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Role of Organic and Mineral Fertilizers in the Availability of Molybdenum in the Rhizosphere and Beyond of Maize

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ABSTRACT

Molybdenum plays an important role as a nutrient for plants. It has an important role in the process of plant growth and fixing nitrogen for the plant. A field experiment conducted in the autumn of 2023 aimed to study how different fertilizer treatments affected the availability of molybdenum in maize (*Zea mays* L.) rhizosphere and non-rhizosphere soils. The treatments included sheep manure at a rate of 8 tons per hectare, urea at 400 kg per hectare, humic acid at 500 cm^3 per liter per dunum, and a control group. The experiment followed a randomized complete block design (RCBD) with three replications, using local maize seeds planted in 3 m by 3 m plots. After applying the treatments, the concentration of available molybdenum was measured in both soil regions at 70 and 100 days after planting. Results indicated that adding fertilizers (sheep manure, humic acid, and nitrogen) increased the concentration of available molybdenum in both soil regions. Specifically, the humic acid treatment had the highest concentration of available molybdenum at both 70 and 100 days, while the nitrogen treatment had the lowest. This highlights the importance of humic acid and organic materials in improving molybdenum availability. Furthermore, molybdenum concentration increased at the 100-day mark for all treatments outside the rhizosphere, except for the control, showing that all treatments enhanced molybdenum content both within and beyond the rhizosphere.

Keywords: molybdenum availability, sheep manure, *Zea mays*, rhizosphere, humic acid.

INTRODUCTION

Molybdenum is present in the soil in smaller quantities compared to other micronutrients like copper, zinc, and iron. It exists in the form of the oxyanion molybdate compound (MoO4-2). Its behavior is similar to that of sulfates and phosphates and often depends on the soil's reaction degree (Xu et al., 2006). Heavy metals generally include elements such as zinc (Zn), arsenic (As), lead (Pb), cadmium (Cd), nickel (Ni), molybdenum (Mo), mercury (Hg), manganese (Mn), iron (Fe), copper (Cu), chromium (Cr), and cobalt (Co), according to SSSA (2008). This element is highly toxic and dangerous, causing numerous health problems even at low concentrations. Its specific gravity is 5 times higher than that of water (the specific gravity of water is 1 at a temperature of 4°C) (Yahaya et al., 2012). Heavy metals are present in various environmental systems, including soil, rocks, sediments, and different types of water bodies (Abegunde and Adelekan, 2011). Molybdenum, a metal found in the Earth's crust at about 1.2 parts per million per gram, typically occurs as molybdate salts. The levels of molybdenum in soil and plants have become a significant focus in research (Rao and Douglas, 2010). Molybdenum was one of the first metals to be isolated, achieved by the Swedish scientist Peter Jacob Hjelm in 1781. Its chemical symbol is Mo, with an atomic number of 42 and an atomic mass of 95.94. The abundance of molybdenum in the Earth's crust is approximately 1.5 mg/kg (Kinniburgh and Smedley, 2017). In a study conducted by Li et al. (2024) during the growth stages of soybeans, MoO_3 NPs was used as a fertilizer, and he found that it was of great importance in increasing the readiness of molybdenum. It also NPs0.05, NPs0.15 maintained the available of molybdenum, and its results proved that the use of MoO_3

NPs fertilizer works to enhance plant growth by providing molybdenum by increasing its readiness, which in turn maintains the nitrogen cycle.

Organic matter can form complex compounds with molybdenum, known as organic matter complexes. During the mineralization of organic matter, molybdenum is converted into a form that plants can absorb. Soils rich in organic matter tend to have higher concentrations of molybdenum compared to soils with lower organic matter content (Sun et al., 2019). According to Wichard et al. (2009), molybdenum can bind with organic matter through bonding and adsorption in the soil. The availability of molybdenum increases with the increase in soil pH, in contrast to other nutrient elements. Therefore, its availability is higher in alkaline soils than in acidic soils. This is explained by the fact that in alkaline soils, anion exchange can occur between the hydroxyl anion dissolved in the soil solution and the adsorbed molybdate anion. The availability of molybdenum increases by ten times with a one-unit increase in soil pH (Ali, 2012; AlJanabi et al., 2019; AlJanabi et al., 2020). Calcium carbonate works to raise the soil pH, which increases the availability of molybdenum in the soil solution. The rise in soil pH releases molybdenum adsorbed on the surfaces of mineral colloids (Gupta, 1997). Molybdate (MoO_4^{-2}) is the most available chemical form of molybdenum, but it is more prone to loss. It can be adsorbed onto clay minerals or carbonates and onto positively charged mineral oxides such as oxides of iron, aluminum, and manganese, as well as carbonates (Sun et al., 2019). This study revealed that the bioavailability of Mo in soil and the increase availability with adding fertilizer.

Experimental

The field experiment was conducted on a farm in Al-Daghara District, Al-Diwaniyah Governorate, located about 18 km from the center of Al-Diwaniyah District. The soil was clay loam, and the experiment was conducted during the autumn season of 2023. The field was prepared by plowing, leveling, and smoothing, and three main irrigation channels were created along the field's length, with secondary channels for each plot. The field was divided into three blocks with 1.5 meters between each block, and each block was further divided into four plots (experimental units) measuring 3 × 3 meters (9 square meters each). A distance of 1 meter was left between each experimental unit. The experiment followed a Randomized Complete Block Design (RCBD) with three replications, each containing four treatments randomly distributed among the experimental units in each block. The treatments are shown in Table 1 and included:

- Mineral fertilizer (M): applied at 400 kg/ha in two stages: the first within 15 days post-planting and the second 35 days after the initial application (Ali, 2012 ; Mohammed et al., 2019).
- Organic fertilizer (O): sheep manure applied at 8 tons/ha, mixed with topsoil prior to planting.
- Humic acid (H): administered at 500 cm³ per liter per dunum, added with irrigation every 10 days until harvest.

Maize seeds (*Zea mays* L.) of a local variety were planted on 29/07/2023 in rows spaced 70 cm apart, with 25 cm between plants. Each plot contained four rows, with a plant density of 53,333 plants per hectare. Initially, three seeds were sown per hole and thinned to one plant per hole 10 days post-germination, resulting in 48 plants per plot. NPK fertilizer was applied at 400 kg/ha across all experimental units. Corn stem borer (*Sesamia cretica*) was controlled using granular diazinon (10% active ingredient) applied twice to the growing tips: 25 days post-germination and 10 days later. Mealybug control involved spraying with Lambda cyhalothrin (EC 5%). Manual weeding was performed as necessary, and regular surface irrigation was applied based on the plants' requirements Hassan et al., 2021.

Table 1. Shows the treatments involved in the experiment and their respective symbols

Symbol	Addition
Nitrogen fertilizer M	400 kg/ha - urea
Organic fertilizer O	8 tons/ha - sheep manure
Humic acid H	500 $cm^3 \cdot L^{-1}$ per donum - humic acid
Control	No addition

Table 2. Some physical and chemical properties of the field soil before planting

Parameter		Value	Unit
1:1 pH		7.68	–
1:1 EC		3.17	ds·m^{-1}
CEC		19.14	Cmol·kg^{-1}
Carbonates minerals		183.9	gm·kg^{-1}
Organic matter		7.2	gm·kg^{-1}
Soluble cations	Ca^{+2}	11.05	mmol·L^{-1}
	Mg^{+2}	9.73	
	Na^{+1}	5.08	
	K^{+1}	0.42	
Soluble anions	CO_3^{-2}	Nil	
	SO_4^{-2}	8.60	
	HCO_3^{-1}	2.15	
	Cl^{-1}	18.41	
Available molybdenum		0.0208	mg·kg^{-1}
Bulk density		1.24	Mg·m^{-3}
Soil fractions	sand	257	gm·kg^{-1}
	Silt	414	
	clay	329	
Texture		Clay loam	

Statistical analysis

The results were statistically analyzed using the analysis of variance (ANOVA) method, considering the experiment as a randomized complete block design (RCBD). The least significant difference (LSD) was calculated to test the differences between treatments at a 0.05 probability level, following the method of Elsahooki and Wehaib (1990), using the Genstat software.

RESULTS AND DISCUSSION

Concentration of available molybdenum in soil 70 days post-planting

Table 3 illustrates the effects of treatments involving organic fertilizer (sheep manure), nitrogen fertilizer (urea), and humic acid on the concentration of available molybdenum in the rhizosphere and surrounding soil of maize plants 70 days after planting. The results indicated significant differences at the 0.05 significance level for the treatments compared to the control, except for the nitrogen fertilizer treatment, which showed no significant difference from the control.

The control treatment had the lowest concentration of available molybdenum in both the rhizosphere soil and beyond, with values of 0.080 and 0.027 mg/kg, respectively, and an average of 0.0535 mg/kg. In contrast, the humic acid treatment yielded the highest concentration and average of available molybdenum inside and outside the rhizosphere soil 70 days after planting, with values of 0.247 and 0.156 mg/kg, respectively, and an average of 0.2015 mg/kg, representing increases of 67.6% and 82.6% compared to the control.

Humic acids enhance micronutrient chelation, improve photosynthesis, increase cation exchange capacity, and boost root activity in plants (Walia, 2019). Melo et al. (2016) state that humic acids dissociate functional groups and form complexes with cations by generating negative charges. These acids improve soil properties such as permeability, aeration, aggregation, and water retention. Furthermore, humic acids promote microbial growth, activate hormones, assist in the mineralization of organic compounds, and supply micronutrients through chelation with nitrogenous cations (Yilmaz and Cimrin, 2005; Hassan et al., 2021; Jafaar et al., 2023).

The use of organic fertilizer (O) significantly outperformed the control, resulting in higher concentrations of available molybdenum in both rhizosphere and non-rhizosphere soils. In the rhizosphere, the concentration reached 0.179 mg/kg, while in the non-rhizosphere soil, it was 0.102 mg/kg, with an average of 0.140 mg/kg. These values represent increases of 55.3% and 73.5% compared to the control, respectively. This

Table 3. Effect of fertilizer type on the concentration of available molybdenum (mg kg^{-1} soil) 70 days after planting

Fertilizer type	Inside rhizosphere		Outside rhizosphere	
Control		0.080		0.027
Nitrogen fertilizer M		0.128		0.059
Organic fertilizer O		0.179		0.102
Humic acid H		0.247		0.156
LSD$_{0.05}$	Fertilizer	0.052	Rhizosphere	0.037

improvement is attributed to organic matter's ability to form complex compounds with molybdenum, converting it into an available form through mineralization (Sun et al., 2019). Wichard et al. (2009) also found that molybdenum binds with organic matter through bonding and adsorption in the soil, supporting these findings.

On the other hand, the nitrogen fertilizer treatment (M) resulted in molybdenum concentrations of 0.128 mg/kg and 0.059 mg/kg in rhizosphere and non-rhizosphere soils, respectively, with an average of 0.093 mg/kg. While this represented increases of 37.5% and 54.2% compared to the control, there were no significant differences. This lack of significant difference is explained by the fact that nitrogen fertilizers lower soil pH, leading to molybdenum adsorption onto mineral colloids such as iron, aluminum, and manganese oxides, which have strong binding capacities. This fixation reduces molybdenum availability, hindering microbial absorption of the nutrient (Ali et al., 2014; Ali et al., 2021; Akol et al., 2021; Hassan et al., 2023).

The results in Table 2 showed that the values of available molybdenum for all fertilizer treatments were higher in both the rhizosphere soil and non-rhizosphere soil. Based on the aforementioned discussion, the fertilizer treatments followed this order after 70 days of growth from planting: M < O < H. This sequence indicates that humic acid and organic residues provided a greater amount of available molybdenum compared to the nitrogen fertilizer treatment Jafaar et al., 2020; Hassan et al., 2021; Jafaar et al., 2022.

Concentration of available molybdenum in the soil 100 days after planting

The results in Table 4 show the effect of organic and nitrogen fertilization levels and humic acid on the concentration of available molybdenum in the rhizosphere soil and non-rhizosphere soil after 100 days of planting. The concentration of available molybdenum was found to be higher than its content at the first interval (70 days), except for the control treatment outside the rhizosphere, which was lower than the first interval at 0.007 mg/kg. This increase is attributed to the effect of fertilizers in enhancing availability. The results indicated significant differences between all treatments compared to the control treatment, with all treatments outperforming the control both inside and outside the rhizosphere.

The treatment involving humic acid fertilization resulted in the highest concentrations of available molybdenum in both rhizosphere and non-rhizosphere soils, with values of 0.618 mg/kg and 0.337 mg/kg, respectively, and an average of 0.477 mg/kg. This represents an increase of 83% and 97.9%, respectively, compared to the control treatment. This increase is attributed to the ability of humic acids to interact with nutrient ions, organic compounds, and hydroxides, thereby enhancing nutrient availability, especially those in low concentrations. Humic acids also help reduce or prevent the loss of elements through adsorption, leaching, or precipitation, ultimately leading to improved crop productivity and quality (Abi-Ghanem and Cooper, 2019).

Table 4. Effect of fertilizer type on the concentration of available molybdenum (mg·kg^{-1} soil) after 100 days of planting

Fertilizer type	Inside rhizosphere		Outside rhizosphere	
Control	0.105		0.007	
Nitrogen fertilizer M	0.221		0.138	
Organic fertilizer O	0.404		0.219	
Humic acid H	0.618		0.337	
LSD$_{0.05}$	Fertilizer	0.050	Rhizosphere	0.036

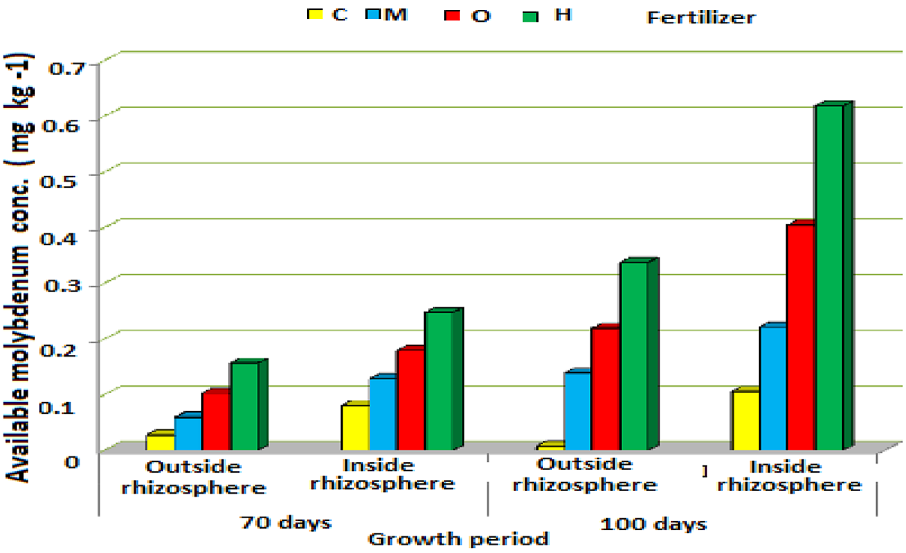

Figure 1. Effect of growth duration (70, 100 days) on the concentration of available molybdenum in the soil ($mg \cdot kg^{-1}$ soil)

The addition of organic matter, specifically sheep manure, significantly increased molybdenum availability in the soil. This treatment outperformed the control, with molybdenum concentrations in rhizosphere and non-rhizosphere soils reaching 0.404 mg/kg and 0.219 mg/kg, respectively, averaging 0.311 mg/kg. This represents increases of 74% and 96.7%, respectively, compared to the control. This improvement is attributed to organic matter's role in enhancing soil chemical properties. As organic matter decomposes, it releases organic acids and CO_2, lowering soil pH and aiding in the dissolution of elements from complex compounds and minerals. Additionally, organic matter positively affects soil biological properties by increasing the number, diversity, and activity of microorganisms, providing them with energy sources (Jarallah and Al-Hasmoti, 2023), and enhancing the release of micronutrients in the soil (Awad et al., 2017).

Furthermore, adding nitrogen fertilizer to the soil significantly improved molybdenum availability compared to the control. The molybdenum concentration reached 0.221 mg/kg and 0.138 mg/kg in rhizosphere and non-rhizosphere soils, respectively, with an average of 0.179 mg/kg. This represents increases of 52.4% and 94.9%, respectively, attributed to urea addition, which lowers soil pH through nitrification and the action of the urease enzyme, increasing micronutrient availability (Havlin et al., 2005).

The concentration of available molybdenum followed the sequence M < O < H at 100 days of growth after planting, consistent with results at 70 days, where humic acid fertilization provided the highest molybdenum availability. Although nitrogen fertilization was the lowest in both periods, its concentration at 100 days was higher than at 70 days. Figure 1 shows that the concentration of available molybdenum increased for all treatments except the control outside the rhizosphere over the 100-day period, indicating that added fertilizers increased molybdenum availability in the soil. The highest molybdenum concentration in rhizosphere soil after 100 days was in the humic acid fertilization treatment, while the lowest concentration outside the rhizosphere was in the control treatment for the same period.

CONCLUSIONS

Fertilization with humic acid outperformed the available and total molybdenum at 70 and 100 days of planting. Fertilization with organic waste also outperformed the available and total molybdenum preparation at 70 and 100 days of planting. Nitrogen fertilization also outperformed the preparation of molybdenum.

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