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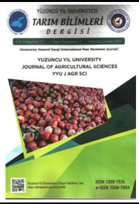

Araştırma Makalesi

Effect of Enhanced Elemental Sulphur Doses on pH Value of a Calcareous Soil

Ayşen AKAY*, Cevdet ŞEKER, Hamza NEGİŞ

Selcuk University, Faculty of Agriculture, Department of Soil Science, 42079, Konya, Turkey
*Sorumlu yazar e-mail: aakay@selcuk.edu.tr

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Abstract: Due to the lime content, the high pH value of the soils usually can limit the availability of some plant nutrients including phosphorus. Elemental sulfur (S) applications are one of the leading methods used for lowering soil pH value. Although S application is an economic resource used for reducing pH value in the rhizosphere, recommended S doses are often ineffective in lowering soil pH value. For this reason, this study was carried out to look into the effects of both the recommended sulphur doses and the intense doses of sulphur additions on the soil pH value. The effect of different S application doses in weight percentages as 0-0.01-0.02-0.04-0.08-0.16-0.32 and0.64 % of elemental S, on soil pH was determined in the pot experiment. The soil sample was taken at 0-30 cm Sarıcalar Experimental area of Agricultural Faculty of Selcuk University in Konya. The soil sample used in the study has light alkaline pH value (7.97), calcareous (12.25%), low salty less salty, organic matter content and available phosphorus concentration. At first, S were added soil samples at the pot experiment, then after, water content was brought to field capacity using pure water and incubated at 28°C for the period of 10 weeks. Weekly, pH measurements were made throughout the incubation period and regular pure water additions were made to ensure that the soil steadily remains at the field capacity. All applications led to a decrease in soil pH values, while pH is inclined to increase again during the course of time in the pot experiments.

Arttırılmış Elementel Sülfür Dozlarının Kireçli Bir Toprağın pH Değerine Etkisi

Makale Bilgileri

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Anahtar kelimeler
Kireçli toprak,
Elementel sülfür,
Toprak pH değeri

Öz: Toprakların yüksek pH değeri kirecin etkisiyle; genellikle fosfor dahil olmak üzere birçok bitki besin elementlerinin alınabilirliğini sınırlamaktadır. Elementel kükürt (S) uygulamaları, toprak pH'sını düşürmek için kullanılan başlıca yöntemlerden bir tanesidir. S uygulamaları rizosferdeki pH değerini azaltmak için kullanılan ekonomik bir kaynak olmasına rağmen, önerilen S dozları toprak pH'sını düşürmede sıklıkla etkisiz kalmaktadır. Bu nedenle, yapılan çalışmada hem pratikte önerilen kükürt dozlarının hem de yoğun kükürt ilavesinin toprak pH' sı üzerindeki etkileri araştırılmıştır. Elementel kükürdün ağırlık esasına göre % 0-0.01-0.02-0.04-0.08-0.16-0.32 ve 0.64 oranlarındaki uygulamalarının toprak pH'sı üzerindeki etkisi inkübasyon çalışmasında, saksı denemeleri ile belirlenmiştir. Çalışmada kullanılan toprak örneği Konya, Selçuk Üniversitesi Ziraat Fakültesi Sarıcalar deneme alanından 0-30 cm derinlikten alınmıştır. Denemede kullanılan toprak örneği, hafif alkali (pH 7.97) reaksiyonlu, kireçli (%12.25), az tuzlu, düşük organik madde ve yarayışlı fosfor kapsamlıdır. Başlangıçta kükürt eklenmiş olan toprak örnekleri, saf su ile tarla kapasitesine getirilmiş ve 10 hafta boyunca 28 °C'de inkübasyona bırakılmıştır. İnkübasyon dönemi boyunca haftalık olarak pH ölçümleri yapılmış ve toprağı tarla kapasitesi su içeriğinde tutmak için düzenli olarak eksilen kadar saf su ilave edilmiştir. Tüm uygulamalar toprak pH'sında sınırlı bir azalmaya neden olurken, zaman içerisinde pH değerleri tekrar artma eğilimi göstermiştir.

1. Introduction

The reactivity of $CaCO_3$ is considered a leading soil property which effects on soil chemical composition and root zone continuum (Loeppert and Suarez, 1996). In order to quality crop production must be take into account management of soil pH at optimum plant nutrient availability (Slaton et al. 2001). The high pH values of the soils limit to uptake of many plant nutrients including phosphorus by plants. The practice of suchlike nutrients to this soil, become inactive for nutrient elements rapidly turn into an unavailable usable form of the plant. Elemental S, which is applied in a constricted line to lower pH in the root zone and enhance nutrient availability to the product, is an economically practicable resolution. Elemental S which implement on a constricted line to lower pH in the root zone and enhance nutrient availability to the crop is an economically practicable solution (Wiedenfeld, 2011). The acidity generated during S oxidization ratchet up the availability of nutrients such as phosphorus, manganese, magnesium, calcium, and sulfate in soils (Lindemann et al., 1991). Various factors like soil moisture, particle size, pH, element situation, temperature and microbial activity of the soils influence the oxidation of S in calcareous soils (Soaud et al., 2011).

During the four-years of field study, the S application rates which lie in 0-1120 kg S ha^{-1} indicated pH changes. The impact of S application on soil pH gradually induced a decrease in the practice line after one year, and it lasted longer thereby continuously resulting in soil pH decline during the after four years. Soil sulfate and available phosphorus levels increased with an increase of S doses application. According to the results of this research, a single practice of S up to exactly 1120 kg S ha^{-1} at planting is recommended for sugarcane on a soil containing high $CaCO_3$ (Wiedenfeld, 2011). The large part of the agricultural area of Turkey comprises comparatively high amounts of $CaCO_3$ and pH and low organic matter content. Over 63% of these soils had a pH higher than 7.5 and approximately 59% of these soils included more than 5% $CaCO_3$ Eyüboğlu (1999). Also, Turkey's soil, the deficient of phosphorus and trace elements in the soils is one of the most important problems. In solving this problem, the application of sulfur to the soil is an important solution way. In recent years, interest in the land use of elemental sulfur to increase the solubility of phosphorus and micronutrient elements, which have been observed in soil with high pH and calcareous soils, has increased (Kashirad and Bazargani, 1972; Abd-Elfattah and Hilal, 1985; Hilal and Abd-Elfattah, 1987).

Nevertheless, the wideness of free $CaCO_3$ in calcareous soils raises the pH of the whole soil profile. A possible alternative would be to reduce the pH of the soil in a small zone directly accessible to the crop root system (Wiedenfeld, 2011).

According to the other conducted study, elemental sulphur was applied at different rates to calcareous soils. As a results, pH value significantly decreased with S applied at a rate of 0.5%, but EC, extractable P, Mn, Fe and Cu increased with S applications (Modaihsh et al., 1989).

Concerning the study conducted in Iran, when the effects of sulfur applied at doses of 0, 20, 40, and 60 t da^{-1} were examined. At last of the study, the deterioration rate was very low and only 1.5, 2.3, and 2.0% of the applied agricultural sulfur level was oxidized to sulfate, respectively (Sameni and Kasraian, 2004).

Another study has been carried out the effects of elemental S and S-containing waste (40, 80 and 120 kg S da^{-1}). From the results indicate that the practices of elemental S and S-containing waste resulted in a decreased soil pH, while these applications increased available nutrient concentration and had a favorable effect on element uptake of plants (Kaya et al., 2009).

This study was carried out under the land of Central Anatolia region in Turkey, in which frequently occurs phosphorus, iron and zinc deficiencies in plants because of having the higher plethora of lime. In the first stage of the ongoing project, it was aimed at decreasing the pH value by applying elemental sulfur at different doses to a soil possessing a high pH and lime content.

2. Materials and Methods

The soil sample was taken at 0-30 cm soil depth from Sarıcalar Experimental area of Agricultural Faculty of Selcuk University in Konya. Particle size analysis was done by the hydrometer method (Gee and Bauder, 1986), soil pH and EC was measured in water (1:2.5 soil: distilled water), $CaCO_3$ equivalent by Scheibler calcimeter method. Organic matter content was determined by modified Walkley-Black method (Walkley and Black 1934), available phosphorus by the Olsen sodium bicarbonate method (Olsen and Sommers, 1982), and trace elements by DTPA soil test of Lindsay and Norvell (1978).

Some of chemical and physical properties of the study soil are given in Table 1. The soil sample used in the study has light alkaline pH value (7.97), calcareous (12.25%), low salty organic matter content and available phosphorus concentration.

Table 1. Some physical and chemical properties of the experiment soil

	Textural class	$CaCO_3$	pH (1/2.5)	EC (µS/cm)	Organic matter (%)	Field capacity (%)
Soil Properties	Loam sand	12.25	7.97	235	2.02	28.37
	Fe (mg/kg)	**Cu (mg/kg)**	**Mn (mg/kg)**	**Zn (mg/kg)**	**P (mg/kg)**	**K (mg/kg)**
	7.67	1.28	9.12	1.37	5.14	840

The effect of different elemental S with low doses (0-0.01-0.02-0.04-0.08 %), and high doses (0.16-0.32-0.64%) on soil pH value was determined by in the pot experiment. The collected soil samples were air dried, then passed through a 4 mm sieve, weighed (1000 g pot^{-1} oven dry weight) and filled into the pots. The experiment was being carried out as for that to the randomized block design with 3 replications including the control. Eight different treatments were applied as follows: 0 (Control (C))-0.01% (S_1)-0.02% (S_2)-0.04% (S_3)-0.08% (S_4)-0.16% (S_5)-0.32% (S_6)-0.64% (S_7) elemental S in percentages (Elemental S contained 90% S) which were mixed with the soil in the pot during January 2018. Soil samples, which were control and added S, were brought to field capacity water content by using pure water and incubated at 28 °C for the period of 10 weeks. During the experiment, weekly measurement of soil pH was taken from the soil samples. Data were analyzed by SPSS-22 software. The comparison of the means was done based on One-way Anova and Tukey Test at %5 probability level.

3. Results

It was observed that the effect of elemental S application on soil pH at all sampling times was significant (Table 2). Changes in pH due to sulfur application over time are shown in Figure 1. These changes may have been due to the neutralization of free carbonates in the soil. When all periods were examined, there were a decrease in soil pH over time, and these decreases ranged from 0.28 to 0.60. When Table 2 was examined, a large decrease of 0.60 units in soil pH was seen after applying of 0.64 S doses at 42nd day. Similar result was also reported by (Kaplan and Orman 1998). Soil pH decreased from 0.16 to 0.25 units with an increasing of S doses at 70th day and these changes were at 2.04-3.22%.

Elemental S application decreased soil pH during the first 56th day, whereas, after which pH tended to increase. At these S applications (S_1, S_2, S_3, and S_4), the pH value outraced the control at the end of the 70th day (Figure 2). However, this is not observed on the 70th day in high-dose S applications (Figure 3). Referring to the conducted research, the effect of different doses was for due to the strong buffering capacity of the calcareous soils (Beverly and Anderson 1987). When the incubation period of the control group was examined, there were no significant differences in pH values. When different days of all sulfur doses were examined, there was a decrease in pH compared to the control, as well as a significant decrease in pH values with an increase in doses. When Table 2 was examined, it was found that there was a decrease from the 28th day in the first low doses S application, whereas a significant difference was found in the high doses sulfur application after the 7th day. High calcium carbonate level in soil counteracts the acidifying effects of elemental S oxidation by making amendment effects temporary and minimally effective (Beverly and Anderson, 1987).

Table 2. Soil pH in incubated soil as affected by elemental S

Dose/Period	7th day	14th day	21th day	28th day	35th day	42th day	49th day	56th day	63th day	70th day
C	$7.92 \pm 0.09^{A, ns}$	$7.92 \pm 0.07^{A, ns}$	$7.90 \pm 0.10^{A, ns}$	$7.93 \pm 0.01^{A, ns}$	$7.89 \pm 0.11^{A, ns}$	$7.94 \pm 0.12^{A, ns}$	$7.81 \pm 0.04^{A, ns}$	$7.79 \pm 0.01^{A, ns}$	$7.84 \pm 0.06^{A, ns}$	$7.84 \pm 0.03^{A, ns}$
S_1	$7.91 \pm 0.01^{AB, a}$	$7.90 \pm 0.02^{A, a}$	$7.90 \pm 0.01^{A, a}$	$7.90 \pm 0.01^{A, a}$	$7.89 \pm 0.10^{A, ab}$	$7.88 \pm 0.04^{AB, abc}$	$7.80 \pm 0.01^{A, bcd}$	$7.78 \pm 0.02^{A, d}$	$7.79 \pm 0.02^{AB, cd}$	$7.86 \pm 0.02^{AB, abcd}$
S_2	$7.90 \pm 0.01^{AB, a}$	$7.88 \pm 0.03^{AB, ab}$	$7.88 \pm 0.01^{A, ab}$	$7.88 \pm 0.01^{A, ab}$	$7.84 \pm 0.08^{AB, abc}$	$7.81 \pm 0.05^{AB, abc}$	$7.76 \pm 0.01^{AB, c}$	$7.76 \pm 0.02^{AB, c}$	$7.77 \pm 0.04^{AB, c}$	$7.80 \pm 0.01^{BC, bc}$
S_3	$7.84 \pm 0.01^{ABC, ab}$	$7.81 \pm 0.02^{AB, abc}$	$7.87 \pm 0.01^{A, a}$	$7.83 \pm 0.01^{B, ab}$	$7.74 \pm 0.06^{ABC, de}$	$7.79 \pm 0.03^{B, bcd}$	$7.73 \pm 0.03^{B, de}$	$7.72 \pm 0.01^{B, e}$	$7.73 \pm 0.01^{B, de}$	$7.76 \pm 0.02^{C, cde}$
S_4	$7.83 \pm 0.02^{BC, ab}$	$7.83 \pm 0.03^{AB, a}$	$7.75 \pm 0.01^{B, bc}$	$7.73 \pm 0.02^{C, cd}$	$7.66 \pm 0.08^{BCD, def}$	$7.62 \pm 0.02^{C, ef}$	$7.61 \pm 0.02^{C, ef}$	$7.61 \pm 0.01^{C, f}$	$7.63 \pm 0.04^{C, ef}$	$7.67 \pm 0.01^{D, cde}$
S_5	$7.80 \pm 0.01^{C, a}$	$7.79 \pm 0.02^{B, a}$	$7.66 \pm 0.02^{C, b}$	$7.62 \pm 0.04^{C, b}$	$7.57 \pm 0.06^{CDE, cd}$	$7.56 \pm 0.02^{CD, cde}$	$7.51 \pm 0.01^{D, de}$	$7.50 \pm 0.01^{D, e}$	$7.57 \pm 0.01^{C, cd}$	$7.58 \pm 0.03^{E, c}$
S_6	$7.77 \pm 0.02^{C, a}$	$7.64 \pm 0.06^{C, b}$	$7.53 \pm 0.02^{D, c}$	$7.61 \pm 0.02^{D, b}$	$7.50 \pm 0.05^{DE, cd}$	$7.49 \pm 0.01^{D, cd}$	$7.42 \pm 0.02^{E, de}$	$7.40 \pm 0.05^{E, e}$	$7.61 \pm 0.01^{C, b}$	$7.52 \pm 0.02^{F, c}$
S_7	$7.64 \pm 0.01^{D, a}$	$7.56 \pm 0.08^{C, ab}$	$7.46 \pm 0.01^{D, cd}$	$7.43 \pm 0.01^{E, d}$	$7.40 \pm 0.04^{E, de}$	$7.34 \pm 0.03^{E, ef}$	$7.33 \pm 0.02^{F, ef}$	$7.31 \pm 0.01^{F, f}$	$7.47 \pm 0.01^{D, cd}$	$7.50 \pm 0.02^{F, bc}$

C: without elemental S, S_l: 0.01 elemental S added to soil, S_2: 0.02 elemental S added to soil, S_3: 0.04 elemental S added to soil S_4: 0.08 elemental S added to soil S_5: 0.16 elemental S added to soil S_6: 0.32 elemental S added to soil S_7: 0.64 elemental S added to soil.
Statistically significantly data are given that with different letters in the same row and column ($P < 0.05$).
Capital letters show differences between the soil samples and lower letters present the differences between the storage times.3

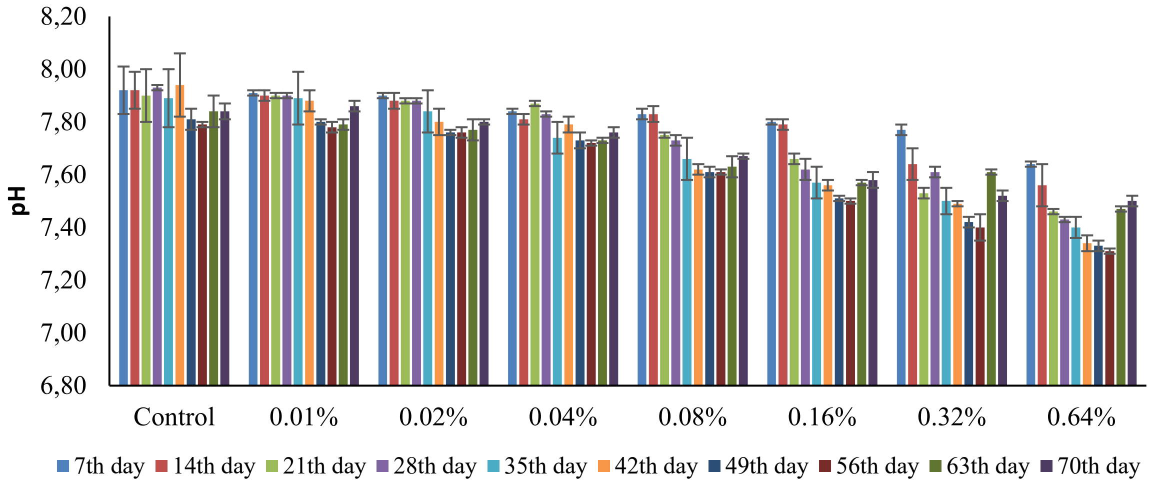

Figure 1. The effect of elemental S application on change in pH value depending on time (n=3).

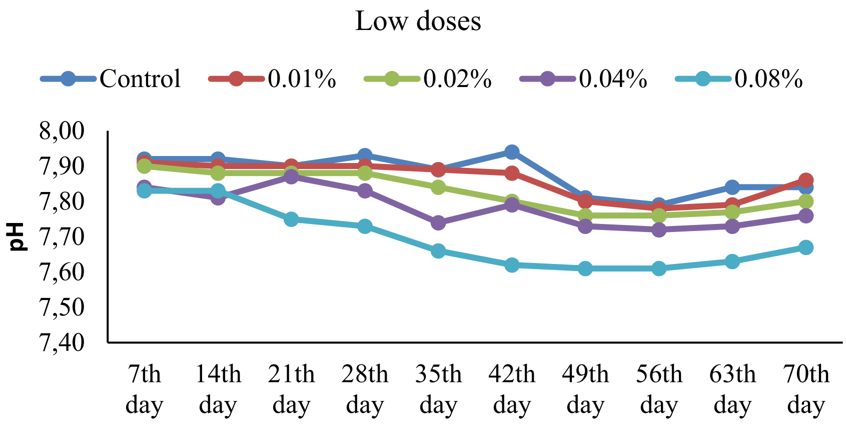

Figure 2. Effect of low dose S application on pH change (n=3).

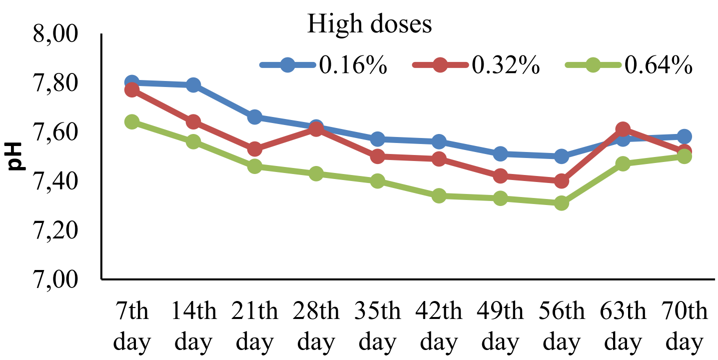

Figure 3. Effect of high dose S application on pH change (n=3).

Table 2 shows that S oxidation is slower at low doses. From the 28th day for the first five doses, the decrease in pH values is statistically significant compared to the control. However, the S oxidation at high doses from the beginning 7th day was started. When the pH values measured at 49th and 56th day, it was seen that the effect of S application was the most in these days (Figure 4). In a similar study; it was observed that the application of S in a calcareous soil resulted in a sharp reduction of soil pH in the first 6 weeks, and then remained stable within 8 weeks, and a slow decrease in pH, but after the 16th week, pH increased again (Tisdale and Nelson, 1958).

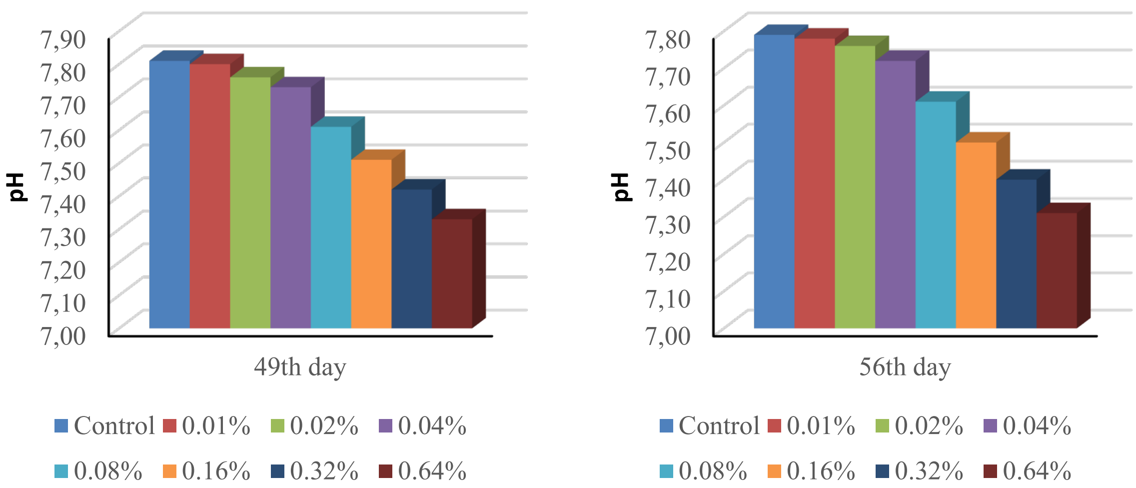

Figure 4. Effect of different dose S application on pH change at 49th and 56th days (n=3).

4. Discussion and Conclusion

The results showed that the elemental S application reduced the pH value of the soil, but the effect was lower at low doses, with no continuity during the incubation. However, it was observed that the effect of S application at high doses continued throughout the incubation period. As a result, at least 800 kg da^{-1} (0.32% S; the value was calculated from soil bulk density for 1.25 g cm^{-3} in 0-20 cm soil depth) of S can be applied in the field conditions in order to increasing in the availability of plant nutrients by lowering the pH value in soil with high lime content. Although 800 kg da^{-1} of S application reduces the soil pH to the desired level; it cannot be recommended in field conditions because of this application unpractical and high cost. Application of the elemental S form necessitates inoculation with suitable S bacteria to achieve rapid oxidation of sulfur dioxide. Another solution is to accelerate the oxidation time of the S application in the form of the appropriate sulphate. Since this work was a pioneering work, it was planned to find a holistic approach to increasing the availability of sulfur and reducing the amount of S content to be used.

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