Effect of Elemental Sulphur on Solubility of Soil Nutrients and Soil Heavy Metals and Their Uptake by Maize Plants

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Abstract: Pot experiment in green house at national research center was conducted on loamy sand soil (polluted soil by industry wastes) to study the influence of elemental sulphur on solubility of soil Cd, Ni, pb and Cu, Zn, Mn, and their uptake by maize plant. Three rates of elemental sulphur applied (100, 200 and 300 kg/ha). The result showed that with S application at 300Kg/ha, soil pH decreased about 0.7 unit compared with control, extractable sulfate concentration increased with increase S application and the all parameters of plants and the concentration of chlorophyll were increased with increasing rates of suphur application, The concentration of N, P and K in maize plant was increased with sulphur application. The solubility of the Fe, and Cd was significantly increased in all treatments with S application, however, the solubility of pb and Ni increased little by the treatment with S. soil extractable copper and Zinc concentration remained at a stable level or little change with all treatment of sulphur. Mn, Pb and Cd content in the plant markedly increased with increased rates of sulphur application; on the other hand, Nikel concentration had adverse effects with sulphur application. Application of elemental sulphur can enhance uptake of Zn by Maize plant. Removal of pb and Cd did not significance increase with application of S. because Maize plant was sensitive to the toxicity of pb/Cd.

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1. Introduction:

Soil contamination by heavy metals ions important issue around the world because some metals are very toxic to microorganisms, plants and animals. With a rapid increase in industry and city population in most cities Egypt. There is considerable interest in the development of technique for remediation of sites contaminated with heavy metals at minimal cost with the least environmental side effects.

In recent years, phytoremedation (especially phytoextraction) has been considered as a cost – effective approach to remediate soil contaminated by heavy metals. The success of phytoremediation depends on several factors, e.g., plant must produce sufficient biomass while accumulating a high concentration of the certain metal. The metal-accumulating plants also need to be responsive to agricultural practices to allow repeated planting and harvesting of the metal-rich tissues (Blaylock et al., 1997). Therefore, enhancing metal accumulation in existing high yielding crop plants without diminishing their yield is the most feasible strategy in the development of phytoremediation and maize is often used as a metal accumulator in phytoremediation experiments (Huang et al., 1997; Brennan and Shelley, 1999; Bricker et al., 2001).

In the process of phytoremediation, the bioavailability of heavy metals is an important factor. There are two main approaches that have been used to increase the bioavailability of heavy metals in soils and the mobility of heavy metals within plants: lowering soil pH (Salt et al., 1995; Chlopeka et al., 1996; Blaylock et al., 1997) and adding synthetic chelates (Blaylock et al., 1997) such as ethylenediaminetetra acetic acid (EDTA), nitrilotriacetic acid (NTA) and diethylenetriaminepenta acetic acid (DTPA). A decrease in soil pH can be achieved by application of mineral or organic acids or acid-producing fertilizer such as ammonium chloride (Salt et al., 1995; Huang et al., 1997; Wasay et al., 1998). However, these methods have some limitations due to negative effects on the chemical, physical and biological properties of the soil, or may lead to groundwater pollution through leaching. To avoid some of these constraints, the use of elemental S to decrease soil pH and increase the solubility of heavy metals in soils has been suggested (Tichy et al., 1997; Seidel et al., 1998; Kayser et al, 2000). However, more investigation are needed to evaluate the feasibility of this method as a tool for the enhancement of metal solubility and uptake by a metal accumulator, especially in alkaline or neutral soils contaminated by different concentrations of heavy metals when applied 25 kg-ha^{-1} in the sulphate kind. The content of Cu, Zn, Mn (except Fe) in the dry mass and uptake these elements by yield of dry mass of potato tuber was significantly determined by S fertilization. The highest content of Cu and Zn in the dry mass and uptake these elements by yield of dry mass of tuber was after applying 50 kg $S\text{-}ha^{1-}$ in elemental kind and on the control plots (without sulphur). Content and uptake of Mn by tuber was after applying 50 kg $S\text{-}ha^{-1}$ in elemental kind and on the control plots (without sulphur). Content and uptake of Mn by tuber was reduced by sulphur fertilization, and the contents and uptake of the Fe by tuber increased as a result of increasing doses of sulphur (although not confirmed that statistically). Elemental sulphur in dose 50 $kg\text{-}ha^{-1}$ substantially reduced the pH value of the soil. It was a significant correlation between the pH value of the soil and the contents of Cu (negative), Zn (positive) and Mn (different values depending on years of research) in the dry mass and uptake these elements by yield of dry mass of potato tuber (Hanna Klikocka, 2011)

In a study by Kayser et al., (2000), the application of elemental sulfur and a decrease in soil pH increased the solubility of heavy metals.

Some elements, including zinc and copper, precipitate as sulfides and sulfates, to produce forms that are relatively immobile in the soil profile (Kabata-Pendias and Pendias 1992). Cadmium, on the other hand, can form inorganic ligands with S-SO_4^{2-} (Mclaughlin et al., 1996) therefore, the objectives of this study were to investigate the effect at different rates of sulphur (0, 100, 200, 300ppm) on metal solubility of soil and investigate the potential to increase metal uptake and accumulation by Maize plant through application of sulphur.

2. Material and Methods:

Pots experiment was conducted in green house at national research centre; loamy sand soil was collected from the top 20 cm of profile in Helwan, Cairo, Egypt. (Pollution soil by industrial wastes) some physical and chemical properties of the use soil are determined and represented in Table (1). Maize (Cv. Giza hybrid 321) was germinated and five uniform seedlings were planted in each pot and thinned to leave two plants in each pot. Soil moisture content was adjusted regularly by weight to about 60% of water holding capacity and the plants were grown for 60 days. The experimental designs were carried out in design randomized was factorial experimental in completely with three replicates in plastic pots; the pots were filled with 10 kg of arid soil.

Elemental Sulphur was applied and mixed thoroughly with the soil before sowing at four rates 0 (S_0), 100(S_1), 200 (S_2), 300 (S_3). Fertilizer was applied at the rates of 100mg N (as ammonium suphate) and 200 mg of potassium dihydrogen phosphate as a source for P and K.

The soil samples were taken at 30 and 60 days after sowing or measuring pH value and SO_4 concentration in wetted sample, then air dried, sieved passing through a 2- mm sieve and analyzed for pH, SO_4 and the available of Zn, Mn, Cd, Ni, Pb and Cu in soil (DTPA extractable) and determination by atomic absorption spectrophotometer. The plant sample taken at the end of experiment (60 days after sowing).

Table (1): Some chemical and physical properties of the studied soil.

Site	Clay%	Texture	PH (1:2.5)	E.C. (dsm^{-1})	Cations meq/L				Anions meq/L		
					Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO^{-}_3	Cl	SO_4^{--}
Helwan	17.3	Loamy sand	8.5	1.31	11.2	38.0	38.2	44.3	7.6	151	1.45

Site	OM%	$CaCO_3$%	DTPA available heavy metals (µ/g/g)				Total heavy metal (µ/g/g)			
			Cd	Ni	Pb	Cu	Cd	Ni	Pb	Cu
Helwan	1.05	3.35	0.47	5.9	3.92	4.8	10.7	25.2	20.2	25

All the plants were harvested after the end of experiment (60days after sowing) and the plant samples were rinsed with distilled water, oven dried at 70°C, ground and digested and analyzed for determined some macronutrients, micronutrients and some heavy metal chlorophyll was also estimated according to Lichtenthalar and Wellburn (1983).

The digested plant solutions were analyzed for N using Micro kjeldoh technique. Micronutrients Fe, Mn, Zn and Cu determination by atomic absorption spectrophotometer.

3. Results and discussion

Soil pH Soil pH decreased in all the treatment with application of S compared to control (table 2), one important fact is the oxidation of S by certain groups of acidophilic bacteria notably thibacillus spp. In the soil (Lee et al., 2000). Kayser et al. (2000) reported that adding 36 mol sm^{-2} to the soil led to a decrease in soil pH from 7.2 to 6.9. In the present experiment adding S also acidified the soil especially with high rates at sulphur and at 60 days after application, which caused the soil pH to decrease about 0.7 units within 60 days compared with control (His Kwierawska et al., 2012 and Yanshan et al. 2003)

Table (2): Change in pH and SO_4'' under different rates of S application after 15 and 60 days

Sulphur rates (kg/ha)	30 days		60 days	
	pH	SO_4'' mg/100g	pH	SO_4'' mg/100g
S_0: control	8.5	18.5	8.3	40.0
S_1: 100	8.3	25	8.0	55
S_2: 200	8.0	40	7.7	105
S_3: 300	7.8	55	7.6	150

The elemental sulphur addition resulted in a noticeable presence of SO_4'' concentration in the soil. However, the magnitude and timing of sulfate formation differed with the of sulphur application.

Sulfate concentration increase with all rates of sulphur the high concentration obtained with the rate of 300 ppm of sulphur at 60 days.

Table (3): Effect of different rates of sulphur on some available nutrients in the soil after experiment (mg/kg soil)

Sulphur rates	Zn	Cu	Mn	Pb	Cd	Ni
Control	0.8	0.31	1.31	3.9	0.32	2.53
100	0.7	0.3	1.52	4.8	0.45	2.81
200	0.9	0.32	1.60	5.2	0.53	2.42
300	0.8	0.34	1.71	6.3	0.65	2.66

Changes in natural heavy metal content of soil fertilized with elemental sulphur at a dose of 0, 100, 200, 300 mg/kg soil were studied after the experimental (Table 3).

At the end of experiment, soil extractable **Zn** concentration change a little with or without S application zinc concentration ranged from 0.7 to 0.9 mg/kg, irrespective of sulfur doses, application of sulphur increase the Zn available in soil. Kayser et al. (2000) demonstrated that the application of elemental sulfur increased zinc solubility in the soil and utilization by plants. Kaya et al. (2009) reported that the application of sulfur and sulphur –containing waste resulted in decrease in soil pH, but it also increased the concentration of nutrients available to plants, such as Zn, Cu and Mn. Different results were obtained by Abou et al. (2011).

Copper concentration remained at a stable level in all treatments copper concentration tended to increase in the treatment with a 300mg/kg dose of elemental sulfur fertilization and no significant effect on change in the copper content of soil. (Tichy et al. 1997, Seidel et al. 1998, Martimez et al., 2000).

Mn, pb, Cd markedly increased with soil pH decrease for all the rates of sulfur application one of the adverse effects of sulfur contamination is an increase in manganese solubility and the mobilization of heavy metals from both natural and anthropogenic sources (James and Riha 1984). The highest concentrations of Mn were 1.71mgkg^{-1} at 300mgkg^{-1} of sulfur application as the same the pb concentration (6.3 mg kg^{-1}) and Cd (0.65 mgkg^{-1}).

Nickel content ranged between 2.53 to 2.81mg kg^{-1}, Nikel content increased with increased rates of sulfur application nickel content depletion was observed in high rate of sulphur probably due to increased nickel uptake by plants. Our results corroborate the findings of Holah et al. (2010).

Plant dry matter biomass was also affected by application of S (table 4) The dose of the elemental sulphur in dose of 300 kg/ha^{-1} cause highest weight of shoots and roots of maize plants but change in weight of dry matter of shoots a little with or without sulphur application one of those possibilities was that the soil pH decreased, which may have introduced of the heavy metal. Grains and phatak, (2002) found that increase sulphur levels significantly increased the dry weight of corn, soybean, tomato, cowpea laps and soy bean roots. phytotoxicity by increasing the solubility and bio availability

Table (4): Some parameters of Maize plant and some micronutrients content under different rates of sulphur application.

Sulpur rate kg/ha	Fresh weight (g/plant)	dry weight (g/plant)	F.w root(g/plant)	D.w. root(g/plant)	Choloblyl mg/gm	N%	P%	K%
0	109	13.7	24.3	3.4	0.62	1.76	0.53	1.6
100	111	14.7	28.7	5.5	0.60	2.27	0.63	2.6
200	119	13.8	39.6	6.4	0.73	2.5	0.66	2.0
300	124	16.4	42.7	8.2	0.86	2.3	0.7	2.7

Koyser et al. (2000) reported that shoot weight in some plants did not significantly with s application Hanna a klikocka (2001) reported that, the yield of dry mass was greatest when applied 25kg/ha S in sulphute and elemental kind.

Addition of elemental sulphur increased the total chlorophyll content especially when addition 300kg ha^{-1}. This might be due to the acidification of soil caused by the oxidation of sulphur. (Rending and Mc comb, 1991) indicated that the chlorotic condition of leaves in sulphur deficient plants was visual evidence of disturbance in photosynthesis. They suggested that sever deficiency enough to disrupt normal photosynthesis would ultimately be reflected on the changes in the kinds and amounts of carbohydrates.

Nitrogen: Application of Sulplur was more effective concerning N concentration. It was observed that addition of 300 $kg.ha^{-1}$ increased the nitrogen concentration to 2.3% as compared with control (1.76%) oxidation of sulphur may regulate the pH of soil, (McNaught and chrisloffels, 1991) indicated that sulphur addition enhanced nodulation, sulphur may have increased nodulation by increasing growth and nitrogen demand.

P-concentration, data in Table (4). Results revealed that application of sulphur increased the p-concentration due to the acidification effect of the rizospher through oxidation products of sulphur which can mobilize considerable amounts of phosphorous. (Khater, 1981) showed that application of sulphur generally increased available P in alluvial soil. (Shadfan and Hussein, 1985) found a significant increase in $NaHCO_3$ extractable P from 10-13.5 ppm by applying 500 ppm S and 8 weeks of incubation in a loamy sand soil.

Potassium concentration affected by S-application k-concentration increased when added sulphur at rate 200kg ha^{-1}, but gave the same value with 100 or 300kg ha^{-1}. In field experiments, (Singh et al. 1995) found that, application increased concentration of N, k and S of groundnuts plants grown on alkaline calcareous soils. Also, added that ph of leaf sap, P and Fe concentration were significantly reduced by sulphur application

Some micro nutrients and heavy metal in maize plant

Table (5) indicated that sulphur application affected highly Fe content, Fe content increased with increased suphur rates this may be attributed to formed sulpluric acid and consequently decreased soil pH which increased iron availability in the soil however, no significant change could be observed in Mn or Cu content relation to rates of S-application.

Table (5): some micronutrient content and some heavy metal in maize plant under effect of sulphur (mg/kg)

Sulphur rates (kg/ha)	Fe	Mn	Zn	Cu	Cd	Ni	pb
0	163	127	38	11.4	46.5	6.53	2.86
100	180	124	36	9.7	4.8	8.5	2.91
200	211	115	38	8.8	5.1	6.2	3.0
300	256	97	39	13.7	5.5	6.5	3.1

On the other hand, the concentrations of pb, Zn and Cd in plants increased with the increased application of sulphur than without sulphur.

It is well known that pb is an immobile metal in soil since it readily forms a precipitate with a low aqueous solubility within the soil matrix and in many cases it is not readily bioavailable, especially in alkaline or neutral soil (Blay Lock et al., 1997; Martinez and Motto, 2000). In addition, many plants retain pb in their roots via sorption and precipitation with only minimal transport to the aboveground harvestable plants portion (Kumar et al., 1995; Huang and Cunningham, 1996; Brennan and Shelley, 1999). In the present experiment, the increase of pb concentration in maize plant is lower than that of Zn and Cd.

Compared to without application of S, concentrations of Zn in maize plant increased by 18.75 and 21.8% with application of S at the rate of 200, 300 kg. ha^{-1}. (Biddappa et.al, 2002) found that the Pb and Cu ions were less mobility than other heavy metal under the lead

Concentration of Cd in lettuce plant increased by 13.3 and 22.2% with application of S at the rate of 200 and 300 kg.ha^{-1} (Table 5). There are a number of reasons for this result in high plant uptake and accumulation of these heavy metals; however, the main reason is most probably that the increase of solubility of Zn and Cd leads to an improvement in metal bioavailability with a decrease of soil pH by application of S. There are certain groups of acidophilic soil bacteria in the soil, predominantly the genus thiobacillus, which can oxidize S and change it to SO_4^{2-} when soil pH has decreased (Lee et al., 1998; Tichy et al., 1997; Kayser et al., 2000). M-claughlin et al. (1998) reported that increasing SO_4^{2-} in soil could increase shoot Cd concentration, In the present experiment the increasing SO_4^{2-} in soil were given may be cause that increased the Cd content.

Conclusions:

Soil pH-decreased and SO_4^{2-} concentration increased with S application and the solubility of the Zn and Cd was significantly increased in all treatments with S application, however, the solubility of pb, and Ni increased little by the treatment with S. application of elemental sulphur can enhance uptake of Zn by lettuce. Removal of pb and Cd did not significance increase with application of S. because maize was sensitive to the toxicity of pb/Cd.

Although the application of S can increase uptake of some metals by plants by enhancing metal mobility, there is also a potential risk of movement risk, an appropriate in the field so that environmental risk can be minimized.

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