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# Amelioration of Some Chemical Properties of Magnesium Affected Soils

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**Abstract**: Magnesium is an important nutrient for plant growth; yet, its high hydrated energy makes soil absorb more water while negatively affects soil infiltration rate. To improve soil characteristics, three integrated approaches were adopted in this study, i.e., amending a Mg affected soil with Ca-additive gypsum or phosphogypsum (factor1), selecting the appropriate N-fertilizer (calcium nitrate vs urea) for plants grown under such stressful conditions (factor 2) and using amino acids to increase the available content of Ca in soil to substitute exchangeable Mg (factor 3). To attain these aims, these additives were included in two experiments. The first one was a column experiment of 5 cm inner diameter cm and 70cm long. The leachate was collected from the column after 45 and 90 days then analysed for its content of salts. Thereafter, analysed for soil chemical characteristics and Mg hazards within the surface (0-30 cm) and sub-surface (30-60 cm) soil layers. The second one was conducted to the pot experiment for a study in which an Mg affected soil was planted with barley plants in presence of the above treatments for 90 days during the winter season of 2020/2021. The results indicate that gypsum exhibited higher efficiency to leach out more Mg and Na from the soil column after 45 days versus phosphogypsum. On the other hand, phosphogypsum recorded higher soil EC values while lessened the Mg hazards beyond those attained for gypsum. A point to note is that the highest increases in exchangeable Ca was attained for the application of phosphogypsum versus gypsum within both the surface and subsurface layers while these additive decreased considerably exchangeable Na and Mg contents. Likewise, $Ca(NO_3)_2$ and amino acids raised significantly the leached out of Mg from the soil profile on the short time period only (45 days after application); thereby decreased the Mg hazards in soil. Overall, all these additives raised macro-nutrient contents within plant tissues in the pot experiment; and also boosted plant growth. The "treatment phosphogypsum + calcium nitrate" with amino-acid addition resulted in the biggest increase in plant dry weight, which was 2.25 times more than the control. As a result, this integrated method is certain to improve the properties of an Mg-affected soil.

**Key words**: Mg affected soil; gypsum; phosphogypsum; urea; calcium nitrate; amino acids; barley.

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**Future Science Association**

**Available online free at**
www.futurejournals.org

**Print ISSN:** 2687-8151

**Online ISSN:** 2687-8216

**DOI:**
10.37229/fsa.fja.2024.11.07

**Received:** 14 September 2024
**Accepted:** 25 October 2024
**Published:** 7 November 2024

**Publisher's Note:** FA stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

## 1. Introduction

Salt affected soils exist in several parts of Nile Delta of which are high-magnesium soils with improper properties. **Abou El-Soud *et al*. (2016)**. Magnesium is an important nutrient for many physiological and biochemical processes within plants **(Farhat *et al.*, 2016)**. Nevertheless, its high existence in soil may lead to adverse effects on plant growth and productivity because of its high hydrated energy **(Hailu and Hagos, 2021)** that makes soil absorb more water and flocculates **(Vyshpolsky *et al.*, 2010)**, similar to what occurs in sodic soil **(Qadir *et al.*, 2018)**. If Mg content in the soil solution exceeds that of Ca; then the Mg hazards originated and the soil becomes a Mg affected soil **(Rengasamy and Marchuk, 2011)**. Additionally, high-Mg levels in soil may lead to surface sealing and erosion **(Dontsova and Norton, 2002)**. Furthermore, high concentrations of Mg in soil may induce its toxicity; yet magnesium toxicity symptoms are not easy detectable on plants **(Verbruggen and Hermans, 2013)**.

In general, no criterion was found for evaluating Mg toxicity in soil **(Yang *et al.*, 2014)**; yet in some references it was defined by the soils whose exchangeable Ca/Mg ratio are less than 1.0 **(Chung and Kang, 2001).** A point to note is that Mg is weakly sorbed on soil colloids **(Farhat e*t al.*, 2016)** and can be easily substituted by Ca **(Qadir *et al.*, 2018)** which is found in either gypsum or phosphogypsum. The latter is a by-product of phosphate manufacturing from phosphate rock, which is composed mainly of gypsum. Generally, these two additives may reduce the exchangeable magnesium percentage in soil, improve water movement **(Vyshpolsky *et al.*, 2010)** and increase the productivity of plants grown on salt affected soils **(Farid *et al.*, 2020)**.

Free amino acid contents are responsible of osmoles concentration in some halophytes **(Nasir *et al.*, 2010)** Probably, adding these bio stimulants (as soil additives or as a foliar spray) enhance plant growth and yield by chelating immobile nutrient to increase their bioavailability to plants **(Popko *et al*., 2018),** and also stimulate ion transport and modulating stomata opening **(Rai, 2002).** It is then thought that application of amino acids can increase the solubility of soil-Ca to substitute Mg; and improve the characteristics of the Mg affected soil. The current study aims at analysing the impacts of using either gypsum or phosphogypsum for reclamation of an Mg- affected soil. A barely plant was selected to check the effectiveness of used additives on its growth and nutrient uptake. It is well known that soil salinity alters the normal pathways of N transformations in soil **(Akhtar *et al.*, 2012)**.

Accordingly, selecting the appropriate N-fertilizer (calcium nitrate vs urea) for plants grown under salt stress conditions is the second objective of this study. Moreover, the usage of amino acids for increasing the availability of Ca to substitute exchangeable Mg in the reclamation process of this salt affected soil; hence improving crop growth thereon is third target of this study. Specifically, we anticipate that gypsum and phosphogypsum have comparative effects for reclamation of an Mg-affected soil, with superiority for phosphogypsum on plant growth, because of its relatively high content of P **(**hypothesis 1**)**. Also, calcium nitrate is preferable than urea because of its content of Ca that improves the characteristics of this soil **(**hypothesis 2). We also anticipate that the application of amino acids chelates soil Ca; hence increases its capability to replace Mg on the exchange complex; hence lessen its hazards **(**hypothesis 3**)**. Finally, the combinations between these factors may have further impacts on soil reclamation and plant growth than application of each one solely **(hypothesis 4)**. This is probably one of the few studies on reclamation of Mg-affected soil to increase its productivity in Egypt.

## 2. Materials and Methods

### 2.1. Experimental soil

A surface soil sample (0-30 cm) was collected from a salt affected soil at Mares El-Gamal village, Kafr El-Sheikh Governorate, North Nile Delta, Egypt, during the winter season of 2021/2022. This location is situated at 31° 12’ 43.00” N and 30° 59’ 40.00” E. Soil sample was than air dried, crashed and sieved to pass through a 2 mm sieve then analysed for its some physicochemical characteristics as outlined by **Klute (1988)** and **Sparks *et al.*, (2020)**. The obtained results are presented in **Table 1.**

**Table (1). Physicochemical characteristics and available macro and micro-nutrient of the investigated soil**

| **Parameter** | | **Value** | **Parameter** | | **Value** |
|---|---|---|---|---|---|
| **Physical characteristics** | | | | | |
| **Particle size distribution** | **Sand (%)** | 16 | **Bulk density (Mg $m^{-3}$)** | | 1.44 |
| | **Silt (%)** | 25 | **Soil moisture characteristics** | **SP (%)** | 78.00 |
| | **Clay (%)** | 59 | | **FC (%)** | 46.00 |
| | **Textural class** | Clay | | **WP (%)** | 20.25 |
| **Chemical characteristics** | | | | | |
| | **pH** | 8.29 | **OM** | **(g $kg^{-1}$)** | 6.00 |
| | **EC (d$Sm^{-1}$)** | 12.43 | **$CaCO_3$** | **(g $kg^{-1}$)** | 3.21 |
| **Soluble cations (mmol$_c$ $L^{-1}$)** | **$Na^+$** | 64.34 | **Soluble anions (mmol$_c$ $L^{-1}$)** | **$CO_3^=$** | 0.00 |
| | **$K^+$** | 1.55 | | **$HCO_3^-$** | 4.36 |
| | **$Ca^{2+}$** | 25.7 | | **$Cl^-$** | 71.92 |
| | **$Mg^{2+}$** | 34.96 | | **$SO_4^=$** | 49.27 |
| **Mg /Ca** | | 1.36 | **SAR** | | 11.70 |
| | | | **ESP%** | | 13.96 |
| **Available macronutrients (mg $kg^{-1}$)** | | | **Available micronutrients (mg $kg^{-1}$)** | | |
| **N** | | 28.00 | **Fe (mg $kg^{-1}$)** | | 0.818 |
| **P** | | 9.00 | **Mn (mg $kg^{-1}$)** | | 0.156 |
| **K** | | 262.00 | **Zn (mg $kg^{-1}$)** | | 0.248 |
| | | | **Cu (mg $kg^{-1}$)** | | 0.082 |

## 2.2. Materials

1. Gypsum containing 98% $CaSO_4.2H_2O$ (235 g $kg^{-1}$ Calcium, 186 g $kg^{-1}$ total sulphur, 7.27 g $kg^{-1}$available sulphur, 2.15 g $kg^{-1}$ total Phosphorus and 0.32 g $kg^{-1}$ available Phosphorus)
2. Phosphogypsum containing 92% CaSO4.2H2O (220 g $kg^{-1}$ Calcium, 174 g $kg^{-1}$ total sulphur, 15.89 g $kg^{-1}$available sulphur, 37.45 g $kg^{-1}$ total Phosphorus and 11.62 g $kg^{-1}$ available Phosphorus).
3. . Gypsum and phosphogypsum were obtained from the Egyptian Agricultural Authority, Ministry of Agriculture and Land Reclamation and Aboukir Fertilizers and Chemical Industries Company, respectively.
4. Amino acids were prepared as mentioned by **Kenawy, (2017)** by acidic hydrolysis of dry yeast protein and adjusted to pH 6 with alkaline hydrolysis of dry yeast protein; included amino acids and its shown amino acids composition in **Table 2.**
5. Farmyard manure was obtained from a private company and its characteristics are presented in **Table 3.**
6. Seeds of barley "***Hordeum aestivum L.***" (Giza 134) were obtained from the Central Administration of Seed Certification, The Ministry of Agriculture, Egypt.

**Table (2). Amino acids composition, % (g. 100m$L^{-1}$)**

| Aspartic | Threonine | Serine | Glutamic | Proline | Glycine | Alanine | Valine | Isoleucine |
|---|---|---|---|---|---|---|---|---|
| 2.77 | 1.43 | 1.51 | 3.14 | 1.27 | 1.28 | 1.84 | 2.11 | 1.40 |
| Leucine | Tyrosine | Phenylalanine | Histidine | Lysine | Arginine | Cysteine | Methionine | |
| 2.35 | 0.98 | 1.18 | 0.95 | 2.48 | 1.55 | 0.57 | 0.70 | |

**Table (3). Some chemical characteristics of farmyard manure**

| EC($dSm^{-1}$) | pH | C/ N ratio | O.M ($gkg^{-1}$) | N | P | K | Fe | Zn | Mn |
|---|---|---|---|---|---|---|---|---|---|
| | | | | (%) | | | ($mgkg^{-1}$) | | |
| 3.05 | 7.90 | 1:10 | 273 | 1.59 | 1.5 | 0.90 | 27.2 | 23.8 | 44.4 |

EC and pH were determined in a suspension prepared with a rate of (1:10), O.M: organic matter

### 2.3. Methods of study and the experimental design

In this part, Ca requirements were calculated to lessen the Mg hazards using the **Schoonover's method** of gypsum requirement determination as mentioned by **USDA (1954),** i.e., 9 Mg $ha^{-1}$, (Mg = metric tons; 1 fed = 0.42 ha). The needed amount of Ca was added in the form of either gypsum or phosphogypsum. Concerning the N-source, urea (100kg N $ha^{-1}$) and calcium nitrate (290 kg $feddan^{-1}$) were added to satisfy the recommended rate of applied N (for barely 45 kg N $fed^{-1}$), according to the recommendations of the Egyptian Ministry of Agriculture. For amino acids (20%), it was sprayed on half of the plants at 3 equal doses at a rate of 283 L $ha^{-1}$ after 3, 6 and 9 weeks of planting, while the other half was sprayed with distilled water. Similarly, column experiment, amino acids were added at same rates and timings as pot experiment. All experiments (Column and pot) received mineral fertilizers at the recommended doses for barley crop 200 kg $fed^{-1}$ mono-superphosphate (15.5% $P_2O_5$), 50 kg $fed.^{-1}$ potassium sulphate, (48% $K_2O$) and 10 $m^3$ $fed^{-1}$ farmyard manure during soil preparation.

**The experiments (Column and pot) included nine treatments as follow:**

The experimental design was randomized complete block, factorial (three factors), calcium source "gypsum or phosphogypsum" **(factor1)**, N-fertilizer "calcium nitrate or urea" **(factor 2)** and amino acids addition "with or without" **(factor 3)** and each treatment was replicated three. There were nine treatments in the experiment as follow: -

1. Control (without additions).
2. Gypsum + urea+ without amino acids.
3. Gypsum + urea+ amino acids.
4. Gypsum + calcium nitrate + without amino acids.
5. Gypsum + calcium nitrate + amino acids.
6. Phosphogypsum + urea+ without amino acids.
7. Phosphogypsum + urea+ amino acids.
8. Phosphogypsum + calcium nitrate + without amino acids.
9. Phosphogypsum + calcium nitrate + amino acids.

#### 2.3.1. Column experimentation

In this trial, PVC cylindrical columns of 5-cm inner diameter and 70-cm long were used. The bottom of these columns was placed by a layer of scrubbed gravel to facilitate water leaching out of the column; then soil portions (equivalent to 1 kg, mixed with the abovementioned treatments) were uniformly packed in these columns. Soil moisture content was maintained at the field capacity (on weight bases) using tap water while considering the leaching requirements throughout the experimental study which lasted for 3 months. At 45 and 90 days of incubation, soil columns were flushed with tape water then EC, Mg and Na ion concentrations were determined in the leachate. By the end of the experimental study (90 days of incubation), soil samples were collected from the columns (not subjected to water flushing) then analyzed for their chemical characteristics as outlined by **Sparks *et al.* (2020).** Mg hazards were estimated according to **Yuan *et al.* (2007)**

### 2.3.2. The pot experiment

Plastic pots (20 cm diameter× 25 cm depth) were uniformly packed with soil portions (equivalent to 3 kg). All pots were planted with barley (Giza 134) seeds at a rate of 5 seedlings per pot during the winter season of 2020/2021. Soil moisture content was maintained at the field capacity using tap water during the experimental period plus leaching requirements. After 3 months, plants were harvested. Plant samples were then oven dried at 70 ºC for 48 h then their dry weights were determined. Plant portions, equivalent to 0.5 g were acid digested using a mixture of $H_2SO_4$ and $HClO_4$ (1:1) and their contents of macro-and micro- nutrients were determined in the plant digest. The digests were then exposed to the estimation of N, P, K, Na and micronutrients according to **Cottenie *et al.* (1982).**

### 2.4. Data analyses

Data were subjected to analyses of variance (3-way ANOVA) and Dunken's text via the statistical software SPSS ver 18. For greenhouse results, one-way ANOVA and Dunken's test was followed for data comparison. Figures were then plotted via Sigma plot 10.

## 3. Results and Discussion

### 3.1. Column experimentation

#### 3.1.1. Effect of the used additives on the salinity (EC) and concentrations of both Mg and Na in the leachate

In this experiment, soil leachate was collected via splashing tap water through soil columns of 60 cm length twice (45 and 90 days after application of the investigated additives) and the obtained results are presented in **Fig. 1**.

**1- Effect on EC values of the leachate**

No significant variations in leachate electrical conductivity (EC) values due to the applied calcium (Ca) source, whether it be gypsum or nitrogen (N) source, were detected until 45 days had passed. However, after 90 days, a decrease in soil salinity was observed for all treatments. This result suggests that it takes more than 45 days for the Ca source to exert noticeable effects on the soil, leading to an increase in salt leaching from the soil. In this particular context, the application of gypsum resulted in leaching out fewer salts compared to phosphogypsum. Both of these amendments, in general, enrich the soil with Ca to replace other cations in the soil complex and enhance soil structure, thereby alleviating salinity stress **(Bello *et al.*, 2021).** However, it is worth noting that excessive concentrations of Ca additives, if not leached out of the soil profile, may exacerbate soil salinity **(Moreira *et al.*, 2014).**

Calcium nitrate application also recorded significantly higher losses in salinity (EC) compared to urea after a period of 90 days of application. This can be attributed to the fact that Ca ions, found in calcium nitrate, were observed to be sorbed on soil particles, as highlighted by **Qadir *et al.*, (2018)**. Consequently, this phenomenon resulted in the improvement of soil aggregation, as indicated by **Rengasamy and Marchuk, (2011)**. It is worth noting that the concentrations of soluble salts (EC) in the leachate during the two periods of study remained unaffected by amino acid applications.

**2- Leaching Mg out of the soil profile**

Both gypsum and phosphogypsum increased the leaching out of Mg from the soil after 45 and 90 days of application, with superiority for gypsum. This result indicates that Ca increased soil porosity thus increase salt leachate from the top soil (**Amer and Hashem, 2018)**. Likewise, $Ca(NO_3)_2$ and amino acids raised significantly the leached out Mg from the soil profile versus urea; yet variation between these two treatments were detectable only on the short time period only (45 days after application).

**3- Leaching Na out of the soil profile**

Calcium, nitrogen-source, and amino acids recorded significant impacts on the leaching amounts of Na within the first 45 days of application. This finding implies that these factors play a crucial role in the overall Na leaching process. However, it is interesting to note that this effect was not noticeable on the longer time period of 90 days of application. It suggests that the initial impact of calcium, nitrogen-source, and amino acids diminishes over time. In addition, the type of calcium source used also influences the leaching of Na. Specifically, gypsum has been found to leach out more Na compared to phosphogypsum. This difference in leaching behaviour may be attributed to the varying chemical properties of these calcium sources. Furthermore, the form in which calcium is applied significantly affects the loss of Na via leaching. Specifically, the presence of Ca $(NO_3)_2$ increased the loss of Na after 90 days of application, whereas urea did not exhibit the same effect. This suggests that the utilization of Ca $(NO_3)_2$ as a calcium source may enhance the leaching of Na from the soil. Another factor worth considering is the application of amino acids. It has been observed that amino acid applications exhibit high efficiency in chelating insoluble calcium into readily soluble forms, as highlighted by **Harouaka *et al.* (2020).** This process facilitates the substitution of adsorbed sodium ions, allowing them to be leached out of the soil column more easily. Overall, the findings suggest that the initial 45-day period is crucial for the impact of calcium, nitrogen-source, and amino acids on Na leaching. While gypsum and $Ca(NO_3)_2$ have been found to enhance the leaching of Na, amino acid applications offer an efficient solution for chelating insoluble calcium and promoting the leaching of Na from the soil column.

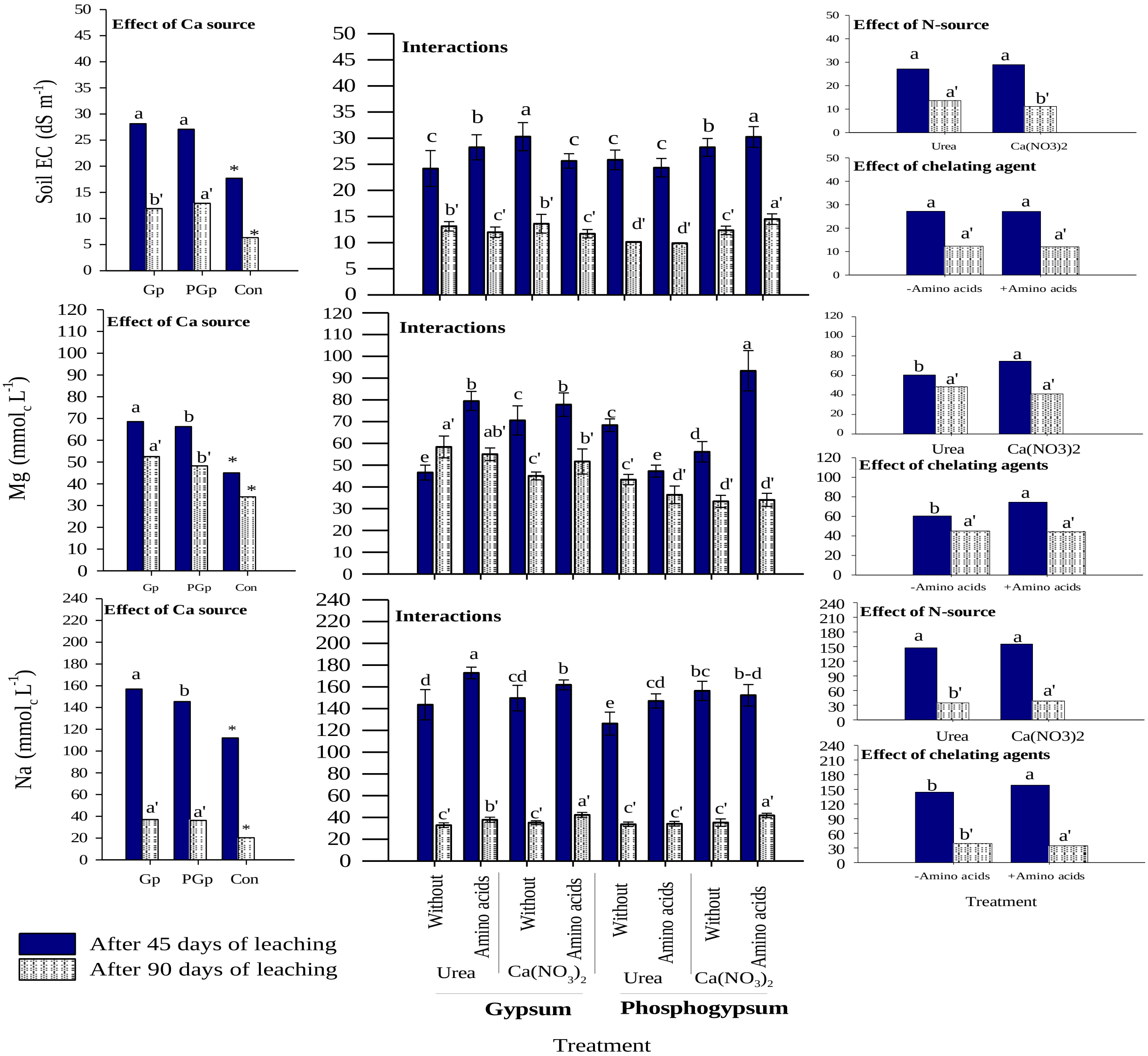


**Fig. (1). EC, Soluble concentrations of Na and Mg (mean± standard deviation) in the leachate of the soil column as affected by application of different ameliorating additives. Similar letters indicate no significant variations among treatments. GP: gypsum, PGP: phosphogypsum**

**4- Effectes on soil pH, EC and Mg hazards**

Slight and insignificant variations were found in soil pH between gypsum versus phosphogypsum, yet these two treatments decreased soil pH versus the control. Likewise, there were no significant variations in soil pH between urea and calcium nitrate treatment, or even for the treatments that received amino acids versus the non-amended ones (Fig. 2). Such a result might be attributed to the high buffering capacity of the soil, particularly because of its clay content **(Jeon and Nam, 2019)**. On the other hand, soil EC and Mg hazards decreased significantly by gypsum and phosphogypsum application as compared to control. However, phosphogypsum recorded higher values of soil EC than gypsum, while phosphogypsum decreased the Mg hazards in soil beyond the values attained for gypsum. Similar results indicate that this additive (phosphogypsum) decreased significantly soil EC (**Moreira *et al.*, 2014).** Likewise, calcium nitrate decreased Mg hazards versus urea, with no significant effect on soil EC. Furthermore, amino acid application recorded no significant impacts on soil EC, while diminished Mg hazards. Mostly, Ca in calcium nitrate substituted Mg on soil particles **(Qadir *et al.*, 2018)** and also mediated soil organic carbon stabilization in soil; and in turn increased soil aggregation **(Rowley *et al.*, 2018**). Accordingly, leaching Mg salts increased from the top soil while decreased the magnesium hazards and soil EC.

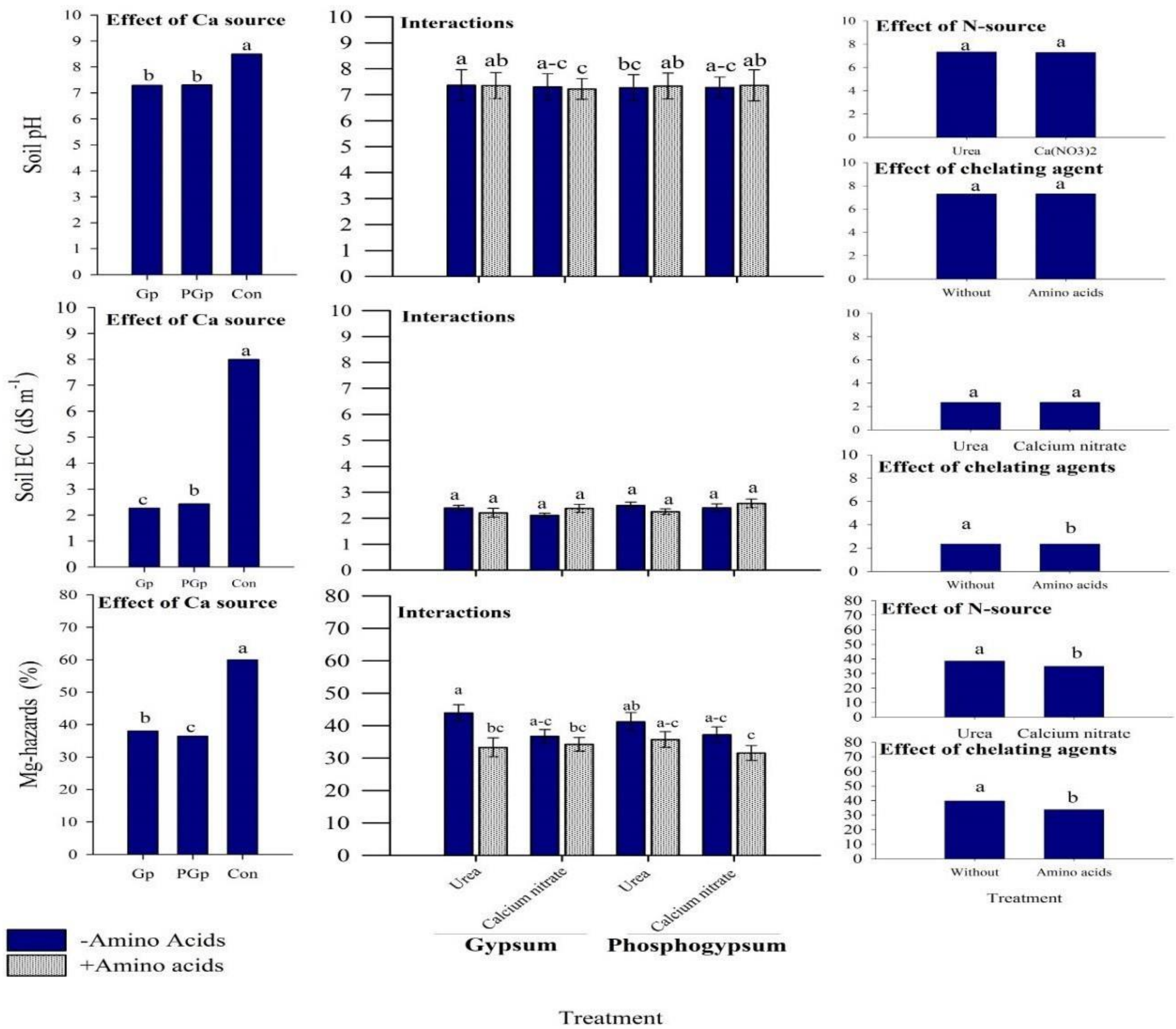


**Fig. (2). Soil pH, EC and Mg hazards in the Mg affected soil as affected by application of different ameliorating additives. Similar letters indicate no significant variations among treatments. GP: gypsum, PGP: phosphogypsum**

### 3.1.2. Effect of the investigated additives on soluble Ca, Mg and Na in soil

Soluble-Ca markedly increased in soil owing to the application of all additives, yet these treatments significantly diminished the soluble concentrations of Na and Mg in soil (**Fig. 3**). In particular, gypsum application decreased soluble Mg in comparison to phosphogypsum, while the reductions in soluble Na were higher in the case of phosphogypsum application versus gypsum. Similarly, the application of amino acids resulted in slight but significant variations in soluble Mg content, with no significant effect on either the soluble Ca or Mg contents in soil. This is because amino acids are known for their capability as surface-active complexing agents (**Bordes and Holmberg, 2015**) that chelate Ca **(Wang *et al.*, 2018)** and other metal cations by binding to carbonyl, amino, and sulfur groups **(Basak. *et al.*, 2015),** thereby increasing their mobility in soil. However, the low application rate of amino acids may not be sufficient to cause substantial increases in the mobility of Ca and Na salts in the soil. On the other hand, the effect of the source of N was not detectable on soluble Ca, Mg, and Na ions in the soil. There might exist an equilibrium between their exchangeable and soluble forms in the soil, and the applied Ca in the form of Ca $(NO_3)_2$ was not enough to significantly diminish the exchangeable Na and Mg forms.

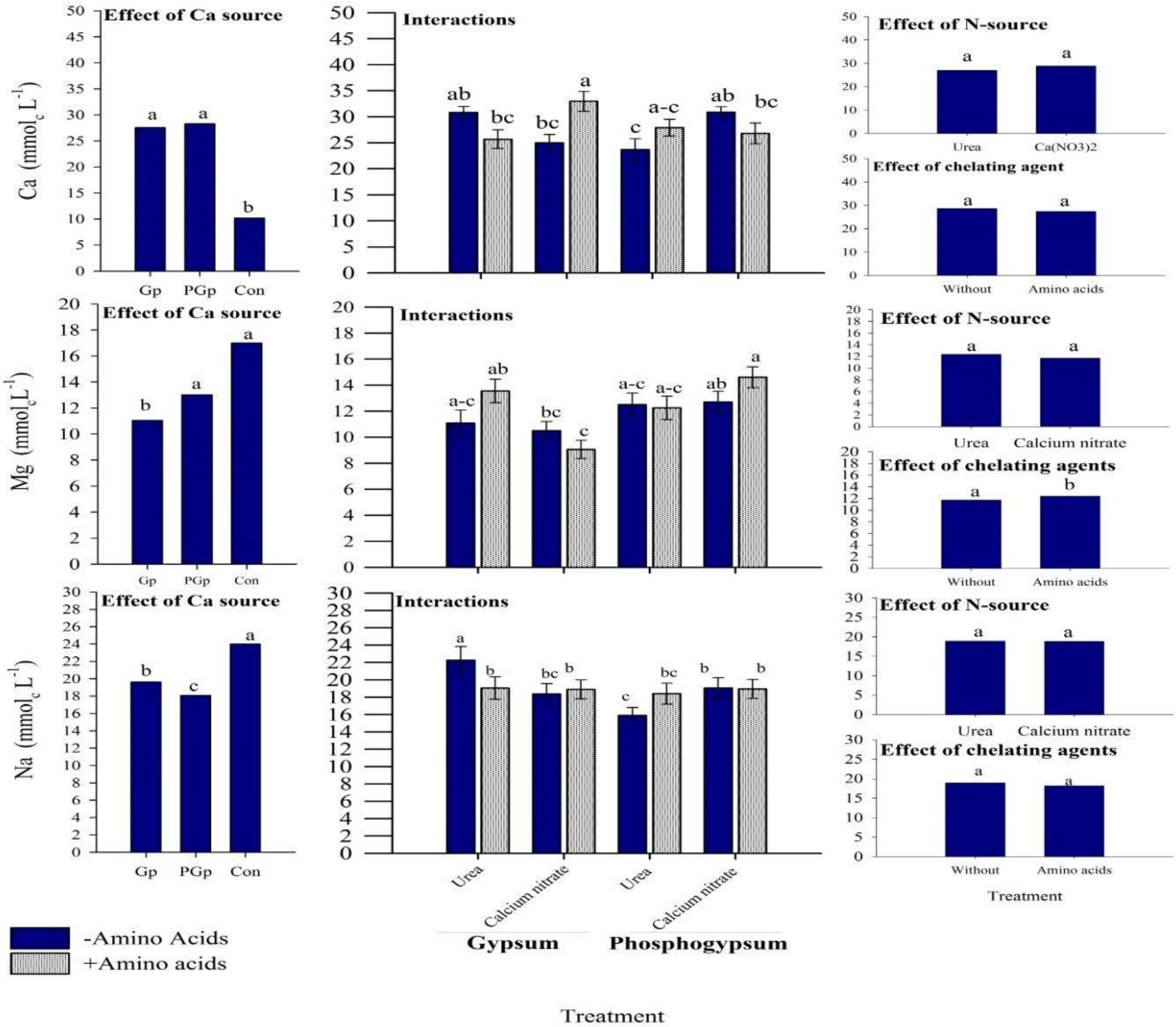


**Fig. (3). Soluble concentrations of Ca, Na and Mg (mean± standard deviation) in a Mg affected soil as affected by application of different ameliorating additives. Similar letters indicate no significant variations among treatments. GP: gypsum, PGP: phosphogypsum**

### 3.1.3. Effect of the investigated additives on exchangeable Ca, Na and Mg cations in soil

To evaluate the impacts of investigated additives on metal sorption on soil particles, the exchangeable amounts of Na, Ca and Mg were determined within both the surface (0-30 cm) and subsurface (30-60 cm) soil layers via subtracting the soluble concentrations of these metal ions, by the end of the experimental period from the $CH_3COONH_4$ extractable amounts, and the results are presented in **Fig.4.**

***Exchangeable-Ca:*** This fraction increased markedly within the top layer (0-30 cm) of soil owing to application of all additives, while the exchangeable Na and Mg decreased noticeably within this soil layer. In particular, exchangeable Ca content increased significantly in soil owing to the application of phosphogypsum versus gypsum. Also calcium nitrate raised significantly the exchangeable Ca content to values exceeding those recorded for urea. Likewise, the chelating agent (amino acid) raised significantly this fraction in soil over the control. This is because of the surface-active complexing agents of amino acids **(Bordes and Holmberg, 2015)** that chelated insoluble Ca **(Wang *et al.*, 2018)** and increased its mobility in soil to be sorbet on soil particles.

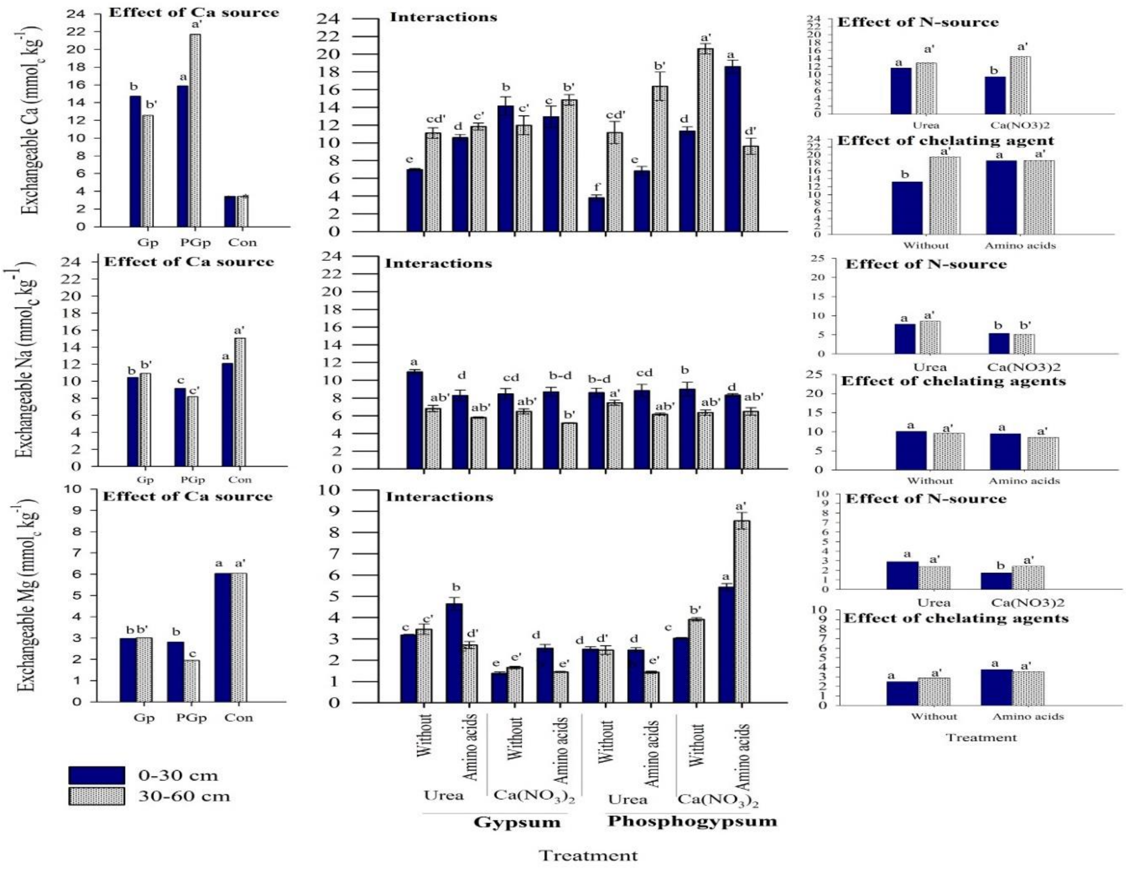


**Fig. (4). Exchangeable Ca, Na and Mg (mean± standard deviation) in the investigated soil as affected by application of different ameliorating additives. Similar letters indicate no significant variations among treatments. GP: gypsum, PGP: phosphogypsum**.

In the sub-sequent soil layers (30-60 cm), concentrations of exchangeable Ca also increased significantly owing to the application to all additives. In particular, application of phosphogypsum led to higher significant increases in Ca exchangeable content versus gypsum. Probably, this amendment was more capable of increasing soil aggregation than gypsum (Nayak et al., 2013); yet, Ca ions became more mobile in soil and reach subsequent soil layers. On the other hand, Ca exchangeable content did not vary significantly between calcium nitrate and urea. Concerning the effect of chelating agents on exchangeable Ca, no ***s***ignificant variations were detectable within the subsurface layer.

***Exchangeable Na:*** Application of gypsum recorded higher soil exchangeable contents than phosphogypsum; in spite of that both recorded significant lower values than the non-amended control. This result postulates that the latter additive increased the mobility cations, which substitute Na ions and increase its mobility to the lower soil layers **(Li, *et al.*, 2020)**. Likewise, Ca $(NO_3)_2$ decreased significantly Na exchangeable content in this layer versus urea. May be Na was lost by leaching from this layer after being substituted by Ca ions **(Rengasamy and Marchuk, 2011)**. On the other hand, the effect of chelating agents was not detectable on the exchangeable Na content in soil. It probably chelated the released Na and kept it in a soluble form. In general, exchangeable Na was lower in the amended soil versus the non-amended control one.

***Exchangeable Mg:*** Regarding Mg, all treatments diminished its exchangeable content within this subsurface layer. In particular, phosphogypsum decreased this exchangeable content versus gypsum. May be, the phosphate ions in phosphogypsum diminished Mg solubility and in turn its sorption on clay minerals. The effect of Ca (NO3)2 was only detected versus urea within the surface soil layer.

### 3.2. The pot experiment

#### 3.2.1. Effect of the investigated additives on pH ,EC, Na ,Ca, Mg and Mg/Ca ratio in soil

Data in Table (4) indicated that, slight and insignificant variations were found in soil pH between gypsum versus phosphogypsum, yet these two treatments decreased soil pH versus the control. Similarly, there were no significant variations in soil pH between urea and Ca $(NO_3)_2$ treatment, or even for the treatments that received amino acids versus without additions ones. This may be due to the buffering capacity of the soil, especially due to its clay content, (**Dvořáčková, *et al.*, 2022)**. On the other hand, soil EC, results indicate a significant decrease in all treatments comparison between control. For example, indicate that the application of Gypsum + Calcium nitrate + amino acid treatment resulted in the highest decreased soil EC (9.21 $dSm^{-1}$). Similar results indicate that this additive (phosphogypsum) decreased significantly soil EC, (**Chhabra and Chhabra, 2021)**.

Similarly, Soluble-Ca content in the soil was significantly increased by the use of all additives, these treatments significantly reduced the soluble sodium and magnesium concentrations in the soil, (Table 4). Application of gypsum + Calcium nitrate + Amino acids recorded higher soluble calcium (42.30 mmolc $L^{-1}$) and the lower was phosphogypsum + Urea + without amino acids (33.00 mmolc $L^{-1}$); in spite of that both recorded significant increase than the control. These results are in agreement with those obtained by **(Rashmi *et al.*, 2022)** who reported that, addition of gypsum leads to an increase in the percentage of dissolved calcium in the soil solution to replace absorbed sodium, thereby overcoming the effects of sodium dispersion and improving soil structure in dispersed soils. Which, the decaying organic matter increases soil CO2 concentrations and releases $H^+$ when it dissolves in water. The released $H^+$ enhances CaCO3 dissolution and liberates more calcium for sodium exchange**, (Amer and Hashem, 2018).** On the other hand, Soluble-Mg content data cleared that the highly significant decreased due to application of gypsum + Calcium nitrate + Amino acids (15.70 mmolc $L^{-1}$) compared with the control (32.36 mmolc $L^{-1}$). Also, Application of Phosphogypsum decreased soluble Mg.

Generally, the positive effect of applied treatments on Mg/Ca ratio, the obtained data indicated that Mg/Ca ratio was decreased by application of gypsum + Calcium nitrate + Amino acids (0.38) compared with the control. Also, Mg/Ca ratio was slightly affected by Phosphogypsum with urea and/or Calcium nitrate and/ or amino acids with or without. Gypsum or Phosphogypsum application increased $Ca^{2+}$ and modifies the ratio $Ca^{2+}$ to $Mg^{2+}$ on the exchange complex in soil, (**Pliaka and Gaidajis, 2022).** Salts of $Mg^{2+}$ & $Na^+$ mainly consisted of Na2SO4, MgHCO3, MgSO4, and NaCl. The amounts of $Ca^{2+}$ salts as CaSO4) were much less than the amounts of $Mg^{2+}$ and $Na^+$ salts, **(Outbakat *et al.*, 2022).**

**Table (4). Effect of the investigated additives on EC, soluble Ca, Mg. Na and Mg/Ca ratio studied soil**

| G.T | N.F | | pH | EC ($dSm^{-1}$) | Soluble cations ($mmol_c L^{-1}$) | | | | Mg/Ca |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg2^+$ | - |
| Gypsum | Urea | Without | 7.74d | 10.35b | 41. b | 2.53b | 36.30d | 20.86 cd | 0.56c |
| | | Amino acids | 7.75cd | 9.36 c | 33.62bc | 2.78b | 39.80c | 22.58 c | 0.57c |
| | Calcium nitrate | Without | 7.73d | 9.89 bc | 32.94c | 2.53b | 33.30d | 17.29d | 0.51de |
| | | Amino acids | 7.76cd | 9.21c | 33.44c | 2.82b | 42.30a | 16.70e | 0.40f |
| Phosphogypsum | Urea | Without | 7.80b | 10.43b | 38.87d | 2.55b | 33.00d | 19.92d | 0.60 d |
| | | Amino acids | 7.79bc | 9.75bc | 31.89c | 2.78b | 38.37c | 20.01cd | 0.52ef |
| | Calcium nitrate | Without | 7.79bcd | 10.30bc | 33.99c | 2.78b | 39.40 c | 26.56 b | 0.63b |
| | | Amino acids | 7.79bcd | 9.28c | 32.53c | 2.81b | 41.77b | 23.69c | 0.57c |
| Without additions | | | 8.09a | 12.84a | 55.81a | 1.70a | 26.67e | 32.36a | 1.21a |

**G.T:** Gypsum type, **N.F:** Nitrogen fertilization pH: & EC: in saturated paste extract and $SO_4^{2-}$ : calculated by difference between cations and anions and Mg /Ca ratio calculated according to **Yuan *et al.*, (2007)**. Similar letters indicate no significant variations among treatments. The soil without any additive was in data analyses (one way anova) for result comparison.

### 3.2.2. Effect of the investigated additives on macro and micronutrient availability of soil

The data presented in **Table 5** shows the available macro and micro nutrients in the tested soils. Clearly, indicate that the application of Gypsum + calcium nitrate + amino acid treatment resulted in the highest nitrogen content (189.67 mg $kg^{-1}$) in soil, while the use of gypsum without amino acid led to the lowest nitrogen content (141.33 mg $kg^{-1}$). Overall, the addition of amino acids generally increased nitrogen levels for both calcium sources (**Xing *et al.*, 2021**). In terms of phosphorus, the highest phosphorus content was observed in phosphogypsum + calcium nitrate + amino acid (14.82 mg $kg^{-1}$), with the lowest levels found in the control group (9.32 mg $kg^{-1}$). The addition of amino acids also, resulted in increased phosphorus content, especially when applied with phosphogypsum (**Pérez Álvarez *et al.*, 2021**). As for potassium, gypsum + calcium nitrate + amino acid treatment showed the highest potassium content (113.80 mg $kg^{-1}$), while gypsum + urea without amino acid showed the lowest (84.80 mg $kg^{-1}$).

The application of amino acids to soil appeared to positively impact potassium absorption. When considering micro nutrients such as Fe, Mn, Zn and Cu, it was observed that the use of amino acids generally led to lower Fe content, with the highest levels found in gypsum without amino acid treatment (**Harouaka, *et al.*, 2020**). Calcium nitrate with amino acid application to soil resulted in the highest Mn content (0.57 mg $kg^{-1}$), while the lowest was found in phosphogypsum without amino acids (0.26 mg $kg^{-1}$). The addition of amino acids also resulted in slightly higher copper content, particularly in calcium nitrate treatments (**Perveen *et al.*, 2022**). Overall, it is evident that applications of calcium nitrate combined with amino acids to soil is the most effective combination for improving both macro- and micro-nutrient contents in soil, particularly for nitrogen and potassium (**Shafeek *et al.*, 2020 and Kheir *et al.*, 2021**). The inclusion of amino acids consistently enhanced nutrient uptake, which is crucial for plant growth. These findings highlight the importance of using specific combinations of calcium sources and amino acids to optimize soil nutrient levels and promote healthy plant development.

**Table (5). Effect of additives on macro and micronutrient availability (mgkg$^{-1}$) of studied soil**

| Calcium source | Nitrogen source | | Macro-nutrient contents (mg kg$^{-1}$) | | | Micro-nutrient contents (mg kg$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | **N** | **P** | **K** | **Fe** | **Mn** | **Zn** | **Cu** |
| **Gypsum** | **Urea** | **Without** | 141.33± 3.21$^{d}$ | 11.83± 0.64$^{b}$ | 84.80± 1.93$^{e}$ | 1.04± 0.06 $^{bcd}$ | 0.45± 0.06$^{b}$ | 0.18± 0.01$^{a}$ | 0.05± 0.01$^{bc}$ |
| | | **Amino acids** | 171.67± 7.02$^{abc}$ | 13.43± 0.67$^{ab}$ | 103.00± 4.211$^{bc}$ | 0.82± 0.18 $^{bcd}$ | 0.40± 0.02$^{bcd}$ | 0.19± 0.02$^{a}$ | 0.06± 0.01$^{a}$ |
| | **Calcium nitrate** | **Without** | 164.67± 5.13$^{bcd}$ | 13.82± ab$^{ab}$ | 98.80± 3.08$^{cd}$ | 0.74± 0.08$^{bcd}$ | 0.26± 0.01$^{a}$ | 0.16± 0.01$^{ab}$ | 0.03± 0.0$^{d}$ |
| | | **Amino acids** | 189.67± 2.08$^{a}$ | 13.25± 0.59$^{ab}$ | 113.80± 1.25$^{a}$ | 0.83± 0.02$^{bcd}$ | 0.57± 0.06$^{a}$ | 0.14± 0.01$^{b}$ | 0.06± 0.0$^{a}$ |
| **Phospho-gypsum** | **Urea** | **Without** | 147.00± 13.45$^{cd}$ | 13.31± 0.24$^{ab}$ | 101.60± 1.93$^{bc}$ | 0.70± 0.01$^{cd}$ | 0.42± 0.04$^{bc}$ | 0.17± 0.001$^{a}$ | 0.04± 0.0$^{cd}$ |
| | | **Amino acids** | 169.33± 3.21$^{abc}$ | 13.67± 1.17$^{ab}$ | 90.90± 5.48$^{de}$ | 0.71± 0.02$^{cd}$ | 0.33± 0.02$^{cde}$ | 0.17± 0.01$^{a}$ | 0.07± 0.0$^{a}$ |
| | **Calcium nitrate** | **Without** | 163.33± 16.56$^{bcd}$ | 13.66± 0.83$^{ab}$ | 108.70± 1.84$^{ab}$ | 0.90± 0.0$^{abc}$ | 0.33± 0.02$^{cde}$ | 0.19± 0.01$^{a}$ | 0.05± 0.01$^{bc}$ |
| | | **Amino acids** | 173.83± 11.07$^{abc}$ | 14.82± 0.98$^{ab}$ | 108.89± 2.49$^{ab}$ | 0.94± 0.02$^{ab}$ | 0.32± 0.04$^{cde}$ | 0.18± 0.01$^{a}$ | 0.06± 0.01$^{bc}$ |
| Without additions | | | 167.0± 0.0$^{abc}$ | 9.32.± 0.06$^{c}$ | 100.20± 0.20$^{e}$ | 0.68± 0.01$^{d}$ | 0.30± 0.01$^{de}$ | 0.16± 0.01$^{ab}$ | 0.04± 0.01$^{cd}$ |

Similar letters indicate no significant variations among treatments. The soil without any additive was in data analyses (one way anova) for result comparison.

### 3.2.3. Effect of the investigated additives on plant dry weights, its content of macro- and micronutrients

Application of phosphogypsum significantly boosted the dry weights of barley plants versus the application of gypsum (**Table 6**). This by-product of phosphate fertilizer (phosphogypsum) that contains calcium, sulphate, silicon, iron, magnesium and manganese ions, **(Chernysh *et al.*, 2021)** can be used as a fertilizer besides being a soil conditioner, **(Saadaoui *et al.*, 2017)**. Moreover, phosphogypsum elevates activities of antioxidant enzymes and proline **(Elloumi *et al.*, 2015)** that are needed to overcome the drought and salinity stresses, **(Lalarukh *et al.*, 2022)**. In this concern, calcium nitrate + phosphogypsum recorded significantly higher dry weight values than the corresponding ones that received only urea. The effect of amino acids on plant growth may be supplementary to the abovementioned additives in enhancing plant dry weight. Generally, the highest increases in plant dry weights were recorded for "phosphogypsum +calcium nitrate" + amino-acid addition. This treatment recorded 2.25 folds higher than the control.

#### 3.2.3.1. Effect on macro-nutrient status within plants

Application of all additives raised significantly N content within plant tissues versus the control (without additives). In this context, the effects of gypsum and phosphogypsum seemed to be comparable. These two sources of calcium may increase the stability of plant cell membrane under the adverse conditions of the salt affected soils **(Akladious *et al.*, 2018)**. Consequently, increase membrane permeability and nutrient uptake by plants **(Tuna *et al.*, 2007)**. On the other hand, N content was higher in plant tissues amended with urea versus the corresponding ones applied with calcium nitrate. Probably, N-$NO_3$ was rapidly lost via leaching from the top soil in the form of gases (**Mahmoud *et al.*, 2021**).

Concerning P-content within plant tissues, significant variations were recorded owing to the application of phosphogypsum versus gypsum and also for using amino acid application. Still, all treatments raised significantly P- content within plants versus the control treatment that did not receive any ameliorating agent. Likewise, K content varied significantly between gypsum and phosphogypsum, with superiority for phosphogypsum, especially with urea. The increases in plant biomass, especially with using phosphogypsum, might be responsible for such increases in K content. This amendment increased root elongation to absorb more K-salts from the media., K-content was lower in urea treated plants versus calcium nitrate treated ones, yet the results of amino acid application on K-content within plants were confusing.

#### 1.1.1.1. Effect on micro-nutrient contents

All treatments resulted in a significant increase in Zn and Cu concentrations within the plant tissues. Specifically, the treatment "phosphogypsum + urea +amino acids" showed the highest increase in Zn content, while the highest Cu content was observed in plants treated with "phosphogypsum + calcium nitrate +amino acids". Conversely, the control plants exhibited higher Fe and Mn contents compared to many other additives. This reduction could possibly be attributed to a dilution effect. Nevertheless, the plant tissues of "gypsum + calcium nitrate" treated plants recorded the highest Fe content, whereas the plants amended with "gypsum + urea" showed the highest Mn content.

**Table (6). Effect on plant dry weights, its content of macro- and micronutrients**

| G. T | N.F | | Dry weight (g. pot$^{-1}$) | Macro-nutrient contents | | | Micro-nutrient contents | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | N | P | K | Fe | Mn | Zn | Cu |
| | | | | g kg$^{-1}$ | | | mg kg$^{-1}$ | | | |
| Gypsum | Urea | Without | 38.77± $1.01^{d}$ | 22.67± $1.70^{b}$ | 2.02± $0.19^{d}$ | 47.69± $0.81^{bc}$ | 183.67± 45.39 $^{e}$ | 69.67± 4.83a | 1.03± $0.60^{g}$ | 13.09± $1.26^{c}$ |
| | | Amino acids | 40.1± $1.16^{d}$ | 20.77± $1.16^{bc}$ | 2.39± $0.33^{bc}$ | 41.40± $2.91^{d}$ | 195.00± 83.36 $^{e}$ | 17.67± $4.04^{b}$ | 2.22± $0.60^{e}$ | 14.89± $1.73^{b}$ |
| | Calcium nitrate | Without | 36.3± $0.46^{de}$ | 21.10± $2.93^{bc}$ | 2.18± $0.25^{cd}$ | 43.96± $6.66^{cd}$ | 328.67± 29.40 $^{a}$ | 15.67± $2.52^{bc}$ | 4.84± $2.90^{b}$ | 14.84± $2.90^{b}$ |
| | | Amino acids | 49.3± $1.78^{c}$ | 19.83± $1.15^{c}$ | 2.43± $0.24^{bc}$ | 41.40± $1.07^{d}$ | 176.00± 11.56 $^{e}$ | 13.67± $1.52^{c}$ | 4.31± $1.94^{d}$ | 14.42± $1.97^{b}$ |
| Phospho gypsum | Urea | Without | 70.3± $1.27^{a}$ | 25.87± $1.30^{a}$ | 2.72± $0.35^{b}$ | 61.64± $2.82^{a}$ | 241.67± $38.21^{cd}$ | 12.67± $1.15^{c}$ | 4.07± $0.77^{d}$ | 11.70± $1.47^{d}$ |
| | | Amino acids | 61.0± $2.10^{b}$ | 20.00± $0.17^{c}$ | 2.66± $0.30^{bc}$ | 61.18± $3.22^{a}$ | 232.33± $37.58^{d}$ | 14.67± $1.15^{bc}$ | 5.54± $3.34^{a}$ | 12.03± $1.17^{cd}$ |
| | Calcium nitrate | Without | 72.3± 1.29a | 19.00± 4.39c | 2.43± $0.17^{bc}$ | 40.71± $2.02^{d}$ | 262.67± $11.32^{bc}$ | 17.33± $0.58^{b}$ | 4.54± $1.07^{c}$ | 12.43± $0.76^{cd}$ |
| | | Amino acids | 74.3± 1.29a | 20.07± $1.20^{c}$ | 3.37± $1.63^{a}$ | 49.08± $8.73^{b}$ | 282.67± $90.64^{b}$ | 16.00± $1.00^{bc}$ | 2.93± $0.42^{e}$ | 16.20± $2.59^{a}$ |
| Without additions | | | 33.2± $0.17^{e}$ | 7.80± $0.01^{d}$ | 1.54± $0.02^{e}$ | 49.52± $0.03^{b}$ | 236.00± $1.02^{d}$ | 14.33± $0.58^{bc}$ | 1.75± $0.11^{f}$ | 1.48± $0.08^{e}$ |

Similar letters indicate no significant variations among treatments. The soil without any additive was in data analyses (one way anova) for result comparison.

## 2. Conclusion

Application of phosphogypsum to ameliorate a Mg affected soil increased the leach out of salts from the soil column versus gypsum; and also recorded better plant growth performance. In spite of that, gypsum recorded the highest capability to substitute exchangeable Mg and Na and set these ions free to be lost via the leachate. The efficiency of phosphogypsum on exchangeable Na appeared within the first 45 days of application while this process lasted for 90 days on Mg. These results validate the first assumption. Concerning the effect of the nitrogen source, calcium nitrate application led to higher losses of salinity (EC) and leached out more Mg and Na than did the urea; thus, it decreased soil EC and Mg hazards in soil to values beyond those attained for the application of urea. This authenticates the second assumption. Likewise, the effect of amino acids was notable on reducing Mg hazards in soil and improving plant growth; yet in only presence of gypsum; while its effect was nearly absent on plant growth or even negative when using phosphogypsum for soil amelioration. May be it increased the availability of impurities found in phosphogypsum than affected negatively plant growth.

Accordingly, these results certify partially the third hypothesis. Overall the combination between the different ameliorating agents decreased Mg hazards; while improved considerably plant growth and this supports the fourth hypothesis.

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