EFFECT OF SULFUR APPLICATION ON SOIL COPPER FORMS

Christos D. Tsadilas, E. Evangelou, M. Tziouvalekas

Hellenic Agricultural Organization DEMETER, Institute of Industrial and Forage Crops *Email: christotsadilas@gmail.com*

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Introduction

Sulfur (S) is applied to soils as an essential nutrient for plant growth or as a soil amendment for reducing soil pH of alkaline soils. Heavy metal contamination is serious concern worldwide since they can be released under changing physicochemical conditions and pose a potential threat to human health and the environment. Heavy metals have both natural and anthropogenic origins with human activities supplementing natural geochemical background values of the pollutants. Copper (Cu) is an essential to plants micro-element but at the same time it is a basic constituent of fungicides used extensively in agriculture such as in vine culture to control fungal diseases. This practice lead to Cu contamination of agricultural soils especially those cultivated with vineyard (Komarek et al., 2010). Copper availability to plants depends on several factors one of the most important being soil pH. Soil pH change affects seriously the distribution of heavy metal forms. In general, as soil pH decreases, available heavy metal fractions increase increasing thus their availability to plants and the possibility of metal leaching (Tsadilas, 2001). Chick-pea is an interesting crop in Greece suffering from root rot disease controlled by fungicides containing Cu which causes soil contamination. The purpose of this study was to investigate the influence of elemental sulfur application to a Greek representative agricultural soil cultivated with chick-pea on the basic soil properties and Cu forms.

Methods

A pot experiment was conducted with an alkaline medium textured soil classified as Typic Xerochrept in which chik-pea was grown in a non heated greenhouse. In three kg of air dried soil, elemental sulfur was applied at rates 0 g S/per pot (control, S_0C), 2 g S/pot (S_2), 4 g S/pot (S_4), and 6 g S/pot (S_6). The mixtures were transferred into plastic pots, wetted up to field capacity, left for two weeks and then they were sown with ten chick-pea seeds per pot which were thinned to three after one month of their emergence. The plants were irrigated up to field capacity by weighting once a week and harvested by cutting the above ground plant parts three months after emergence. Plant samples were dried, ground and incinerated at 450 °C, the ash was diluted with dilute HCl solution and analyzed for basic elements and Cu content. At the same time soil samples were collected from all the pots, air dried, ground to pass a two mm sieve, and analyzed for pH, electrical conductivity (EC) and copper after extraction with the 0.005 M DTPA, pH 7.3 (Cu_{DTPA}) (Lindsay and Norvell, 1978). In addition, Cu was fractionated in exchangeable (Cu_{ex}), organic matter (Cu_{om}), Mn oxides (Cu_{Mnox}), amorphous Fe oxides (Cu_{Feaox}) and crystalline Fe oxides (Cu_{Fecox}) associated forms and residual fractions (Cu_{res}) according to Emmerich et al., 1984). Total Cu was also determined according to Baker and Amacher, 1982). Analysis of variance was performed by using the LSD test at the probability level $p<0.05$ and regression analysis where needed.

Results

From the properties tested, it was revealed that S application resulted in significant change of soil pH and electrical conductivity. Soil pH decreased gradually from 8.00 in the control up to 5.72 in the treatment with the highest S rate (S_6) while EC increased about three times i.e. from 0,943 to 2,627 mmhos/cm. This EC change affects seriously the quality of soil and the plants grown on it. Cu_{DTPA} and plant tissues Cu were not significantly changed (Table 1).

Table 1. Influence of sulphur application on soil pH, electrical conductivity and available Cu

Treatments	Soil pH	EC, mmhos/cm	Cu_{DTPA}, mg/kg	Plant-Cu, mg/kg
S_0	8,00a*	943c	1,30a	7,25a
S_2	6,95b	1885b	1,45a	8,67a
S_4	6,35bc	2139b	1,37a	7,33a
S_6	5,72c	2627a	1,50a	7,50a

*Values in the same column followed by different letters differ significantly ($p<0,05$, LSD test)

The effect of S application on soil Cu fractions is presented in Table 2, from which it is obvious that S addition affected significantly only Cu_{ex}, and Cu_{om} **in an opposite way.** $\mathbf{Cu_{ex}}$ **tended to decrease with the increasing S rate while** $\mathbf{C_{om}}$ **increased.** $\mathbf{Cu_{DTPA}}$ **was negatively correlated with pH (r=-0,73**) showing that pH decrease results in increasing** $\mathbf{Cu_{DTPA}}$**, although this indicator is effective for chick-pea plants since its tissue concentration showed a non significant correlation with Cu content of chick-pea tissues (r=0.34, ns). Soil pH was significantly correlated with** $\mathbf{Cu_{ex}}$ **(r=0,742**) and** $\mathbf{Cu_{Mnox}}$ **(r=0,549***) but negatively with** $\mathbf{Cu_{om}}$ **(r=-0,682**) and** $\mathbf{Cu_{Fecox}}$ **) r=-0,533*). A multiple regression forward elimination procedure showed that about 87% of the variation of the** $\mathbf{Cu_{DTPA}}$ **depends on the parameters as it is shown by the equation:** $\mathbf{Cu_{DTPA} = 1,845-0,179*pH+0,231Cu_{Fecox}+Cu_{total}-0,532C_{om}}$, $\mathbf{R^2 = 0,869^{***}}$**.**

Table 2. Influence of sulphur application on Cu fractions

Treat	Cu_{ex}	Cu_{om}	Cu_{Mnox}	Cu_{Feaox}	Cu_{Fecox}	Cu_{res}	Sum	Cu_{total}
S_0	0,053a	0,27b	0,027a	2,73a	0,63a	23,35a	27,02a	25,0a
S_2	0,031ab	0,24b	0,0170a	2,75a	0,60a	23,62a	27,24a	23,0a
S_4	0,016b	0,42a	0,021a	2,47a	0,62a	25,13a	28,65a	21,2a
S_6	0,006b	9,43a	0,004a	2,50a	0,96a	25.47a	28,48a	19.7a

*Values in the same column followed by different letters differ significantly ($p<0,05$, LSD test)

Conclusion

Elemental sulfur application to alkaline soils significantly decreases soil pH and increases electrical conductivity. Soil Cu fractions are seriously affected by S application, especially those associated with exchangeable, Mn oxides forms (positively) and with organic matter and crystalline Fe oxides (negatively). A percentage about 87% of the variation of Cu_{DTPA} is explained by soil pH, total Cu, and Cu fractions associated with crystalline Fe oxides and organic matter.

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