10

Effect of Elemental Sulfur and Compost of Peanut Residues on Mobilization of Lead and Nickel in Elgabal-Elasfar and Kaluob Soils

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I NCUBATION experiment was conducted to study the potential effects of elemental sulfur (S) and organic matter on availability of soil Pb and Ni in two soils. The first soil (Elgabal-Elasfar) is representing the contaminated area with sludge and the other representing the contaminated area with industrial contaminants (Kaluob). Four rates of elemental sulfur was applied at 0(S0), 50(S50), 100(S100) and 150(S150) mmole kg^{-1} soil. Compost was applied at four rates 0(C0), 0.5(C0.5), 1(C1) and 2(C2) %. The results showed that with S application, acidification was intense at all sulfur dosages applied in Elgabal-Elasfar soil, pH had dropped by 1.2, 2.2 and 2.5 units for the three dosages compared with the control at termination of the experiment. In the Kaluob soil, pH did not decrease as much as in Elgabal-Elasfar soil.

DTPA-extractable Pb and Ni increased up to 7 and 6-fold, respectively, in Elgabal-Elasfar soil, while in the Kaluob soil, maximum increases were 6 and 4-fold.

Lead and nickel fractionation were performed by using a sequential extraction procedure. Applied sulfur altered concentration of Pb and Ni forms in the studied soils. Application of elemental sulfur to soils redistributed Pb and Ni from complex form to the more exchangeable one thus increasing Pb and Ni availability. In both studied soils, elemental sulfur addition was the highest in increasing the exchangeable form of Pb and Ni.

No significant differences in pH and solubility of Pb and Ni values were found between the control and compost- treated soils. Application of compost to the tested soils led to decrease carbonate and oxides Pb and Ni fractions, organic Pb and Ni forms increased. While exchangeable and residual Pb and Ni fraction were not affected.

Keywords: Elemental sulfur, Peanut compost, pH, Mobilization, Lead, Nickel, Fraction.

Heavy metals are natural components of the earth crust (Wedepohl, 1991). In addition to this native origin, some heavy metals may be supplied to soils by atmospheric deposition and by agronomic practices such as fertilizer and

pesticide applications as well as the disposal of municipal wastes such as composts and sewage sludge on agricultural land (Sticher & Schmidt, 1991).

The remediation of metal contaminated sites often involves expensive and environmentally invasive, civil engineering based, practices. This may prohibit their use at many sites, where consequently no action is taken to adequately assess and when necessary, reduce the risks to human health and the environment. Without some remediation efforts, the soil from these contaminated areas remains exposed to human contact and to erosion that may carry contaminants off site.

Some materials traditionally used in agriculture, like animal manures and peat, have been recently employed in different experiments on the bioremediation of soils contaminated with heavy metals (Clemente *et al.,* 2007 and Walker *et al.,* 2004). These materials improve soil fertility and generally increase plant production and can also increase heavy metals availability. Fresh organic wastes, such as animal manures, are rich in soluble organic compounds which can increase the solubility of metals shortly after the addition of these materials to the soil (Almas *et al.,* 1999), through formation of soluble organo-metallic complexes, decreasing for instance Zn adsorption, particularly in sandy soils (Shuman, 1999a).

Organic amendments such as composts or peat, which contain a high proportion of humified organic matter (OM), can decrease the bioavailability of heavy metals in soil by adsorption and by forming stable complexes with humic substances (Shuman, 1999b), thus permitting the re-establishment of vegetation on contaminated sites (Tordoff *et al.,* 2000). This OM can re-distribute heavy metals from soluble and exchangeable forms (extractable with solutions of neutral salts such as $CaCl_2$) to fractions associated with OM or carbonates and the residual fraction (Shuman, 1999b). Also, the use of organic wastes as sources of organic matter for agricultural or ecological benefit is a way of recycling them, in accordance with European Union Policy (Commission of the European Communities, 1996).

The effects of OM amendments on heavy metal bioavailability depend on the nature of the organic matter, and on the particular soil type and metals concerned (Clemente *et al.,* 2005), usually involving the formation of insoluble contaminant species, less likely to leach through the soil profile (Berti & Cunningham, 2000). Organic amendments can decrease heavy metal bioavailability, shifting them from "plant available" forms to fractions associated with OM, carbonates or metal oxides (Walker *et al.,* 2004), with consequent reductions in the metal uptake by the installed plants. For example, Walker *et al.* (2004) reported lower Zn tissue concentration in *Chenopodium album* L. plants grown in compost and manure amended soil. Clemente *et al.*(2005) found the same behavior for *Brassica juncea* L. Czern grown in OM amended contaminated soil. However, no reduction in the accumulation of Zn was demonstrated for Agropyron elongatun

and Trifolium repens growing in Zn/Pb mine tailings amended with pig manure (Ye et al., 1999).

Heavy metal solubility, mobility and, therefore, bioavailability in soils depend on the characteristics of the metal, but they are generally very low in neutral and calcareous soils (Kabata-Pendias, 2001). A potential strategy to enhance heavy metal availability is the lowering of soil pH; this can be achieved through application of mineral acids, organic acids or acid-producing fertilizers like sulfur-containing materials (Kaplan et al., 2005). Elemental sulfur is oxidized to H_2SO_4 by sulfur-oxidizing microorganisms, which may decrease soil pH. The rate of sulfur oxidation in soils has been related to a wide number of factors such as temperature, moisture, sulfur particle size, aeration and microbial biomass (Germida and Janzen, 1993).

Chemical speciation plays an influential role in solubility and potential bioavailability of heavy metals in soils. The sequential extraction procedure (SEP) was proposed by Tessier et al. (1979), in which soil Pb was operationally fractionated into water soluble (WS), exchangeable (EX), weakly specifically adsorbed (SP), Fe/Mn oxides-bound (OX), organically bound (OR) and residual (RE) portions (Tessier et al., 1979 and Planquart et al., 1999). Results from the SEP studies showed that in contaminated soils, Pb occurred primarily in the residual, carbonate and exchangeable fractions (Yang et al., 2004), whereas 48.5 and 42.5% of soil Pb were bound to organic and carbonate fractions, respectively, in a Pb battery dump soil (Pichtel et al., 2000). However, in unpolluted soils, most Pb was found in the residual fraction (Wong et al., 2002). The bioavailability and mobility of heavy metals in soil strongly depend on their physicochemical forms in soils, i.e., chemical fraction or speciation (Kabata-Pendias, 1993) and consequently, on soil physicochemical characteristics (Planquart et al., 1999). Therefore, it is important to understand chemical speciation of Pb in order to assess Pb availability and toxicity to crop plants in a contaminated soil.

The aim of this work was to study the effect of different dosages of elemental sulfur and organic matter (compost) on soil pH, Pb and Ni dynamics in used soils in an incubation experiment.

Material and Methods

Soils

Soil samples were taken from two polluted sites enduring of heavy metals contamination for a rather long time. These sites are Elgabal-Elasfar, Cairo Governorate, Egypt which received sewage effluent as a solely source of irrigation and the second site from Alex-Cairo Agricultural Road, Kaluob Governorate (Kaluob). The first site representing the contaminated area with sludge and the other representing the contaminated area with industrial contaminants. Top soil material was sampled from small pits of 0-20 cm depth from the two locations and transported to the laboratory. Collected soils were air

dried, ground and sieved passing through a 2mm sieve, homogenized with a shuffle and stored until analysis of experiment.

Soil pH was measured using glass electrode in a soil to water ratio of 1:2.5 (Cottenie *et al.*, 1982). Electrical conductivity of soils was measured using soil to water ratio of 1:2.5(Cottenie *et al.*,1982). The organic carbon content was determined using the Walkley and Black Wet Combustion Method (Cottenie *et al.*, 1982).The soil particles size distribution was analyzed according to Dewis and Feritas (1970). Soils were also characterized for calcium carbonate content (Cottenie *et al.*, 1982).The acid neutralization capacities (ANC) of the soils were determined by pH titration according to the method described by Susser (1987). Available Pb and Ni were analyzed as described by Lindsay & Norvell (1978). The supernatant was decanted and saved for Pb and Ni determination by atomic absorption spectrophotometer (Perken Elmer - 2380). The total Pb and Ni concentration in soils were digested by aqua regia digestion according to Cottenie *et al.* (1982) and determined using atomic absorption spectrophotometer.

Sequential extraction

The method of sequential extraction used in this study was outlined by Tessier *et al.* (1979). Nickel and lead were partitioned into five operationally defined fractions; exchangeable, bound to carbonates, reducible (bound to Fe-Mn oxides), oxidizable (bound to organic matter and /or sulfides) and residual.

Preparation of incubation experiment

An incubation experiment was performed to assess the influence of elemental sulfur or compost on mobilized Pb or Ni in used soils. The organic matter used in this study was compost resulting from peanut residues. The characteristics of compost were shown in Table 1.

TABLE 1. Chemical properties of peanut compost.

OM. %	Total N %	C/N ratio	pH (1:10)	EC dSm⁻¹	Available nutrients %		DTPA extractable (mg/kg)					
					P	K	Ni	Pb	Cd	Fe	Mn	Zn
36.81	1.4	26.3	6.5	0.62	1.6	9.8	0.01	0.2	1.10	30	9	11.6

100g dry soil was weighed into 200ml polyethylene pots. Sulfur was applied and mixed thoroughly with the soils at three rates, 50 (S50), 100 (S100) and 150 (S150) mmol kg-1 soil. Other sets for two soils were mixed with compost at rates level, 0.5 (C 0.5), 1 (C1) and 2 (C2) % and the control for two soils without sulfur or compost application. There were 7 treatments with three replicates. Fertilizer was applied at the rates of 0.05g of ammonium sulfate, 0.02g of potassium sulfate and 0.025g of calcium super phosphate / 100g soil. During the experiment, soil moisture content was maintained at 60 % of the water holding capacity, by weight with water added every two days. The sample time was after 2, 4, 6 and 8 weeks of incubation.

After incubation time, the soils were air dried ground and sieved through a 2mm sieve for chemical analysis.

Results and Discussion

Physico-chemical properties of the used soils

The physico-chemical characteristics of Elgabal-Elasfar and Kaluob soils are summarized in Table 2. Soil collected from Kaluob was alkaline in nature (pH 8.0), while those from Elgabal-Elasfar was neutral (pH 7.1). In general, the Elgabal-Elasfar and Kaluob soils have slight salinity, the EC values were 0.27 and 0.37 dS/m, respectively. The soils had very slight carbonate (CO_3^{-2}) contents (0.4 and 1.2 % respectively). Kaluob also had relatively high clay content (47 %), in contrast, the Elgabal-Elasfar soil had higher sand content (71%) and lower clay content (16 %). Total Pb and Ni metals content was observed in the Elgabal-Elasfar and Kaluob soils which was 70 and 98 mg kg^{-1} for Pb and 78 and 87 mg kg^{-1} for Ni, respectively.

TABLE 2. Some physical and chemical properties of the investigated soil samples.

Location	pH 1:2.5	EC 1:2.5 dS/m	CaCO₃ %	O.M %	Particle size distribution				Texture	Ni (mg/kg)		Pb (mg/kg)		ANC mcqkg⁻¹
					C.S %	F.S %	Silt %	Clay %		Tot.	Av.	Tot.	Av.	
Elgabal Elasfar	7.1	0.27	0.4	4.9	22.6	48.4	13	16	S.L	78	4.5	70	3.5	75
Kaluob	8.0	0.37	1.2	1.0	9.8	17.1	26.1	47	Clayey	87	2.5	98	4.5	225

ANC= Acid neutralization capacity (Susser, 1987).

Soil pH

Sulfur addition resulted in a decrease of soil pH over time in the two soils, and clearly showed dosage dependence (Fig. 1). One important fact is the oxidation of sulfur by certain groups of acidophilic bacteria, notably *Thiobacillus* spp. in the soil (Tichy *et al.*, 1997 and Kayser *et al.*, 2000). Tichy *et al.* (1997) reported that 156 mmol of different types of elemental sulfur per kilogram of soil were added to a gleyic cambisol with an initial soil pH between '5 and 5.5, the soil pH decreased to 3.3 within 80 days. Kayser *et al.* (2000) reported that adding 36 mol S m^{-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, which caused the soil pH to decrease about 0.4 – 2.5 units within 8 weeks.

In the Elgabal-Elasfar soil, acidification was intense at all sulfur dosages applied, pH had dropped by 1.2, 2.2 and 2.5 units for the three dosages compared with the control at termination of the experiment (8 weeks). The magnitude of the drop in soil pH increased with increasing the incubation time up to 8 weeks.

In the Kaluob soil pH did not decrease as much as in the Elgabal-Elasfar soil. The decrease in soil pH was slight in S50 treatment. In contrast, the higher dosage led to markedly lower soil pH. A decrease from 7.4 to 6.0 was observed

in the S150 treatment between the beginning and the termination of the experiment.

Effects of sulfur application on acidification were consistent with the acid neutralization capacity (ANC, Table 2) of the treated soils and therefore decreased in the order Elgabal-Elasfar < Kaluob.

The ANC of the Kaluob soil is accounted for to a large extent by the dissolution of $CaCO_3$. According to Schwertmann *et al.* (1987) and Furrer & Sticher (1999) the dissolution of 1 mole of $CaCO_3$ will result in the consumption of 2 or 3 moles of protons, respectively. Given the data shown in Table 2 and assuming that only 2 protons are consumed per equivalent of $CaCO_3$, the ANC of the Elgabal-Elasfar and Kaluob soils were made up to approximately 94% of $CaCO_3$.
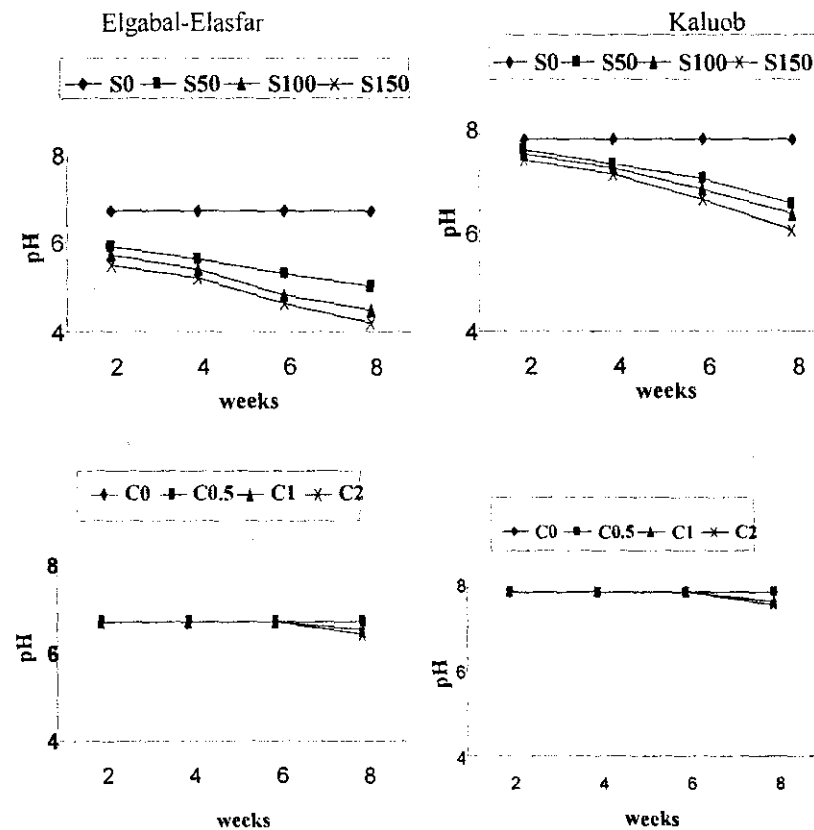

Fig. 1. Changes in soil pH after sulfur and compost application during 8 weeks of incubation.

The oxidation of 1 mole of sulfur will result in the production of 2 moles of protons. Hence, if all sulfur applied to the soil was oxidized, this would 3 fold the ANC of the Elgabal-Elasfar soil in the S100 treatment, while it would only account for 80% of the ANC of the Kaluob soil. At the highest dosages the m moles of protons in Elgabal-Elasfar was more exceed than Kaluob soil. The percentages of mmoles of protons in Kaluob soil were 80 and 133.3 % of ANC at the rate 100 and 150 m moles, respectively. While they were 266 and 400 % of ANC in Elgabal-Elasfar. Consequently, if proton buffering capacity was not kinetically or spatially limited, a shift in pH would be expected in the Elgabal-Elasfar soil. The fact that pH decreased also in the Kaluob soil when compared with controls, hence indicates kinetic and/or spatial limitation of proton buffering capacity most likely attributable to heterogeneous distribution of sulfur in the soil matrix. Mixing of sulfur powder with soil material may result in predominant coverage of the surfaces of soil aggregates that leads to a heterogeneous distribution of zones of sulfur enrichment. When the sulfur is oxidized, protons will be produced equally heterogeneously.

As a result, the sulfur coated surfaces of soil particles may be exposed to greater acid production than the remainder of the soil, as was also indicated in an aggregate fractionation experiment performed by Kayser et al. (2000). Reactive soil components involved in acid neutralization, on the other hand, may be distributed differently than the sulfur particles mixed into the soil and may be outcompeted at sites of intensive acid production. This could result in local acidification even in soils with a high ANC.

This hypothesis is in agreement with findings obtained from a comparative study on the proton buffering behavior of disturbed and undisturbed forest soils using batch suspensions and undisturbed soil columns (Kaupenjohann and Hantschel, 1987). Results showed that less acidity could be neutralized in the percolated soil columns than in the suspensions.

No significant differences in pH values were found between the control and compost-treated soils (Fig. 1) due to the high buffering capacity of these soil or the high C:N ratio of the used compost (26.3:1). Romero et al. (2005) found that the pH of mine tailings was scarcely affected by the application of sludge of olive mill waste (SOMW). Piotrowska et al. (2006) found no significant differences between unamented soil and soil treated with olive-mill wastewater at different rates (18 and 36 ml 100 g^{-1} of soil), for a slightly alkaline soil. However, Nogales et al. (1997) showed a decrease in soil pH (0.6 unit) after olive-mill wastewater disposal in a calcareous soil, whilst Clemente et al. (2007) found that the pH of the calcareous soil used in their experiment decreased by 0.3 units in a field experiment with SOMW (51 ton of SOMW per ha).

Solubilization of Pb and Ni

The relative efficiency of elemental sulfur in enhancing soil Pb and Ni solubility in the soils were assessed and is presented in Fig. 2 a and b. When sulfur was added, the extracted Pb concentrations in the soil extracts was higher by four to seven times and one to six times compared to no sulfur treatments in Elgabal-Elasfar and Kaluob soils, respectively. For Ni, it was higher by three to seven times and two to four times compared to no sulfur treatments in Elgabal-Elasfar and Kaluob soils, respectively.
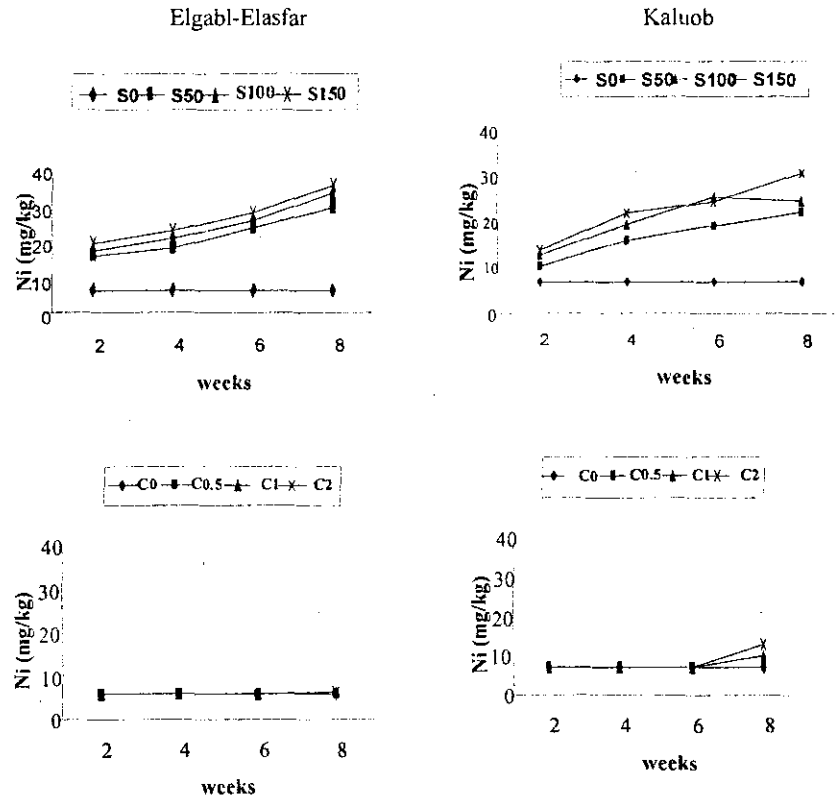

Fig. 2a. Changes in availability of nickel after sulfur and compost application during 8 weeks of incubation.

The addition of elemental sulfur significantly increased the concentration of extracted Pb and Ni in soils. For example, without elemental sulfur addition, the concentration of extractable Pb in Elgabal-Elasfar and Kaluob soils were 5.5 and 5mg kg^{-1}, which increased immediately to average 38 and 30 mg kg^{-1} at the highest rate of elemental sulfur. Our results also demonstrate that increasing the rate of elemental sulfur addition resulted in a significant increase in mobilized Pb over the study period.
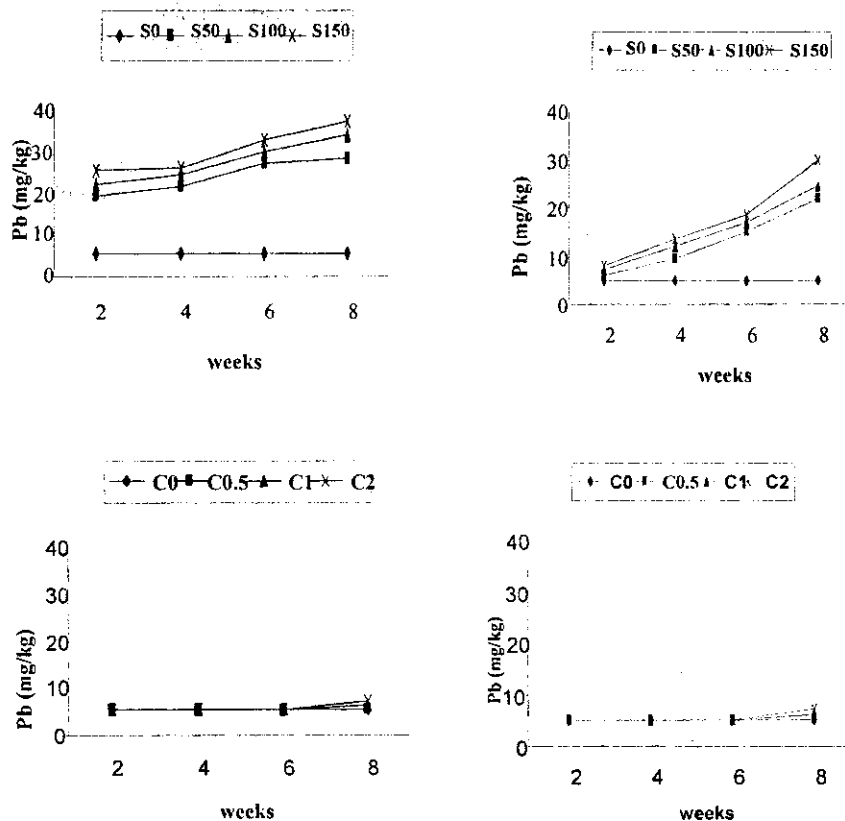
Fig. 2b. Changes in availability of lead after sulfur and compost application during 8 weeks of incubation.

Concentration of Pb and Ni extractable by DTPA showed a clear relation to soil pH. Fig. 3 shows that metal solubilization increased with decreasing pH in the two soils. Lead concentrations increased 7-folds in Elgabal-Elasfar soil between pH 6.7 and pH 4.2 between the control and the highest rate of elemental sulfur (S150) treatment measured at the end of the experiment. The highest concentration accounted for 54.3% (38 mg kg^{-1}) of the total Pb present in the soil. For Kaluob, this increase was less pronounced (6-folds), leading to an increase in DTPA-extractable Pb to 30 mg kg^{-1} at pH 6.0, or 30.6 % of the total Pb.

Nickel solubility increased with decreasing soil pH. Its concentrations increased 6-folds in Elgabal-Elasfar soil between pH 6.7 and pH 4.2 between the control and the highest rate of elemental sulfur (S150) treatment measured at the end of the experiment. The highest concentration accounted for 44.9 % (35 mg kg^{-1}) of the total Ni present in the soil. For Kaluob, this increase was less pronounced (4-folds), leading to an increase in DTPA-extractable Ni to 30.5 mg kg^{-1} at pH 6.0, or 35.1 % of the total Ni.

Generally, our results are in good agreement with findings of other investigators who described soil pH as a key factor governing the solubility of Pb and Ni in soils (Arnfalk *et al.*, 1996).

Differences existed, however, between soils. At a given pH, much higher soluble metal concentrations were found in Elgabal-Elasfar soil, as can be seen in Fig. 3, where the percentage of total solubilized metals are presented. Moreover, the proportion of the total contents of these metals solubilized was different between soils, suggesting that metal speciation is different in the Elgabal-Elasfar and Kaluob soils, presumably as a result of different origin of the pollutants. This is supported by our next findings from sequential extraction performed on these soils.
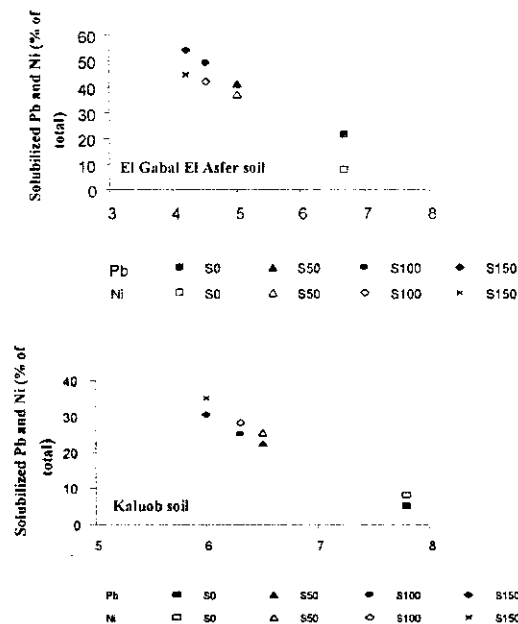

Fig. 3. Percentage of solubilized Pb and Ni as a function of soil pH.

The obtained results of adding compost to soils are presented in Fig. 2. Availability of Pb and Ni were not significant increase with increasing compost application to the soil. Except, at the highest level of compost (2%) at the end of the incubation experiment caused a slight increase in extractable Pb and Ni in both Elgabal-Elasfar and Kaluob soils. This may be due to small change in soil pH, soil pH in Elgabal-Elasfar and Kaluob soils range of 6.7-6.4. Tandy *et al.* (2004) reported that Pb extraction by EDTA, at low chelate to metal ratio, depends on soil pH and shows a strong positive relation up to a soil pH of 6.0. The effects of OM amendments on heavy metal bioavailability depend on the nature of the organic matter and on the particular soil type and metals concerned (Clemente *et al.*, 2005) usually involving the formation of insoluble contaminant

species, less likely to leach through the soil profile (Berti and Cunningham, 2000). Organic amendments can decrease heavy metal bioavailability, shifting them from "plant available" forms to fractions associated with OM, carbonates or metal oxides (Walker *et al.,* 2004) with consequent reductions in the metal uptake by the installed plants.

Lead and Nickel distribution in chemical fractions

The behavior of heavy metals in soils depends not only on the level of contamination as expressed by the total content, but also on the form of the metal. Sequential extraction techniques which provide a useful tool to understand the chemistry of metals in soils. As described previously, the partitioning of the metals in the studied soils is based on the sequential extraction procedure of Tessier *et al.* (1979) that evaluates the distribution of metals among the exchangeable, carbonate, oxide, organic and / or sulfide and residual fractions or forms. A high significant correlation coefficient value was obtained between the determined total metal in soils and sum of the different extracted fractions yielding 0.96 and 0.94 for Pb and Ni, respectively. Therefore, the fractionation procedure used proved to be satisfactory.

In untreated soils, in Elgabal-Elasfar, Pb and Ni were mainly present in the Res. and Org. forms, where the lowest values were for Exch. form, with the order being: Res.> Org.> Oxide> Carb.>Exch. (Fig. 4). On average, the metal part existing in the Res., Org., Oxide, Carb., and Exch. fractions were represented by 34.6, 29.7, 14.4, 11.3 and 9.3 % of the sum of Pb fractions, respectively. A strong association of Pb with organic matter was described by Kabata-Pendias and Pendias (1992) based on the results of many investigators. For Ni, they were represented by 25.6, 23.4, 23.1, 15.3 and 12.5 % of the sum of Ni fraction, respectively. While in Kaluob soil, Pb and Ni were mainly found in the Res. form followed by Oxide, while the lowest values were for Exch.form. Chlopecka *et al.* (1996) and Ramos *et al.* (1994) however, found most of the Pb to be bound to Fe and Mn oxides.

Concerning distribution of Pb and Ni in soil fraction due to application of sulfur through successive extraction of Elgabal-Elasfar soil, data presented in Fig. 4 show that application of elemental sulfur decreased Carb., Oxide, Org. and Res.-Pb, while increased Exch.-Pb, which reached 6-folds than that of the control. Also, application of elemental sulfur to this soil decreased Carb., Oxide, Org. and Res.-Ni by 57.1, 63.2, 37.5 % and 4.7% less than the control treatment, respectively. In contrast, Exch.-Ni increased with the application of elemental sulfur recording 3.6-folds than that of the control treatment.

Application of organic compost to the tested soils led to decrease Carb. and Oxide-Pb. The decrease represented 58.8 and 16.7 % compared to the control, respectively. For Ni, these decrease recorded 15 and 20% compared to that control, respectively. On the other hand, Org.-Pb and Ni forms increased with compost application reaching 48.9 and 22.9 for Pb and Ni above the control, respectively, while Exch and Res-Pb and Ni fractions were not affected.
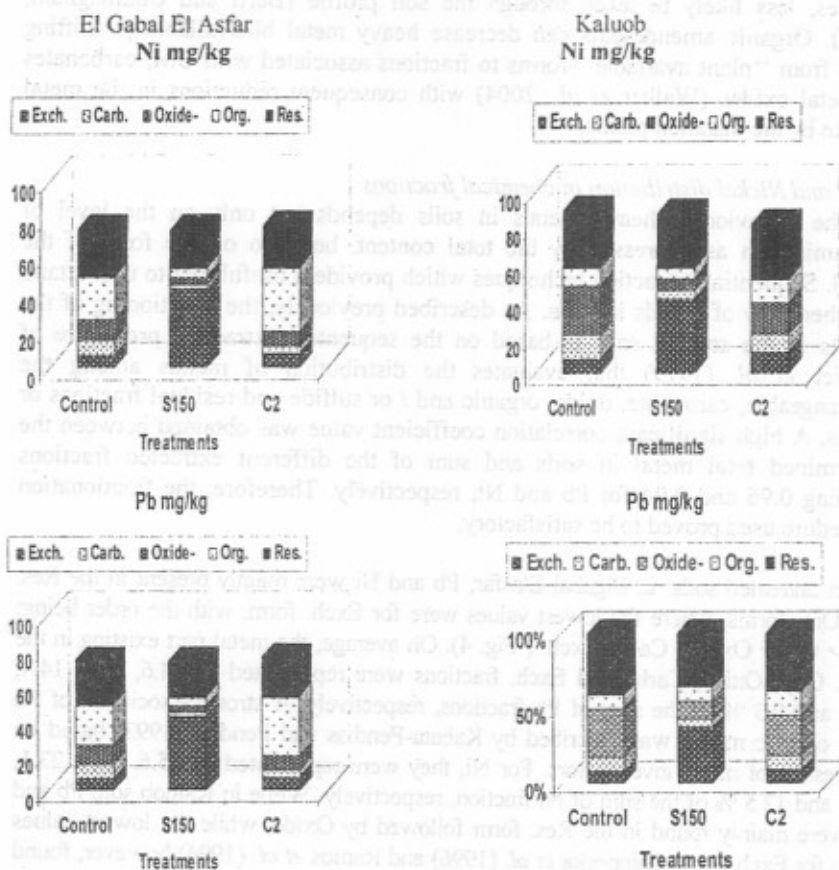
El Gabal El Asfar
Ni mg/kg

■ Exch. ▨ Carb. ■ Oxide- □ Org. ■ Res.

Kaluob
Ni mg/kg

■ Exch. ▨ Carb. □ Oxide- □ Org. ■ Res.

Pb mg/kg

■ Exch. ▨ Carb. ■ Oxide- □ Org. ■ Res.

Pb mg/kg

■ Exch. ▨ Carb. ■ Oxide- ▨ Org. ■ Res.

Fig. 4. Effect of sulfur and organic compost application on Pb and Nifractions in Elgabal-Elasfar and Kaluob soils.

In Kaluob soil, data presented in Fig. 4 show that application of elemental sulfur decreased Carb. Oxide and Res.-Pb, such decreases recorded 55, 60.6 and 15.9% less than control, respectively, but elemental sulfur application did not alter Res.-Pb fraction. Similarly, elemental sulfur also decreased Carb. Oxide and Org.-Ni, such decreases recorded 63.6, 75.6 and 42.6 % less than control, respectively, while Res.-Ni in the two soils seemed to be not affected. Exch.-Pb showed similar trend to those of Ni recording 5-folds that of the control. Application of organic compost to the tested soils led to the same trend in Elgabal-Elasfar soil.

References

Almas, A., Singh, B.R. and Salbu, B. (1999) Mobility of cadmium-109 and zinc-65 in soil influenced by equilibration time, temperature and organic matter. *J. Environ. Qual.* **28**: 1742–1750.

Arnfalk, P., Wasay, S. A. and Tokunaga, S. (1996) A comparative study of Cd, Cr(III), Cr(VI), Hg and Pb uptake by minerals and soil materials. *Water, Air and Soil Pollution* 87: 131-148.

Berti, W.R. and Cunningham, S.D. (2000) Phytostabilization of metals. In: *"Phytoremediation of Toxic Metals: Using Plants to Clean Up the Environment"*, I. Raskin and B.D. Ensley (Ed.), pp. 71-88, John Wiley & Sons Inc., New York.

Chlopecka, A., Bacon, J.R., Wilson, M.J. and Kay, J. (1996) Heavy metals in the environment. *J. Environ. Qual.* 25: 69-79.

Clemente, R., Paredes, C. and Bernal, M.P. (2007) A field experiment investigating the effects of olive husk and cow manure on heavy metal availability in a contaminated calcareous soil. *Agri. Ecosyst. Environ.* 118: 319-326.

Clemente, R.,Walker, D.J. and Bernal, M.P. (2005) Uptake of heavy metals and as by *Brassica juncea* grown in a contaminated soil in Aznaco llar (Spain). The effect of soil amendments. *Environmental Pollution* 138: 46-58.

Commission of the European Communities (1996) Commission decision of 24 May 1996 adapting annexes IIA and IIB to council directive 75/442/EEC on waste. O.cial *J. European Communities* (L135): 32-34.

Cottenie, A., Verloo, M., Kieken, L., Velgh, G. and Camerlynck, R. (1982) Chemical analysis of plant and Soil. Lab. Anal. Agrochem., State Univ., Ghent ,Belgium.

Dewis, J. and Feritas, F. (1970) Physical and chemical methods of soil and water analysis. *Fao, Rom, Soil Bulletin*, No. 10.

Furrer, G. and Sticher, H. (1999) Chemische Verwitterungsprozesse. In: *"Handbuch der Bodenkunde"*, pp. 1-15, Ecomed.

Germida, J.J. and Janzen, H.H. (1993) Factors affecting the oxidation of elemental sulfur in soils. *Fert. Res.* 35: 101-114.

Kabata-Pendias, A. and Pendias, H. (1992) *"Trace Elements in Soils and Plants"*, CRC Press, Boca Raton, USA.

Kabata-Pendias, A. (1993) Behavioural properties of trace metals in soils. *Appl. Geochem. (Suppl. Issue* 2): 3-9.

Kabata-Pendias, A. (2001) *"Trace Elements in Soils and Plants"*, 3rded., CRC Press, Boca Raton, FL.

Kaplan, M., Orman, S., Kadar, I. and Koncz, J. (2005) Heavy metal accumulation in calcareous soil and sorghum plants after addition of sulfur-containing waste as a soil amendment in Turkey. *Agri. Ecosyst. Environ.* 111: 41-46.

Kaupenjhann, M. and Hantschel, R. (1987) Die kurzfristige pH- Pufferung von gestorten und ungestorten Waidboenproben. *Z. Pflanzenernahr. Bodenk* 150: 156-160.

Kayser, A., Wenger, K., Keller, A., Attinger, W., Felix, H.R. and Gupta, S.K. (2000) Enhancement of phytoextraction of Zn, Cd, and Cu from calcareous soil: the use of NTA and sulfur amendments. *Environ. Sci. Technol.* **34**:1778–1783.

Lindsay, W.L. and Norvell, W.A. (1978) Development of DTPA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Amer. J.* **42**: 421-428.

Nogales, R., Gallardo-Lara, F., Benitez, E., Soto, J., Hervas, D. and Polo, A. (1997) Metal extractability and availability in a soil after heavy metal application of either nickel or lead in different forms. *Water Air Soil Pollut.* **94**: 33–44.

Pichtel, J., Kuroiwa, K. and Sawyer, H.T. (2000) Distribution of Pb, Cd and Ba in soils and plants of two contaminated sites. *Environ. Pollut.* **110**: 171–178.

Piotrowska, A., Iamarino, G., Rao, M.A. and Gianfreda, L. (2006) Shortterm effects of olive mill waste water (OMW) on chemical and biochemical properties of a semiarid Mediterranean soil. *Soil Biol. Biochem.* **38**: 600–610.

Planquart, P., Bonin, G., Prone, A. and Massiani, C. (1999) Distribution, movement and plant availability of trace metals in soils amended with sewage sludge composts: application to lowmetal loadings. *Sci. Total Environ.* **241**: 161–179.

Ramos L., Hernandez, L.M. and Gonzales, M.J. (1994) Sequential fractionation of copper, lead, cadmium and zinc in soil from or near Donana national park. *J. Environ. Qual.* **23**: 50–57.

Romero, E., Benitez, E. and Nogales, R. (2005) Suitability of wastes from olive-oil industry for initial reclamation of a Pb/Zn mine tailing. *Water Air Soil Pollut.* **165**:153–165.

Schwertmann, U., Susser, P. and Natscher, L. (1987) Protonen – Puffersubstanzen in Boden. *Z. Pflanzenernahr. Bodenk* **150**: 194-202.

Shuman, L.M. (1999a) Effect of organic waste amendments on Zn adsorption by two soils. *Soil Sci.* **164**: 197–205.

Shuman, L.M. (1999b) Organic waste amendments effect on zinc fractions of two soils. *J. Environ. Qual.* **28**: 1442–1447.

Sticher, H. and Schmidt, H.W. (1991) Heavy metal compounds in the soil. In: *"Metals and their Compounds in the Environment"*, E. Merian (Ed.), pp.311– 331,VCH/Verlagsgesellschaft, Weinheim,

Susser, P. (1987) Art, Menge and Wirkungsweise Von puffersubstanzen in Mineralbodenhorizontem forstlich genutzter Boden des Fichtelgebirges. *Ph.D.* Dissertation, Techical Universty of Munich, Fakultat fur Landwirtschaft und Gartenbau, Lehrstuh fur Bodenkunde.

Tandy,S., Bossart, K., Muller, R., Rilschel, J., Hauser, L., Schulin, R. and Nowack, B. (2004) Extraction of heavy metals from soils using biodegradable chelating agents. *Environ. Sci. Technol.* **38**: 937–944.

Tessier, A., Campbell, P. G. C. and Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**: 844-850.

Tichy´, R., Fajtl, J., Kuzel, S. and Kolar, L. (1997) Use of elemental sulfur to enhance a cadmium solubilization and its vegetative removal from contaminated soil. *Nutr. Cycl. Agroecosyst* **46**:249– 255.

Tordoff, G.M., Baker, A.J.M. and Willis, A.J. (2000) Current approaches to the revegetation and reclamation of metalliferous mine wastes. *Chemosphere* **41**: 219–228.

Walker, D.J., Clemente, R. and Bernal, M.P. (2004) Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste. *Chemosphere* **57**: 215-224.

Wedepohl, K.H. (1991) The composition of the upper earth's crust and the natural cycles of selected metals. In: *"Metals and their Compounds in the Environment"*, E. Merian (Ed.), pp. 3–17, VCH/Verlagsgesellschaft, Weinheim,

Wong, S.C., Li, X.D., Zhang, G., Qi, S.H. and Min, Y.S. (2002) Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environ. Pollut.* **119**: 33–44.

Yang, Q.W., Shu, W.S., Qiu, J.W., Wang, H.B. and Lan, C.Y. (2004) Lead in paddy soils and rice plants and its potential health risk around Lechang Lead/Zinc Mine, Guangdong, *China. Environ. Int.* **30**: 883–889.

Ye, Z.H., Wong, J.W.C., Wong, M.H., Lan, C.Y. and Baker, A.J.M. (1999) Lime and pig manure as ameliorants for revegetating lead/zinc mine tailings: a greenhouse study. *Bioresource Technology* **69**: 35-43.

تأثير إضافة الكبريت العنصري ومكمورة الفول السوداني على حركة الرصاص والنيكل في أراضي الجبل الأصفر وقليوب

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صممت تجربة تحضين لدراسة تأثير إضافة الكبريت العنصري و المادة العضوية (مكمورة الفول السوداني) على صلاحية كل من الرصاص والنيكل للإمتــصاص بواسطة النبات في تربة من الجبل الاصفر ملوثة بمياه الصرف الصحي واخـرى من قليوب ملوثة بمخلفات الصرف الصناعي. أضيفت ٤ معدلات مـن الكبريـت العنصري (صفر–٥٠–١٠٠–١٥٠ ملليمول /كجم تربة) , كما أصـيفت المـادة العضوية (مكمورة الفول السوداني) بــ ٤ معدلات (صفر –٠,٥– ١–٢٪ / كجم تربة).

أشارت النتائج الي أن إضافة معدلات الكبريت كان لها تأثير عالي في تربـة الجبل الأصفر حيث ادى الى انخفاض الــ pH بمقـدار ١,٢–٢,٢–٢,٥ نتيجـة اضافة ٥٠ ، ١٠٠ ، ١٥٠ ملليمول كبريت عنصري /كجم تربة على التـوالى مقارنة بالتربة الغير معاملة بالكبريت أما تربة قليوب فإن انخفاض رقم الــ pH بها لم يصل لدرجة الإنخفاض التي حدثت في أرض الجبـل الــصفر. كمـا زاد الرصاص المستخلص بالــDTPA فى تربة الجبل الاصفر و قليوب بمعـدل ٧، ٦ مرات علي التوالي والنيكل المستخلص في تربة الجبل الاصفر و قليـوب بمعدل ٤، ٤مرات علي التوالي .

تم تقدير المفصولات المختلفة لكـل مــن الرصـاص والنيكـل باسـتخدام الأستخلاص المتتابع حيث تم دراسة تأثير إضافة الكبريت العنصري علي تركيز النيكل والرصاص في تلك المفصولات حيث زاد التركيز في المفصول المتبـادل بينما انخفض في المفصولات الأخري وهو السبب الأساسي لزيادة تيسر الفلـزين في الترب محل الدراسة. على الجانب الاخر لم تؤثرإضافة المعدلات المختلفـة للمادة العضوية (مكمورة الفول السوداني) علي كل من رقم الـــ pH وزيـادة الرصاص و النيكل بالمقارنة بالأرض الغير معاملة.

ولقد أدت إضافة المادة العضوية الي إنخفاض المفصول المرتبط بالكربونات وكذلك مفصول الأوكسيد بينما زاد المفصول العضوي لكل من فلزي الرصاص والنيكل بحيث لم يتأثر المفصول المتبقي لكل من فلزي الرصاص والنيكل.