# Factors Controlling Potential Toxic of Heavy Elements Speciation in Arid Soils

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**Abstract:** Three groups of some Egyptian surface soil samples (G1, GII, and GIII), located in; El-Gabal El-Asfar, Zenin, and El-Khanater were collected in this study, these groups of soils were classified under two orders i. e. *Typic torrerts* and *Typic psamments* according to the American taxonomy. The source of contamination in the first and second groups was created from applying sewage sludge and irrigation with wastewater for more than 50 years in the first group (G1), for about 10 years in the second group (GII). The third group of soils (GII), however, was affected by its location beside traffic road beside, its treatments with organic fertilization types. All groups of soils were investigated for distribution, chemical fractions of Pb, Ni, Cu and Zn and their mobility as affected by different soil properties of these groups. The obtained results indicated that neither the time of exposure to sewage sludge applied nor wastewater irrigation treatments influenced heavy metals concentration in different soil samples. In addition, the decreasing order of different heavy metals distribution generally was: Residual (Res) > Fe-Mn oxide > carbonate (carb) $\sim$ organic (org.) > exchangeable (exch.) > water-soluble (WS). In some cases, however, the organically bound form of heavy metal was the predominant form, especially in GIII. Correlation analysis between soil properties and heavy metals distribution in different forms indicated that clay content, surface area and organic matter were the most soil properties contributing to the relative distribution of the studied pollutants in different fractions.

**Keywords:** heavy metals, speciation, arid soil, soil properties

## INTRODUCTION

Heavy elements especially, Cadmium and nickel are major environmental contaminants, and elevated levels in soils can cause toxicity stress of plants and adversely affect human health.

In Egypt, increasing awareness of the hazard that heavy metals can cause to the environment and human health through the presence of these pollutants in soils and their uptake by different crops, is presently pressuring society to comply with environmental regulations and develop management strategies to minimize their adverse impacts. These strategies, however, should be built according to the distribution of these trace elements in the soil system.

Many factors affect the toxicity of heavy metals and their forms in the soil, the most important of which are the organic matter calcium carbonate, the pH, and the type of soil mineral.

Primarily, concerning the properties of the soil, Loganathan et al. (2012) stated that properties of the solid and liquid phase critically influence specific and non-specific sorption of Cd in soils. Tamer and Saleem (2019) stated that the two chemical cadmium and nickel interacting in the soil are highly dependent on different soil properties, especially since the statistical analyzes revealed the important role of the mutual effect of pH, CEC, TC, silt, clay, and CaCO3 on Cd and maximum Ni absorption capacities. Liao et al. (2013) found that after sorption-desorption, large amounts of Ni residues were bound to carbonates, Fe-Mn and OM oxides along with the partially irreversible Ni fractions. In this point, Elbana and Selim (2010) added that cadmium is distributed into carbonates/oxides and highly bonded fractions in alkaline soils; Whereas, cadmium was bound to interchangeable fractions as an oxide and highly bonded fractions on acidic soil. They also showed very limited kinetic of Cd release in alkaline calcareous soil compared to acidic soil. Adhikari and Singh (2003) explained the increase of Cd affinity to soils with increasing pH, organic carbon, CEC, Clay, and CaCO3. For the calcareous soil, Wahba, et al. (2016b) reported that the quantity of adsorbed heavy metals was in the sandy soil more than in calcareous soils due to the charges on the surface sand particle and the big surface area. Zhao et al. (2014) showed that calcareous soils exhibited lower desorption rates and exchangeable Cd fraction compared with non-calcareous soil.

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On the other hand, Caporale and Violante, (2016) declared that heavy metal's adsorption and absorption processes control their mobility and bioavailability in the soil and water environment. Cationic heavy metals exhibit mechanisms associated with surface complexes simultaneously, such as electrostatic interactions of outer-sphere complexes and strong chemical binding of inner field complexes.

Secondary, for the role of organic matter, Wahba et al. (2015) studied the effect of compost on the movement of zinc and cadmium and recorded that increasing the rate of applied compost from 2% to 10% in lanced greatly the mobility of both elements and consequently their concentration in the leachate. At this point, Wahba et al. (2014) reported that the soluble organic acids may combine with metal ions and form soluble complexes, which can be removed from heavy metals in leaching. Also, these organic acids reduce soil pH and increase the solubility and mobility of these heavy metals from soils. Another role of the organic manure is increasing the surface area and cation exchange capacity of the soil particularly sand soil which affects the equilibrium between soluble and exchangeable metal ions. On the other hand, Walker et al.2004 found that cow manure is capable of preventing soil acidification and decreasing heavy metal bioavailability. In addition, they expressed that the increase of soil pH caused by manure addition is the main factor reducing metal availability. Burgos et al. (2006) reported that the application of organic and inorganic amendment increased soil pH and total organic carbon content and decreased as, Cd, Cu, Pb and Zn, solubility.

Thirdly, for the type of clay mineral, González-Costaet al. (2017) emphasized that silt exhibited the highest importance role in Ni sorption followed by mica and sand contents. Wahba et al. (2016a) reported that the role of zeolite was more pronouncing in enhancing the adsorption of heavy metals than bentonite due to its specific molecular structure and high surface area. Therefore, it is recommended to be applied as a remediation material in polluted soils by heavy metals. Added that, Wafaa et al. (2017) recorded that the role of zeolite, as a remediation material, was more effective on the adsorption of heavy metals than montmorillonite and bentonite, respectively. This was related to the specific structure of zeolite's high cation exchange capacity and large surface area. Recently, wahba et al (2020) used clay minerals such as zeolite, bentonite and montmorillonite to reduce the hazardous of nickel from aqueous solutions. The adsorption capacity of each of them was the zeolite gave the highest adsorption results of nickel followed by montmorillonite and then bentonite.

The primary objectives of this study are to investigate the effect of source of contamination, type of irrigation water and soil properties of some Egyptian soils collected from agricultural soils treated with sewage sludge and continuously irrigated with effluent water for different periods ranging from 10 to more than 50-year period and that collected from location beside the traffic road, on the distribution of Pb, Cu, Ni and Zn in polluted soil. The results of this study may be a guide for selecting the suitable remediation strategy(s) that should be applied according to conditions of pollution.

## MATERIAL AND METHOD

Soils: Twelve different soils divided into three groups collected from El-Gable El-Asfar, Zenen and El-Kantar El- Khirya areas. The source of pollution in the first and second group soils created from irrigation of these soils with effluent water and application of sewage sludge for more than 50 years (GI) and about 10 years (GII) respectively. The third group of soils irrigated with non-polluted water and the source of pollution comes from its location beside the traffic rode. Routine analyses for these samples were carried out according to conventional methods EPA (1993). Some physical and chemical properties are presented in Table 1.

### *Heavy metals distribution:*

In the studied samples heavy metals distributions were conducted according to Tessier et al. (1979) and modified by Ma and Rao, 1997. The following fractions were obtained: the water soluble, exchangeable, carbonate, Fe-Mn oxides, organic, and residual. The method could be summarized as follow:

Step1. Water-soluble: soil soluble, soil sample extracted with 15 ml of deionized water for 2 h.

Step2. Exchangeable: The residue from water-soluble fraction is extracted with 8 ml if 1M MgCl2 (pH7.0) for 1h.

Step3. Carbonate-Form: The residue from exchangeable fraction is extracted with 8 ml of 1 M NaOAc (adjusted to pH 5.0 with HOAc) for 5H.

Step4. Fe-Mn Oxides-Form: The residue from carbonate fraction is extracted with 0.04M NH2OH.HCL in 25% (v/v) HOAc at 96oCwith occasional agitation for 6H.

Step5. Organically form: The residue from Fe-Mn oxide fraction is extracted with 3 ml of 0.02M HNO3 and 5ml of 30% H2O2 (adjusted to pH 2 with HNO3). The mixture is heated to 85oC for 2h, with occasional agitation. A second 3-ml aliquot of 30% H2O2 (pH 2 with HNO3) is added and the mixture heated again to 85oC for 3h with intermittent agitation.

After cooling, 5 ml of 3.2M NH4OAc in 20% (v/v) HNO3 is added and the samples diluted to 20 ml and agitated continuously for 30 min.

Step 6. Residual Fraction: The residues from organic fraction are digested using a HF-HCl/HNO3.

### *Statistical analysis:*

Different statistical analysis such as relationships among heavy metal fractions and soil properties were evaluated by correlation analysis, which carried out taking into consideration all metal fractions with all soil properties on the four soil profiles. (SAS institute, 1985).

## RESULTS AND DISCUSSION

### *Heavy metals distribution in the studied soil samples*

In Egypt, soils have long been regard as repository for different society's wastes, by time and biogeochemical process these wastes gradually mobilized. In addition to different human activities such as chemicals applied in agricultural systems led to increase heavy metals in soils, these contaminants can also pollute water supplies and impact food chains (Ma and Rao, 1997). Heavy metals such as Pb, Cu, Ni and Zn all are potential soil pollutants soils consist of heterogeneous mixture of organic and inorganic solid components as well as a variety of soluble substances. Therefore, distribution among specific forms varies widely based on the metal's chemical properties and soil characteristics (Soon and Bates, 1982). Thus it is important to evaluate the availability and mobility of heavy metals to establish environmental guidelines for potential toxic hazards and to understand chemical behavior and fate of heavy metal contaminants in soils (Davies, 1980)

The sequential extraction used in this study is one of the useful issues to indirectly assess the potential mobility and bioavailability of heavy metals in soils Ma and Rao, 1997. Also, Sequential extraction procedures provide useful information for risk assessment since the amount of metals mobilisable under different environmental conditions can be estimated.

The six chemical fractions are potentially defined by an extraction sequence that follows the order of decreasing solubility (Xian, 1989; Clevenger and Mullins, 1982; Soon and Bates, 1982). Assuming that bioavailability is related to solubility, then metal bioavailability decreases in the order: water soluble> exchangeable > Carbonate > Fe-Mn oxides > organic > residual. This order offers qualitative information about metal bioavailability. According to study of Ma and Rao, 1997, we assumed that metals in the nonresidual fractions are more bioavailable than metals associated with the residual fraction.

**Table 1.** Some chemical properties of the studied soils

| Soil No. | Irrig. period | pH | EC | OM | CaCO₃ | Clay % | Silt % | S. area | Tot. Pb | Tot. Ni | Tot Cu | Tot Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | El-Gabl El-Asfar | 7.07 | 0.33 | 0.78 | 0.45 | 4.6 | 25.1 | 14.5 | 139.4 | 32.5 | 73.2 | 281 |
| 2 | | 7.27 | 0.24 | 0.96 | 0.31 | 5.2 | 4.8 | 12 | 130.4 | 88 | 87.4 | 344 |
| 3 | | 7.94 | 0.26 | 2.97 | 0.89 | 29.0 | 30.0 | 149 | 135.1 | 101 | 99.0 | 298 |
| 4 | | 7.16 | 0.31 | 2.62 | 0.89 | 39.1 | 28.9 | 161 | 134.8 | 42 | 72.4 | 380 |
| 5 | | 7.61 | 0.31 | 2.72 | 0.45 | 41.9 | 13.1 | 165 | 133.9 | 74 | 70.3 | 483 |
| 6 | | 7.64 | 0.25 | 1.04 | 0.05 | 5.3 | 13.2 | 14 | 128.2 | 64 | 52.8 | 395 |
| 7 | | 7.31 | 0.38 | 1.72 | 0.89 | 25.3 | 24.3 | 131 | 123.6 | 113 | 69.1 | 382 |
| 8 | Zenin | 7.73 | 2.10 | 2.91 | 0.65 | 51.1 | 26.7 | 244 | 129.6 | 117 | 86.2 | 302 |
| 9 | | 7.46 | 4.39 | 2.33 | 1.23 | 45.3 | 43.2 | 230 | 133.5 | 110 | 114 | 359 |
| 10 | | 7.78 | 3.33 | 2.92 | 0.45 | 48.6 | 40.4 | 239 | 138.2 | 100 | 107 | 298 |
| 11 | El-Kanater | 7.89 | 0.41 | 2.91 | 2.23 | 53.0 | 34.0 | 248 | 98.31 | 49.1 | 24.3 | 135 |
| 12 | | 7.87 | 0.57 | 2.97 | 2.23 | 58.5 | 27.0 | 258 | 97.9 | 44.8 | 23.8 | 117 |

***Lead (Pb) distribution***

Figure (1) represents distribution of Pb in the six fractions: water soluble (WS), exchangeable (EXC), carbonate (CA), Fe–Mn oxides (Fe–Mn), organic matter (OM) and residual (RES) fractions for the studied three groups of soils. Generally, results refereed that the decreasing order of the six fractions applied in this study is residual (Res) >> Fe-Mn > carbonate (carb) ~ organic (org.) > exchangeable (exch.) > water soluble (WS).

Data also showed that residual fraction ranged between ~30 and 53 % of total Pb concentration in GI, the higher value was observed in S5 and the lower one in S1. In GII, the range was ~ 45 % from the total Pb and was ranged between 56-59% in GIII. The comparison between residual and non-residual forms, data showed that increasing of clay content in GI and GIII, led to increase residual fraction over the non-residual forms, however, this trend was not observed in GII.

In G1 (El-Gabal El-Asfar site), data showed that Pb distribution consistently related to soil properties of soils with respect to variation of soil properties in this group according to its containing the two studied orders. In course texture like S1, S2 and S6, data showed that the summation of WS and Exch. forms of these soils are higher than other soils have high clay percent. In G2, the sum of WS and exchangeable fractions ranged between ~7-11% from the total concentration of Pb in different soils of the group, the higher value was observed in S8 followed by S9 and the lost value is in S10. In G3 which represents organic faming selection in this study, worth to mention that both soil0s in this group almost gave the same value especially in the exchangeable form.

The higher values extracted in step 3 was observed in S1, S2 and S6 in G1, moderately in S7 and the lowest values in S3, S4 and S5. In G2, data showed that Pb associated with carbonate form take the decreasing order S9 > S10 >S8 and S12 >S11 in G3, this result indicate the association of Pb with Fe-Mn oxides take different trends in different groups of used soils.

**(Group 1)**
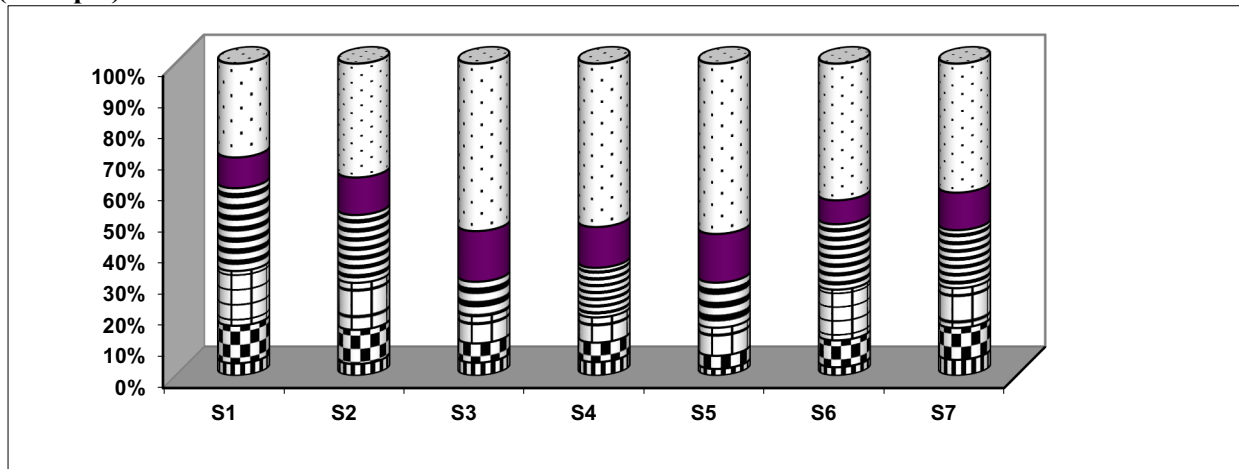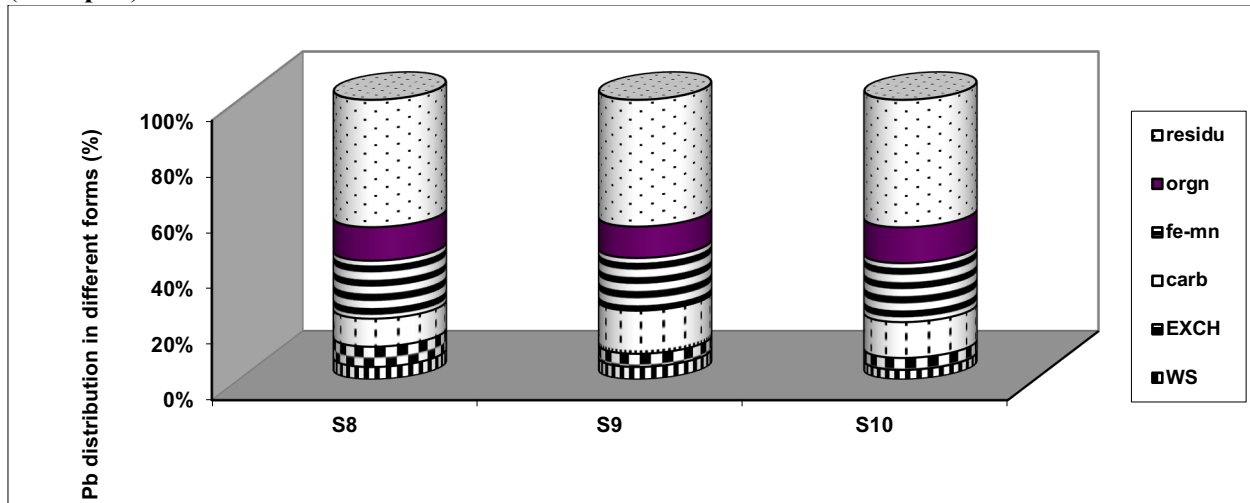
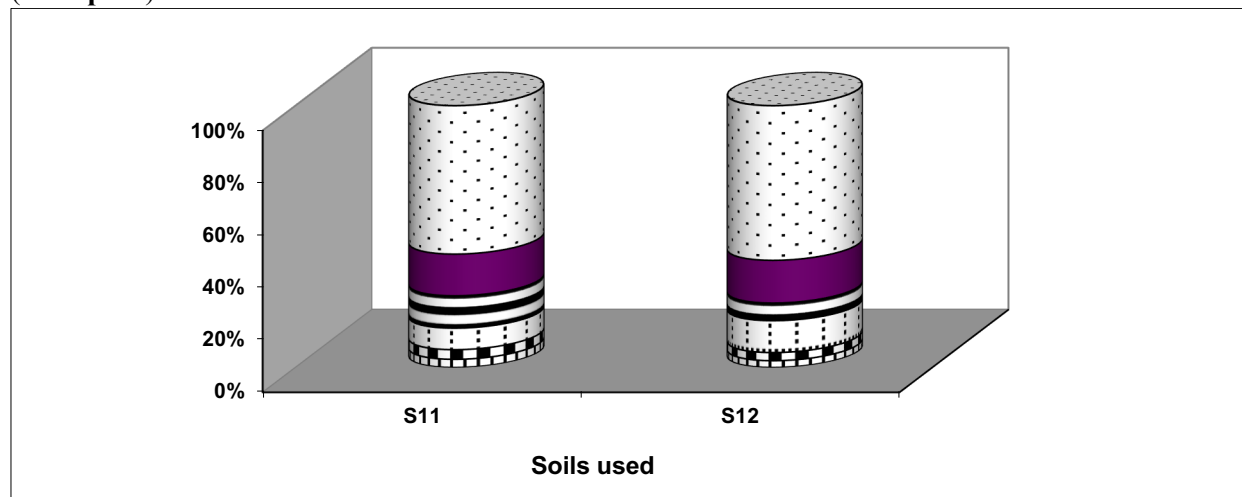

**(Group II)**

**(Group III)**



**Figure 1.** Pb distribution in different soil samples as affected by source of pollution, time of irrigation with effluent water

Data of step 4 extraction gave almost the abovementioned trend of Step 3 with increasing % values of total in all soils. These higher concentrations compared with other fraction in different groups can be understood only in terms of occurrence of the added Pb in Fe-Mn oxides with low solubility, in addition, data of GII gave higher percentage values of total of Pb associated with Fe-Mn in most cases with that of G2 and G3 represent the effect of time and this result will be discussed in more details in discussion.

Lead (Pb) in residual fraction (step 6) showed percent value vary with time of irrigation with waste water and inside the different groups related with soil properties.
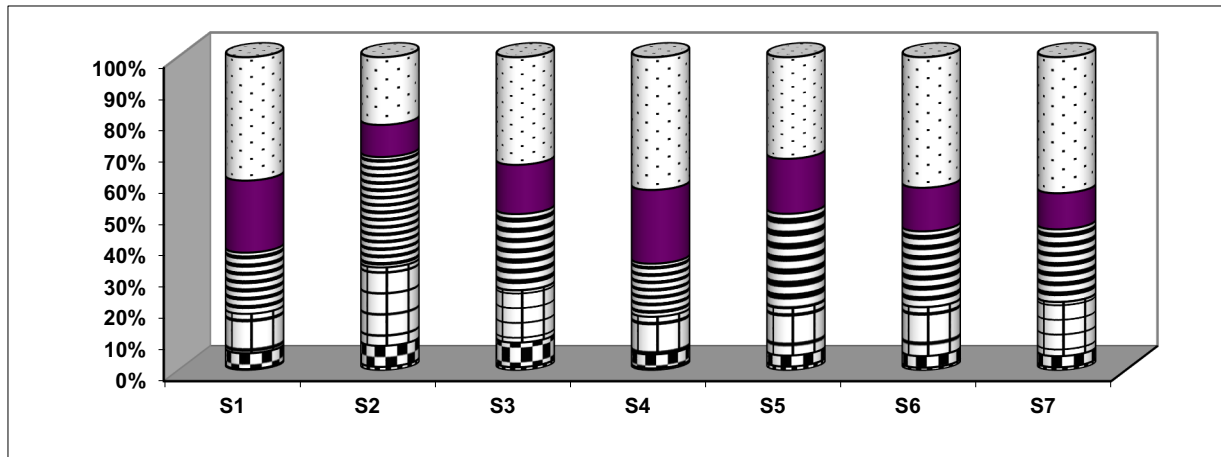
*Ni distribution*

Unlike Pb, data depicted in figure (2) showed that in different groups of used soils, the percent of Ni distributed in nonresidual form (sum of WS, Exch., Carb., Fe-Mn and org. forms), was higher than residual form (step 6). Nevertheless, Ni in residual fraction (step 6) was the most important fraction for Ni in all studied groups ranging from 21-43 % of total in G1, ~ 51% in G2 and 33-61.5 % in G3.

In non-residual fraction, Ni was found in all fractions with different percentages of total. The Fe-Mn oxides and carbonate fraction contained most of Ni in used soils. The higher percent value of Ni was observed in Ni associated with Fe-Mn oxide (17-35 %) of total in all groups, followed by (12-25 %) in carbonate fraction, the organically bound Ni was ranged between 10 and 22.5 % and then WS and Exch. forms gave the lowest percent values.
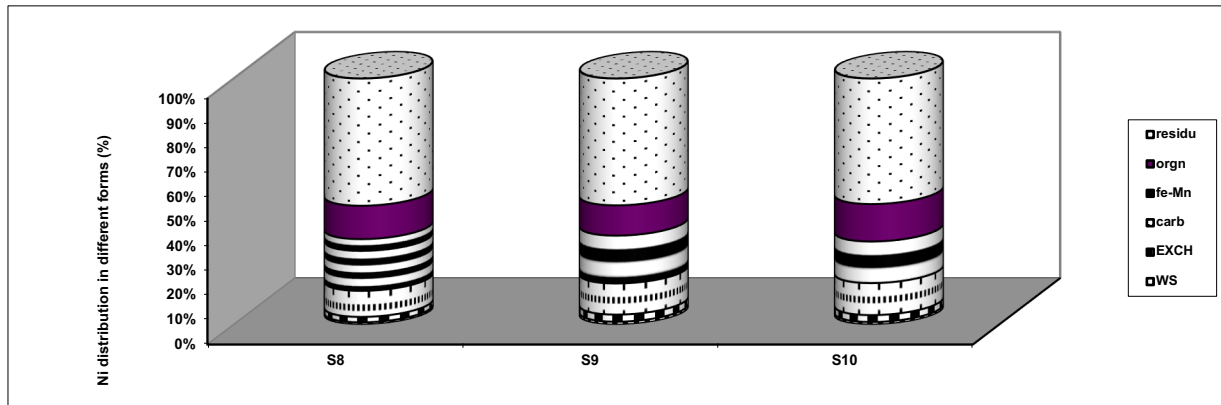
The effect of concentration in Ni distribution showed that increasing of Ni concentration in soils led to increasing residual fraction over non-residual ones, a reverse trend, however, was observed with decreasing the concentration of Ni, for example, data showed that total concentration of Ni ranged between about 44-49 ppm in GIII, the relative percent values were 58, 66 % and 33, 42 % for non-residual and residual forms in S11 and S12 respectively.

In GII, although the higher concentration in this group ranged between 100-117 mg kg-1, was observed, the percentages of non-residual and residual fractions were very narrow and ranged between about 48% and 51 % form the total Ni. Worth to mention that increasing the application of sewage sludge and irrigation with waste water did not influence the total concentration of Ni.
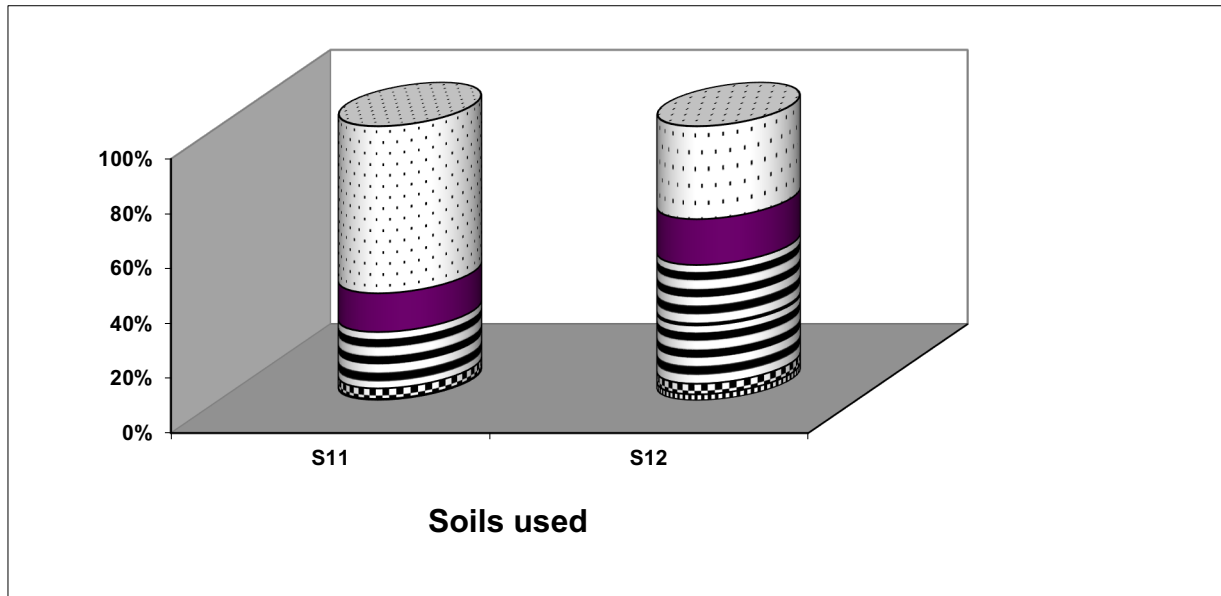I

**Figure 2.** Ni distribution in different soil samples as affected by source of pollution, time of irrigation with effluent water

### *Copper distribution*

Data in Figure (3) indicate that most of Cu found in these soils were found in residual fraction in most cases. In group I, the percentages of Cu in residual fraction were ranged between 37-80% from the total Cu content. The higher percent of Cu was pronounced in S6 and the lower one was in S4.

In G2, soil irrigated with effluent water and treated with sewage sludge for less than 10 years, the residual fraction percentages were ranged between 26-49% from the total content of Cu, the respective

values for G3 were 51-36 % for S11 and S12 respectively. As a percent of total, most of non-residual fraction, most of Cu are concentrated in Fe-Mn oxide followed by that associated with carbonate fraction.

In these two forms, the obtained results indicated that about more than 50 % of total are associated with these two fractions in most cases of G2 soils. These percentages were decreased in G2 and reach the lowest value in S11 of G3. The percentages of organically bound Cu in the studied soil groups were observed to be the important fraction hold soil Cu after carbonated and Fe-Mn fractions in the case of decreasing their values. Data showed that higher organically bound Cu was reported in G3 (17-23 % of total), the respective values were ranged between 14-21 % and 3-17% in G2 and G3 soils.

Worth to mention that the smallest percentage of Cu in all soils were detected for exchangeable (exch.) and water soluble (WS). Forms in all groups of tested soils had some reasonable exceptions detected in both G1 and G3.
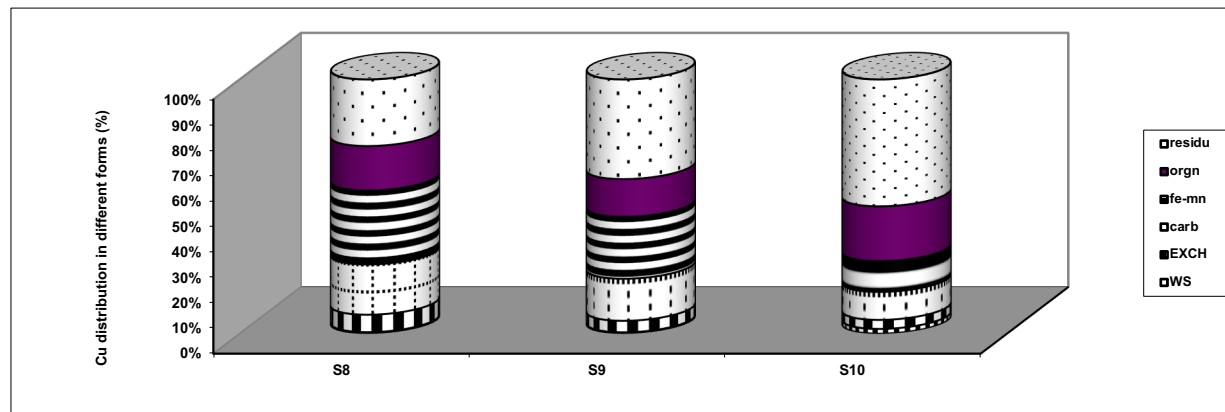
### *Zinc distribution*

In this pollutant fractionation study, data showed that residual fraction of Zn showed the higher worked fraction compared with other fractions. Results showed that 28-55% of total Zn was retained in soils of G1, this ration was decreased in G2 to be about from 36-42% and reached the maximum recorded values in G3 (59 and 67 % of total Zn). The amount of Zn in non-residual fraction ranged between 33 and 83% of total Zn.

Among the non-residual fraction, the Fe-Mn oxide fraction contained the greatest amount of Zn in most soils in the studied groups with some exceptions found in soils of G3 in which the organically bound Zn had the greatest amount of Zn compared to other fractions of Zn in this group of soils.
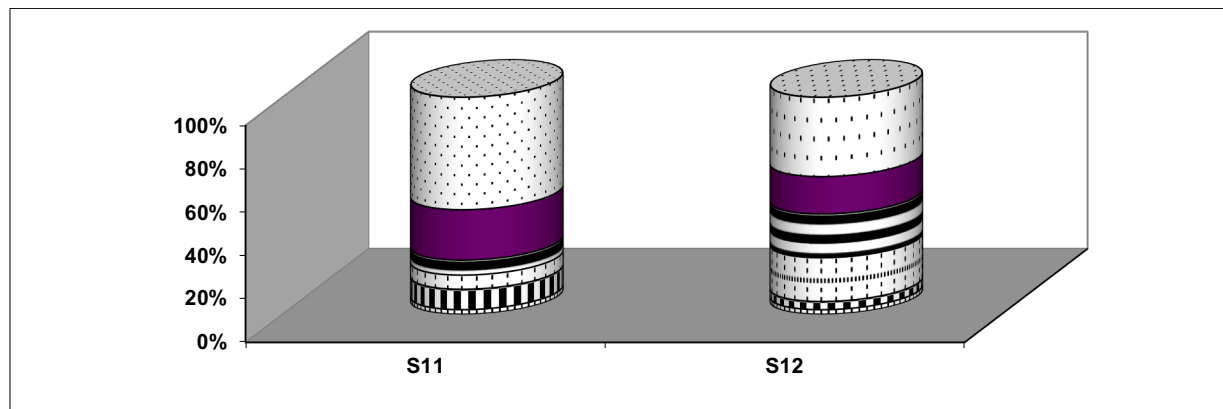
GI
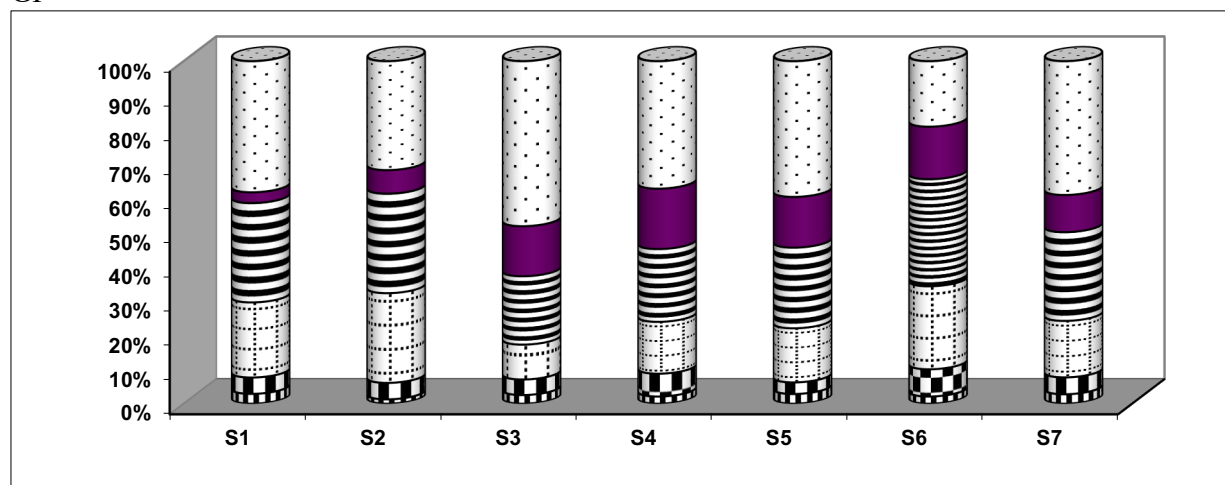


GII

GIII



**Figure 3.** Cu distribution in different soil samples as affected by source of pollution, time of irrigation with effluent water

The dominating chemical form for Zn was varied between different groups according to source and time of receiving the studied pollutants. The Fe-Mn oxide-bound Zn represent about from 17-50 % of total in G1and 28-33 %, 2 % of total in G2 and G3 respectively, which represent higher bound form with the carbonate-bound Zn.

In G3, data represented in Fig (4) showed higher carbonate bound Zn compared with other groups which suggested that Zn had a preference for carbonate at the expense of the Fe-Mn oxide fractions. In some cases, however, some soils in G1 retained Zn in carbonate fraction reached to about 26% of total content of Zn in this soil. The org. bound Zn in the studied group samples were potentially varied according to the source of pollutants and perhaps according to the soil components. Data showed that org-Zn ranged between 4 and 36 % of total Zn in all groups, the higher values were reported in G3 were 25 and 36 %, the same values was 4-7% in G1 and 4-8% of total Zn in G2. In all soil groups, worth to mention that again water soluble followed by exchangeable fraction gave the lowest percent of total Zn retention with significant particular values of exchangeable fraction were reported in G1.

***Correlation analysis between soil properties of different groups and pollutants fractionation***
Correlation analysis was conducted between soil properties of different groups of used soils and Pb, Cu, Ni and Zn fractionation in these soils to represents most soil factors controlling studied heavy metals distribution in different fractions under our experimental conditions. Data in table 2 showed that in most cases pH and EC parameters did not gave significant correlation with fractionation of different pollutants, in some cases, however, for pH, organically pound Pb, Cu gave significant correlation at 0.01 level and at 0.05 for Zn. For EC only Ni gave high significant correlation compared with other pollutants.

Organic matter combined with the studied pollutants showed significant correlation with some of fractions of these trace elements. Data showed that most of organically bound-trace form gave highly and significant correlation, for example, the respective values of correlation between OM content of the studied soil samples with the organically bound form were 0.66**, 0.80** and 0.85** with Pb, Ni and Zn while it was 0.55* for Cu.
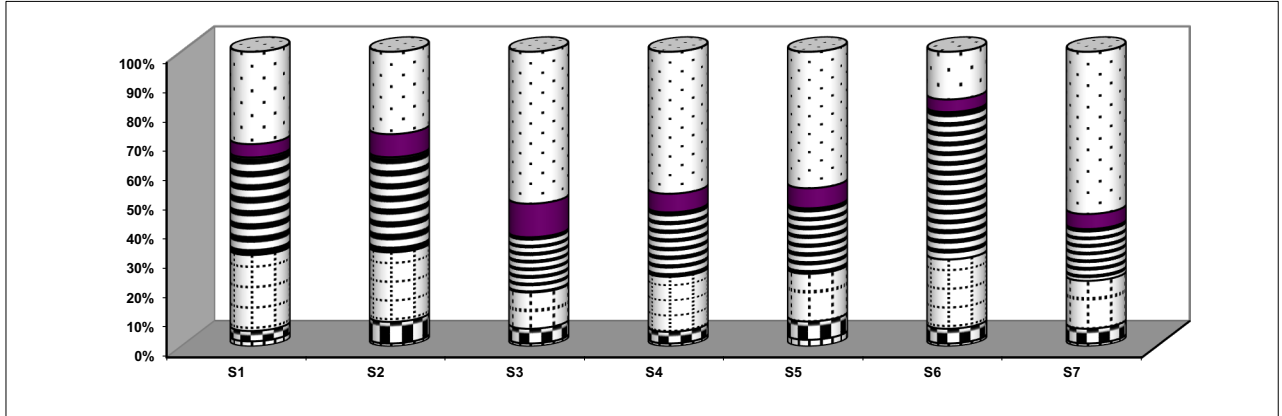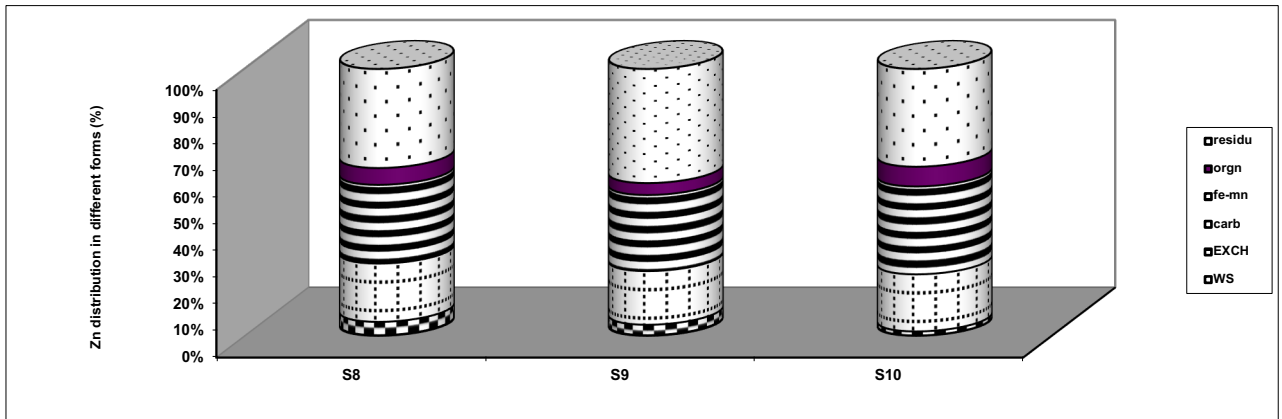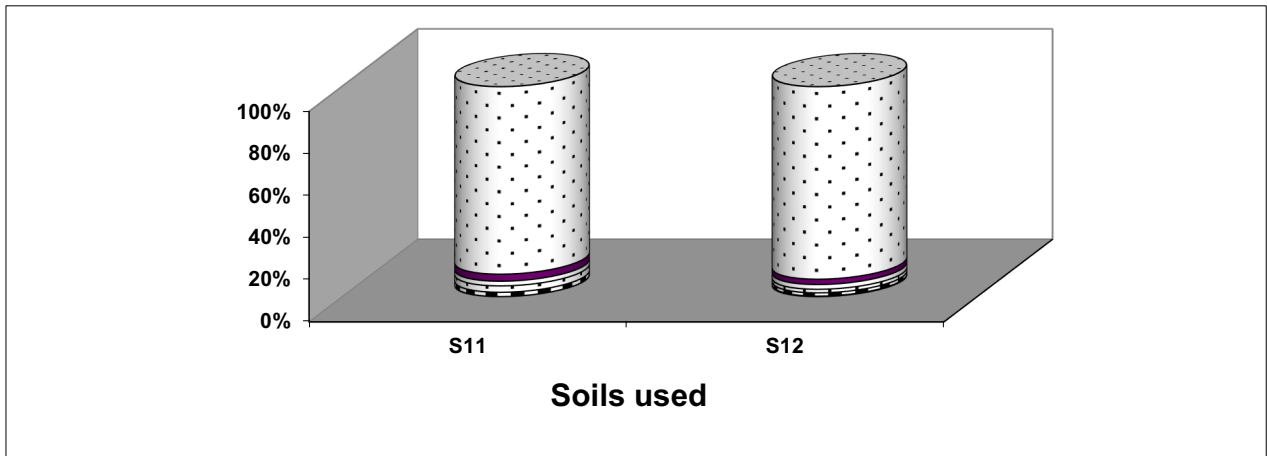
**Figure 4.** Zn distribution in different soil samples as affected by source of pollution, time of irrigation with effluent water.

The same parameter showed positive and high correlation with residual Pb (0.86**), Ni in carbonate form, and Res.-Zn, while it was highly and negative values with cu in Carb. and Fe-Mn oxide forms. Worth to mention that some fractions like Org-Cu, Res-Cu and Carb-Zn, and Zn in Fe-Mn forms showed significance at 0.05 level.

Although the studied soil samples are not calcified as calcareous soil, correlation analysis showed significant correlation relationship between Pb in organic and residual forms. In Ni and Cu, however, data indicated only carbonate and Fe-Mn oxide forms gave high (at 0.01 level) and low (at 0.05 level) respectively, the other forms did not give any significant correlation with $CaCO_3$ content. In contrast, the correlation analysis values between $CaCO_3$ content in the studied soils and different forms of Zn,

were highly and significant positive correlation with organic and residual forms (0.86** and 0.84**), and negatively with other forms ranged between 0.66** and 0.89**.

Mechanical analysis represented by clay and silt showed more or less significant correlation with some forms of studied pollutants. For clay content, correlation analysis showed that organic and residual forms of Pb gave high and positive significant correlation with this soil parameter. In Ni, the correlation between carbonate form of Ni gave high and positive correlation with clay (0.97**).

For Cu and Zn pollutants, most fraction low significant with clay content such as Carb, Fe-Mn and residual forms of Cu and Carb, Fe-Mn for Zn. The high and significant correlation were just only recognized in organically bound- Cu gave significant correlation with clay content (0.79**). Although all forms of studied heavy metals distribution in the studied soil fractions gave no or low significant correlation with silt content in these soil samples, only Ni in Fe-Mn, Cu in carbonate, and Zn in Exch. forms gave high and significant correlation with silt contents.

Surface area of the studied soil samples represents an important parameter affecting heavy metals retention in soils. Results showed that like clay content, high significant correlation between organic and residual forms and soil surface area ranged between 0.81** and 0.83**. The same significant correlation with surface area was observed for carbonate form of Ni (0.94**), Fe-Mn and organically bound Cu. In Zn heavy metal data showed that both high negative and positive correlation were detected for carbonate and Fe-Mn forms for the negative one and residual form for the other type.

**Table 2.** Correlation analysis between soil properties of different groups and pollutants distribution in these groups

| Fractions | pH | EC | OM | CaCO$_3$ | Clay | Silt | S. area |
| | | dsm$^{-1}$ | % | % | % | % | m$^2$/g |
|---|---|---|---|---|---|---|---|
| | | | | Pb | | | |
| Exc | 0.27ns | 0.09ns | 0.32ns | 0.26ns | 0.22ns | 0.07ns | 0.19ns |
| Carb | -0.18ns | 0.47ns | -0.46ns | -0.11ns | -0.21ns | 0.11ns | 0.16ns |
| Fe-Mn | -0.44ns | 0.48ns | -0.41ns | -0.62* | -0.29ns | -0.07ns | -0.23ns |
| Org. | 0.64** | 0.01ns | 0.66** | 0.76** | 0.86** | 0.34ns | 0.81** |
| Res. | 0.69** | 0.10ns | 0.86** | 0.72** | 0.88** | 0.37ns | 0.83** |
| | | | | Ni | | | |
| Exc | 0.15ns | -0.11ns | -0.03ns | -0.22ns | -0.30ns | -0.17ns | 0.29ns |
| Carb | 0.56* | 0.41ns | 0.86** | 0.68** | 0.97** | 0.51ns | 0.94** |
| Fe-Mn | -0.09ns | 0.38ns | -0.36ns | -0.51ns ns | -0.47ns | -0.84** | -0.57* |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Org. | -0.31ns | 0.28ns | 0..80** | 0.01ns | 0.02ns | 0.12ns | -0.06ns |
| Res. | 0.21ns | 0.75** | 0.29ns | -0.15ns | 0.33ns | 0.48ns | 0.43ns |
| Cu | | | | | | | |
| Exc | 0.09ns | -0.23ns | -0.06ns | 0.18 ns | -0.03ns | -0.01ns | -0.03ns |
| Carb | -0.49ns | -0.17ns | 0.73** | -0.47ns | -0.61* | -0.67** | -0.64* |
| Fe-Mn | -0.53* | -0.14ns | -0.67** | -0.62* | -0.64* | -0.59* | -0.65** |
| Org. | 0.72** | 0.30ns | 0.55* | 0.46ns | 0.79** | 0.61* | 0.78** |
| Res. | 0.06ns | -0.25ns | -0.52* | -0.34ns | -0.59* | -0.47ns | -0.59* |
| Zn | | | | | | | |
| Exc | -0.37ns | -0.26ns | -0.38ns | -0.66** | -0.49ns | -0.70** | -0.59* |
| Carb | -0.36ns | 0.20ns | 0.61* | -0.89** | -0.64* | -0.30ns | -0.69** |
| Fe-Mn | -0.36ns | 0.20ns | -0.61* | -0.89** | -0.64* | -0.30ns | -0.82** |
| Org. | 0.56* | -0.21ns | 0.85** | 0.86** | 0.53ns | 0.15ns | 0.49ns |
| Res. | 0.35ns | -0.11ns | 0.67** | 0.84** | 0.68** | 0.43ns | 0.67** |

## DISCUSSION

Barrier to discuss fractionation of the studied pollutants in more details, it should be mentioned that we faced inconsistent result that the time of using waste water in irrigation of the studied soils i.e. >50 years using waste water in irrigation (case I), > 15 years irrigation with waste water (case II) and organically farm used ordinary irrigation water and the source of pollution of these soils comes from their location beside traffic road (case III), all cases did not gave relative concentrations according to time and source of pollution parameters. The total concentration in G1 ranged between 131-166, 42-113, 53-99, 281-483 ppm for Pb, Ni, Cu, Zn; the respective values for G2 were from 170-180, 100-117, 86-114, 298-359 ppm. For G3, the total concentration values were ranged from 176-193, 69-75, ~ 24, 117-135 ppm for Pb, Ni, Cu and Zn respectively. Consequently, in this study we used percent (%) of total expression instead of actual concentration of these pollutants in explaining heavy metal distribution in different fractions. In addition, using of % expression was applied to understand the actual bioavailable form(s) of these pollutants in used groups of soils according to graduation in their distribution which was explained by Ma et. al., 1997 that WS and exch. fractions would be readily

bioavailable to the environment, whereas the metals in the residual fraction are tightly bound and would not be expected to be released under natural conditions. The same result was reported by Xian, 1989; Cleveger, and Mullins, 1982. The other fractions of fractionation analysis i.e. carbonate, Fe-Mn oxide and organically bound metal would be a reserve source to be replenish under decreasing concentration of these heavy metals in soils.

For non-residual and residual distribution of the studied pollutants, results indicated that more or less the higher or lower of these two forms are generally related to three main factors controlling heavy metals distribution in soil system represented by type of pollutant(s), soil properties of soils investigated source of pollution and specifically to the different forms of pollutants present in sewage sludges Corey et al., 1987 especially for GI and GII. Numerically, In GI and GII increasing of clay content in soil samples, led to increasing of N-residual form (sum of all fractions except residual) compared with residual one for most pollutants. For example, In G1, data showed that non residual Cu increased to about 62% of total by increasing clay content to 39%, in GII also increasing clay content to 51% led to increase Cu and Zn in non-residual form to reach about 74 and 63% from the total respectively. Some exceptions, however, were obviously observed in Pb pollutant represented by increasing of non-residual form with decreasing clay content only in GI (50 years' application of sewage sludge and waste water), perhaps this result related to easier behavior of this pollutant to change to unavailable form with long time of land use compared with other pollutant. In soils of GIII, distribution of pollutants in residual or non-residual forms was depending on type of pollutant. In this group, results showed that Pb and Zn were specifically retained in residual form whereas, other pollutants i.e. Ni and Cu were more concentrated in non-residual one. These results are more related to the types of organic fertilization applied in group of soils and the interaction between organic matter and different pollutants which will be specifically discussed in distribution of non-residual form of the studied pollutants.

Lead (Pb) distribution in non-residual form was more concentrated in more resistant fraction like Fe-Mn oxide form in GI, and GII. The presence of metal in Fe-Mn oxide form was reported by Carmen and Murray 2001 to be an important sunk of different pollutant in soils. However, it was found in organic form in some cases of soils in GI higher in organic matter and all soils in GIII. Similar results were reported by Sposito et al. 1982 in fine-loamy, mixed, thermic Xerollic Calciorthid soils and they differed from the results which were reported by Xian 1989, who found that the organic fraction was higher than the other fractions of Pb in sludge amended soils. It should be mentioned that in GI and GII the decreasing order of different non-residual fractions according to the mean value expression were:

$$Fe\text{-}Mn > Carb. > Org. > Exch. > WS$$

The preference of Mn oxides over Fe oxides for Pb has been reported before by Tipping et al. 1985 and by McGrath, et. al. 1992, who found that the adsorption to Mn oxides was approx. 40 times greater than that of Fe oxides.

The respective arrangement of GIII was:

$$Org. > Carb. > Fe\text{-}Mn > Exch. > WS$$

According to data of total concentration of Pb, irrespective of Zn concentration, Pb was high in GIII compared with other groups. For the location of this group vicinity of the highways, result emphasized that Pb should be high consistent with the observations of Harrison et al. 1985 and with data given in a literature survey by Scanlon 1991.

Data of mean values of non-residual Ni distribution, data showed that Nickel (Ni) was mainly associated with Fe-Mn oxide followed by carbonate and organic forms in GI with some exceptions in increasing organically bound Ni in the case of increasing organic matter. By increasing of clay content in GII (45-51%) most of Ni associated with Fe-Mn, followed by organic and then carbonate. Despite soils of GIII represented organic farming type by mainly applied organic fertilization technique, Org-Ni

comes in the third category after Fe-Mn and organic forms. These results may be due to the different locations of Ni in the soil which could be attributable to the different forms of Ni present in sewage sludges Corey et al., 1987. Worth to mentioned that in GI there are some cases of increasing of Fe-Mn bound Ni, compared with other used soils in the same group (S2 and S5), these soils contain more than 30% of Ni associated with Fe-Mn oxide and it should be mention that both soils have relative high Zn concentration which could be influencing Ni accumulation in this form over other forms analyzed. The decreasing order, however of Ni distribution in the three groups are as follow:

Fe-Mn oxide > organic = carbonate > exch. > WS (GI & GII)
organic > Fe-Mn oxide = carbonate > exch. > WS (GIII)

Like Ni, copper (Cu) take the same trend in its distribution in GI with some exception in high OM soils i.e. S3 and S4, however, the organically pound Cu was the dominant form in GII and GIII. This result represents the importance of OM content in sludge amended soils on heavy metals distribution in Org-form. Soil organic matter has been recognized as a critical component in the retention of heavy metals in soils. The increase of organic matter in soil would help to reduce the metal ions from exchangeable sites and acidic conditions (Eillott et al., 1986; Weng et al., 2002). Moreover, Anxiang Lu et al., 2005 stated that soil with high OM content could bind more metals in organic matter fraction. Results of this work could be helpful for us to clarify the distribution of anthropogenic heavy metals in soil. This conclusion by different authors may be the main reason in finding more that 31 % of about 42 % (non-residual form of Zn in organic form of GIII. On the other hand, decreasing of the same parameters in GI and GII, led to concentrate soil Zn in Fe-Mn oxide, followed by carbonate and at least the other fractions with some exception present in S3 in GI where high OM was observed ked to increase organically bound Zn.

Correlation analysis conducted between different soils parameters and different fractions of Pb, Ni, Cu and Zn perhaps emphasized the above results. Organic matter content in different soils highly correlated at 0.01 level with Pb, Ni and Zn and at 0.05 level with organically bound fraction. The same parameter was also correlated with carbonate fraction of Ni and Cu. In the same analysis, clay content and surface area of soil samples are the most important soil parameters controlling studied heavy metals distribution in soils. Relationships between soil parameters and metal fractions are complex and may be different for different soils. It may also be one reason for the contradiction between different studies McLaren and Crawford 1973 and Iyengar et al. 1981 reported a statistical relationship between metal fraction and soil parameters, whereas Miller and McFee 1983 found no significant relationships in their regression analyses. Moreover, Ramos et al. 1994 reported that the distribution of metals in the various chemical fractions was dependent on the total metal content of the soils. Under our experiment condition soil pH which considered as the most important parameters controlling heavy metals distribution did not show any significant with different fractions with one exception related with high correlation observed in organically bound all heavy metals.

## CONCLUSION

Our goal was to achieve a set of parameters estimated capable of describing the adsorption-adsorption regardless of the concentration of the applied heavy metals. Therefore, we also try to obtain only one set parameter capable of predicting the concentration of all entries and the entire focus range. Moreover, the estimated absorption capabilities of different soil types were subsequently associated with clay content, surface area, organic matter, calcium carbonate and type of clay mineral of soil. This information is a prerequisite for understanding the fate and behavior of pollutants in the environment.

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