Original Article

The Effectiveness of Foliar Applications of Synthesized Zinc-Amino Acid Chelates and $ZnSO_4$ on the Nutritional Status of Wheat Plant Cultivated in a Soil Contaminated with Cd and Diesel Oil

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Abstract

Aims: This study was done to evaluate the effectiveness of foliar applications of synthesized zinc-amino acid chelates and $ZnSO_4$ on the nutritional status of wheat plant in a soil contaminated with Cd and diesel oil. **Materials and Methods:** Treatments were consist of foliar application of Zn amino acid chelate $(Zn(Arg)_2$ and $(Zn(His)_2)$ and $ZnSO_4$ at the rate of 0, 0.1, and 0.2% (W/V) in the soil co-contaminated with Cd (0, 10, and 20 mg Cd/kg soil) and diesel oil (0 and 8% [W/W]). **Results:** Application of Zn amino acid chelates had a significant effect on increasing plant nutrient status, however, soil pollution with Cd and diesel oil had an adverse effect. Based on the results of this study, application of 0.2% (W/V) $(Zn(Arg)_2$ and $(Zn(His)_2)$ significantly increased the grain Zn concentration of the plants grown in the soil polluted with Cd (10 mg Cd/kg soil) and diesel oil (8% [W/W]) by 11.3% and 10.1%, respectively. For co-contaminated soil with Cd and diesel oil, it was increased by 9.8%. Soil microbial respiration has affected by Zn amino acid chelate and soil pollution. According to our results, application of 0.2% (W/V) $Zn(Arg)_2$ chelate significantly increased the soil microbial respiration in the soil polluted with Cd (10 mg Cd/kg soil) and diesel oil (8% [W/W]) by 12.5% and 13.1%, respectively. **Conclusion:** Zn amino acid chelate had a significant effect in increasing plant nutrient status such as Zn and Fe that is a positive point environmental study.

Keywords: Cd, chelate, diesel oil, soil microbial respiration, Zn

Introduction

Soil is one of the most important environmental components, which are receiving all kinds of waste, toxins, and fertilizers. There are various additives that can cause soil contamination.[1,2] Therefore, it is necessary to know the nature and chemical behavior of pollutants in the soil and their remediation methods. Soil contamination with heavy metals due to their toxicity, stability in the environment, and concerns for the general health of humans and living organisms has the great importance.[3-5] Therefore, among soil and environmental pollutants, the study of heavy metals has been considered by many researchers over the past few decades and now. Heavy metals are important environmental pollutants, some of which are toxic even in low concentrations.[6,7] The natural concentration of heavy metals in the soil depends on the type and chemical composition of the parent material from which the soil is origin, but other sources such as human activities have also led to increased concentrations of these elements.[8,9] Different heavy metals such as Pb, Cd, and Zn have received a

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great deal of environmental attention in recent decades due to their ability to harm the health of humans and living organisms, and efforts have been made to prevent them from entering the natural cycle as much as possible. At the same time, the use of their application and production in industries is essential to achieve industrial progress.[10,11]

Among the heavy metals, Cd has many destructive effects on human health.[12-14] In addition, it is a very mobile element in the environment and can easily absorb by plants.[15] Cadmium concentration in nonpolluted soil is <1 mg/kg soil and its critical concentration in soil is reported to be 1.5–2.5 mg/kg soil. Therefore, it is necessary to use a suitable solution to help reduce the availability of heavy metals such as Cd in the soil, although in many soils, simultaneous contamination of heavy metals with petroleum compounds can complicate the remediation processes.[16,17]

There are various methods such as washing soils contaminated with heavy metals, treatment of industrial effluents in treatment plants, excavation and landfilling, and biological methods such as microbial bioremediation to reduce soil and water pollution. However, among the mentioned methods, the engineering method is very difficult and expensive and causes pollution of another part of the environment.[18,19]

In this case, phytoremediation can be used as a cheap and safe method to remediate soils contaminated with heavy metals, although the physical and chemical conditions of the soil have an important role on remediation of soils contaminated with heavy metals. Steliga and Kluk investigated the role of *Festuca arundinacea* in phytoremediation of soils contaminated with Pb, Ni, Cd, and petroleum hydrocarbons and concluded that plant cultivation has a significant effect on degradation of petroleum hydrocarbons in the soils that simultaneously polluted with heavy metals and petroleum hydrocarbons which was related to the role of root exudate on increasing soil microorganism.[20] However, the phytoremediation efficiency depends on different factors such as contaminant properties, plant species, and conditions prevailing in the environment. Due to the fact that the phytoremediation process is relatively slow, it is necessary to select plants that had extensive roots that can grow quickly and are resistant to contamination. Quickly growing plants are preferred in phytoremediation due to their ability in production of large amounts of biomass and accumulating moderate amounts of metals in their tissues.[21] However, it is important to note that in arid and semi-arid regions, due to high pH, plants are often faced with the problem of nutrient deficiency that affects plant growth and reduces phytoremediation efficiency. On the other hand, in many industrial areas of the country, there is a problem of simultaneous contamination of heavy metals and petroleum compounds that can affect plant growth.[22]

Considering the antagonistic effect of heavy metals with nutrient elements, it is better to find a suitable solution to reduce the plant heavy metal uptake by increasing the absorption of nutrients by plants. In arid and semi-arid regions, Fe and Zn deficiency is very common problem, and soil application of such compounds has low efficiency due to high soil pH. According to the results of Seddigh *et al*., foliar application of Zn fertilizer relative to soil application of them may increase the plant nutrient uptake.[23] However, plant physiology, the type and amount of organic chelate, and the type of soil pollution have an important role in phytoremediation processes. Due to the fact that in the industrial areas of the country, remediation of contaminated area with heavy metals or petroleum compounds is difficult, we need to find the good approach to reduce the uptake of these contaminants by plants and consequently decrease the entering of pollutant in human food chain. Accordingly, this research aims to investigate the effectiveness of foliar applications of synthesized zinc-amino acid chelates and $ZnSO_4$ on the nutritional status of wheat plant in a soil contaminated with Cd and diesel oil.

Materials and Methods

To comparing the effectiveness of foliar and soil application of different Zn fertilizers on Cd uptake by wheat in a diesel oil-polluted soil, a nonsaline soil with low organic carbon was selected from the Pakal village area in Markazi province. The physico-chemical properties of soil used in this study are shown in Table 1.

This research was done as a factorial experiment in the layout of completely randomized block design in three replications. Treatments consist of foliar application of Zn amino acid chelate ($Zn(Arg)_2$ and ($Zn(His)_2$) and $ZnSO_4$ at the rate of 0, 0.1, and 0.2% (W/V) in the soil co-contaminated with Cd (0, 10, and 20 mg Cd/kg soil) and diesel oil (0 and 8% [W/W]). The plant used in this experiment was wheat (*Triticum aestivum* cvs. "Back Cross") that was the most commonly cultivated in Iran and it was Zn-deficiency tolerant. The selected chelates are soluble in water and had a stimulating effect on growth of wheat.[24]

Selected soil samples were polluted with Cd at the rates of 0, 10, and 20 mg Cd/kg soil and incubated for 2 months to equilibrium. Before planting, the soil received 50 mg K, 100 mg

Table 1: Some selected physico-chemical properties of soil used in this study

Characteristic	Unit	Amount
Soil texture	-	Loam
pH	-	7.2
EC	dS/m	1.2
Organic carbon	%	0.1
$CaCo_3$	%	7
Pb availability	mg/kg	ND*
Cd availability	mg/kg	ND
Cr availability	mg/kg	ND
Ni availability	mg/kg	ND
Soil CEC	meq/100g soil	11.8

*ND: Not detectable by AAS. AAS: Atomic absorption spectroscopy

P, and 200 mg N/kg soil in the form of K_2SO_4, $CaHPO_4.2H_2O$, and urea. Then, the soil samples amended with diesel oil at the rates of 0 and 8% (W/W) and for 2 weeks were incubated. Thereafter, 5 kg of soils was filled in plastic pots. Ten seeds of wheat plants were sown in each pot and were placed in a greenhouse condition. The climatic conditions were set to an 8 h day/night cycle, a light intensity of 12,000 Lux, a day/night air temperature of 22/14°C, and a relative air humidity of 40%–45% [Figure 1].

After 3 weeks, plants were thinned to 4 seedlings per pot and daily watered by deionized water. At tillering, 50 mg urea in the liquid form was added to each pot at 2–4 d intervals. The plants were harvested at the maturity of grains. The above ground biomasses of plants were harvested and the grains were separated from the husk, dried at 60°C in a forced-air oven to reach a constant weight, and ground to a fine powder.

To measure the concentration of cadmium in wheat plant, first, the plant seeds were washed 3 times with distilled water in order to remove dirt, dust, and pollution, and then, the samples were dried in an oven at 75°C for 72 h. Then, the plant samples were digested according to the wet digestion method. Accordingly, 0.2 g of the sample was taken in 100 mL volumetric flask and about 4 mL of HNO_3 was added and solution was allowed to stand for few hours; then, it was carefully heated over water bath till red fumes coming from the flask completely ceased. Flask was allowed to cool at room temperature and then about 4 mL of perchloric acid was added and then flask was heated again over water bath to evaporate till a small portion which was then filter through filter paper no. 42 and made up the volume using distilled water till 100 mL. Plant Cd and Zn concentration were also measured using atomic absorption spectroscopy (AAS).[25] Soil microbial respiration was measured according to Besalatpour *et al*.[26]

Statistical analyses were calculated according to the ANOVA procedure. The mean differences were considered according to the least significant difference (test). The 95% (P = 0.05) probability value was considered to determining the significant difference.

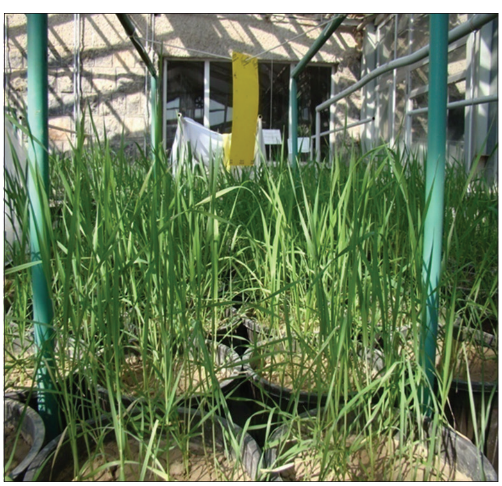

Figure 1: The cultivated plant in this experiment

Results

Shoot Cd concentration

Regardless of the type of soil pollution sources, application of Zn fertilizer had a significant effect on decreasing shoot Cd concentration. Based on the results of this study, application of $Zn(Arg)_2$ and $Zn(His)_2$ at the rate of 0.2% (W/V) significantly decreased the Cd concentration of the plant cultivated in the Cd-polluted soil (20 mg Cd/kg soil) by 10.2% and 8.9%, respectively [Table 2].

The greatest shoot Cd concentration was belonged to the soil that was polluted with the greatest level of Cd and diesel oil. Increasing soil pollution with diesel oil significantly increased the shoot Cd concentration [Table 2], as the results of this study showed that increasing soil pollution with diesel oil from 0% to 8% (W/W) significantly increased the shoot Cd concentration by 14.4%. The type of Zn fertilizer had a significant effect on shoot Cd concentration. Accordingly, the greatest and lowest effectiveness of applying Zn fertilizer on decreasing shoot Cd concentration has belonged to the foliar application of $Zn(Arg)_2$ and $ZnSO_4$, respectively. However, soil contamination with Cd and diesel oil has played an effective role in changing the Cd concentration of the plant. Regardless of the applied Zn source, soil pollution with Cd and diesel oil had an additive effect on increasing shoot Cd concentration. The shoot Cd concentration was increased by 12.4%, when the soil was simultaneously polluted with 20 mg Cd/kg soil and 4% (W/W) diesel oil.

Shoot Zn concentration

The greatest shoot Zn concentration [Table 2] has belonged to the plants cultivated in the nonpolluted soil and sprayed with $Zn(Arg)_2$ amino acid chelate at the rates of 0.2% (W/V), while the lowest that was measured in the plant grown on the soil irrigated with Cd-polluted soil (20 mg Cd/kg soil) and sprayed with $ZnSO_4$ at the lowest rate (0.1% [W/V]).

Shoot Zn concentration in cultivated in control soil was not detectable by AAS. Regardless of the amount of soil pollution, increasing the level of foliar application of Zn-amino acid chelate significantly increased the shoot Zn concentration, as the results of the this study showed that with increasing the application rate of $Zn(Arg)_2$ from 0.1% to 0.2% (W/V) significantly increased the shoot Zn concentration cultivated in Cd (20 mg Cd/kg soil) and non-Cd-polluted soil by 11.2% and 13.4%, respectively. For $Zn(His)_2$ chelate application, it was increased by 10.1% and 11.5%, respectively. Foliar application of $ZnSO_4$ showed the similar trend. Based on the results of this study, foliar application of $ZnSO_4$ at the rates of 0.2% (W/V) significantly increased the Zn concentration of the plant grown in the Cd-polluted (10 mg Cd/kg soil) and non-Cd-polluted soil by 8.2% and 9.3%, respectively. However, soil pollution to Cd or diesel oil had a negative effect on shoot Zn concentration, as the results of this study showed that increasing soil pollution with diesel oil from 0% to 2% (W/W) significantly decreased the shoot Zn concentration by 11.3%.

Grain Cd concentration

The greatest grain Cd concentration [Table 3] was belonged to the plants cultivated in the soil with the greatest level of Cd and diesel oil, while the lowest that was measured in the plant that was sprayed with the highest level of $Zn(Arg)_2$ chelate with the lowest level of soil Cd pollution (10 mg Cd/kg soil).

The grain Cd concentration in nonpolluted soil was not detectable by AAS. Increasing soil pollution to Cd or diesel oil significantly increased the grain Cd concentration. Based on the results of this study, increasing soil pollution with Cd from 0 to 20 mg Cd/kg soil in the soil that simultaneously polluted with 4% (W/W) diesel oil significantly increased the grain Cd concentration by 14.2%. Among this, using Zn sources via $ZnSO_4$ or amino chelate decreased the grain Cd concentration in the plant that cultivated in the soil polluted with Cd or diesel oil. The results of our study showed that application of $Zn(Arg)_2$ chelate at the rate of 0.2% (W/V) significantly decreased the grain Cd concentration by 11.2%. For $Zn(His)_2$ chelate and $ZnSO_4$, it was decreased by 10.8% and 8.3%, respectively.

Grain Zn concentration

Foliar application of Zn sources significantly increased the grain Zn concentration [Table 3]. Our results indicated that foliar application of $Zn(Arg)_2$, $Zn(His)_2$, and $ZnSO_4$ at the

Table 2: Effect of type and application rate of Zn fertilizer, Cd, and diesel oil on shoot Cd and Zn concentration

Diesel oil (%)	Soil Cd (mg/kg)	Zn fertilizer								
		$Zn(Arg)_2$ (% [w/v])			$Zn(His)_2$ (% [w/v])			$ZnSO_4$ (% [w/v])		
		0	0.1	0.2	0	0.1	0.2	0	0.1	0.2
		Shoot Cd concentration (mg/kg)								
0	0	Nd*	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
	10	9.22q**	9.13r	9.02t	9.11r	8.72u	8.55v	9.00t	8.51w	8.33x
	20	18.55c	18.33f	18.25g	18.31f	18.11i	18.03j	18.17h	18.00k	17.53l
8	0	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
	10	9.49m	9.38o	9.21q	9.41n	9.27p	9.12r	9.22q	9.08s	8.71u
	20	18.74a	18.61b	18.53	18.55c	18.41d	18.12i	18.34e	18.12i	18.00k
		Shoot Zn concentration (mg/kg)								
0	0	28.4p	70.1b	71.7a	28.3p	69.7c	70.2b	28.3p	65.4g	68.8d
	10	26.9r	68.4d	67.9e	26.5r	67.3e	68.3d	26.8r	64.5h	66.4f
	20	25.3s	65.9g	66.4f	25.7s	64.1h	63.5i	25.9s	60.3k	62.8j
8	0	27.8q	68.4d	70.1b	27.3q	66.8f	67.7e	27.0q	62.7j	59.4j
	10	26.5r	65.3g	66.3f	26.3r	63.2i	65.4g	26.2r	59.7j	55.4n
	20	21.9t	62.8j	64.1h	21.5t	60.2k	60.4k	21.5t	56.5m	53.2o

*Nd: Not detectable by AAS, **Means with the similar letters in each parameter are not significantly different. AAS: Atomic absorption spectroscopy

Table 3: Effect of type and application rate of Zn fertilizer, Cd, and diesel oil on grain Cd and Zn concentration

Diesel oil (%)	Soil Cd (mg/kg)	Zn fertilizer								
		$Zn(Arg)_2$ (% [w/v])			$Zn(His)_2$ (% [w/v])			$ZnSO_4$ (% [w/v])		
		0	0.1	0.2	0	0.1	0.2	0	0.1	0.2
		Grain Cd concentration (mg/kg)								
0	0	Nd*	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
	10	8.00l**	7.76n	7.45r	7.77n	7.45r	7.32s	7.51q	7.32s	7.12t
	20	17.01b	16.57c	16.22e	16.22e	16.12f	16.00h	16.01h	15.85i	15.72j
8	0	Nd*	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
	10	8.12k	8.00l	7.81m	8.00l	7.82m	7.63o	7.77n	7.54p	7.32s
	20	17.14a	17.00b	16.56c	17.01b	16.58c	16.34d	16.21e	16.12f	16.10g
		Grain Zn concentration (mg/kg)								
0	0	26.4n**	65.3c	68.9a	26.9n	63.7e	66.4b	26.6n	61.4g	62.9
	10	25.3o	63.7e	65.8c	25.1o	61.9g	63.8e	25.2o	59.5i	60.4h
	20	24.3p	61.8g	63.2e	24.2p	59.7i	61.2g	24.5p	58.8j	59.4i
8	0	25.6o	63.2e	66.3b	25.3o	61.4g	63.2e	25.1o	58.3j	60.2h
	10	24.1p	61.7g	64.9d	24.4p	60.3h	62.7f	24.5p	56.5l	58.3j
	20	23.3q	59.2i	62.7f	23.2q	58.7j	60.4h	23.5q	55.4m	57.1k

*Nd: Not detectable by AAS, **Means with the similar letters in each parameter are not significantly different. AAS: Atomic absorption spectroscopy rates of 0.2% (W/V) significantly increased the grain Zn concentration by 11.9%, 10.7%, and 9.1%, respectively.

Although, soil pollution with Cd or petroleum hydrocarbons significantly decreased the grain Zn concentration. For instance, increasing soil contaminated with Cd from 0 to 10 mg Cd/kg soil significantly decreased the Zn grain concentration of the plants that sprayed with 0.2% (W/V) $Zn(Arg)_2$. The similar results was found for grain Zn concentration of the plants that grown in soil polluted with diesel oil, as, with increasing soil pollution with diesel oil from 0% to 4% (W/W), the grain Zn concentration was decreased by 11.9%.

Grain Fe concentration

The effect of Zn on grain Fe concentration [Table 4] was dependent on the fertilizer type and its rate application. The greatest grain Fe application was belonged to the plants with the greatest and lowest Zn and Cd concentration, respectively.

Application of $Zn(Arg)_2$ amino acid chelate at the rate of 0.2% (W/V) significantly increased the grain Fe concentration by 12.3%. For $Zn(His)_2$, it was increased by 11.1%. Soil pollution with Cd or diesel oil had a negative effect on grain Fe concentration. Increasing soil pollution with Cd from 0 to 20 mg Cd/kg soil significantly decreased the grain Fe concentration of the plants that was sprayed with 0.2% (W/V) $Zn(Arg)_2$ and $Zn(His)_2$, respectively. Soil pollution to diesel oil showed the similar results, as we found that increasing the rate of diesel oil from 0% to 8% (W/W) significantly deceased the grain Fe concentration by 14.3%. However, simultaneous effect of soil pollution with Cd and diesel oil had an additive effect on decreasing grain Fe concentration. Meanwhile, the application of Zn-amino chelate has been able to reduce the negative role of soil pollution on grain Fe concentration. Our results indicated that foliar application of $Zn(Arg)_2$ at the rate of 0.2% (W/V) significantly increased the grain Fe concentration in the plants grown in the soil polluted with 4% (W/W) diesel oil.

Grain yield

Foliar application of Zn fertilizer had a significant effect on increasing wheat grain yield [Table 4] even in soil polluted with Cd or diesel oil. The greatest wheat grain yield was belonged to the plants grown in nonpolluted soil and sprayed with the greatest rate of $Zn(Arg)_2$ amino acid chelate.

Increasing soil pollution to Cd or diesel oil had a negative effect on grain yield. According to the results of our study, increasing soil pollution with Cd from 0 to 20 mg Cd/kg soil decreased the grain yield of wheat sprayed by 0.2% (W/V) by 14.5%. In addition, simultaneous effect of soil pollution to Cd and diesel oil had an additive effect on decreasing grain yield. Our results indicated that soil pollution with Cd (20 mg Cd/kg soil) and diesel oil (8% [W/W]) significantly decreased the grain yield of the plants sprayed by 0.2% (W/V) $Zn(Arg)_2$, $Zn(His)_2$, and $ZnSO_4$ by 13.9%, 12.4%, and 10.3%, respectively.

Increasing soil pollution with Cd significantly decreased the soil microbial respiration. According to the results of this study, increasing soil pollution to Cd from 0 to 20 mg Cd/kg soil significantly decreased the soil microbial respiration by 12.5%. Among this, foliar application of Zn-amino chelate significantly had effect on soil microbial respiration. However, the type and application rate of Zn fertilizer showed the significant differences. According to our results, foliar application of $Zn(Arg)_2$, $Zn(His)_2$, and $ZnSO_4$ at the rate of 0.2% (W/V) significantly increased the microbial activity in the Cd-polluted soil (20 mg Cd/kg soil) by 13.2%, 12.1%, and 10.6%, respectively. Soil pollution to diesel oil also showed the similar results.

Table 4: Effect of type and application rate of Zn fertilizer, Cd, and diesel oil on grain Fe concentration and grain yield

Diesel oil (%)	Soil Cd (mg/kg)	Zn fertilizer								
		$Zn(Arg)_2$ (% [w/v])			$Zn(His)_2$ (% [w/v])			$Znso_4$ (% [w/v])		
		0	0.1	0.2	0	0.1	0.2	0	0.1	0.2
Grain Fe concentration (mg/kg)										
0	0	70.4p*	119.4b	120.5a	70.8p	117.3d	119.3b	70.3p	114.7g	117.1d
	10	68.9q	118.6c	119.3b	68.1q	115.2f	116.9g	68.9q	110.6k	113.8h
	20	67.3r	115.2f	117.2d	67.6r	112.7i	115.4f	67.8r	106.8n	110.2k
8	0	68.4q	117.7d	119.5b	68.1q	114.7g	118.8c	68.7q	110.9k	114.2g
	10	66.2s	114.3g	118.4c	66.6s	111.4j	114.3g	66.0s	107.4m	111.8j
	20	65.7t	111.7j	115.8f	65.2t	108.7l	110.9k	65.7t	104.2o	108.2l
Grain yield (g/pot)										
0	0	0.99n*	1.19c	1.22a	0.98n	1.15e	1.18c	0.99n	1.08j	1.13f
	10	0.95o	1.15e	1.19c	0.96o	1.13f	1.16d	0.95o	1.02l	1.10h
	20	0.93p	1.13f	1.16d	0.93p	1.09i	1.13f	0.94p	0.99n	1.06k
8	0	0.86s	1.16d	1.20b	0.86s	1.11g	1.15e	0.85s	1.00m	1.10h
	10	0.84t	1.13f	1.17d	0.85s	1.06k	1.12fg	0.84t	0.92q	1.05k
	20	0.82u	1.11g	1.15e	0.81u	1.00m	1.06k	0.81u	0.85s	1.00m

*Means with the similar letters in each parameter are not significantly different

Soil microbial respiration

The greatest soil microbial respiration was measured in soil under cultivation of the plants that was sprayed with the greatest level of $Zn(Arg)_2$ amino chelate (0.2% [W/V]), while the lowest was obtained from the soil with the greatest level of Cd and diesel oil [Table 5].

Discussion

Generally, application of Zn fertilizer has an effective agronomical practice in crop production, with substantial influence on both yield and particularly grain quality. Ghasemi *et al*. investigated the effect of foliar applications of Zn-amino acid chelates and $ZnSO_4$ on increasing grain nutritional quality and biomass of wheat plant and concluded that using Zn fertilizers had significant effects on increasing plant Zn concentration that is similar to our results.[24] Our results showed that foliar application of Zn fertilizer had a significant effect on decreasing plant Cd concentration that can be related to the interaction effect of Cd and Zn that is mentioned by different researchers.[27,28] Mohtadi and Hooshyari reported that increasing plant Zn concentration can inhabit the Cd uptake by plant.[29] Due to the similarity between Cd and Zn, Cd mimics the physiological role and functions of Zn, but unlike Zn, Cd is toxic to plants[30] that are similar to our results.

Based on the results of our study, foliar application of Zn-amino acid chelates and $ZnSO_4$ has different effects on increasing plant Zn and Fe concentration and consequently decreasing Cd concentration, respectively, that is an important point in environmental studies. Amino acids are nitrogen sources for plant nutrition, and therefore, using these compounds has a positive effect on plant nutrient status that is an important point in phytoremediation studies. Nitrogen uptake by plants can effect on the activity of the number of Zn- and Fe-carrier proteins on the root cell membranes and thereby increases uptake and translocation of nutrient elements of the plant tissues. In this regard, Kutman *et al*. reported that improving plant nitrogen status enhances plant Fe and Zn concentrations both in the whole grain and the endosperm fraction of wheat.[31] Accordingly, increasing plant Zn or Fe concentration can help to decrease the plant Cd concentration.

Due to the fact that in the central regions of the country due to the high pH and low soil organic matter, the concentration of different nutrient element especially micronutrient such as Fe and Zn is low. Thus, it is necessary to finding a suitable way to increase the availability of plant nutrients Bagheri *et al*. investigated the role of iron-enriched vermicompost on corn Fe availability in a Cd-polluted soil and concluded that increasing plant nutrient availability can decrease the soil and plant Cd concentration[32] that is similar to our results. Tabarteh *et al*. also reported that enrichment of organic amendment with nutrient elements can help to decrease the heavy metal uptake by plants and thereby can increase plant biomass.[33] Despite the mentioned information about the positive role of using organic fertilizers enriched with nutrients on reducing plant heavy metals availability, it seems that foliar application of these fertilizers can lead to further reduction in heavy metal uptake by the plant.[34] Hussain *et al*. investigated the role of soil and foliar Zn application on grain yield and grain Zn concentration in Cd contaminated soil and concluded that Zn and Cd concentration in grains was influenced more by soil + foliar than sole soil Zn application.[35]

Based on the results of this study, foliar application of Zn fertilizer had a significant effect on decreasing plant Cd concentration, but it had less efficiency on the plants grown in the soils co-contaminated with Cd and diesel oil which can be related to the greater soil Cd availability in the soils co-contaminated with Cd and petroleum hydrocarbons. Wong *et al*. investigated the degradation of crude oil in a soil co-contaminated with Pb and Cd and resulted that soil polluted with heavy metals has a negative effect on degradation of crude oil in the soil which was related to the toxic effect of heavy metal on soil microbial activity.[36] Accordingly, the results of our study showed that the lowest soil microbial respiration has belonged to the soil co-contaminated with the greatest level of Cd and diesel oil. Moreover, increasing the application rate of Zn amino acid chelates increased the microbial activity and reduced the Cd concentration of the plants grown in the soil that was co-contaminated with 10 mg Cd/kg soil and 4% of diesel oil (W/W), indicating that the foliar application of Zn amino acid chelates has a positive effect on yield and nutritional quality of wheat plant. In this regard, Oliver *et al*.

Table 5: Effect of type and application rate of Zn fertilizer, Cd, and diesel oil on soil microbial respiration (mg C-CO_2/kg soil)

Diesel oil (%)	Soil Cd (mg/kg)	Zn fertilizer								
		$Zn(Arg)_2$ (% [w/v])			$Zn(His)_2$ (% [w/v])			$ZnSO_4$ (% [w/v])		
		0	0.1	0.2	0	0.1	0.2	0	0.1	0.2
0	0	10.65l	15.81b	15.94a	10.61l	15.55e	15.79c	10.65l	15.34g	15.55e
	10	10.55m	15.75c	15.82b	10.57m	15.41f	15.61d	10.52m	15.21h	15.25h
	20	10.23o	15.65d	15.70c	10.20o	15.34g	15.55e	10.24o	15.11i	15.11i
8	0	10.43n	15.66d	15.83b	10.41n	15.32g	15.51e	10.44n	15.141	15.32g
	10	10.31	15.51e	15.74c	10.33	15.12i	15.32g	10.35	15.00j	15.14i
	20	9.51p	15.32g	15.62d	9.53p	15.00j	15.26h	9.59p	14.71k	15.03j

*Means with the similar letters are not significantly different reported that foliar application of Zn fertilizer would be particularly useful in the areas where the possibility of high grain Cd concentration.[34] However, they did not consider the simultaneous effect of soil contamination with heavy metals and petroleum compounds. Seddigh *et al*. conducted the effectiveness of zinc-amino acid chelate application compared with application of $ZnSO_4$ in improving yield and zinc availability of wheat grain and concluded that application of amino acid chelate such as $Zn(Arg)_2$ has reduced the phytic acid to Zn molar ratio of wheat grain. In addition, using of $Zn(His)_2$ and $Zn(Arg)_2$ could be an alternative approach for soil application of Zn-sulfate to overcome Zn deficiency in calcareous soils.[23] In addition, their results showed that with considering higher grain protein content of wheat genotypes at $Zn(Arg)_2$ and $Zn(His)_2$ treatments, application of these chelates is an effective approach to improve availability of wheat grain Zn for human.[23] However, the effectiveness of Zn-amino acid chelates in improvement of grain quality and yield of the wheat cultivars are dependent on the amino acid type, plant genotype, and soil physico-chemical properties. In our study, regardless of the type of soil pollutant, the effectiveness of applying foliar application of Zn fertilizer on decreasing plant Cd concentration and increasing plant Zn and Fe concentration was in order: $Zn(Arg)_2 > Zn(His)_2 > ZnSO_4$. Among this, the effeteness of applying Zn sources was lower in polluted soil relative to nonpolluted soil. Our results showed that applying 0.2% (W/V) Zn amino acid chelate had the best effect on reducing the Cd concentration in the soil polluted with the greatest level of diesel oil.

Conclusion

Based on the results of this study, foliar application of Zn amino acid chelate had a significant effect on increasing plant Zn and Fe concentration and decreasing plant Cd concentration. However, soil pollution to Cd or diesel oil had an adverse effect of plant nutrient status and plant growth that its mechanisms should be studied in the future research. Among the Zn fertilizer used in this study, the greatest and lowest efficiency on increasing plant nutrient elements such as Zn or Fe was belonged to the $Zn(Arg)_2$ and $ZnSO_4$, respectively. In contrast, the plant Cd concentration was decreased. Accordingly, application of $Zn(Arg)_2$, $Zn(His)_2$, and $ZnSO_4$ at the rates of 0.2% (W/V) significantly decreased the Cd concentration of the plants grown in Cd (20 mg Cd/kg soil) and diesel polluted soil (8% [W/W]) by 13.2%, 11.8%, and 9.6%, respectively. Furthermore, our results demonstrated the positive trend between Zn fertilizer usages with soil microbial activity. It can be concluded that using Zn organic acid chelate in a soil simultaneously polluted by heavy metal or petroleum hydrocarbon is a suitable way to decrease the uptake of heavy metals by wheat. However, the plant physiology, the type, and amount of soil pollutant cannot be ignored.

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Conflicts of interest

There are no conflicts of interest.

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