Effect of Fertilizer Type and Growth Duration on the Availability of Zinc in the Rhizosphere of Maize (Zea mays L(.

Ahmed Murad AL-Zayadi1 Raid Shallan Jarallah1

1Department of Soil Science, College of Agriculture, Al-Qadisiyah University
ahmed.murad@qu.edu.iq raid.jarallah@qu.edu.iq

Abstract

The current study aimed to investigate the effect of fertilizer type and vegetative growth duration on the availability of zinc elements in the rhizosphere and bulk soils of maize crop. Six fertilizer treatments were applied, including mineral fertilizer, organic waste, and humic acid (each at two levels), and the control, with three replications. Soil samples were taken 70 and 100 days after cultivation to estimate available zinc in the rhizosphere and bulk soils. The humic acid treatments resulted in the greatest values of the available zinc concentration of 1.40 and 1.31 mg kg-1, respectively, at 70 days for the rhizosphere and bulk soils. Poultry waste application resulted in the greatest values of the available zinc concentration 1.40 and 1.12 mg kg-1 100 days after cultivation for the rhizosphere and bulk soils, respectively. The results present a decrease in the concentration of available zinc with the increase in growth periods

K**eywords: Maize; Zink; fertilization; rhizosphere; organic fertilizer; humic acid**

Introduction

Zinc is one of the eight microelements that are essential for the healthy growth of plants. Zinc, copper, boron, iron, nickel, chlorine, manganese, and molybdenum are required by plant tissues in small quantities of 5-100 mg. kg-1 [1]. It plays an essential role in many plant physiological processes. Zinc is an essential element for proper plant growth. Its presence in large quantities causes contamination of soil, water, and food chains. Soil predominantly zinc-deficient is sandy, calcareous, saline, and moist [2]. Most plants contain 100-300 mg. kg-1 of zinc in the dry matter, which, when exceeded, becomes toxic. Maize, rice, sorghum, beans, citrus, and grapes are the most sensitive plant species to zinc deficiency. Therefore, biofortification is essential for accumulating high concentrations of zinc and alleviating human health problems caused by zinc deficiency [3]. It is considered an essential phytonutrient that participates in the physiological processes in the plant.

Zinc is essential in crop resistance against drought stress, stimulates antioxidant enzymes, and is needed by more than 300 enzymes as a mineral cofactor. Foliar application of zinc and manganese increases grain yield in wheat grown under drought stress [4]. In addition, when water supplies are scarce, zinc increases photosynthesis, pollen activity, and the number of grains per spike, thus raising water use efficiency and increasing micronutrient concentration in the grain .

Microelements are found in soil naturally in low concentrations. However, zinc is one of the components of many compounds emitted into the environment, and agriculture is one of the primary sources of soil pollution [5]. The average total zinc concentration in the soil is about 55 mg.kg-1 from a typical range of 10-

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300 mg.kg-1. The global average for zinc is 64 mg.kg-1. Soils containing large amounts of zinc could have originated from parent rocks containing weathered zinc minerals such as zinc sulfate, zinc carbonate, and zinc oxide [1]. Zinc in the soil can be evaluated based on particle size or chemical analysis and divided into three main parts: the first is the water-soluble zinc (found in the soil solution and associated with soluble organic matter), and the second part is the absorbent and interchangeable part in the colloidal part (linked to clay and iron particles, aluminum hydroxides and humic compounds), and the third is insoluble zinc aggregates in the solid phase [6]. The main soil factors that control the availability of zinc in the soil are those that affect the amount of zinc in the soil solution, the most important of which are: total zinc, clay content, redox potential, the activity of microorganisms in the soil, and the presence of nutrients Others, climatic conditions [2]. One of the most significant adverse effects of increasing zinc concentrations in the soil is the inhibition of soil enzymes [7]. The inhibition is more significant in sandy soils than in clay soils because clay soils work to protect the enzyme activity and the resulting harmful effects on the vital activities of the plant and the availability of many nutrients in the soil.

Zinc availability is low in Iraqi soils because of its high content of carbonates and silicic minerals and its high pH, which exposes zinc to adsorption and fixation reactions[8]. As a result, zinc presents, as is the case with other trace elements, in different forms [1 and 9 :[

- Water-soluble zinc is found in soil solutions.
- Exchangeable zinc: includes ions associated with soil particles through electric charges
- Organically bound zinc: adsorbed or chelated ions or complexes are formed by organic bonds.
- Zinc adsorbed on clay minerals and hexagonal oxides.
- With other minerals that can turn into soluble parts after exposure to weathering processes.

The following factors influence zinc availability:

Soil pH

Soil pH dramatically affects the solubility of zinc. Zinc precipitates as slightly soluble zinc hydroxides and carbonates when the pH values are raised. It leads to a decrease in plant readiness. The adsorption of heavy elements increases with the increase in pH due to the decrease in competition with hydrogen ions [10]. Therefore, alkaline soils suffer from a permanent zinc deficiency due to adsorption processes on clay surfaces and calcium carbonate or precipitation in the form of carbonate and poorly soluble zinc hydroxides. The Iraqi soil contains high levels of active lime. Most of the nutrients are subjected to stabilization processes, and thus their availability decreases [11-13.[

Organic matter

Organic matter has a vital role in the availability of zinc for plants through the formation of organic complexes, soluble and insoluble with it, and accordingly, the effect of organic matter is positive or negative on the availability of zinc [14.[

Soil texture and content of hexagonal oxides

The adsorption of heavy metal ions on the surfaces of metal oxides in the soil plays a vital role in the fate and transport of heavy metal ions in the natural environment [15]. Therefore, more significant amounts of zinc aggregate with iron and manganese oxides tend to be more available to plants. In

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addition, the type of clay minerals also affects the soil zinc content, such as vermiculite and gibbsite [16,17 .[

Soil immersion with water

Indicated that zinc availability decreases when the soil is immersed in water due to the interaction of zinc with free sulfide. Therefore, it is recommended to add zinc sulfate in rice fields, in contrast to iron and manganese elements. The lack of zinc availability in the submerged soils is its deposition in zinc sulfur or the mineral ZnFe2O4 franklinite[18,19.[

Level of phosphorus in the soil

The process of adding phosphorus in large quantities to the soil is one of the reasons that reduce the availability of zinc. Researchers have mentioned several reasons for this situation, which leads to the precipitation of zinc in the form of zinc phosphate, which leads to a decrease in the zinc concentration in the soil solution. The second opinion is that phosphorus slows down the transfer of zinc to the roots, and some oppose this explanation because zinc phosphate is poorly soluble and they believe that the negative effect is due to the mutual physiological effect between phosphorus and zinc inside the plant and not in the soil [18-21]. The adsorption process of zinc occurs on soil joints, especially clay, which outperforms the rest of the joints by adsorption due to the high ratio of expanded minerals of type 2:1, such as smectite mineral, and the specific surface area rise [16,22,23]. When clay is compared with other aggregates, which are characterized by a decrease in the specific surface area and thus less adsorption. zinc interacts with all the anions present in the soil, which include nitrates, phosphates, sulfates, chlorides, and molybdates. There is no problem with zinc availability to plants in the presence of nitrates, sulfates, and chlorides dissolved in water[20]. Molybdate and borate have little effect on zinc availability. Phosphates reduce zinc absorption .

Most of the zinc, applied to the soil as fertilizers, is subjected to adsorption and precipitation reactions during incubation, which does not exceed two weeks. Therefore, the amount of zinc retained may decrease with the increase in the sand in the soil. In addition, studies indicate that heavy elements are subjected to severe sequestration due to the exposure of the ions of these elements to fixation, especially in conditions of high pH in calcareous soils [24.[

Nitrogen-containing fertilizers are among the most efficient and effective fertilizers in increasing vegetative growth and the size of roots. However, this increase makes the plant need to supply the rest of the nutrients, which leads, if not added, to a deficiency in supplying it to plant[1.[

Using nitrogen in the absence of zinc could lead to a decrease in zinc absorption through the significant depletion of zinc from the rhizosphere resulting from increased vegetative growth and the need for continuous supply to continue the physiological activities of the plant [24]. It was noted that there were no significant differences in the amount of ready zinc when adding nitrogen and phosphorous [26]. The interaction of using nitrogen fertilizers with the application of zinc led to an apparent increase in the productivity of grain crops such as wheat and maize. There is a great need for a balanced application of many micronutrients to avoid the occurrence of a shortage in the supply and readiness of these elements, which negatively affects the yield [27]. The dynamics and transformations of zinc and copper in soils are subject to various factors.

Organic matter is among the most critical factors and directly and indirectly, affects

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nutrient transformations. Organic matter is a source of organic carbon in the soil, accounting for approximately 60% of the organic matter content [28]. There is an affinity between the dissolved organic matter and the elements copper and zinc through cationic bridges [22]. The sequential addition of the dissolved organic matter led to a higher affinity than the simultaneous addition, as the binding sites on the iron oxides were coated with the dissolved organic matter. The study showed differences in the effect of the application of dissolved organic matter on zinc and copper retention. Humic acids are organic substances with large molecular weights ranging from (2-1300 kDa) characterized by their ability to dissolve entirely in alkaline media, partially in the water, and insoluble in acidic media. It contains many functional groups such as phenols, carboxyl, hydroxyl, ketone, and ethers, which are the main reason for the high affinity of humic acids to bind with nutrients. It works through it to transfer micronutrients from the soil to the plant, remove heavy metals from soil and water, inhibit the formation of free radicals, and reduce and stabilize metal nanoparticles. In addition, it can form chelates with positive metal ions in the soil solution and is very important in the movement of nutrients and their readiness for the plant.

The process of complexing with positive ions occurs by dissociating functional groups from humic acids, mainly phenolic and carboxyl groups, which are more effective, leading to the formation of a negative charge on the acid, which is directly associated with the positive ions dissolved in the soil solution (and this process is affected by pH) [30-33]. Accordingly, the research aimed to study the effect of fertilizer type and growth periods on zinc readiness in the rhizosphere soil of yellow corn plants and outside it (bulk soil.(

Materials and Methods

This research studied the effect of several fertilizer treatments on the availability of zinc elements inside and outside the rhizosphere of the maize (Zea mays L.). A field experiment was conducted during the fall season in 2022 in Al-Diwaniyah Governorate-Iraq, in Sumer county, which is 25 km north of the city of Al-Diwaniyah X: 4992010, Y: 3766942. The soil texture of the field was clay loam. The yellow corn crop was cultivated, and the experiment included the application of the following fertilizer treatments:

- Control treatment.
- M1= Nitrogen fertilization treatment (urea 46% N) 400 kg ha-1
- M2= Nitrogen fertilization treatment (urea 46% N) 200 kg ha-1
- H1= Fertilization treatment with liquid humic acid 1000 ml per 100 ml water per dunum
- H2= Fertilization treatment with liquid humic acid 500 ml per 100 ml water per dunum
- O1= Fertilization treatment with organic waste (poultry waste) 8 tons ha-1
- O2= Fertilization treatment with organic residues (poultry waste) 4 tons ha-1

A factorial experiment was conducted using a Randomized Complete Block Design (R.C.B.D) with three replicates. The treatments were distributed randomly. Seeds of a local variety of maize (Zea mays L.) were sown on 7/17/2022. The plantation is done on lines, and the distance between one line and another is 75 cm, with 4 lines per plot and 25

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cm between one planting point and another within a line. The planting density was 53333 plants ha-1. Three maize seeds were planted at each planting point, and after 10 days of germination, the plants were thinned to a single seedling.

The whole field was fertilized with DAP fertilizer at 400 kg ha-1 for all experimental units. The corn stalk borer insect (Sesamia cailica L.) was controlled by using diazinon granular 10% effective substance, inoculated on the growing tops of the plants twice, the first after 25 days of germination and the second after 10 days of the first one. Manual hoeing of bushes was carried out whenever needed. The irrigation was carried out in equal amounts, regularly according to the plant's needs. Soil samples were randomly taken from the field before planting at a 0-30 cm depth. They were mixed well and homogenized to obtain a composite sample representative of the entire field. The sample was air-dried in the laboratory, then ground with a wooden hammer, and passed through a sieve with a diameter of 2 mm to conduct the physical and chemical analyses shown in Table (1 .(

Table 1: Chemical and physical Characteristcs of field soil before planting

Trait		Value	Unit
PH		7.8	
Electrical conductivity		3.23	$Ds.m^{-1}$
Ionic exchange capacity		20	$Cmol.Kg^{-1}$
Carbonate minerals		240	$gm.Kg^{-1}$
Organic matter		12.4	$gm.kg^{-1}$
Cations	Ca^{+2}	60	$mmol.L^{-1}$
	Mg^{+2}	36.	$mmol.L^{-1}$
	Na^{+1}	14.7	$mmol.L^{-1}$
Anions	$SO4^{-2}$	43.6	$mmol.L^{-1}$
	$HCO3^{-1}$	6.5	$mmol.L^{-1}$
	Cl^{-1}	9.1	$mmol.L^{-1}$
zinc	Total	31	$Mg.Kg^{-1}$
	Available	1.6	$Mg.Kg^{-1}$
Texture	Sand	208	gm. Kg^{-1} soil
	Silt	407	gm. Kg^{-1} soil
	Clay	385	gm. Kg^{-1} soil
Soil Texture		Clay loam	
Bulk Density	1.18		Mega $gm.Kg^{-1}$

Results and Discussion

Available zinc at 70 days after planting

Table 2 presents the effect of applying levels of mineral fertilizer, organic fertilizer, and humic acid on the values of zinc concentration availability in the rhizosphere and bulk soil after 70 days of sowing maize crops. The statistical analysis results present significant differences at a significant level of 0.05 between the levels of fertilizer treatments in the rhizosphere compared to the control. The treatment of humic acid (H1) fertilizer at the recommended dose resulted in the highest significant effect on the available zinc

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concentration in the soil of the rhizosphere, 1.40 mg kg-1, with an increase of 21.7% compared to the control, 1.15 mg kg-1. On the other hand, it decreased the available zinc concentration in the bulk soil by 1.42 mg kg-1 compared to the half-recommendation treatment (H2). This may be due to the increased level of plant uptake of available zinc in the soil rhizosphere and the movement of nutrients from outside the rhizosphere into the interior by mass flow or diffusion from an area of high concentration to a low concentration. It is consistent with what [34] mentioned. As for the half-recommendation treatment (H2), its concentration of available zinc in the soil of the rhizosphere was 1.31 mg kg-1, with an increase of 13.9% compared to the control treatment. In the bulk soil, this level resulted in significant differences compared with the control, and the available zinc concentration was 1.56 mg kg-1, with an increase of 11.4%. It is due to the role played by the available humic acid in the formation of chelates with positive metal ions in the soil solution, which are influential in the movement of nutrients and their availability for the plant, as well as in reducing the pH in the rhizosphere and thus increasing the availability of nutrients. These results are consistent with what was found by[31], who stated that the complexation process occurs with positive ions by dissociating functional groups from humic acids and forming a negative charge on the acid associated with a positive ion .

A decrease in zinc in the bulk soil with the fertilization at the recommended dose compared to the half-recommendation treatment. This confirms the decrease of zinc in the soil outside the rhizosphere in the fertilizer recommendation compared to the half-recommendation treatment, which confirms what we have reached of the element moving towards the soil of the rhizosphere. The available zinc concentration in the recommended treatment for nitrogen fertilization M1 was 1.29 mg kg-1, with an increase of 12.1% compared to the control treatment. It showed a significant effect compared to the control treatment. As for the soil outside the rhizosphere, the available zinc concentration was 1.37 mg kg-1, lower than the control treatment that gave a ready zinc concentration of 1.40 mg kg-1, with a decrease of 2.1%. The reason may be due to the rhizosphere's rapid depletion of available zinc. This is consistent with what was found by Erenoglu et al. (2010), who reported that plants deplete zinc in high-nitrogen soils faster than in soils with a lower nitrogen concentration. It leads to a transfer of zinc dissolved in the soil solution towards the rhizosphere in the manner of diffusion until reaching the state of equilibrium.

The other treatment (half recommendation), M2, resulted in a concentration of available zinc in the soil of the rhizosphere of 1.25 mg kg-1, with an increase of 8.6% compared to the control. In the bulk soil, it was 1.58 mg kg-1. It is due to the effect of nitrogen fertilizers in reducing the pH and the significant depletion of zinc due to the effect of these treatments on increasing the vegetative growth of the plant and the size of the roots, which leads to the absence of a supply of zinc through fertilization to a severe deficiency that affects the physiological processes of the plant. Furthermore, it is consistent with what [35] found that increasing nitrogen supply improved root density, surface area, and dry weight, which led to increased zinc uptake. Therefore, it was concluded that the combination of good nitrogen supply,

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breeding, and improvement of plant species

improvement in the uptake of roots and the accumulation of zinc in grains.

The O1 treatment significantly affected the available zinc concentration in the soil of the rhizosphere by 1.25 mg kg-1, with an increase of 9.2% compared with the control treatment. As a result, the bulk soil resulted in a concentration of available zinc of 1.54 mg kg-1. On the other hand, the O2 treatment resulted in a significant decrease compared to the control treatment in the soil of the rhizosphere and sulk soil. The reason may be due to the high ability of the organic matter to retain heavy elements such as zinc due to its high specific surface area. It is consistent with

with a sound root system could lead to an

the findings of [36], who indicated that zinc uptake in the soil is primarily controlled by organic matter, which determines its bioavailability in soil.

From the above results, we find that the concentration of zinc in the studied treatments in the soil of the rhizosphere followed the following pattern during the growth period of 70 days of cultivation:

H1>H2>M1>M2 = O1>O2

This sequence presents that the treatments that represent half of the recommendation (O2, M2, H2) were the lowest in the supply of zinc for all types of studied fertilizers.

Table 2. The effect of fertilizer type on the available zinc concentration in the soil after 70 days of planting mg kg-1.

Fertilizer Type	Rhizosphere soil	Bulk soil
Cont.	1.1 5	1.40
M1	1.29	1.37
M2	1.25	1.58
H1	1.40	1.42
H2	1.31	1.56
O1	1.25	1.54
O2	1.17	1.39
L.S.D at 0.05	0.03540	

Available zinc after 100 days of planting

Table 3 presents the effect of nitrogen and organic fertilization treatments and humic acid levels on the available zinc concentration in the rhizosphere soil and outside it after 100 days of cultivation. The concentration of available zinc in all treatments was less than its content in the first period (70 days). It may be due to the increase in solid growth and nutritional needs in this period (the stage of maturity) and the occurrence of absorption of nutrients from the soil to carry out the vital activities of the plant. The results present significant differences at a significant level of 0.05 between all treatments and the control. All treatments outperformed the control treatment in rhizosphere soil regarding zinc availability .

The treatment of fertilization with poultry waste O1 resulted in the highest concentration of available zinc in the rhizosphere soil, 1.16 mg kg-1, compared with the control treatment, 0.93 mg kg-1, with an increase of 24.7%. As

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for the O2 treatment, it produced the available zinc values in the soil of the rhizosphere 1.12 mg kg-1 with an increase of 20.4% compared to the control. The reason for this treatment in this period may be due to the increase in the decomposition of organic matter with time and the release of dissolved organic carbon (DOC) and cations. This is consistent with what was found by [37], who mentioned that the peak availability of zinc in the soil treated with organic matter occurs when the organic matter decomposes and the dissolved organic carbon flow increases, especially with the rise in temperature, which leads to the release of these nutrients. The result indicates a significant difference at the significance level of 0.05 between the two treatments of poultry waste. The lowest concentration of available zinc was with humic acid fertilization treatments. The two treatments resulted in a concentration of 1.04 and 0.96 mg kg-1 for the two treatments, H1 and H2, with an increase of 11.8% and 3.2%, respectively, compared with the control. The reason behind this decrease in the concentration of available zinc in humic acid treatments may be due to a decrease in the concentration of the acid as a result of its depletion after 100 days or exposure of the acid to adsorption reactions on the surfaces of the oxides, or its deposition in the form of complexes with zinc. It is consistent with what was found by [30], who stated that zinc liberation depends mainly on the concentration of humic acid, the pH in the solution, and soil properties, which affect the availability of humic acid molecules in the soil solution and the degree of complexation (chelating) with zinc. The precipitation of zinc-humic acid complexes in the soil delays the liberation of zinc because it is affected by the amount of organic matter, clay, and oxides.

Regarding the nitrogen fertilization treatments M1 and M2, the concentration of available zinc in the rhizosphere soil after 100 days was 1.12 and 1.05 mg kg-1, with an increase of 20.4% and 12.9%, respectively, with significant differences compared with the control. The reason for the decrease in the ready zinc concentration in the soil of the rhizosphere after 100 days compared to the period of 70 days may be due to the absorption of ready zinc as a result of high vegetative growth, as well as the exposure of nitrogen to volatilization in the form of ammonia with the help of the urease enzyme present in the soil, which increases with the increase in the activity of microorganisms and is in Its maximum is in the rhizosphere [38.[

The Table shows the high concentration of available zinc in the bulk soil for all treatments. The control treatment resulted in the highest concentration of available zinc in the soil outside the rhizosphere, recording significant differences with all treatments at 1.85 mg kg-1. The reason for the decrease in available zinc in the soil outside the rhizosphere for all treatments compared to the control treatment may be due to the sufficiency of the plant with what is present in the rhizosphere, and therefore it did not generate stress on the zinc present in this region and thus to its accumulation. In addition, the increase in the control treatment is due to the small size of the plant compared to the rest of the treatments and, thus, the decrease in its nutritional needs. As for the rest of the treatments, the concentrations of available zinc in the mineral fertilization treatments were 1.78 and 1.66 mg kg-1, respectively, recording a decrease of 8.5% and 0.210% compared to the control. As for the fertilization treatments with humic acid H1 and H2, it made a concentration of available

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zinc outside the rhizosphere of 1.69 and 1.61 mg kg-1, respectively, with a decrease of 8.6% and 12.9%, respectively, compared to the control .

The poultry waste treatments O1 and O2 resulted in a concentration of available zinc in the bulk soil of 1.69 and 1.62 mg kg-1, respectively, with a decrease of 8.6% and 12.4%, respectively, compared to the control.

The available zinc concentration in the studied treatments in the rhizosphere followed the following form at the growth period of 100 days of cultivation.

O1>O2=M1>M2>H1>H2

The treatments of H2, and M2, resulted in the least values of zinc availability. However, the treatment O2 and M1 had similar values at 70 and 100 days. Therefore, it indicates that the half-recommendation treatment of poultry waste is equivalent to what the recommended treatment of mineral (nitrogen) fertilizer provides. Furthermore, the application of humic acid fertilizer was the highest in zinc processing during the 70 days but the lowest during the 100 days.

Table 3. Effect of fertilizer type on the concentration of available zinc in the rhizosphere and bulk soil after 100 days of planting.

Fertilizer Type	**Rhizosphere soil**	**Bulk soil**
Cont.	0.93	1.85
M1	1.12	1.78
M2	1.05	1.66
H1	1.04	1.69
H2	0.96	1.61
O1	1.16	1.69
O2	1.12	1.62
L.S.D at 0.05	0.1190	

Tables (2 and 3) present a continued decrease in the zinc concentration available for all treatments, with an increase in the growth period in the rhizosphere soil, Figure (1). It indicates the occurrence of zinc absorption from bulk soil to the region of vital activity (rhizosphere) to compensate for its deficiency. The highest depletion of available zinc in the rhizosphere soil was in the two periods (70 and 100) days, and the highest absorption of available zinc was in the rhizosphere during 100 days. As for the soil outside the rhizosphere, it had the highest absorption at the period of 70 days, and this is due to the increase in the nutritional requirements of the plant in the flowering stage on the one hand and to the transfer of zinc to the rhizosphere more than it is in 100 days of cultivation .

The highest supply of zinc was with the humic acid treatments in 70 days, while the highest was in the poultry waste treatments in 100 days. It indicates the role of time in increasing the decomposition of organic matter and the supply of zinc. As for the available zinc, values ranged between 0.93-1.69 mg/kg, higher than the critical values for zinc in adult maize 0.7 mg kg-1 16

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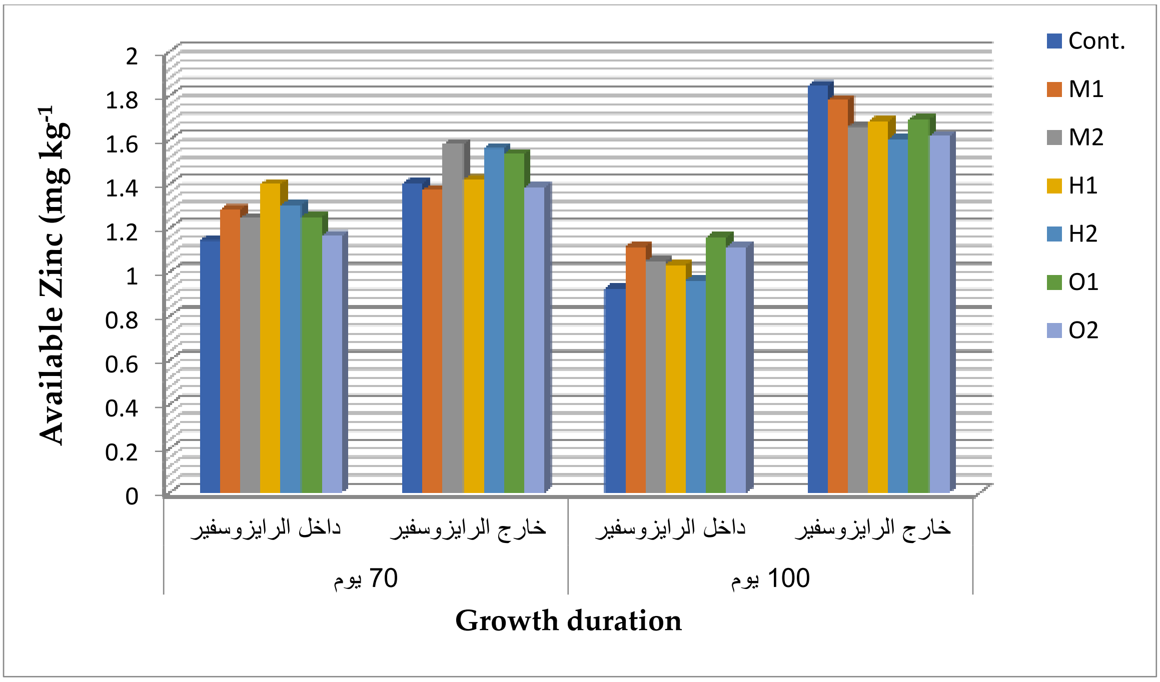

Figure 1: The effect of fertilizer type and growth periods on the available zinc concentration in the soil.

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