

*Short Communication*

# Effect of Fertigation-Applied Sulfuric Acid on Phosphorus Availability and Some Microelements for Greenhouse Cucumber

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## Abstract

Aim of study: Essential nutrient elements such as P, Fe, Zn, Cu, B and Mn are mostly affected by soil pH. In calcareous soils, it is often difficult to obtain a pH of 6-6.5 the optimum soil pH value of phosphorus and micronutrients, as the goal of fertilizer best management practices is to match nutrient supply with crop requirements to optimize yield while minimizing nutrient losses to the environment. Material and methods: In order to study the addition of different amounts of sulfuric acid through irrigation to minimize soil pH value, and to improve the availability of the elements on cucumbers, experiments were carried out on two types of soil textures: Silty Clay Loam (S1) and Silty Clay (S2). The sulfuric acid was applied with different concentrations (0, 0.5, 1, 3, and 5 ml L<sup>-1</sup>). The elements' concentration was studied at three soil depths (D1 = 0-10, D2 = 10-20 and D3 = 20-30) cm. Results: The availability of P and micronutrients primarily increased in C4D3 in S2 soil. The P in this work was a positive correlation with Zn in both soils, while it showed a negative correlation with other micronutrients (Fe, Cu, B and Mn). Element concentration in plant tissue was studied in the plant residues after harvesting. The C3 was highly effective in increasing the elements (P, Fe, Zn, Cu, B, and Mn) in plant tissues in both soils, and had a significant effect on the increase in cucumber yield. Conclusion: The values of soil pH were regularly decreased by increasing sulfuric acid. Then, the availability of the studied elements was enhanced.

**Keywords:** phosphorus, calcareous soil, cucumber yield, soil pH, microelements availability

## Introduction

Cucumber (*Cucumis sativus* L.) is considered to be one of the most important vegetables and is a popular member of the Cucurbitaceae family [1]. Most nutrients are recommended to be necessary to improve cucumber

yield and product quality [2]. However, integrated plant nutrient and soil fertility management share similar objectives namely to ensure efficient nutrient uptake and plant growth with minimal adverse impacts on the environment. Crop yield and quality will be restricted if the rate is too low while excess application can lead to crop damage and negative environmental impacts [3]. Among these nutrients, phosphorus (P) is deemed the most important macro element to the plant, as it is vitally connected to a number of functions in the plant

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including photosynthesis, energy transfer, respiration, and cell division [4]. Also, micronutrients contribute to numerous physiological processes. For example, iron (Fe) is a component of several enzymes involved in various biological processes including respiration and photosynthesis; zinc (Zn) is an important component of many enzymes, and a structural stabilizer of proteins and plant membranes; manganese (Mn) is an active component of the water-splitting system of photosystem II that supplies the electrons necessary for photosynthesis; copper (Cu) is a redox transition element with an important function in photosynthesis, respiration, and the metabolism of carbon (C) and nitrogen (N). Cu also induces protection against oxidative stress, and boron (B) participates in cell division, water relations, ion adsorption, the metabolism of carbohydrates, and the translocations of sugar and fruit [5]. Furthermore, the availability of these nutrients are mainly affected by soil type, in particular, calcareous soils due to a high pH value. Iraqi soils are categorized in this class of soil [6, 7].

Sheikh-Abdullah [8] confirmed that active  $\text{CaCO}_3$  negatively influences the availability of micronutrients

such as Fe, Zn and Mn. Khorsandi [9] stated that better P solubility occurs at a pH ranging between 6-6.5. Several methods have been reported to benefit a reduction in pH value and then increase nutrient availability; for example, adding sulfur to the soils then oxidation into  $\text{H}_2\text{SO}_4$  results in increasing the availability of nutrients by reducing soil pH [10]. However, the direct use of sulfuric acid into the soil to minimize the pH value might be helpful to increase soil nutrient availability [9]. In Iraqi calcareous soils, the factor of adding sulfuric acid to improve nutrient availability has not been carried out; thus, this study aimed to add sulfuric acid at different concentrations to lower soil pH under plastic house conditions, and illustrate its impact on the growth and yield of cucumbers, as well as the availability of P, Fe, Zn, Cu, B and Mn.

### Materials and Methods

The experiments were conducted at the Agricultural Research Station in Grdarasha (412 m,  $36^{\circ}07'10.44''\text{N}$  –  $44^{\circ}00'50.52''\text{E}$ ), about 4 km south of Erbil centre,

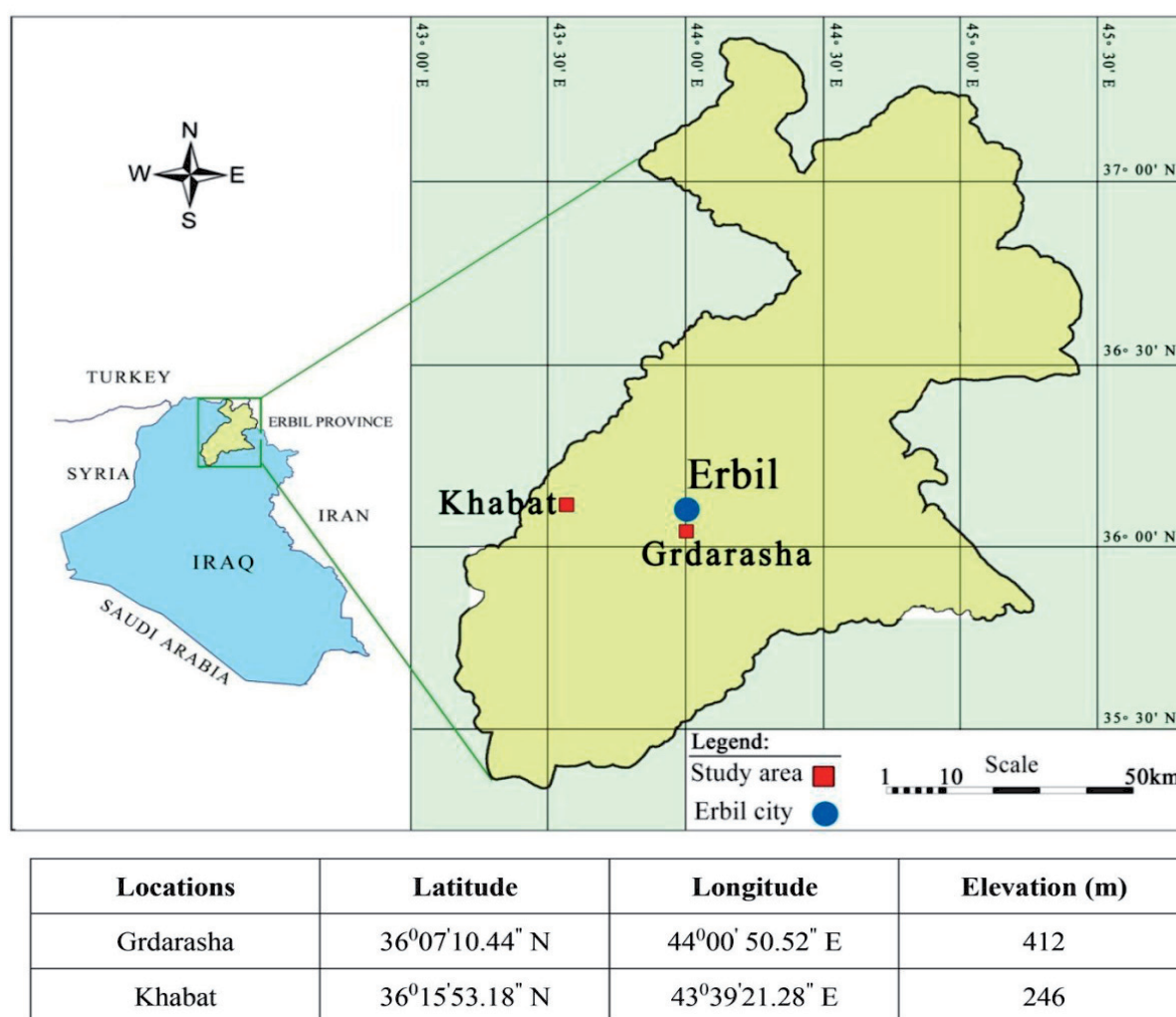


Fig. 1. The experiments location map.

and at Khabat Agricultural Technical Institute (246 m, 36°15'53.18"N – 43°39'21.28"E), 30 km west of Erbil centre, under plastic house conditions during the summer season of 2016 (Fig. 1). The experiments were carried out to evaluate the impact of applying different concentrations of sulfuric acid directly to soils on P and certain micronutrients including Fe, Zn, Cu, B and Mn, and its effect on the growth and yield of the Rainbow variety of cucumber.

At the site of the plastic houses, the land was prepared through ploughing, harrowing and levelling, and two samples from the site were taken (0-30 cm) to determine some of the chemical and physical properties of the soils under study (Table 1). Next, the experimental sites were shaped into mounds. Every experimental unit included a mound of 4 m in length, and ten plants were cultivated in every mound with a spacing of 40 cm between plants. Also, 75 cm was left between every experimental unit. Five concentrations of sulfuric acid (0, 0.5, 1, 3, and 5 ml L<sup>-1</sup>) were applied into the soil surface for two types of soils. This was determined according to the USDA soil textural classification [11], including Silty Clay Loam (SiCL = S1) and Silty Clay (SiC = S2), to the Grdarasha and Khabat soils, respectively. During the experiment, the crop was irrigated every two weeks; the total watering was eight times to avoid acid accumulation in the soil. The study took a chemical analysis of the soil at both locations (pH, P, Fe, Zn, Cu, B and Mn). The soils were sampled by end harvesting with an auger drill at three depths (0-10, 10-20, 20-30) cm. Also, the concentration of P, Fe, Zn, Cu, B and Mn in the plant was analysed by sampling the above-ground plant-parts at the end of harvest, in addition to the cucumber yield. Available Fe, Mn, Zn, and Cu contents of the soil samples were extracted with 0.005 M diethylenetriamine pentaacetic acid + 0.01 M CaCl<sub>2</sub> + 0.1 M triethanol amine, and the extractable elements were determined on an atomic absorption spectrophotometer as described by Lindsay and Norvell [12]. Furthermore, the plant samples were digested and prepared for total element determination by inductively coupled plasma-atomic emission spectrometry [13]. In addition, the experiments were designed according to Factorial Randomized Completely Block Design (RCBD). In all cases, Tukey's H.S.D multiple range tests were applied at (P≤0.05) for comparison between the means of treatments using SPSS 25.0.

## Results and Discussion

### Soil Properties

The results showed the significant effects of sulfuric acid levels at the end of the growing season for both soils at different soil depths in reducing pH in the soil solution. The fourth concentration of sulfuric acid and a 0-10 cm soil depth had a greater decrease of soil pH value compared to other the treatments. As a result,

Table 1. Some physical and chemical properties of two soils before experiment.

Soil type	pH	EC dS m <sup>-1</sup>	O. M. g m kg <sup>-1</sup>	*CaCO <sub>3</sub>	CEC cmol kg <sup>-1</sup>	PSD%			Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	N%	mg kg <sup>-1</sup>					
						Clay	Silt	Sand									P	Fe	Zn	Cu	B	Mn
<b>S1</b>	8.10	0.60	8.70	340	22.20	30.20	57.60	12.20	2.75	1.92	1.39	0.12	1.20	2.08	2.85	0.16	4.15	7.50	2.50	1.20	4.54	2.58
<b>S2</b>	7.90	1.60	9.20	280	24.10	44.30	49.30	6.40	6.28	3.80	4.08	0.14	1.28	4.23	8.10	0.20	7.80	8.40	3.20	1.10	4.85	2.30

S1 (Silty Clay Loam), S2 (Silty Clay), PSD (Particle-Size Distribution), EC (Electrical Conductivity), CEC (Cation Exchange Capacity), O. M. (Organic Matter), \*Total CaCO<sub>3</sub> (gm kg<sup>-1</sup>).

S1 (Silty Clay Loam), S2 (Silty Clay), PSD (Particle-Size Distribution), EC (Electrical Conductivity), CEC (Cation Exchange Capacity), O. M. (Organic Matter), \*(Total CaCO<sub>3</sub> gm kg<sup>-1</sup>).

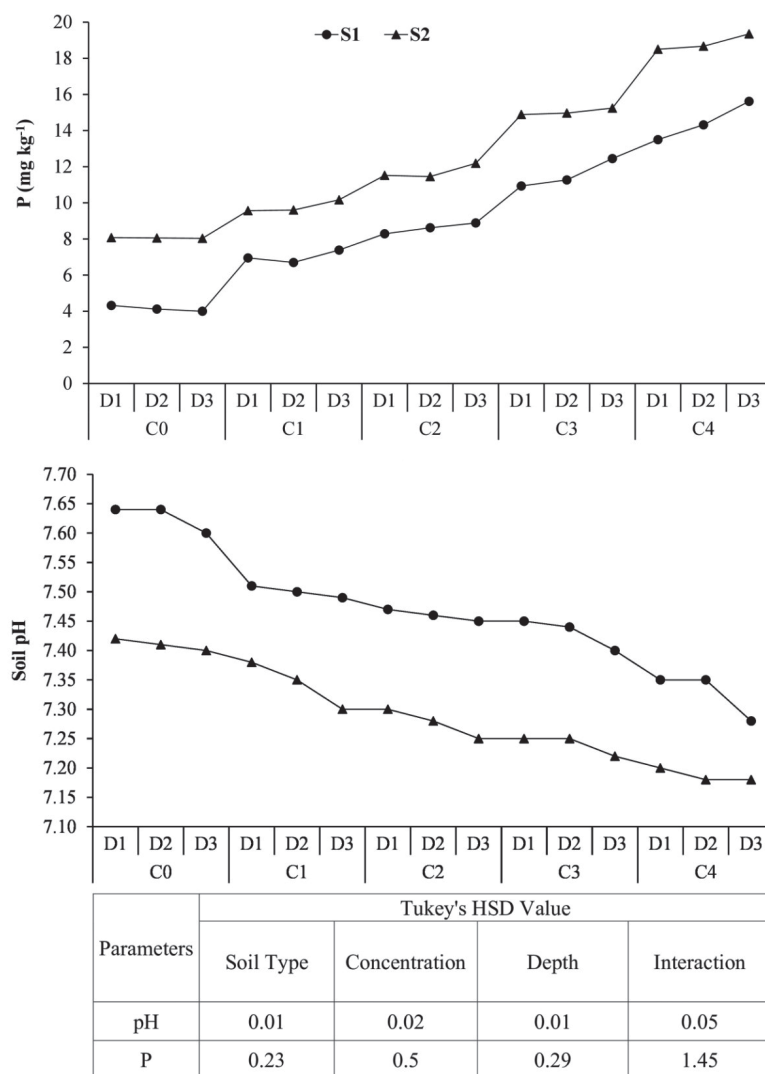


Fig. 2. Effect of sulfuric acid concentrations on pH and phosphorus availability in two different soils (S1= Silty Clay Loam, S2 = Silty Clay, C = Concentration, D = Depth, Significant at  $P \leq 0.05$ ).

the availability of phosphorus was primarily increased, in particular, by a 5 ml treatment of sulfuric acid and 20-30 cm depths for both soils (Fig. 2). Furthermore, the maximum concentration of micronutrients (Fe, Zn, Cu, B and Mn) was obtained by the fourth concentration of sulfuric acid and the third depth of soil in both experiments compared to other treatments. On the other hand, better results for the concentration of micronutrients was obtained in Khabat soils due to the high content of clay particles, particularly in the fourth concentration of the sulfuric acid and the third depth of the soil (Fig. 3). The calcite amount in the soil was diminished, possibly due to the dissolution of the lime by acid. This emphasized that the application of acid to calcareous soils dramatically decreases the pH value of the soil as a result of neutralizing soil  $\text{CaCO}_3$ . A very low soil pH is obtained as the sulfuric acid results in a low pH in the soil solution. As a result, some of the phosphate compounds are dissolved, and then the available phosphorus is released [14]. In addition,

Sumner and Yamada [15] found that soil acidification results in increasing the concentration of some nutrient elements in the soil solution, particularly phosphorus.

It is commonly known that there is a direct relationship between soil pH and  $\text{CaCO}_3$  in soil. When a high concentration of sulfuric acid was added to the soils, the pH tended to an extremely low value, and then the activity of  $\text{CaCO}_3$  was diminished. After the active carbonate calcium was restricted, most of the micronutrients are available. Sheikh-Abdullah [8] found a negative correlation between the availability of Fe, Zn and Mn, and  $\text{CaCO}_3$  activity. Then, the rate of micronutrients markedly increased. In soil with a low pH, most micronutrients are at their peak availability; this is probably due to the strong attraction of  $\text{H}^+$  ions to the negative site on the surface of the soil particles, which is then sufficiently replaced by other cations. Consequently, these cations are released to the soil solution obtaining better availability [16]. In addition, Ghehsareh and Samadi [17] found that acidification

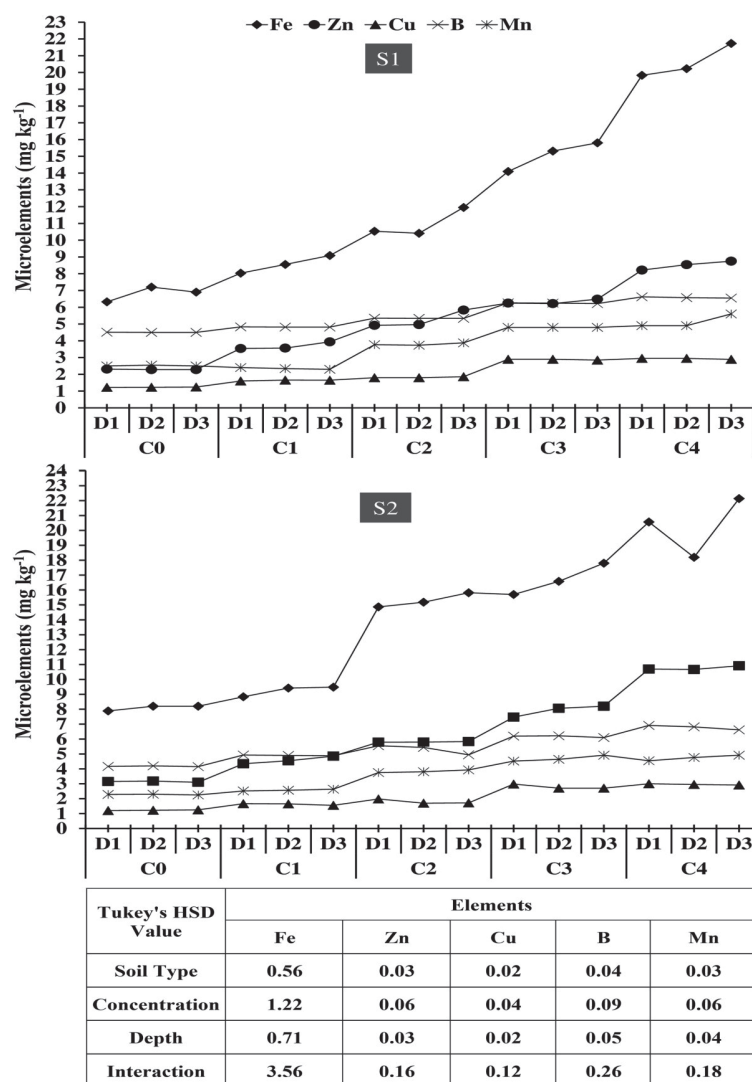


Fig. 3. Effect of different sulfuric concentrations on micronutrient availability in two soils (S1 = Silty Clay Loam, S2 = Silty Clay, C = Concentration, D = Depth, Significant at  $P \leq 0.05$ ).

of soil can result in the dissolution of soil minerals, particularly microelement minerals. In addition, the correlations between P and micronutrients were varied (Fig. 4). The P in this work was a positive correlation with Zn in both soils, while it showed a negative correlation with other micronutrients (Fe, Cu, B and Mn). In contrast, the work of [18] showed different results, as Zn, Cu and B decrease with an increase in P concentration in the soil, whereas Fe and Mn showed a positive correlation.

Besides soil pH as a factor that affects micronutrient availability, soil texture is also deemed an important feature that influences the nutrient elements [19]. However, finer-textured clay soils often display more concentrations of micronutrients and can endure higher pH compared to sandier soils [20]. Silva et. al. [21] explained that soils with a sand texture contain the lowest Fe, Mn, Zn, and Cu, and the researchers stated that the average content of micronutrients in these soils was 4-10 times lower than those of clay loam and

loam texture soils at 0.00-0.20 m layer. In addition, Najafi-Ghiri et. al. [22] in their work on the availability of micronutrients in calcareous soil, found that a better content of clay in the soil showed preferable concentrations of micronutrients. These cations exist in the soil solution and can bind to negative charges of clay minerals by external sphere (ion exchange) or internal sphere (specific adsorption) bonds [21].

In calcareous soils at both locations, a high level of active lime can result in the release of calcium carbonate to the soil solution, which causes an increase in soil pH. As a result, the iron element is precipitated, as iron hydroxide is formed in the soil and is unavailable to be absorbed by the plants. In addition, increasing soil pH can reduce available Cu concentration due to the precipitation of the element as  $\text{Cu}(\text{OH})_2$ . However, the available form of Mn mainly depends on dissolving manganese compounds in soil, which occurs under low soil pH. Also, soil microorganisms, which influence the availability of manganese reduction, rely markedly



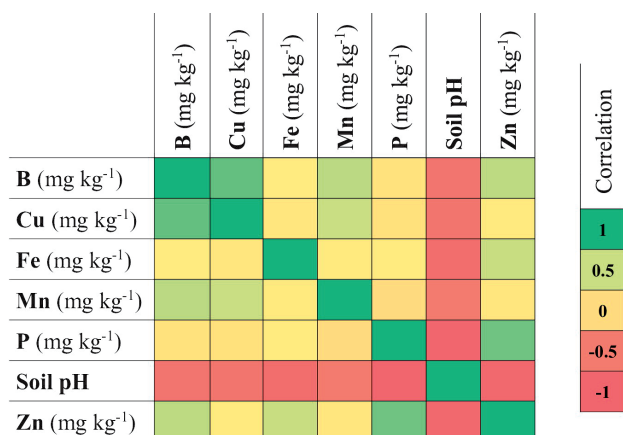
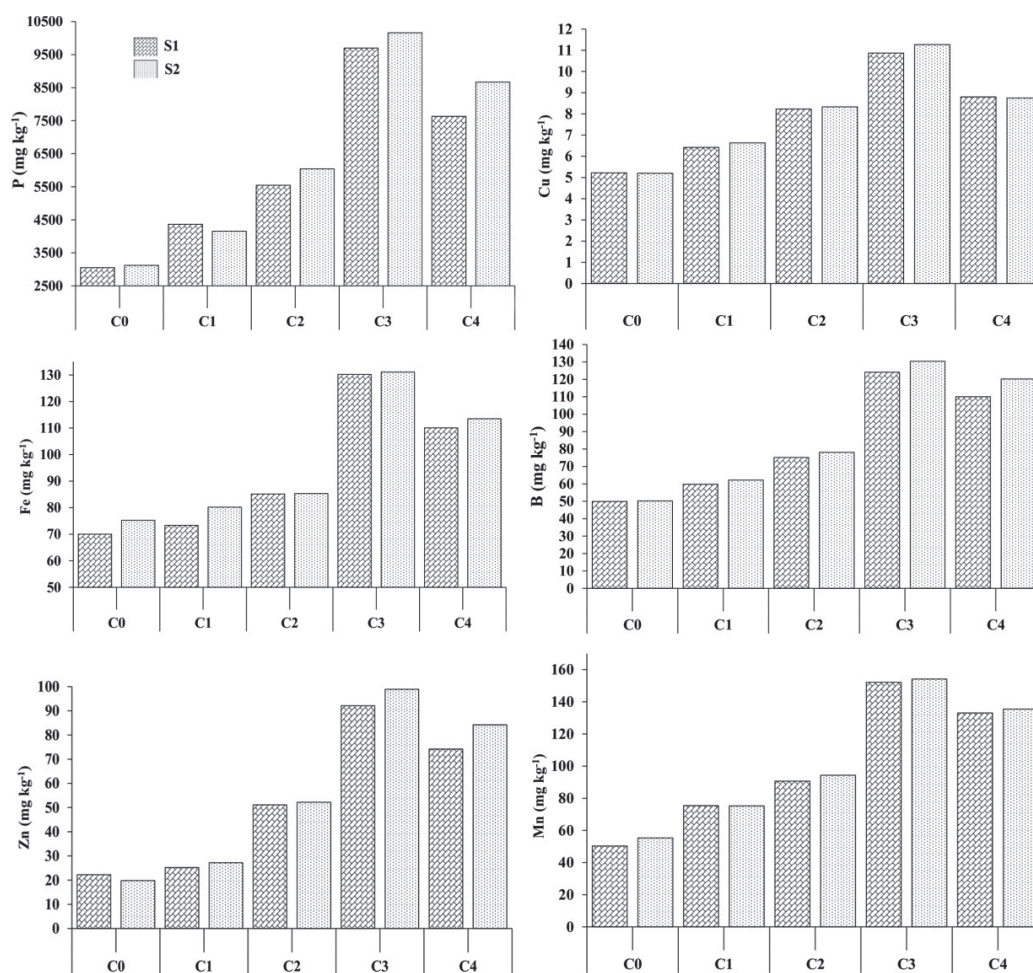


Fig. 4. Heat map of Pearson correlation coefficients between available forms of micronutrients and phosphorus of the studied soil at three depths (0-10, 10-20 and 20-30 cm).

on soil pH, and the optimum value of pH for soil microorganism activity is around 7. Furthermore, the sharp decrease in Zn concentration above pH 7 appears to be the result of the decreased concentration of  $\text{Zn}^{2+}$  species and the increase in hydrolysed forms of  $\text{Zn}(\text{OH})^+$  and  $\text{Zn}(\text{OH})_2$  [22].

### Soil Textures

Micronutrient concentration was higher at soil type S2, which contains higher clay content. It was observed that soils with high clay content have greater adsorptive capacities and higher bonding energies for micronutrients [24]. In addition, Rengel [25] confirms that micronutrients (Fe, Zn, Cu and Mn) have better availability with a relatively higher proportion of clay. Furthermore, the availability of B is greater with higher



Elements		P	Fe	Zn	Cu	B	Mn
Tukey's HSD Value	Soil Type	95.70	5.08	5.08	1.8	0.42	4.34
	Concentration	367.03	10.23	10.23	3.62	0.84	8.75
	Interaction	519.06	14.47	14.47	5.11	1.19	12.37

Fig. 5. Response phosphorus of micronutrients in plant tissues by different concentrations of sulfuric acid in two soils (S1 = Silty Clay Loam, S2 = Silty Clay, C = Concentration, Significant at  $P \leq 0.05$ ).

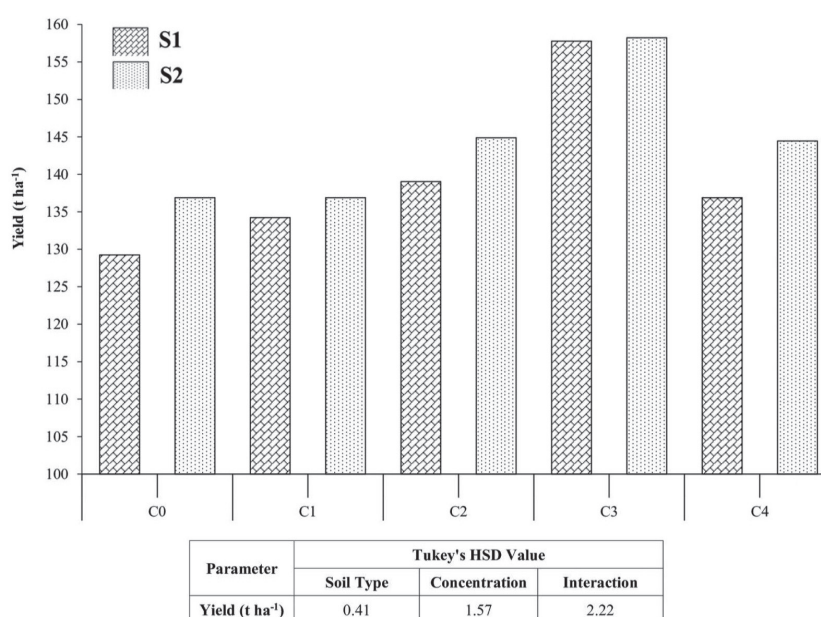


Fig. 6. Effect of different concentrations of sulfuric acid on cucumber yield in the two soils (S1 = Silty Clay Loam, S2 = Silty Clay, C = Concentration, Significant at  $P \leq 0.05$ ).

clay content in the soil, and the mechanism of the B adsorption step is considered to be ligand exchange with surface hydroxyl groups on the clay's particle edges. Therefore, additions of B could be made without it becoming toxic to plants because of a high adsorption capacity [26].

#### Element Concentration in Plant Tissue and Cucumber Yield

The best result for phosphorus, Fe, Zn, Mn, Cu and B in the cucumber stem after harvesting was obtained by the fourth concentration (3 ml L<sup>-1</sup>), as this concentration showed statistically significant ( $P \leq 0.05$ ) effects in increasing the number of elements in the plant stem tissues. The amount of Cu, Fe, B, Mn and Zn in the leaves increased with a decrease in pH in treatments, particularly the fourth factor as well as P concentration (Fig. 5). In addition, the fourth concentration of sulfuric acid ( $P \leq 0.05$ ) had a statistically significant impact on the yield (158.22 t ha<sup>-1</sup>) of the cucumber plant (Fig. 6). The acidification of soil might cause an increase in the dissolution of minerals containing microelements. Also, the absorbance of B by plants in H<sub>3</sub>BO<sub>3</sub> form, and an increase in soil pH, can result in the dissociation of H<sub>3</sub>BO<sub>3</sub> and transformation into H<sub>2</sub>BO<sub>3</sub> form [27]; finally, the availability of boron to the plants would be decreased. As a result, the B uptake is decreased by increasing the pH of the soil solution. However, in this work, the concentration of micronutrients in cucumber leaves was similar to the study of Kreij et. al. [28]. Therefore, it seems that soil acidification to a pH range of about 5.5 improved the provision of micronutrients for cucumber plants. Fageria [29] also explained that a decrease in pH of irrigation water caused an increase

in micronutrient uptake. On the other hand, Ghehsareh and Samadi [17] in their work on corn found that an increase of phosphorus uptake by the crop was obtained by acidifying irrigation water in the corn plantation.

As the availability of microelements and their uptake to the plant are improved by reducing the pH value, the yield is noticeably enhanced. The improvement of this parameter is probably due to an increase in the amount of chlorophyll in the leaves, which results from a decrease in alkalinity. Moreover, the highest amount of chlorophyll in leaves can be obtained from plant leaves in an acidic media, as the amount of chlorophyll in leaves can be an important index in determining the rate of photosynthesis [30]. Also, gains in high yields and good quality of cucumber depend on a convenient supply of macro- and microelements into the plant. Nutrient deficiency, particularly microelements, in plants can cause deterioration in plant resistance to detrimental environmental factors: declining yields and quality can occur [31]. However, the most important nutrients for cucurbits, especially cucumber, which are mainly affected by soil pH are P and micronutrients in the soil [32]. As a result, the pH for cucumber production is managed at 5.5–6.5, levels ordinarily used for plant production, and it has been observed that a target pH of 7.0 resulted in a 9.5% increase in the growth rate compared to the 5.0 treatment when the soil was acidified with an acid to manage the pH value [33].

#### Conclusions

Soil pH values noticeably were decreased by the addition of a low concentration of sulfuric acid. The values of soil pH were regularly decreased by increasing

sulfuric acid (ml L<sup>-1</sup>). The lowest soil pH was obtained by C4 (5 ml L<sup>-1</sup>). The availability of phosphorus and micronutrients (Fe, Zn, Cu, B and Mn) was markedly improved by C4 (5 ml L<sup>-1</sup>), and their concentration in plants were also improved particularly in (S2). As the acid reduces the soil pH temporarily, it would be useful for the elements to be adsorbed by the plant. Consequently, cucumber yield is enhanced, particularly in calcareous soils that have a higher soil pH that restricts the availability of most elements, especially phosphorus.

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### Conflict of Interest

The author declares no conflicts of interest.

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