

Sequential Extraction of Cu and Ni in some Egyptian Contaminated Soils

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THREE GROUPS of some Egyptian surface soil samples (G_1 , G_2 and G_3), from; El-Gabal El-Asfar, Zenin and El-Khanater areas were collected. These groups of soils were classified under two orders, *i.e.*, *Typic torrerts* and *Typic psanments* according to the American taxonomy. The source of contamination in the first and second groups created from applying sewage sludge as main source of organic fertilizer and irrigation with waste water for more than 50 years (G_1), and about 10 years (G_2). The 3rd group of soil, however, was affected by its location beside traffic road and application of organic fertilization sources. All groups of soils were investigated for distribution and chemical fractions of Ni and Cu and their mobility in relation to different soil properties.

The obtained results imply that neither time of exposed to sewage sludge applied nor waste water irrigation treatments used influencing heavy metals (HM) concentrations in different soil samples tested compared with the effect of soil properties which assumed in this study to control heavy metals distribution into different fractions tested. The decreasing order of different heavy metals distribution generally takes the order: Residual (Res) >> Fe-Mn oxide > carbonate (Carb) \approx organic (Org.) > exchangeable (Exch.) > water soluble (WS). In some cases, however, the organically bound form of heavy metal was the predominant fraction especially in (G_3) for the applying of organic fertilizers in these soils. 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 in relative distribution of the studied pollutants into different fractions.

Several metals are listed in the U.S. Environmental Protection Agency's list of 129 priority pollutants due to their abundance and toxicity in various environments; heavy metals contamination of aquatic environments (Li & Shuman, 1996). Except for very acidic soils, heavy metals are sparingly soluble in soils and occur predominantly in a sorbed state or as insoluble compounds. Because of their low solubility, movement of heavy metals in soils has generally been considered either minimal or practically nonexistent. Williams *et al.* (1987)

found no significant movement of Cd, Pb, Cu and Zn in soils treated with biosolids for 8 years and demonstrated that more than 90% of applied heavy metals were found in the top 15 cm of the soil. Their movement is essentially related to the physicochemical forms of the metals in soil.

It is well known that metals, reaching excessive levels, can exert serious impacts on humans, animals, and plants (Kim & Kim, 1999). Metal toxicity associated with solids in the environment is of particular concern since they can be released. Nevertheless, their environmental impact is difficult to evaluate qualitatively due to the complex interactions between metals and ecological systems (Kim & Kim, 1999). It is however, well known that information on the total concentration of toxic metals in contaminated soils is not sufficient for the understanding of their mobility and availability to the biota (Bunzl *et al.*, 1999). For this reason, various sequential extraction procedures have been proposed to study the partitioning (or fractionation) of metals in soils or sediments (Tessier & Campbell, 1988). Use of sequential extraction technique to separate the soil metals into different forms can be helpful in understanding the processes of metal in soil profile.

Copper in most soils is derived mainly from parental rocks (Jenkins & Jones, 1980 and Tiller, 1983) but some copper in some soils is derived from anthropogenic sources. Substantial copper addition to soils can occur from agricultural practices (Tiller & Merry, 1981 and Barzi *et al.*, 1996), where copper compounds are used widely as fungicidal and bactericidal sprays, fertilizers and stimulants of animal growth. The most common, incidental contamination of horticultural soils with copper is due to the use of copper-bearing fungicides that reach soil surfaces directly or indirectly with leaf litter (Richardson, 1997). Despite its environmental and agricultural importance, the concentration, distribution and fractionation of anthropogenic and naturally occurring, copper in soils is poorly known. Although the total copper content in soils is a useful indicator of soil deficiency and/or contamination, it does not provide enough information about its environmental impact. Copper availability to biota (as a nutrient or toxin) and its mobility are the most important factors to be considered when assessing its effect on the soil environment.

Nickel status in soils is highly dependent on the Ni content of parent rock. However, the concentration of Ni in soils also reflects soil forming processes and pollution. Alloway (1995) reported that Ni recently has become a serious pollutant that is released in the emissions from metal processing operations from the increasing combustion of coal and oil. Also application of sludge and certain phosphate fertilizers may be important sources of Ni in soils.

In Egypt, soils has 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 & Rao, 1997). Heavy metals such as Cu and Ni 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 metals chemical properties and soil characteristics (Soon & 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).

El-Gamal (1980) indicated that total Ni content in El-Gabal El-Asfar soils irrigated with sewage water for several years ranges from 162 to 1611 ppm with an average of 675 ppm, while the DTPA extractable Ni varies from 0 to 4.6 ppm with an average of 2.1 ppm. Yaron *et al.* (1996) showed that a close positive relationship was found between Ni in the soils and its content in the soil forming parent materials and a weak relationship with the content of organic matter. Different types of Ni distribution were detected in the soil profiles in different soils depending on the content of clay separates and the pH of the soil solution. Although a voluminous studies discussed the relationship between total and available forms of Cu and Ni in soil systems, the studies concerning with the effect of source of pollution of these metals in relation to their distribution in soils still limit.

The primary objectives of this study are to investigate the effect of source of contamination, quality of irrigation water and properties on Ni and Cu distribution in some Egyptian contaminated soils collected from cultivated lands and treated with sewage sludge and continuously irrigated with effluent water for 50 years (G_1), and 10 years (G_2). However, the soils of third group (G_3) as collected from farms located beside the traffic road and used organic fertilizers. The results of this study may be a guide for select the suitable remediation strategy(s) should be applied according to conditions of pollution.

Material and Methods

Soils

Twelve cultivated soils samples were collected from El-Gable El-Asfar, Zenen and El-Kantar El-Kharya areas and divided into three groups according to the source of pollution. In the first and second group's pollution of soils created from irrigation with effluent water and application of sewage sludge as a main source of organic fertilizer for more than 50 years (G_1) and about 10 years (G_2) respectively. In third group (G_3) the source of pollution comes from its location beside the traffic road, in addition, these soils irrigated with non-contaminated water. Routine analyses for these samples were carried out according to conventional methods Environmental Protection Agency, EPA (1993). Some physical and chemical properties are presented in Table 1.

TABLE 1. Some physical and chemical properties of the studied soils samples.

Location	Soils	pH	EC dSm ²	OM %	CaCO ₃ %	Clay %	Silt %	Surface area m ² /g	Total ppm	
									Ni	Cu
El-Gable El-Asfar	S ₁	7.07	0.33	0.78	0.45	4.6	25.1	14.5	32.5	73.2
	S ₂	7.27	0.24	0.96	0.31	5.2	4.8	12	88	87.4
	S ₃	7.94	0.26	2.97	0.89	29.0	30.0	149	101	99.0
	S ₄	7.16	0.31	2.62	0.89	39.1	28.9	161	42	72.4
	S ₅	7.61	0.31	2.72	0.45	41.9	13.1	165	74	70.3
	S ₆	7.64	0.25	1.04	0.05	5.3	13.2	14	64	52.8
	S ₇	7.31	0.38	1.72	0.89	25.3	24.3	131	113	69.1
Zenin	S ₈	7.73	2.10	2.91	0.65	51.1	26.7	244	117	86.2
	S ₉	7.46	4.39	2.33	1.23	45.3	43.2	230	110	114
	S ₁₀	7.78	3.33	2.92	0.45	48.6	40.4	239	100	107
El-Kantar El-Kharya	S ₁₁	7.87	0.57	2.97	2.23	58.5	27.0	258	44.8	23.8
	S ₁₂	7.89	0.41	2.91	2.23	53.0	34.0	248	49.1	24.3

Heavy metals distribution

In the studied samples (Ni and Cu) heavy metals distributions were conducted according to Tessier *et al.* (1979) and modified by Ma & Rao (1997). The method could be summarized as follow:

Water-soluble (WS): soil sample extracted with 15 ml of deionized water for 2 hr.

Exchangeable (Exch): The residue from water-soluble fraction is extracted with 8 ml of 1M MgCl₂ (pH7.0) for 1hr.

Carbonate-Form (Carb): The residue from exchangeable fraction is extracted with 8 ml of 1 M Na-OAc (adjusted to pH 5.0 with HOAc) for 5hr.

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

Organically form (Org): 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 85°C for 2hr, with occasional agitation. A second 3-ml aliquot of 30% H₂O₂ (pH 2 with HNO₃) is added and the mixture heated again to 85°C for 3hr with intermittent agitation. After cooling, 5 ml of 3.2M NH₄OAc in

20% (v/v) HNO_3 is added and the samples diluted to 20 ml and agitated continuously for 30 min.

Residual Fraction (Res): The residues from organic fraction are digested using a HF-HCl/ HNO_3 .

Availability Index (AI)

Availability index was applied to evaluate the effect of pollution source on HM distribution in different soils. This AI is represented by the equation:

$$\text{AI} = \frac{\{(\text{Readily available pools (RAF)} + \text{Moderately available pools (MAF)})\}}{\{\text{Hardily available pools (HAF)}\}} * 100$$
. Increasing the AI parameter over 100 represents risk situation in tested soil(s).

Where:

RAF: Water soluble + Exchangeable.

MAF: carbonate form + Fe-Mn Oxides-Form + organically form.

HAF: Residual form.

Statistical analysis

Results are the mean values of three replicates. Different statistical analysis conducted between different fractions of heavy metals studied and soil properties were evaluated using SAS software (SAS Institute, 1985).

Results

Total concentration of Ni and Cu in used soil samples

Results in Fig. 1 represent the mean value of total concentrations of Ni and Cu in different groups of soils. Data indicated that Ni concentration was ranged between 56-194 ppm in G_1 , 163-191 ppm in G_2 and 75-82 ppm in G_3 . The concentration of Cu, however, was ranged between 105-166 ppm in G_1 , 164-203 ppm in G_2 and G_3 was 43-85 ppm. As shown in Fig. 1 the mean values of Ni and Cu perhaps emphasized that pollutants concentration were higher than the normal range of in used soils.

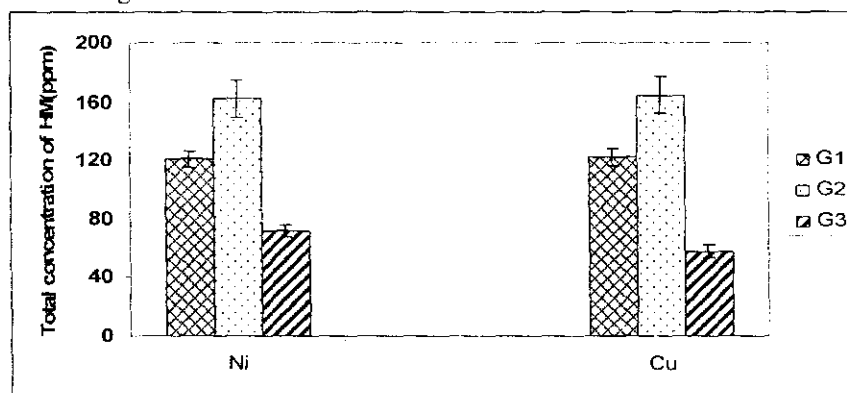


Fig. 1. Mean values of total concentrations of Ni and Cu in used soils.

Moreover, the time of soils exposed to different sources added from different sources was not enough to judge the hazardous of soil to be used in food production. For example, generally in both Ni and Cu the mean values of these pollutants in used soils indicated that values of G₂ (10 years exposed to pollution) were higher than G₁ (50 years exposed to pollution). Also, perhaps some kinds of organic fertilizers applied in agricultural lands may have significant values of pollutants beside the situation of the studied farms as was noticed in third group.

Concerning the results of sequential extraction of Ni and Cu, it should be mentioned that discussion was carried out on the basis of heavy metals distribution into different fractions. Also the evaluation of the results for each metal alone does not take into account possible synergistic or antagonistic effects due to influences of other metals that may be present in the samples (Campanella *et al.*, 1995). The metals in the non-residual or bio-available phases (water-soluble, exchangeable, carbonates bound, Fe-Mn oxides and organic bound) signify anthropogenic inputs from varying sources. This phase constitute potentially more mobile fractions and are often responsible for heavy metal toxicity in plants and animals.

Nickel distribution

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 & Rao (1997). Also, Sequential extraction procedures provide useful information for risk assessment since the amount of metals modifiable 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 (Clevenger & Mullins, 1982; Soon & Bates, 1982 and Xian, 1989). 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 & Rao (1997), we assumed that metals in the non-residual fractions are more available to be uptake than metals associated with the residual fraction.

Data in Table 2 and plotted in Fig. 2, represents Ni distribution into different fractions. Generally, data indicated that in different soils most of Ni was found in residual form (31-55% of total), followed by Fe-Mn oxide form (17-35%), the organically form represented about from 10-24% of total, meanwhile carbonate form represented about from 10-25%. The readily available pools represented by water soluble and exchangeable forms gave the lowest values compared with other fractions in all used soils. Concerning different groups, results showed that significant variation in different groups was observed in the studied fractions related with the time and source of contamination. For example, the average of carbonate form was about 16.5% of total in G₁, decreased to 12.2% in G₂ and then increased to 21% in third one. The respective values of Fe-Mn form were 25, 19 and 52%. These variations were more or less observed in other fractions. Also, the comparison between different soils in different groups, data showed that carbonate bound fraction a significant variation between soils of G₁

compared with G_2 and G_3 in different fractions was observed. In G_1 , data showed that Ni extracted by applying this step was ranged between about 5 ppm in S_4 and 22 ppm in S_2 . The same trend was observed in other readily and moderately available pools studied, in readily available pool, the numerical values for S_2 and S_4 were about 7 and 4.5 ppm, also for readily available pool Fe-Mn oxide associated with Ni the respective values were about 31 and 7 ppm.

TABLE 2. Distribution of Ni fractions mg kg^{-1} in different soil samples as affected by residence time and source of pollution.

Soil Groups	Soil No	WS. form	Exch. form	Carb. Form	Fe-Mn Oxi Form	Org. form	Res. Form
El-Gabl El-Asfar	S1	0.15	1.60	4.00	6.20	7.30	13.25
	S2	1.05	5.90	22.00	31.00	9.00	19.05
	S3	1.10	8.00	17.00	24.80	16.00	34.10
	S4	0.30	1.90	5.10	7.21	10.00	17.50
	S5	0.95	2.60	11.20	22.32	13.00	23.95
	S6	0.60	2.40	10.10	15.72	9.00	26.21
	S7	1.20	4.00	19.52	26.24	13.00	49.12
Zenin	S8	1.09	2.62	12.50	24.89	16.00	60.01
	S9	1.30	3.23	14.00	21.51	13.60	56.42
	S10	1.06	2.81	13.00	16.90	15.20	51.04
El-Kaater	S11	0.26	1.90	10.20	9.50	7.00	20.42
	S12	0.98	1.73	9.55	9.90	7.50	15.20

In G_2 , although the higher concentration in this group ranged between 100-117 mg kg^{-1} , the percentages of non-residual and residual fractions were very narrow and ranged between about 48% and 51 % from 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. In addition, more than 60% of the total Ni was found in the residual fraction at all sites (Fig.1) A larger percentage of Ni was bound in the reducible fraction in the sandy loam soils, whereas an almost equal part of the Ni was present in the oxidizable fraction at all sites. Almost no exchangeable Ni^{2+} occurred in any of the sandy loam profiles, but a larger fraction of Ni was found to be exchangeable in the top soils of the loamy sand soils.

Copper distribution

The concentration of copper associated with different soil fractions were measured for the three groups of soils. Data represented in Table 3 and plotted in Fig. 3 indicated that most of Cu was found in residual fraction in most cases. In the first group G_1 , the percentages of Cu values in residual fraction were ranged between 37-80% from the total Cu content. In this fraction, the higher percent of Cu was pronounced in S_6 and the lower value was observed in S_4 . In G_2 , soils which irrigated with effluent water and treated with sewage sludge for 10 years, data showed that the percentages of residual fraction were ranged between 26-49% from the total content of Cu in these soils; the respective values for G_3 were 51 and 36 % in S_{11} and S_{12} respectively.

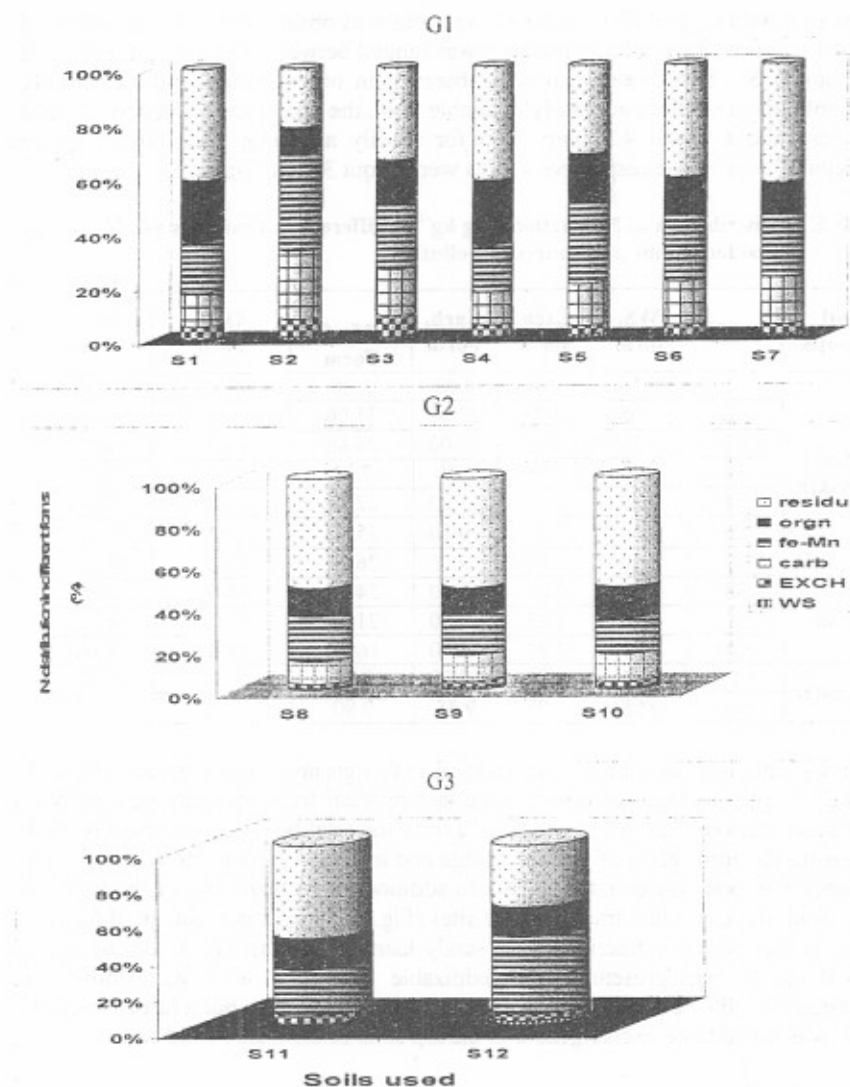


Fig. 2. Nickel distribution in different soil samples as affected by source and time of exposed to pollution.

The water soluble (WS) and exchangeable fractions of metals in soils are considered to be mobile (Kabata-Pendias, 2001), easily mobilizable (Karczewska, 1996) or available to biota (Peijnenburg *et al.*, 2001). These two fractions ranged between 3 and 5.5% of total Cu concentration in G₁, 3-4.5% in G₂ and increased to 7.8 and 4 in S₁₁ and S₁₂ of G₃. Worth to mention that the smallest percentage of Cu in all soils were detected for Exch and WS forms in all tested soils with having some reasonable exceptions detected in both G₁ and G₃.

As a percent of total, most of non-residual fractions 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 G₁ and G₂ soils.

TABLE 3. Distribution of Cu fractions mg kg⁻¹ in different soil samples as affected by residence time and source of pollution.

Soil groups	Soil No	WS. Form	Exch. Form	Carb. Form	Fe-Mn Oxides Form	Org. Form	Res. Form
El-Gabl El-Asfar	S1	2.1	3.5	16.1	21.3	2.3	28.1
	S2	1.1	4.2	22.9	25.4	6.0	59.6
	S3	2.5	4.5	10.1	19.8	14.5	47.8
	S4	1.5	4.8	10.9	15.3	12.7	26.8
	S5	2.0	2.4	11.2	16.7	10.5	28.1
	S6	1.1	4.2	12.8	16.5	8.1	42.7
	S7	1.9	3.4	11.4	17.9	7.5	69.1
Zenin	S8	0.5	5.9	17.0	25.0	15.0	22.5
	S9	0.6	5.2	19.0	28.0	17.0	45.0
	S10	2.0	3.8	11.8	13.0	23.1	53.5
El-Kanater	S11	1.1	4.9	3.4	3.6	12.1	27.0
	S12	0.5	0.9	4.8	4.8	4.1	8.7

Correlation analysis between soil properties and pollutants fractionation

Correlation analysis was conducted between soil properties of different groups and fractions concentration of Cu and Ni to represents most soil factors controlling heavy metals distribution in used soils under our experimental conditions. Data in Table 4 showed that in most cases pH and EC parameters did not give significant correlation with Ni and Cu fractions, in some cases, however, for pH, organically bound Cu gave significant correlation at 0.01 level. For EC only Ni gave high significant correlation compared with other pollutants.

Organic matter contents in used soils were also correlated with the studied pollutants in different fractions. Data showed significant correlation with some fractions of Ni and Cu. Data in the same table showed that most of organically bound-trace metals gave highly and significant correlation with OM, for example, the respective values of correlation between OM content of the studied soil samples with the organically bound form were 0.80** for Ni while it was 0.55* for Cu.

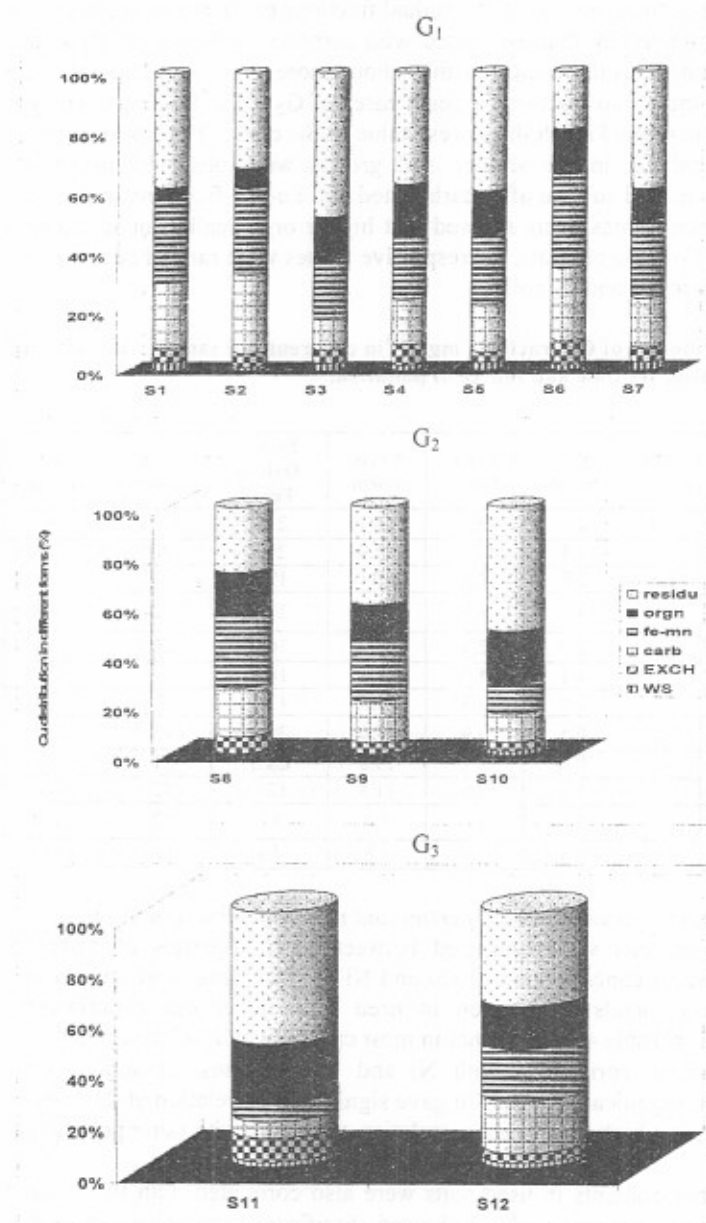


Fig. 3. Cu distribution in different soil samples as affected by source and time of exposure to pollution.

TABLE 4. Correlation analysis between soil properties and Ni and Cu concentrations in different fractions.

Fractions	Soil parameters						
	pH	EC dsm ⁻¹	OM %	CaCO ₃ %	Clay %	Silt %	S. area m ² /g
Ni							
Exc	0.15 ^{ns}	0.11 ^{ns}	-0.03 ^{ns}	-0.22 ^{ns}	0.30 ^{ns}	-0.17 ^{ns}	0.29 ^{ns}
Carb	0.56*	0.41 ^{ns}	0.86**	0.68**	0.97**	0.51 ^{ns}	0.94**
Fe-Mn	-0.09 ^{ns}	0.38 ^{ns}	-0.36 ^{ns}	-0.51 ^{ns}	0.47 ^{ns}	-0.84**	-0.57*
Org.	-0.31 ^{ns}	0.28 ^{ns}	0.80**	0.01 ^{ns}	0.02 ^{ns}	0.12 ^{ns}	-0.06 ^{ns}
Res.	0.21 ^{ns}	0.75**	0.29 ^{ns}	-0.15 ^{ns}	0.33 ^{ns}	0.48 ^{ns}	0.43 ^{ns}
Cu							
Exc	0.09 ^{ns}	-0.23 ^{ns}	-0.06 ^{ns}	0.18 ^{ns}	-0.03 ^{ns}	-0.01 ^{ns}	-0.03 ^{ns}
Carb	-0.49 ^{ns}	-0.17 ^{ns}	0.73**	-0.47 ^{ns}	-0.61*	-0.67**	-0.64*
Fe-Mn	-0.53*	-0.14 ^{ns}	-0.67**	-0.62*	-0.64*	-0.59*	-0.65**
Org.	0.72**	0.30 ^{ns}	0.55*	0.46 ^{ns}	0.79**	0.61*	0.78**
Res.	0.06 ^{ns}	-0.25 ^{ns}	-0.52*	-0.34 ^{ns}	-0.59*	-0.47 ^{ns}	-0.59*

The same soil parameter showed positive and high correlation with Ni in carbonate form, while it were highly and negative values with Cu in Carb. and Fe-Mn oxide forms. Worth to mention that Org-Cu fraction and its distribution in the studied soil fractions gave no or low significant correlation with silt content. While, only Ni associated with Fe-Mn and Cu in carbonate form, gave high and significant correlation with silt contents.

Although the studied soil samples have a small percentages of active CaCO₃ assumed to be associated with Ni and Cu, however, data indicated that 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 gave any significant correlation with active CaCO₃ content. Mechanical analysis represented by clay and silt contents showed more or less significant correlation with some forms of studied pollutants. In Ni, the correlation between carbonate form of Ni gave high and positive correlation with clay (0.97**). For Cu pollutant, most fraction low significant with clay content such as Carb, Fe-Mn and residual forms of Cu. 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, while only Ni in Fe-Mn and Cu in carbonate 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 as with clay content. Results in Table 4 showed that, 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.

Availability index (AI)

Availability index represents the relationship between non-residual and residual forms which subsequently give good indices for availability of heavy metals in soils. Data depicted in Fig. 4. showed that AI values in most of soils were very high than 100 which represent high availability of Ni and Cu in these soils and toxic condition take placing. In G₁, AI values ranged between 130 and 362, for Ni between 107 and 422 while Cu the highest value was observed in S₂ and the lowest value in S₆ and S₇.

In the second group, generally data indicated that AI values for Ni were lower than soils in G₁; these values were less than 100 in all soils. In Cu, however, data indicated that although the same parameter values were lower than G₁, the parameter values were higher than 100. This trend perhaps reflects the contamination hazards expected from using these media for cultivating edible plants in such polluted soils. Moreover, in group three where organic fertilizers applied in these farms, AI parameter values indicated that compared to G₂, a reverse trend was observed. The AI parameter values were higher than 100 in Ni and lower than 100 in Cu, this trend perhaps gave a risk of Ni more than in Cu.

Discussion

Barrier to discuss the fractionation of Ni and Cu in used soils, it should be mentioned that we faced inconsistent result concerned with residence time of applied sewage sludge and using of waste water in irrigation for 50 and 10 years in the first and second groups. Data indicated that total concentration in soils of G₁ ranged between 42-113 and 53-99 ppm for Ni and Cu, while the respective values for G₂ ranged from 100-117 and 86-114 ppm. As unexpected result, this trend indicated that no significant difference between first and second groups in total concentration in Ni and Cu. In third group, the source of pollution in these soils assumed to be created from soils location beside highway, however, pollutants concentration were over the normal range, this trend may also assumed that organic matter applied contain a significant amounts of Ni and Cu as pollutants since it undergoes to the same conditions as soils. The total concentrations values of Ni for G₃ were 69, 75 ppm, and 39, 77 ppm in S₁₁ and S₁₂ for Ni, Cu respectively.

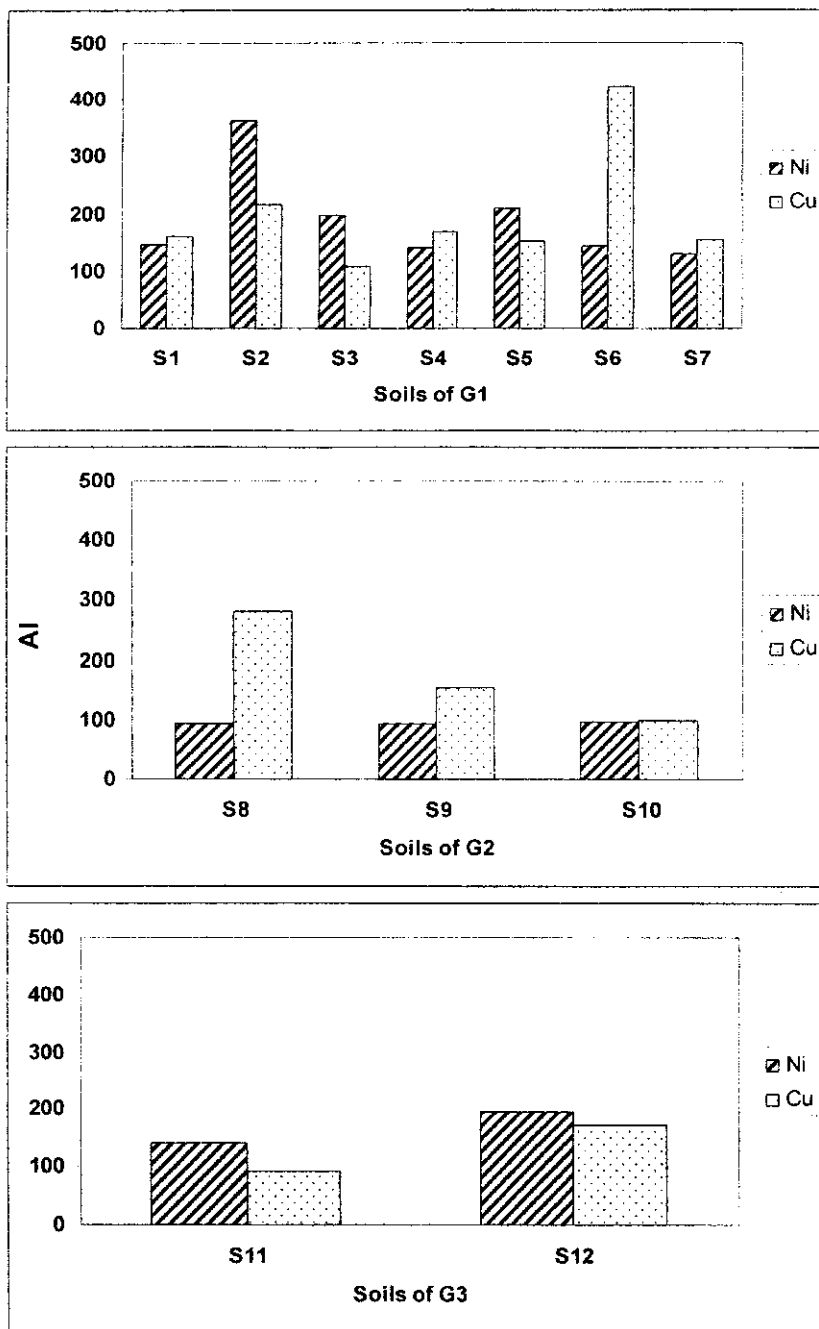


Fig 4. Availability index of Cu and Ni in different groups of soils as affected by time and source of pollutions.

Accordingly, we assumed that the annual application of swage sludge and the continuous irrigation with effluent water in G_1 and G_2 , led to create renewable source of organic materials available to be uptake by growing plants for 50 years (G_1) and no barriers faced these available pollutants to conflict into unavailable forms such as moderately or residual fractions. In this respect, under such conditions the increasing of residual time will be enhanced factor to increase pollutants bioavailability in G_1 over G_2 . Moreover, the comparison between G_1 and G_2 in soil pH, data indicated that generally the pH values in the first group of soils are lower than the second one. The numerical values for these groups were ranged between 7.0-7.6 in G_1 , meanwhile it were 7.5-7.8 in the G_2 , this result perhaps give an opportunity to increase bioavailability of pollutants in the 1st group and subsequently decreased content in this group compared to G_2 .

The availability index AI parameter for these two groups perhaps emphasizes the abovementioned result. Data indicated that in most cases, AI values in G_1 are higher than in G_2 in both Ni and Cu reached in some cases to doubled and tripled in both pollutants studied. This result led to increase consumption of such heavy metals and decrease its contents in soils of G_1 . Increasing the same parameter in G_3 compared to G_2 especially in Ni and in some cases in Cu gave an idea about producing edible crops from farms beside highways is not save to have healthy foods for humane and even for the gathered animals. Also, it should be mentioned here that chemical analysis of organic matter applied must be takes place to use such material(s) as a single source for fertilization.

According to Ma *et al.* (1997) they assumed that water soluble and exchangeable fractions would be readily bio-available to the growing plant; meanwhile the metals in the residual fraction are tightly bound and would not be expected to be released under normal conditions. The same result was reported by Xian (1989) and Cleveger & Mullins (1982).

The other fractions studied, *i.e.*, carbonate, Fe-Mn oxide and organically bound metal would be moderately available pools and considered to be a replenish source to readily available pool under decreasing order of concentration. Distribution study of non-residual and residual fractions of Ni and Cu, 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), properties of investigated soils, source of pollution and specifically to the different forms of pollutants present in sewage sludge applied in G_1 and G_2 (Corey *et al.*, 1987). Numerically, in G_1 and G_2 increasing of clay content in soil samples, led to increasing of Non-residual form (sum of all fractions except residual) compared with residual one for most pollutants. For example, In G_1 , data showed that non residual Cu increased to about 62% of total by increasing clay content to 39%, in G_2 also increasing clay content to 51% led to increase Cu in non-residual form to reach about 74 % from the total and respectively.

In soils of G₃, distribution of Ni and Cu pollutants were more concentrated in non-residual forms. These results may attributed to the types of organic fertilization applied in this group and the interaction between organic matter and different pollutants which will be specifically discussed in distribution of non-residual form of the studied pollutants. Data of mean values of non-residual Ni distribution showed that Ni was mainly associated with Fe-Mn oxide followed by carbonate and organic forms in G₁ with some exceptions observed in increasing of organically bound Ni when organic matter was increased. By increasing of clay content in G₂ to 45 and 51%, most of Ni was associated with Fe-Mn, followed by organic form and then carbonate. Despite soils of G₃ represented organic farming type since it mainly applied organic fertilization technique, org-Ni comes in the third category after Fe-Mn and carbonate forms. These results may attributable to the different forms of Ni in sewage sludge applied (Corey *et al.*, 1987). Worth to mention that in some soils of G₁, data indicated that Fe-Mn bound Ni was increased compared to other used soils in the same group, this trend was observed in S₂ and S₅. These soils contain more than 30% of total Ni associated with Fe-Mn oxide 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 (G₁ & G₂).
Organic form > Fe-Mn oxide = carbonate > exch. > WS (G₃).

Like Ni, Cu take the same trend in its distribution in G₁ with some exception in high OM soils, *i.e.*, S₃ and S₄, however, the organically bound Cu was the dominant form in G₂ and G₃. 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 and Weng *et al.*, 2002). Moreover, Anxiang *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 than 31 % of about 42 % (non-residual form of Zn in organic form of G₃). On the other hand, decreasing of the same parameters in G₁ and G₂, 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 G₁ where high OM was observed led to increase organically bound Zn.

Correlation analysis conducted between different soil parameters and different fractions of Ni and Cu perhaps emphasized the above results. Organic matter content in different soils highly correlated at 0.01 levels with Ni and at 0.05 levels 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 & Crawford (1973) and Iyengar *et al.* (1981) reported a statistical relationship between metal fraction and soil parameters, whereas Miller & 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 showed any significant with different fractions with one exception related with high correlation observed in organically bound all heavy metals. Nevertheless, these important soil parameters play an important role in Ni and Cu consumption by plants in used soils.

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توزيع عنصري النحاس والنيكل في بعض الاراضى المصرية الملوثة بالعناصر الثقيلة

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في هذه الدراسة اخذت ثلاثة مجموعات من الاراضى المصرية تضم اثني عشر أرض (من الطبقة السطحية من صفر - ٣٠ سم) من مناطق الجبل الاصفر (سبع اراضى) وزينين (ثلاث اراضى) والقناطر الخيرية (ارضين)، اختلفت تلك المجموع في صفاتها الارضية المختلفة كذلك في مصادر التلوث وزمن تعرضها لتلك المصادر ، حيث تعرضت المجموعة الاولى لإضافة مخلفات المجارى والرئى بمياه مختلفة الجودة (مياه الصرف الصحى) لمدة خمسون عام اما المجموعة الثانية فقد تعرضت لنفس الظروف السابقة لمدة عشرة سنوات في حين ان المجموعة الثالثة من الاراضى تميزت باستخدامها أسمدة عضوية و كان مصدر التلوث فيها وجودها بجانب الطرق السريعة و في هذه الاراضى تم دراسة توزيع عنصري النحاس والنيكل وعلاقتهم بصفات التربة المختلفة في هذه المجموع وقد اوضحت النتائج المتحصل عليها ما يلي :-

- لم يكن تأثير زمن اضافة مخلفات المجارى او الرئى بمياه مختلفة الجودة للمدد السابق ذكرها ٥٠ سنة أو ١٠ سنوات في المجموعة الاولى والثانية يعادل تأثير العوامل الارضية كمحتوي تلك الاراضى من الطين وغيرها في الكمية الكلية المتراكمة من العناصر تحت الدراسة وتوزيعها.

- في المجموعة الثالثة كان موقع تلك الاراضى بالاضافة الى استخدام الاسمدة العضوية تأثير معنوي في محتوى الاراضى من العناصر تحت الدراسة بمستويات تفوق المعدل الطبيعي وأرجع هذا التراكم الى تواجد تلك المجموعة قرب الطرق السريعة بالاضافة الي إمكانية تواجد تلك العناصر في هذه الاسمدة المضافة يتضح منة وجوب اجراء تحليل كامل لتلك المواد العضوية المضافة .

- ارتبط توزيع العنصرين تحت الدراسة بالصور المختلفة تبعاً لتحليلات تلك الاراضى الا انه بشكل عام كانت الصورة المرتبطة بأكاسيد الحديد والمنجنيز اكثر تركيزاً تلاها الصورة المرتبطة بالكربونات والتي تساوت تقريباً بالصورة العضوية في المجموعة الاولى والثانية ، في حين كان الجزء الذائب والمتبادل اقل تركيزاً في اراضى تلك المجموعتين.

- زادت كمية النحاس والنيكل المرتبطة بالمادة العضوية في بعض الحالات بشكل أكبر من الصور الاخرى خاصة في المجموعة الثالثة التي يتم فيها استخدام الاسمدة العضوية و اوضحت تحاليل الارتباط الاحصائية العلاقة بين الخواص الارضية وتوزيع العناصر تحت الدراسة في مختلف الاستخلاصات ان محتوى الطين ومساحة السطح النوعي والمادة العضوية كانت اكثر العوامل الارضية التي ساهمت بنسب متفاوتة في توزيع تلك الملوثات في نوعية الاراضى تحت الدراسة.

- اوضحت الدراسة من خلال استخدام معامل التيسر الاثر الضار للعنصرين من خلال زيادة قيم ذلك المعامل في معظم اراضى المجموع المختلفة وارتباط قيم ذلك المعامل مع بعض الخواص الارضية التي ارتبطت بالعنصرين.