between pH and available zinc in their 19 studied samples of soil. Studying several sample of acid soils of Canada, Neilson & *et al*. (1986) reported also a direct relationship between the amounts of organic matter in these soil samples and available zinc. The application of plant residues to the soil led to the increase in zinc concentration in the wheat grain, compared to the control. Yilmaz *et al*. (1997) showed in a study that applying various methods of Zinc consumption in different wheat cultivars increased not only the yield significantly, but also the concentration of this element in the grain and resulted in enriched grains. Concentrations of copper and zinc in wheat grain increased through applying organic matter in the soil regardless of the type of organic matter. This increase could be implying that these metals would be carried easily from stem to seed when they were absorbed by the roots (Narwal and Singh, 1998). Release of organic acids from decomposing plant residues of alfalfa is considered as a major part of several mechanisms which improves zinc absorption by plants (Singh *et al*., 2005). The results of correlation between the zinc concentration in wheat grain and the chemical forms of zinc indicated that there was a significant positive correlation between the zinc concentration in wheat grain and the exchangeable, organic and carbonated forms of zinc. It was reported in many studies a significant correlation between the plant response and the exchangeable zinc (Youssef & Chino,1989 ; Rupa & Shukla, 1999). Bansal & *et al*. (1990) reported a significant correlation between the amount of available zinc in the soil and the amount of zinc in the wheat grain. Yasrebi (1991) observed in his studies on calcareous soils that there was a significant correlation between the concentration of carbonated zinc and the concentration of zinc in plant. Also, Stanton & Burger (1967) stated in their study that iron oxide has a high affinity to absorb zinc. But the zinc absorbed by iron oxides in the soil is useless for the plant is.

Conclusion:

Conducting this study, we can conclude that the chemical forms of zinc play important role in its absorption by plants, and plants Can absorb the exchangeable, organic and carbonate forms of zinc. The application of zinc sulfate to the soil resulted in the increase in all forms of zinc, particularly its oxidized and residual forms. That is, the major part of zinc added to soil will turn into non-available form for the plant, but the application of plant residues can change the unavailable added zinc to the soil into the absorbable forms of zinc to be absorbed into the plant through decreasing pH and increasing the dissolved organic carbon. Also the application of zinc along with the plant residues can increase the absorbable forms of zinc (exchangeable, organic and carbonate) and reduce the non-absorbable forms of zinc (oxidized and residual), compared to the application of zinc sulfate alone, and also the zinc concentration is increased further in grain.

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