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Zinc is a Neglected Element in the Life Cycle of Plants

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ABSTRACT

Zinc (Zn) is deficient in most calcareous soils and consequently in plants, animals and human diets. Zn deficiency is common in agricultural products of most countries, where bread and rice are the main staple foods. Its deficiency are due to soil calcareousness, high pH, low organic matter, drought, high bicarbonates in irrigation water, overuse of P-fertilizers and the absence of Zn-fertilizers in farmers' conventional fertilizer practices. Its deficiency causes substantial yield losses in different crops. Zn is a component of the enzyme molecular structure besides being a co-factor in regulating the reactions of many enzymes. The first possible effect of Zn deficiency can be seen in reduced levels of cell RNA which in turn halts the protein synthesis, leading to the accumulation of free amino acids. In the past decade more than 2,500 experiments were carried out on different crops, vegetables and orchards throughout Iran. The results revealed that Zn-fertilizers resulted in increased yield as well as crop quality. The conventional notion that Zn-fertilizers increase crop yield by 10-20% is an understatement. In fact, in some cases, especially with non-efficient cultivars such as Durum wheat, it can increase grain yield about 50% and increase macronutrient use efficiencies. A positive and constructive step taken in Iran is the trend of increasing the application of Zn-fertilizers where, currently 30,000 tons of Zn-fertilizers are produced and used annually in the agricultural sector.

Keywords: Zinc (Zn), soil calcareous, bicarbonate, yield and quality of agricultural products
Abbreviations: OM, organic matter; **PA/Zn**, phytic acid ($C_6H_{18}O_{24}P_6$) /Zn molar ratio; **Zn**, zinc

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INTRODUCTION

Zinc (Zn) is one of the essential elements for plants but it is deficient (less than 1.00 mg kg^{-1} DTPA-extractable Zn) in most calcareous soils and consequently in plants, animals and human diets (Malakouti 1998). Zn deficiency is a widespread problem in crop production, in particular for cereals grown on calcareous soils. Zn deficiency can be related to soil calcareousness, high pH and low organic matter, drought, high bicarbonate in irrigation water, overusing P-fertilizers and absence of Zn-fertilizer application. Zn deficiency has been shown to be more widespread than those of other micronutrients (Malakouti 1998). Many investigations show that some 90% of agricultural soils have available Zn below the critical levels of 1.00 mg kg^{-1} DTPA-extractable Zn. If we are to fortify agricultural products, in addition to bringing the soil Zn level to critical levels, we would have to add Zn fertilizers to every piece of farmland. In other words, since enrichment of crops and forage products is being considered, we would be safe to say that 100% of the agricultural and rangeland soils require Zn-fertilizers (Malakouti and Mashayekhi 1996). The total soil Zn levels depend on the nature of parent materials and soil pH and it ranges between 10 to 300 averaging about 35 mg kg^{-1} (Havlin *et al*. 2005). In calcareous soils, its concentration in soil solution is very low due to high pH and the formation of Zn carbonate. In clays, Zn hydroxides and organic Zn compounds become surface adsorbed, lowering its concentrations in the soil solution (Malakouti and Davoudi 2003). Zn deficiency in soils has been reported worldwide, particularly in calcareous soils of arid and semiarid regions. In a global study, Sillanpaa (1982, 1990) found that more than 50% of the soil samples collected in 25 countries was Zn deficient but in the author's view, more than 90% were deficient in Zn especially if enrichment of the crops, pastures and forages was desired (Malakouti and Lotfollahi 1999). Zn deficiency is a particularly widespread micronutrient deficiency in different crops including wheat, leading to severe de-

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Invited Review

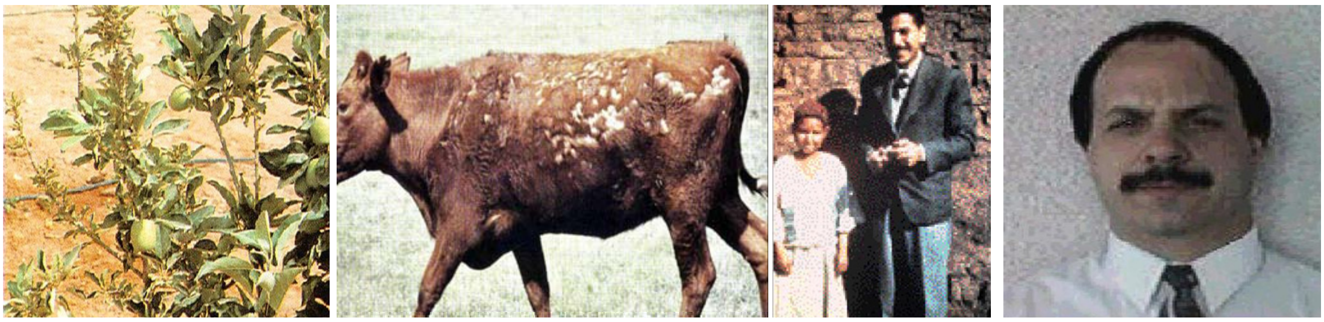

Fig. 1 The signs of Zn deficiency in apple tree, calf and humans (from Malakouti *et al*. 2006b).

pressions in wheat production and nutritional quality of grains. Foods derived from these types of calcareous soils are not only low in Zn, but also due to overuse of P-fertilizers are rich in phytic acid compounds and high in PA/Zn molar ratio depressing bioavailability of Zn to humans (Erdal *et al*. 1998; Malakouti 2000).

Plant genotypes greatly differ in Zn deficiency, either in the ability to absorb Zn from soils or to utilize Zn internally. In detail, enhanced root growth, release of Zn-mobilizing phytosiderophores from roots and Zn uptake capacity of the roots are attributed as main casual factors for Zn efficiency. Also, internal utilization of Zn within in a plant has been discussed as an important mechanism involved in experiments of Zn efficiency in cereal genotypes (Hajiboland *et al*. 2001). To determine the potentials of some indigenous fluorescent Pseudomonads for siderophore production and their effects on ^{65}Zn absorption, 201 strains of *Pseudomonas putida*, *P. fluorescens*, and *P.* aeruginosa were isolated from different locations representing rhizosphere of wheat. The results revealed that among the three most effective siderophores producing strains considered; the *P. putida* produced a siderophore complex that showed efficiency of 83%, compared with the standard siderophore in the uptake of Zn. The effect of bacterial siderophores in the uptake of labeled ^{65}Zn by wheat was significant, indicating that the chemical structures of the siderophores from various strains were different. The effects of wheat variety on ^{65}Zn translocation to shoots was also significant, where the efficient Tabasi variety contained 46% more Zn in shoots than the inefficient Yavarous variety. It was concluded that the siderophore complex from *P. putida* was the most effective in translocation Zn to shoots, particularly in efficient Tabasi genotype (Rasouli *et al*. 2007).

Why are arable soils faced with Zn deficiency?

Zn deficiency is especially widespread in plants, animals and human beings due to the calcareous nature of soils, high pH, low organic matter, salt and drought stresses, high temperature, high bicarbonates in irrigation water (e.g. irrigation water with HCO_3^- concentration of four meq/L = 244 mg/L added to a field crop or an orchard at a rate of 5000 m^3 per hectare per year, the amount of added HCO_3^- to soil will exceed 1220 kg ha^{-1} per year (Malakouti *et al*. 2006a), overuse of P-fertilizers and imbalanced application of fertilizers. The following reactions show why high pH and high bicarbonate reduce the availability of Zn in calcareous soils:

$$CaCO_3 + H_2O \rightleftharpoons Ca(OH)_2 + CO_2$$

$$CaCO_3 + H_2O \rightleftharpoons HCO^-_3 + Ca^{++} + OH^-$$

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons 2HCO^-_3 + Ca^{++}$$

$$CaCO_3 + 2H^+ \rightleftharpoons 2HCO^-_3$$

$$HCO^-_3 \rightleftharpoons CO^{\uparrow}_2 + OH^-$$

$$2OH^- + Zn^{++} \rightleftharpoons Zn(OH)_{2\downarrow}$$

$$CaCO_3 + ZnSO_4.\ X\ H_2O \rightleftharpoons ZnCO_{3\downarrow} + SO_4Ca$$

So, by producing more HCO_3^- and OH^- in the rhizosphere, the pH of the soil solution, and consequently, pH of plant sap will increase enough to cause the precipitation of $Zn(OH)^2$ or $ZnCO_3$, lowering its availability. Physiological reactions of plants, animals and humans to Zn deficiency are quite similar. **Fig. 1** shows Zn deficiency symptoms in apple tree mainly as leaf rosetting and hair loss in animals and human (Malakouti *et al*. 2006b).

Malakouti and Mashayekhi (1996), Rashid and Rafique (1998) and Cakmak *et al*. (1999) announced that in Iran, Pakistan and Turkey's calcareous soils, micronutrient deficiency especially Zn is widespread. These factors are causing substantial yield and quality losses in different crops, i.e. wheat, rice, corn, potato, vegetables, fruit crops. However, a general awareness hardly exists about this important area of plant nutrition. Based on the analysis of more than 50,000 soil samples collected from most provinces of Iran, more than 90% of the studied soils are Zn deficient. Deficiency of Zn in soils on such a large scale, and thus in plant foods, has been suggested to be one of the major causes of the widespread occurrence of Zn deficiency in animals and humans (Malakouti *et al*. 2006b).

Why does Zn availability not comply with the soil organic matter?

Relationship between soil properties and Zn availability revealed that organic matter (OM) and clay contents have synergistic effects while other soil properties such as pH, free $CaCO_3$ and phosphates have antagonistic interactions on the availability of Zn. So, application of OM improves soil conditions and Zn availability. A soil having greater quantity of clay provides extensive surface area for ion exchange and thus contributing towards DTPA extractable Zn. These results are in conformity with the findings of Minakshi *et al*. (2005). Soil pH has an inhibitory effect on the availability of Zn. In the alkalinity conditions, the availability of Zn is reduced due to the precipitation process. In alkaline range, Zn forms negatively charged ions. The change in pH may alter the stability of soluble and insoluble organic complexes of Zn or the solubility of antagonistic ions.

The availability of Zn is decreased at the range of more than 1% free $CaCO_3$ due to the possibility of precipitation or transformation of available Zn into carbonates. The OM content of the soil increases the available Zn status due to the supply of chelating agents and thereby protects the metal ions from precipitation into unavailable forms which is similar to the observations of Sharma *et al*. (2003). These soil factors promote precipitation and adsorption of Zn and reduce transport of Zn to plant roots (Jegan and Subramanian 2007). In calcareous soils, Zn is mostly unavailable due to sorption by clays and carbonates, co-precipitation with carbonates or formation of insoluble calcium zincate (Bradl 2004). Agbenin and Olojo (2004) found that the distribution coefficient K-d is five times greater for Cu than Zn. It seems that reactions with organic matter (OM) and amorphous oxides are the major controls on Cu, whereas Zn might be largely sorbed by clay minerals. The metal

Table 1 Extent of micronutrient deficiencies and organic matter distribution in soil samples from four provinces (adopted from Ali Ehyaee 2001).

Province	No of soil samples	pH	OM % (Mean)	TNV (%)	Fe < 5 (%)	Mn < 5 (%)	Zn < 1 (%)	Cu < 1 (%)	B < 1 (%)**
Qom	650	8.2	0.69	28	91	62	76	71	5
Tehran	882	7.9	1.03	17	65	30	63	28	30
Kermanshan	1238	7.8	1.62	22	33	23	73	13	40
Golestan	1062	7.8	2.29	15	22	9	72	9	10

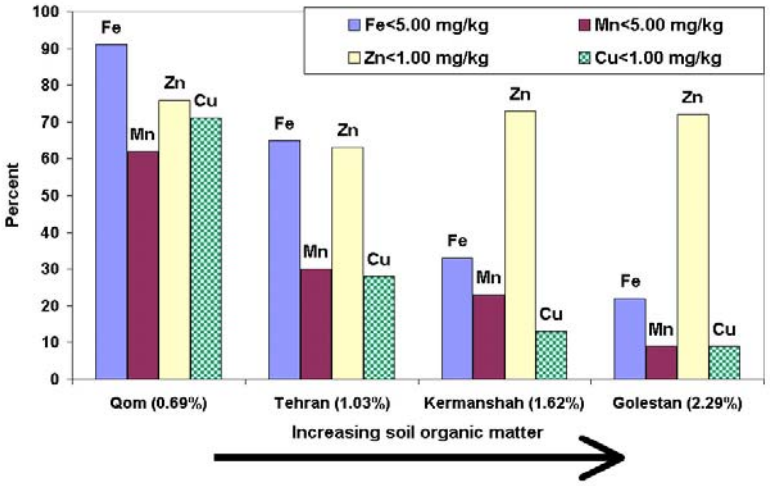

Fig. 2 The trend of soil micronutrient deficiency percentages as related to soil organic matter content in four provinces in Iran (from Malakouti 2006).

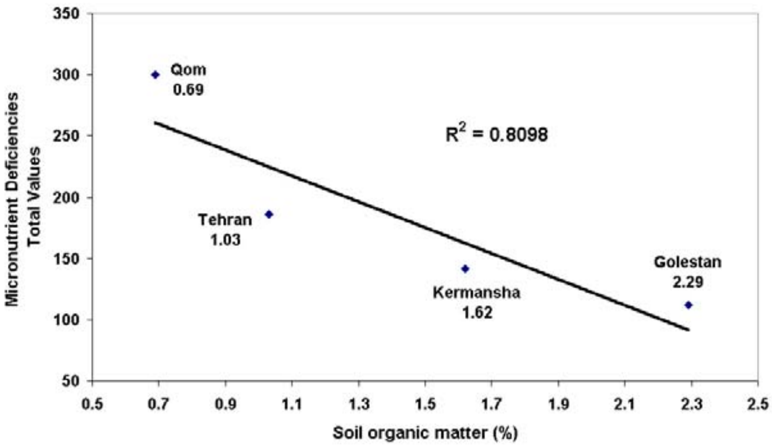

Fig. 3 Relationship between mean values for soil organic matter and total values of micronutrient deficiency in four provinces (from Malakouti 2006).

binding sites in the amorphous hydrous oxides and OM were more selective for Cu than Zn. In a study with 18 Colorado state soils, it has been shown that there is a very strong inverse relationship between soil OM and soluble Zn in rhizosphere (Catlett *et al*. 2002).

To find out which factor, i.e. soil $CaCO_3$, pH and/or OM content, is the most limiting factor in Zn availability, 3,832 soil samples were collected from 4 provinces, i.e. Qom, Tehran, Kermanshah, and Golestan, Iran. Soil samples were analyzed for their $CaCO_3$, organic carbon, and micronutrients content. Data were categorized according to the critical levels of micronutrients in soils, i.e. Fe<5, Mn<5, Zn<1 and Cu<1 (**Table 1**). A negative relationship was found between %OM and the occurrence of micronutrient deficiencies (**Fig. 2**). The mean of OM and total absolute values for micronutrient deficiencies in these provinces were 0.69, 1.03, 1.62 and 2.29 percent and 300, 186, 142 and 112, respectively. The correlation coefficient between %OM and micronutrient deficiency was found to be -0.81. Such a negative correlation was not found for Zn alone. In fact, the concentration of DTPA-Zn in calcareous soils was calculated to be dependent on pH variations. That is, it may be explained in terms of competition between DTPA and soil OM for metal ions which also affect the rate of attainment of chemical equilibrium during extraction. In most cases, Zn deficiency depends on soil chemical and physical properties such as high pH, high level of free $CaCO_3$ and high bicarbonate in the irrigation water (**Fig. 3**). Our soil analysis data demonstrated that there was a good correlation between the rate of micronutrient deficiency and soil OM, but no such correlation was found for Zn, possibly due to two points: a) pH is relatively high in calcareous soils that affects on the solubility of micronutrient minerals and b) Formation of complex between soil OM and Zn is weaker than its complexes with Fe, Mn and Cu.

ROLES OF Zn IN PLANTS

In plant physiology two parts play important roles, one is the process of production of photosynthesis material (the source) and secondly storing the photosynthesized material in the storage tissues (the sink). Zn affects both the source and the sink in a positive way. Zn functions in plants in important ways. It is first of all a structural component in many enzymes involved in energy and metabolism, and is important for the synthesis and degradation of carbohydrates, lipids, proteins and nucleic acids. It also plays an important role in genetic expression (Oliver 1997). Zn is found as a part of enzymes including carbonic anhydrase (transport of CO_2 in photosynthesis), ribulose bi-phosphate carboxlyase (starch formation), RNA polymerase (protein synthesis), superoxide dismutase (converting superoxide radicals to hydrogen peroxide and water), several dehydrogenases such as alcohol dehydrogenase and glutamic dehydrogenase (Alloway 2004).

According to Marschner (2005), the metabolic functions of Zn are based on its strong tendency to form tetrahedral complexes with N-, O- and particularly S-ligands and it thereby plays both a functional and a structural role in enzyme reactions. Although more than 70 metalloenzymes containing Zn have been identified, these only account for a relatively small proportion of the total Zn in a plant. A deficiency of Zn can cause a reduction in net photosynthesis by 50-70% depending on the plant species and the severity of deficiency. This reduced efficiency of photosynthesis could be due, at least in part, to a reduction in the activity of the enzyme carbonic anhydrase especially in C_4 plants. Enzymes involved in the formation of sucrose, such as aldolase, are adversely affected by Zn deficiency. A decline in the level of sucrose in sugar beet and maize is due to lower activity of sucrose synthetase activity.

The amount of protein in a Zn-deficient plant is greatly reduced but the composition remains almost unchanged. In Zn-deficient leaves, the concentration of free amino acids was 6.5 times greater than in controls but it decreased and the protein content increased after Zn application within 3 days. The mechanism by which Zn deficiency affects protein synthesis is considered to be due to a reduction in RNA and the deformation and reduction of ribosomes. In the meristem of rice seedlings, it was found that the level of RNA and the number of free ribosomes was dramatically reduced by Zn deficiency. Zn is necessary for the activity of the enzyme RNA polymerase and it protects the ribosomal RNA from attack by the enzyme ribonuclease. High levels of ribonuclease activity are a typical feature of Zn deficiency in higher plants. As a consequence of this, the earliest causal effect of Zn deficiency is a sharp decrease in the level of RNA. However, the reduction in RNA can occur before the increase in ribonuclease activity. The importance of Zn in protein synthesis suggests that relatively high Zn concentrations are required by meristematic tissue where cell division as well as synthesis of nucleic occurs. Zn is also known to be required for the maintenance of membranes through the interaction with phospholipids and sulphydryl groups of membrane proteins. The loss of membrane integrity is considered by some to be the earliest biochemical change caused by Zn deficiency (Alloway 2004).

The importance of Zn for crop production in Iran and Turkey was recognized only during the past decade. The effects of Zn deficiency on crop production in Iran and Turkey have received attention only since the early 1990 and 1995s. In 1982 after a soil survey study in different countries, however, Sillanpaa (1982) stated that concentration of Zn in the soils of Middle East countries were among the very lowest recorded. Many experiments were carried out in these regions to test the effect of soil applied Zn and other micronutrients on growth and grain yield of wheat cultivars. The results revealed that grain yield was significantly depressed only in the absence of Zn fertilization. Based on these results, it has been suggested that Zn deficiency is of critical importance for the wheat production in the Middle East countries. These observations and findings on Zn deficiency in cereals raised questions about the extent and importance of Zn deficiency in soils, plants, foods and humans (Cakmak 2006; Malakouti *et al*. 2006b).

EFFECTS OF Zn APPLICATION ON THE YIELD AND QUALITY OF CROPS

Crop yield and quality

Application of Zn-fertilizers to soils with Zn deficiency problems has been associated with improved yield and crop quality for cereals, corn, sorghum, beans, forages. By applying Zn-fertilizers on 1000 wheat fields in various provinces of Iran in the last decade, Zn significantly improved the yield. The average yield increase amounted to 406 kg ha^{-1} and the maximum increase of 1731 kg ha^{-1} was obtained in Khorasan. In these studies the grain protein content also improved. Yield components such as weight of a thousand seeds index, number of seeds per ear and the carbohydrate and starch contents of the seeds also improved (Malakouti and Mashayekhi 1996; Malakouti 2000; Malakouti *et al*. 2004). Majidi and Malakouti (1998) in their experiments found that Zn-fertilizers significantly increased wheat grain yield in both rainfed and irrigated conditions. Zn concentration also was increased in wheat grain in both conditions. The effect s of Zn sources, i.e. zinc sulphate and zinc oxide were similar in their effects on grain yield and Zn uptake. Increasing wheat grain yield and community's health through the use of zinc sulphate was tested in different wheat fields (Malakouti 1998). The results demonstrated that application of Zn-fertilizer increased grain yield and quality considerably in the Zn-deficient (<1.00 available Zn) calcareous soils.

The role of Zn in improving the grains protein content has been reported by many researchers (Malakouti 2000). The average protein content of the grain was found to be 13.05%. With Zn deficiency the rate of RNA polymerase enzyme declines strongly and the rate of transport of amino acids also declines and the rate of RNA decomposition as

Table 2 Effect of Zn fertilization on the grain yield and 1000 kernel weight index in greenhouse experiments. Average of 25 fields with three replications (from Malakouti *et al*. 2005).

Field №	Grain yield (g/pot)		Relative Increases (%)	1000 kernel weight (g)		Relative increases (%)
	Control	Treated		Control	Treated	
Ave.	7.1	8.3	17	44.0	48.4	10

Table 3 Effect of Zn fertilization on grain yield and on 1000 kernel weight index. Average of 140 fields for two-year experiments in different provinces (from Malakouti *et al*. 2005).

Region	Grain yield (kg ha^{-1})		Change (%)	C.V. (%)	1000 kernel weight (g)		Change (%)	C.V. (%)
	Control	Treated			Control	Treated		
Fars	3904	4476	14.5^{**}	17.29	37.73	36.75	-2.6^{ns}	6.12
Hamadan	5496	6418	16.8^{**}	7.63	36.07	37.21	$+3.2^{**}$	2.38
Illam	4428	4565	3.1	6.50	36.36	36.86	$+1.4^{**}$	1.41
Esfahan	5843	6287	7.6^{**}	11.50	40.97	42.26	$+3.2^{**}$	7.05
Khuzestan	2546	2555	0.4	9.52^{ns}	34.91	34.71	0.6^{ns}	4.30
Tehran	4480	4835	7.9^{**}	10.19	47.33	47.22	-0.2^{**}	1.63
Zabol	2800	2877	2.8	22.69^{ns}	37.87	37.73	$-0\text{-}4^{ns}$	10.22
Semnan	4705	4448	-5.5	12.99^{ns}	43.87	41.88	-4.5^{*}	6.69
Yazd	3698	4500	21.7^{**}	13.52	40.61	40.97	0.9	5.16
Varamin	5200	5925	14.0^{**}	3.73	40.87	39.87	-2.5^{ns}	4.74
Kordestan	5023	5387	7.3^{**}	9.81	33.31	33.99	2.0^{ns}	5.43
Average	4353	4640	6.6^{**}	10.77	38.49	38.94	1.2^{**}	5.51

* Significant differences at 5% level; ** Significant differences at 1% level ; *** The main reason for decrease of 1000 kernel weights index in the field studies was due to existence of some limiting growth factors such as soil salinity in some provinces. ns - no significant differences between treatments.

Table 4 Influence of Zn application methods on winter wheat yield and quality (from Majidi and Malakouti 2007).

Parameter / Treatment	Control (NP)	NPK	NPK + SA	NPK + ST	NPK + FA	NPK + SA + FA	NPK+ FA+ST
1000 kernel weight (g)	46.3 e	45.2 f	48.8 ab	46.9 de	47.6 cd	49.4 a	48.32 bc
Grain yield (Kg ha^{-1})	4352 e*	4996 d	6073 b	4706 de	5602 c	6490 a	5572 c
Protein content (%)	11.6 c	12.2 b	13.1 a	12.5 b	13.2 a	13.3 a	13.3 a
Zn concentration in grain (mg kg^{-1})	22.6 d	24.0 d	28.0 c	21.3 d	48.4 a	47.7 a	43.9 b

* Note: Averages in the same column followed by the same small letter are not different at the 0.01 probability level

well as the activity of the RNAase increased resulting in a strong reduction in the rate of protein synthesis. Zn is also an essential component of the ribosomes (Marschner 1995).

Yilmaz *et al*. (1997) and Malakouti (2000) demonstrated that Zn significantly increased 1000 kernel weight and grain yield. They also reported that effect of Zn on the number of spikes per square meter was most pronounced so that the latter parameter had increased by 81% and 1000 kernel weight by 26%. Thousand kernel weight had increased from 28 to 32 g in soil application and to 35 g for foliar sprays of zinc sulphate. In another series of experiments which carried out on some 815 irrigated wheat fields across Iran during 1995-2000, the effect of zinc sulphate on increasing the yield of wheat grain was evaluated. The results demonstrated that yield and quality were increased significantly. The highest yield was obtained by Zn fertilization (Malakouti 2000).

It was commonly believed that 1000 kernel weight index was genetically determined and that nutrient management would not affect such a parameter in wheat. This notion was tested in greenhouse and fields in 1996-1998. The results revealed that the kernel weight index increased from 44.0 to 48.4 g (17% increase) and grain yield increased from 7.1 to 8.3 $g.pot^{-1}$, an increase of 10%, significant at α=1% level in greenhouse experiment. The field experiments also showed mean yield increases from 4353 to 4640 kg ha^{-1} as well as increases in the mean weight of 1000 kernel weight from 38.49 to 38.94 g. The effect of Zn fertilization on the average value of grain yield and on 1000 kernel weight index for different wheat cultivars tested in 140 fields in different provinces are shown in **Tables 2** and **3** (Malakouti *et al*. 2005). If only one single micronutrient is to be added in calcareous soils, Zn is obviously the best choice for yield improvement. A similar experiment carried out on 433 irrigated wheat fields the following years also showed that by adding Zn to NPK, yields of wheat grain increased. Effect of Zn-fertilizer in increasing wheat grain yields was repeated again during 1999-2000 on 331 wheat fields in the country, where it was again demonstrated that micronutrient-fertilizers additions to NPK increased the yield of wheat grain under irrigated conditions. Another experiment was carried out in Karaj region on the effect of Zn to improve the yield of wheat grain during 1996 also showed that grain yields increased from 3,910 kg ha^{-1} to as much as 4,926 kg ha^{-1}, or up to 26% (Malakouti 2000). Majidi and Malakouti (2002) evaluated the effect of zinc sulphate on the yield of rainfed wheat grain during 1996-97 growing season. They succeeded in increasing the yield from 1,135 kg ha^{-1} in the control plot to 1,241 kg ha^{-1} on the average by applying zinc sulphate. The yield increase averaged 9% in this experiment.

Influence of balanced fertilization as well as Zn sulphate application methods, i.e. soil application (SA), seed treatment (ST), foliar application (FA), combination of SA with FA and ST with FA have been tested in a series of experiments. The results demonstrated that the highest yield increase by Zn-fertilizers was obtained with SA+ FA. ST alone or FA by itself had little effect in overcoming the Zn deficiency symptoms. ST at high rates increased the grain yield but had little effect on increasing the Zn level in the above ground plant tissues or the grain. This was attributed to the dilution effect. The results concerning ST showed the importance of grain Zn for sprouting and early maturity. Once the residual levels of Zn in soil are taken into account, SA method turns out to be the best solution for Zn deficiency soils. Zn fertilization at a rate of 28 kg ha^{-1} zinc sulphate for 4 to 7 years appears to be sufficient to overcome Zn deficiency problems of affected soils. FA is the most effective method for increasing the Zn concentration in the plants foliage tissues as well as the grain, a very important outcome for improving the human food chain. The combination of SA with FA is proven to be the best procedure to obtain high grain yields with high levels of Zn in wheat grains (Yilmaz *et al*. 1997; Malakouti *et al*. 2006b). Effect of different methods of Zn-fertilizer application methods were tested in 10 main wheat grown provinces by Balali *et al*. (2001). They found that significant differences existed among different Zn application method. The highest yield (5,521 kg ha^{-1}), protein content (13.86%) and Zn concentration (39.5 mg kg^{-1}) were obtained from the combination of soil and foliar application methods. In another experiment, balanced fertilization as well as Zn sulphate application methods have been tested by Majidi and Malakouti for three years (2007). The results revealed that Zn application methods increased kernel weight, grain yield, protein content and Zn concentration in the grain of winter wheat, but combination of SA with FA remarkably had the greatest influence on the above factors (**Table 4**). These results corresponded with the findings of Yilmaz *et al*. (1997) and Malakouti (2000) in Turkey and Iran's Zn deficient calcareous soils.

Application of Zn-fertilizers on fruit trees also improved the yield of fruits, i.e. apple, grape, apricot, citrus. Likewise, the quality of fruits had improved (Malakouti 2001). Foliar application of Zn would cause the branches to become longer and heavier, and the roots would become more extensive and more dry matter will be produced. Application of zinc sulphate in manure pits under apple trees along with foliar applications of zinc sulphate solutions increased the Zn content of apple fruits (**Fig. 4**). Furthermore, since increased levels of Zn in fruits meant greater activity of the antioxidants, browning incidence was decreased (Souri and Malakouti 2000). Foliar applications of Zn solutions on apple buds increased the Zn concentrations from 7% in the control to 29% in the treated samples (Hipps and Davies 2001). Foliar applications of Zn and boric acid solutions on cherry trees new buds improved the number of fruits per branch and the total yield.

Soil and Water Research Institute's researchers in their study on different crops in various regions found that by Zn application, the yield of wheat, rice, corn, potato, onion,

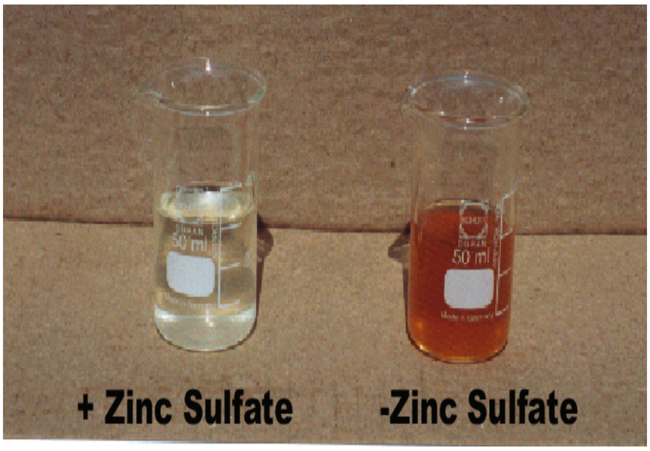

Fig. 4 Effects of zinc sulphate on the discoloration of apple juice (from Souri and Malakouti 2000).

+ Zinc sulphate **– Zinc sulphate**

Fig. 5 Effects of zinc sulphate on the premature of canola (from Malakouti 2003).

Table 5 Average canola yields as affected by Fe and Zn fertilizers (from Malakouti and Tehrani 2005).

Study site №	NPK (kg ha^{-1})	NPK + Fe (kg ha^{-1})	Yield Increase (%)	Study site №	NPK (kg ha^{-1})	NPK + Zn (kg ha^{-1})	Yield increase (%)
1	2,051	2,578	26	1	3,221	3,513	9
2	1,043	1,437	38	2	2,467	3,169	28
3	2,403	3,221	34	3	1,409	1,579	12
4	3,036	3,694	22	4	2,243	3,816	70
5	2,831	3,334	18	5	2,051	2,578	26
Mean	2,273	2,853	28	6	2,278	2,931	29

[8] Soils low in a nutrient but non-responsive due to some other limiting factors or to non-susceptibility of the test crop.

Table 6 Average potato and sesame yields as affected by micronutrients additions (from Malakouti and Tehrani 2005)*.

Potato fields №	NPK (kg ha^{-1})	NPK + Zn (kg ha^{-1})	Yield increase (%)	Sesame field №	NPK (kg ha^{-1})	NPK + Zn (kg ha^{-1})	Yield increase (%)
1	28,800	40,700	41	1	1,433	1,795	25
2	35,000	39,500	13	-	-	-	-
Mean	31,900	40,100	-	-	-	-	-

* Soils low in a nutrient but non-responsive due to some other limiting factors or to non-susceptibility of the test crop.

Table 7 Average potato and sugar beet yields in different provinces as affected by Zn-fertilizer application (from Malakouti and Tehrani 2005)*.

Potato field №	NPK (kg ha^{-1})	NPK + Zn (kg ha^{-1})	Yield increase (%)	Sugar beet field №	NPK (kg ha^{-1})	NPK + Zn (kg ha^{-1})	Yield increase (%)
Semnan	29,000	32,000	10	Fars	6,497	6,561	1
Hamadan	41,500	46,500	12	Khorasan	4,230	4,545	7
Kerman	13,900	17,500	26	Arak	9,858	10,635	8
Karaj	16,900	22,100	31	Karaj	6,450	7,500	16
Ardabil	35,500	36,700	3	-	-	-	-
Mean	27,360	30,960	16	Mean	6,759	7,310	8

* Soils low in a nutrient but non-responsive due to some other limiting factors or to non-susceptibility of the test crop.

Table 8 The effects of seed enrichment and Zn application on the grain yields under field condition (from Savaghebi *et al.* 2001)*.

Zn / Seed	0	5	10	20	Average
Normal seed	6046 G	6218 F	6303 DE	6365 DC	6233 B
Enriched	6276 EF	6390 C	6611 B	6883 A	6540 A
Average	6162 D	6304 C	6457 B	6624 A	6358 A
LSD 1%	Zn x seed = 65.06	Zn = 64	Seed = 32.53		

* Grouping of the averages was done separately for Zn levels, seed, and seed x Zn.

soybean, sugarbeet and sesame were increased significantly. Salimpour *et al.* (2001) in their study found that by Zn application, the yield of canola has been increased significantly and prematured canola almost for two weeks (**Fig. 5**). In another experiment in five provinces, the effects of balanced fertilization on potato and sugar beet yield were tested (average of 20 fields in each province). The results are shown in **Tables 5, 6, 7** (Malakouti and Tehrani 2005). In the case of severe deficiency condition, the yield increase could increase to over 100% (Sillanpaa 1990; Malakouti and Kalantari 1998; Malakouti 2006). In different experiments, wheat, rice and grape yields, increased from 3,220, 4,697 and 10,540 kg ha^{-1} to 4,117, 7,508 and 19,040 kg ha^{-1} (28, 60 and 81%), respectively. But, in ordinary situation, the average yield increase in wheat, rice, corn, potato, onion and oil seed plants were 10, 30, 25 and 15%, respectively (**Fig. 6**). In other words, application of Zn-fertilizers to the calcareous soils with Zn deficiency problem has been associated with improved yield and crop quality (Malakouti 2006).

Seed enrichment

Research results indicated that planting Zn treated seeds can be used as a measure to prevent low yields caused in Zn deficient soils. The effect of Zn-fertilizers in seed enrichment and on wheat production has been studied in Iran's calcareous soils for the past decade. The results revealed that the main and interactive effects of using enriched seeds and Zn-fertilizers on the grain yield the straw and the total yield became significant at 1% level. The average grain yield for normal seed was 6,233 kg ha^{-1} while it was 6,540 kg ha^{-1} for the enriched seed; therefore, enrichment increased the grain yield by 307 kg or 4.92% (**Table 8**). The average grain yield for Zn_0 was 6,162 kg ha^{-1} and for Zn_3 it was 6,624 kg ha^{-1}, an increase of 462 kg or 7.5%. The com-

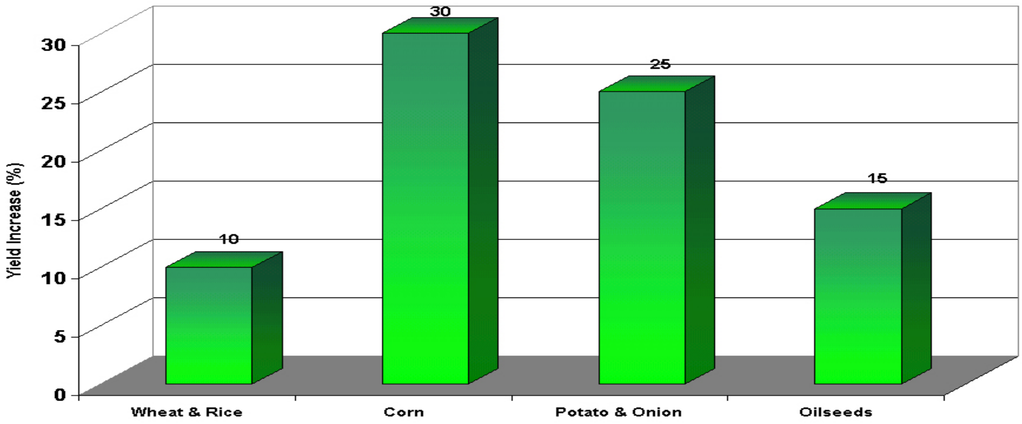

Fig. 6 Average yield increases due to zinc application in addition to expected improvement in crop quality and enrichment in the calcareous soils (from Malakouti 2006).

bined effect of enriched seed and Zn_3 resulted in an increase in the grain yield of 837 kg ha^{-1} or 13.84%, meaning positive interaction between Zn-enriched seed and Zn application, in other word, enrichment of the seeds caused an improved reaction of the plants to the applied Zn (Savaghebi *et al*. 2001).

The main effects and interactive effects of seed enrichment and Zn application on the protein content of the seed became significant at 1% level. The average protein content of the normal seed was 12.73% while it was 13.38% for the enriched seed (5.1% increases). The protein content of the seed for Zn_0 was 12.56 and for Zn_3 it was 13.59% (8.2% increases). The average weight of a thousand seeds in the control (normal seed) was 42 g, in the enriched seed 45 g, and in Zn_0 43.07, in Zn_3 it was 46.20 g, showing 7.1and 7.4% increases, respectively. These results were corresponded with the findings of Rengel and Graham (1995), Yilmaz *et al*. (1997) and Malakouti (2000). Investigations on the effects of Zn-enriched wheat seeds on the yield and quality of wheat grain produced on Zn deficient soils showed yield improvements of about 819 kg ha^{-1} and the grain protein increase of 1.79%. The highest protein content (14.17%) resulted from enriched seed and the use of 10 kg Zn/ha (Tehrani *et al*. 2002). Another experiment was carried out at Tehran University's farm and greenhouse facilities during 1998-99 and at Karaj to study the effect of the enrichment of wheat seeds with Zn on the yield and quality of the resulting wheat crops grown on Zn-deficient soils. The results of the field and greenhouse experiments showed that seed enrichment with Zn significantly increased the seed yield, total yield; the thousand-kernel weight index, the seeds protein content; absorption and the concentration of Zn in seeds, bran and flour. While the yield and the grain protein content in G_1Zn_0 were 6,064 kg ha^{-1} and 12.38%, respectively, the related figures for G_2Zn_3 were 6,883 kg ha^{-1} and 14.17%. In other words, given similar field conditions, seed enrichment increased the grain yield by 11.9% and the grain's protein content by 12.69%. Similarly, the two-year trials showed that the average yield resulting from the fortified seeds was greater than those from the control seeds. It became evident, therefore, that fortified seeds, especially grown in fertile soils, play an important part in improving the wheat yield, as seen by comparing the results from the control seeds and Zn-fortified seeds. This observation emphasizes the superiority of the fortified seeds in Zn-deficient calcareous soils. The average grain yield for normal seed was 6,233 kg ha^{-1} while it was 6,540 kg ha^{-1} for the fortified seed; therefore, enrichment increased the grain yield by 307 kg ha^{-1} or 4.9%. The average grain yield for Zn_0 was 6,162 kg ha^{-1}and for Zn_3 it was 6,624 kg ha^{-1}, an increase of 462 kg ha^{-1} or 7.5%. The combined effect of fortified seed and Zn_3 resulted in an increase in the grain yield of 837 kg ha^{-1} or 13.8%, meaning positive interaction between Zn-fortified seed and Zn application. In other words, enrichment of the seeds caused an improved reaction of the plants to the applied Zn. The yield increase was considerable if you compared the performance of the fortified seeds in Zn-fertilized rich soil with that of normal seeds in Zn-deficient unfertilized soil (Malakouti *et al*. 2005). The main and interactive effects of seed enrichment and Zn application on the concentration of Zn in the grain became significant at 1% level. The average Zn concentration in the control (normal seed) was 21 mg kg^{-1}and in the grain from the enriched seed 36 mg kg^{-1}. The Zn concentration in the grain from Zn_0 was 29.51 mg kg^{-1} and in Zn_3 it was 54.50 mg kg^{-1}. The Zn concentration in the straw from the control treatment was 22 mg kg^{-1} and in the enriched seed treatment it was 27 mg kg^{-1}. Zn application increased the Zn content in the straw from 16 mg kg^{-1} in Zn_0 to 31 mg kg^{-1} in Zn_3. Under Zn deficiency, the wheat crop will show not only Zn-deficiency symptoms and stunted growth and low grain yield, but also low Zn content for the resulting grain. The experimental results of various investigators on the positive effects of Zn application and enriched seeds of the grain and straw have been summarized by Malakouti and Lotfollahi (1999) and Malakouti and Tehrani (2005).

It can be seen from our findings that in soils poor in Zn, enriched seeds yielded better than the control while in the soils with good available Zn level the yield increase due to the use of enriched seed was greater. As a whole, the study shows that enriched seeds would improve the grain yield, the grain protein content, and the Zn concentration in and absorption by the grain in poor soils by producing stronger seedlings than those produced by normal seeds. The stronger seedlings would absorb more soil-Zn or the fertilizer-Zn resulting in improved quality and quantity of the yield. In this investigation the enriched seeds resulted in an increase of 518 kg grain/ha, 1.16% increases in the protein content and an increase of 2.48 g in the weight of a thousand seeds. Also the application of zinc sulphate fertilizer resulted in lower phosphorus content of the grain, flour and bran indicating a negative interaction between Zn and P. With the analyses of samples of flour and bran it became evident that the greatest portion of the major nutrients accumulates in the bran (Malakouti 2000). Besides, human nutrition, increases in Zn content of grains also has desirable consequences for seedling vigor. Seedlings from seeds with low Zn content are very susceptible to various soils-borne and other pathogens and thus, to winter-kill. Seed content of Zn is extremely low in all calcareous soils including Middle East countries. Obviously, seedlings from such seeds might be sensitive to diseases and winter-kill. This would be one reason why seedling rates (200-300) in these regions are almost three times as high as in other countries with similar climate (Cakmak *et al*. 1999). In another study in west Azarbyjan province with Zn application, the wheat yield increased significantly at 5 percent level. The least increase, in the grain yield was 350 (from 5,450 in the check plots to 5,800 in the treated plots), and the greatest increase was 1,900 (from 6,600 kg ha^{-1} in check plots to 8,500 kg ha^{-1} in treated plots). These average grain yield increase in the treated plots in two provinces in tested farms was 954 kg ha^{-1} grains (from 5,242 kg ha^{-1} in the check plots to 6,196 kg ha^{-1} in the treated plots). These results revealed the positive

Table 9 Effects of Zn on the grain zinc content and PA/Zn molar ratio (from Malakouti *et al.* 2006b).

Treatment	P	Zn	PA/Zn
Check plots	0.33 A	14.1 B	23.78
Treated plots	0.31 A	24.5 A	12.46

Table 10 The advantages of using Zn- fertilizer (T_2) on increasing average wheat grain yield, NUE and NARF in 22 studied sites (from Malakouti *et al.* 2006b).

Wheat grain \ Treatments	T_1 = Control	T_2 = Zn treated plots
Yield (kg ha^{-1})*	4,160 B	4,674 A
Protein (%)*	11.66 A	12.01 A
NUE (kg.kg^{-1})	8.8 B	12.2 A
NARF (%)	23.2 B	31.6 A

* LSD for yield = 346 kg ha^{-1} and protein = 0.82%.

role of Zn in increasing wheat yield. Zn application significantly improved the concentration of Zn in grain and conesquently reduced PA/Zn molar ratio (**Table 9**). This was corresponded with the findings of Erdal *et al.* (1998) and Malakouti (2000).

Improving fertilizer use efficiency (FUE)

Zn-fertilizers increased the yield; increased macronutrient-fertilizers use efficiencies and farmers economical return considerably. FUE for different crops can be increased as high as 25 (kg.kg^{-1}) with Zn application. It is recommended that in order to maximize FUE in crop production, Zn-fertilizers should be applied on the basis of soil testing values in all calcareous soils. The average yield increase due to Zn-fertilizer application was 16% (the average yield of potato in different provinces increased from 27,360 to 30,960 kg ha^{-1}). Then the fertilizer use efficiency, by assuming an application rate of 50 kg of Zn-fertilizers per hectare, was 72 kg.kg^{-1}. Considering that in spite of the fact that macronutrient was used, the values for NUE and NARF increased. Therefore, it seems more logical to practice balanced crop fertilization. The data from a series of experiments revealed that, as a whole, T_2 was the best in all studied sites. The average values of grain yields (from all 14 provinces) and of agronomic efficiencies due to balanced fertilization are given in **Table 10**. The maximum recovery rates were obtained with T_2 in most studied sites. In addition to yield increase of 12% with T_2, the NUE increased up to 15 kg grain.kg^{-1} N and NARF values improved by 36%. Zn-fertilizers are highly recommended as a means of improving grain yield as well as fertilizer recovery rates. Results of different experiments on different soils with different soil conditions showed that using Zn-fertilizers had positive results on economic returns (Malakouti *et al.* 2006b).

Zn interaction with other nutrients

Phosphorus (P), iron (Fe) and manganese (Mn) induced Zn deficiency while potassium (K) accelerated the uptake of Zn in plants. Our studies on the interaction between Zn and K in wheat production indicated that application of Zn and K-fertilizers significantly increased the grain yield, protein content and Zn and K concentrations in different wheat cultivars and hence decreased PA/Zn molar ratio in wheat grain (Savaghebi *et al.* 2001). On the other hand, many experiments revealed that application of high P, Fe and Mn-fertilizers, disturbed Zn uptake by plants. While available P in the plant rhizosphere increased, despite of sufficient amount of available Zn in the soils, the uptake of Zn decreased considerably (Malakouti and Samadi 1989). Other greenhouse and field studies with different crops also showed the same results. In a very wide study in 10 main wheat grown provinces, the results revealed that by application of Zn-fertilizers, the average grain yield, protein content and Zn concentration were increased 19, 15 and 22%, respectively, but the levels of Fe and Mn had decreased

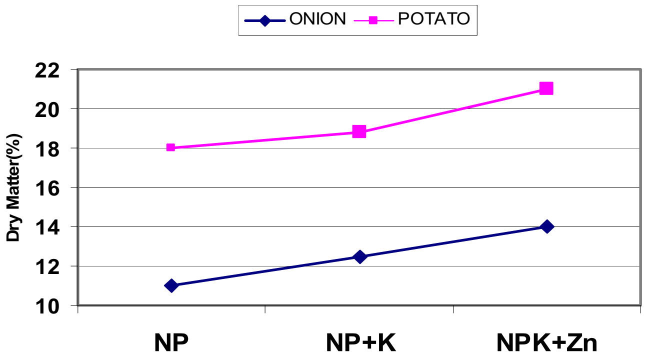

Fig. 7 The role of zinc sulphate on increasing the percentage of dry matter (from Malakouti and Bybordi 2006).

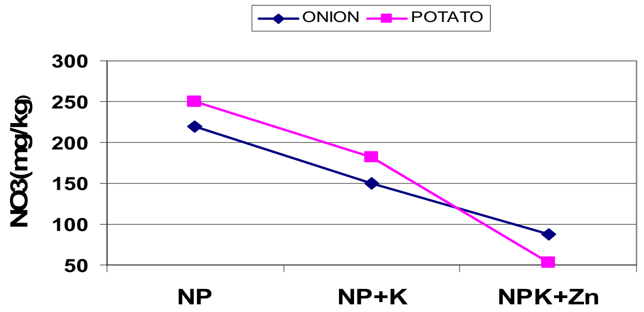

Fig. 8 The role of zinc sulphate on the reduction of nitrate contaminants (from Malakouti and Bybordi 2006).

significantly. Further analysis revealed that a great part of the mineral elements are removed by bran (Malakouti 2000). Malakouti and Bybordi (2006) indicated that there was a positive relationship between K and Zn uptake especially in controlling soil contaminants (NO_3 and Cd). Analysis of variance showed significant differences at 1% level in the potato and onion' the sizes of tubers, the starch content, K and Zn levels in the tubers and yield. There was also a significant difference at 5% level in the NO_3 and Cd contents of the tubers as well as percent of dry matter. The results revealed that the yield, TSS, ascorbic acid, NO_3 and Cd contents in onion bulbs were varied significantly. The highest yield was obtained with 50 kg ha^{-1} zinc sulphate. As for quality, the soil application resulted in onions with higher contents of ascorbic acid and titrateable acidity. The highest NO_3 and Cd contents (220 mg kg^{-1}FW and 0.27 mg kg^{-1} DW) in the onion bulbs was obtained in the control plots. The lowest NO_3 and Cd contents (80 mg kg^{-1}FW and 0.10 mg kg^{-1}DW) were obtained with 50 kg ha^{-1} zinc sulphate (**Figs. 7, 8; Table 11**). In another experiment, while the soils of the surveyed orchards are high in available Zn, with moderate OM, all favoring higher Zn uptake and contents, i.e. apple, peach and citrus orchards, showed insufficient growth and visible Zn deficiency symptoms (leaf rosetting) and low leaf Zn content. The main reason for low Zn uptake was due to high available P, Fe and Mn which are known to be antagonistic to uptake and root surface and translocation the chronic Zn deficiency contributed to the decline and resulted in increase of plant deficiency.

Salinity and anatomical structure of plants

Soil salinity is a major agricultural problem in arid and semi-arid regions. Morphology, anatomy and metabolism of plants are deeply affected by salt stress. Anatomical disturbances in stems due to salinity have been reported (Gadallah and Ramadan 1997). Responses to salinity are often expressed as anatomical and cytological changes. Zn is necessary for root cell membrane integrity. External Zn concentration may mitigate the adverse effect of NaCl by inhibiting Na^+ and Cl^- uptake or translocation (Alpaslan *et al.* 1999). In saline soils, despite higher Zn solubility, its availability decreased with soil salinity. To recognize the possible pro-

Table 11 The role of zinc sulphate on the onion yield, quality, nitrate and cadmium contaminants (from Malakouti and Bybordi 2006).

Treatment	Yield (ton.ha^{-1})	Nitrate (mg kg^{-1} FW)	Cadmium (mg kg^{-1} DW)	Ascorbic acid (mg.100 g^{-1})	Dry matter (%)
NP (T_1)	43.8 C	229 A	0.27 A	12.0 C	11.0 C
NP+K (T_2)	47.5 B	170 B	0.10 B	13.0 B	13.8 B
NPK+Zn (T_3)	49.0 A	80 C	0.10 B	14.0 A	14.0 A

Table 12 Shoot and root dry weights of wheat, Zn, Na concentrations, and K/Na, Ca/Na ratios in shoot as affected by Zn and salinity (from Keshavarz and Malakouti 2007).

Zn (mg kg^{-1})	Salinity (mM)	Dry weight (g.pot^{-1})		Concentration (g.kg^{-1})		K/Na	Ca/Na
		Shoot	Root	Zn	Na		
0	0	7.63 b*	0.921 a	4522 b	2.52 c	10.41 a	1.43 b
	100	2.70 d	0.180 b	1865 d	8.47 a	1.70 c	1.09 c
10	0	7.96 a	0.954 a	7398 a	2.64 c	9.61 a	1.42 b
	100	3.30 c	0.197 b	3740 c	3.49 b	4.50 b	2.75 a

* Values were compared using a Duncan multiple range test at the 95% level.

tective role of Zn against salinity by changes in chemical and anatomical structure of wheat, 20 calcareous soil samples were collected from different regions of Khorasan province in Iran. Pot experiment was carried out on wheat. The soil samples were salinized by adding saline water (100 mM NaCl + $CaCl_2$ prepared with the same equivalents). Zn was applied to the soil at the rates of 0 and 10 mg kg^{-1} of $ZnSO_4.7H_2O$. The plants were harvested 12 weeks after planting, and stem segments were taken from the 2cm above soil surface level (Gadallah and Ramadan 1997). The stem diameters and the thickness of vessels were determined by ocular micrometer using a light microscope. The shoot and root dry matters were determined, the amount of Zn^{2+} and Ca^{2+} concentrations were measured in the shoots with the atomic absorption instrument, and the Na^+ and K^+ concentrations were measured by a flame photometer. The results revealed that root and shoot growth of wheat was restricted by increased salinity. The salinity-induced dry weight reduction was more severe in the roots than in the shoots. However, the dry weight increased with Zn application, respectively, to 4.1% and 18.2% for the shoots, 3.4% and 8.6% for the roots in non-saline and saline soils. The application of 10 mg kg^{-1} Zn increased K/Na and Ca/Na ratios (**Table 12**). Salinity and Zn treatments induced structural changes in the stem of wheat. The stem diameter as well as number of vascular bundles decreased in salinity stressed plants. The relative thickness (RT) of the pith was increased in saline conditions. The Zn application improved the formation of vascular tissues and increased the number of vascular tissues in unstressed and stressed plants. The lower shoot and root dry weight due to salinity is attributed to water stress, Na^+ toxicities, and ionic imbalance in the plant. Although adding Zn alleviated Zn deficiency, it did not offset ill effects of high solubility on plant growth. On the other hand, increasing soil salinity decreased pH and Eh and increased Zn concentration (Keshavarz and Malakouti 2007).

FATE OF APPLIED Zn-FERTILIZER ON THE CALCAREOUS SOILS

Physical and chemical properties of soils influence the distribution of native and applied Zn among its different forms. Low soil test Zn values do not always imply that the soil is not deficient for crop production nor do the higher values necessarily mean toxicities to crops. For a better understanding of Zn dynamics, soil scientists have partitioned total Zn into different pools. After incubation of Zn with soil, the availability of Zn to plant decreases presumably due to transformations of various forms of the Zn added to soil (Ma and Uren 1997). As general rule, Zn is immobile, it is rapidly converted insoluble forms in calcareous soils and hence, will not contribute to the groundwater contamination. However, due to soil erosion, Zn can be formed in flooded rivers, especially during wet season. Results obtained from a series of experiments using sources of irrigation water (Haraz river and underground water) on paddy soils in Mazandaran province indicated that paddy yields were increased significantly with irrigation water from Haraz river mainly due to its Zn content (Malakouti and Davoudi 2003).

Fractionation studies revealed that various fractions of Zn exist in a state of dynamic equilibrium and together constitute the labile pool responsible for plant available Zn. Yasrebi *et al.* (1994) have concluded that in highly calcareous soils, water soluble Zn-fertilizers are rapidly converted to insoluble forms resulting in lower efficiency of such fertilizers. The forms determined were exchangeable Zn (EXZn), sorbed Zn (SRZn), organic Zn (ORZn), carbonate Zn (CRZn), residual Zn (RSZn) and sum of Zn (SMZn) forms. The native SMZn forms ranged from 32 to 67% with a mean of 50%. Application of 10 and 20 mg kg^{-1} Zn as $ZnSO_4.7H_2O$ increased the mean to 58 and 63%, respectively. Concentration of different forms of Zn in the soil was determined to be in order of RSZn>>>CRZn> SRZn>EXZn >ORZn. The concentration of native EXZn+ SRZn+ ORZn forms constituted less than 5% of SMZn, while concentration of CRZn alone ranged from 4 to 16.0%. About 60% of the applied Zn-fertilizer was converted to CRZn. They concluded that conversion of applied Zn-fertilizer to CRZn was mainly responsible for retention of this fertilizer in highly calcareous soils, making it temporarily unavailable to plants, and therefore decreasing its apparent recovery by the first crop. It was also announced that Zn remains available for plants up to 6-crop in sequence mainly due to low availability of $ZnCO_3$ to plants.

Tehrani (2003) studied the fate of applied Zn in soils of India and found that Zn became almost unavailable to plants after a second crop in the sequence of wheat-maize and the major part moved to a residual fraction. He found that Zn application increased dry matter and Zn concentration in wheat and maize. N application enhanced Zn but P-fertilizers reduced Zn concentration and uptake. In terms of the relative abundance of different Zn fractions in soil, the sequence was water soluble < exchangeable < specifically absorbed < amorphous FeO < acid soluble < MnO-occluded < OM-occluded < crystalline FeO <residual fraction. There was no build up of Zn in available form. This means that in a Zn deficient soil, to get higher yield with optimum Zn nutrition, regular application of Zn-fertilizers are necessary. He also observed that more than 90% of applied Zn gets fixed on the soil. In another experiment, Tehrani (2007) studied Zn fractionation at three growth stages; at plantation time, one month after plantation and at harvesting time and its availability to wheat in Zn deficient calcareous soils and he found that the amounts of different Zn forms of the soils under the study were in the order of RSZn >> CRZn > SRZn > ORZn > EXZn which was almost similar to the findings of Yasrebi *et al.* (1994). He concluded that the highest contents of exchangeable and sorbed Zn were observed in the first stage with a mean value of 0.22 and 2.00 and decreased gradually in the second and third stages. Backward stepwise regression analysis indicates that exclusion of each of the Zn fractions from the model decreased the predictability of yields and the total Zn uptake by the crop. The model could not exclude those variables which are in the significant predictability. The highest significant fractions were for sorbed which could predict 38% of the wheat yield variations (Y= 0.795+0.302 SRZn). Total Zn uptake variation were 24% predictable by the carbonate and organic Zn forms (uptake = 3.399+6.434 CRZn+33.833 ORZn). He concluded that application of zinc sulphate resulted in an increase in all forms of Zn. The apparent low recovery of Zn-fertilizers in highly calcareous soils is mainly due to the conversion of applied Zn to the carbonate form.

HOW DO Zn-FERTILIZERS IMPROVE HUMAN HEALTH?

In the third millennium, the promotion of human health should be the priority of the crop producers. So, balanced fertilization should be seriously practiced. To begin with, the wheat produced in Iran is low in Zn and high in PA/Zn molar ratio[1]. Besides, in the bread making process we often waste the Zn containing wheat bran. Therefore, our society will suffer from Zn deficiency. Research work on Zn deficiency carried out recently in the countries where the people's staple foods consist of bread and polished rice has lead the research scientists to address this problem as a worldwide phenomenon (Malakouti 2003). Since bread is our main staple food (500 g/day/person), it should be considered as the main target for enrichment and proper handling. A great portion of wheat grain Zn is contained in the bran which is currently discarded in the process of bread making. Moreover, phytic acid at high concentration would combine with Zn and other micronutrients in the intestine and prevent them from being absorbed. To prevent higher molar ratio of phytic acid to Zn (PA/Zn), soil fertilization with Zn-fertilizers and minimizing phosphate application would be necessary. Zn application improves the yield and quality of agricultural crops and thus with improved quality and abundant food supplied the consumers well being will improve (Malakouti *et al*. 2006b). Zn-fertilizers application significantly improved the concentration of Zn in cereal grains and reduced PA/Zn molar ratio. An application of Zn improved Zn content of wheat grain (enriched) and enhanced human health (Malakouti *et al*. 2006b).

CONCLUSIONS

The occurrence of Zn deficiency in calcareous soils is prevalent and increasing alarmingly year by year. There is an urgent need to target the problem correctly, particularly for precise fertilizer recommendations (Malakouti *et al*. 2006b). In order to achieve the mission of precision agriculture, it is quite appropriate to find out the influence of soil characteristics on Zn availability that can be used for crop management (Havlin *et al*. 2005). This review is intended to establish the importance of Zn in the life cycle of plants (Malakoti and Mashayekhi 1996).

This paper summarizes the extent of Zn deficiency in calcareous soils and the related crops as well as their influence on crop productivity. Among micronutrients, Zn deficiency is the most common problem which causes reduction in yield, total production and Zn malnutrition (Cakmak 2006). Zn is taken up predominantly as Zn^{2+} and at high pH, it is presumably also taken up as $ZnOH^{+}$. In long distance transport in the xylem, Zn is either bound to organic acids or occurs as the free divalent cation and in the phloem sap its concentration is relatively high. There are a large number of enzymes in which Zn is an integral component of the enzyme structure. The metabolic functions of Zn are based on its strong tendency to form tetrahedral complexes with N-, O- and S-ligands and it thereby plays both a functional and structural role in enzymes reactions (Marschner 1995).

Strategies involving application of Zn-fertilizers in soil, seed treatment, foliar sprays or use of organic manure have been proven to sustain optimum yield potential and enhance Zn content in seeds, forages and vegetable crops to curb Zn malnutrition and achieve nutritional balance (Balali *et al*. 2001). The collected data for the relationship between soil properties and Zn availability revealed that free $CaCO_3$ content, bicarbonate in irrigation water, pH value, and available P, Fe and Mn concentrations have antagonistic effects on its availability (Alloway *et al*. 2004). However, soil organic carbon, K, N and Mg concentrations and clay content have synergistic effect on Zn availability (Ma and Uren 1997). Soil salinity and sodicity increase Zn solubility in soil solution but decreases Zn uptake (Rezaei *et al*. 2006).

Calcareous soils that are dominant soil formations in Iran have high pH value (7.7-8.2) and low organic carbon contents (less than 1%), therefore, the crops usually contain lower than average levels of Zn. The low annual precipitation also enhances the Zn deficiency in such regions (Malakouti 2000). The physical and chemical properties of soils influence the distribution of native and applied Zn among its different forms (Yasrebi *et al*. 1994). The low apparent recovery of Zn-fertilizers in highly calcareous soils is mainly due to the conversion of applied Zn to the carbonate form (Tehrani 2007). The DTPA extractable Zn in such soils is often less than 1.00 mg kg^{-1} whereas under favorable conditions it should exceed 1.00 mg kg^{-1}. Zn deficiency limits plant growth and affects the crop yield diversely. Based on the analyses of more than 50,000 soil samples, about 80 percent of the cultivated soils of Iran face Zn deficiency. Field tests on more than 2,500 farms have shown that Zn fertilization had a significant positive effect on crop yields, seeds vigor and their quality. The resulting enriched seeds would improve the grain yield, protein content, Zn concentration, lower the seeding rate and reduce PA/Zn molar ratio (Erdal *et al*. 1998; Tehrani *et al*. 2002).

There is an urgent need for improving Zn nutritional status of calcareous soils. Most farmers and many research institutes were not aware of Zn deficiency in crops until early 1990s (Cakmak 2006; Malakouti *et al*. 2006b). The most effective method of Zn application for improving yield and increasing Zn concentration for different crops such as grains and beans would be soil application of $ZnSO_4.7H_2O$ (Yilmaz *et al*. 1997). Other methods of Zn application include soaking the seeds in zinc sulphate solution, foliar application and fertigation with Zn-EDTA and seed treatment. Zn fertilization in Zn deficient soils has been shown to improve the yields of crops, especially cereals, oilseed plants, vegetables, beans and orchards as well as Zn content of the edible parts of the plants. Currently, annually about 30,000 tons of Zn-fertilizers in the forms of complete fertilizers, powdered, granulated zinc sulfate and Zn-EDTA are applied for crop production in Iran (Malakouti 2006).

Despite the enormous investigations and many research findings that clearly indicate crop productivity improvements by Zn application, Zn-fertilizers are not commonly applied by farmers. This implies that there is a large gap between research, education and extension in transferring the valuable scientific information to farmers and in changing their habits of conventional fertilization practices. Despite these progresses, still more efforts are needed to increase Zn-fertilizers efficiencies, environmental related issues and economical aspects to achieve sustainable agriculture for food security and human health.

[1] According to WHO (1996) and Gibson (1998) the molar ratio of phytic acid to zinc (PA/Zn) should be less than 15.

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