

Assessing Heavy Metals Speciation and their Concentrations in Vegetables Grown on Peri-Urban Soils

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ABSTRACT

In this study, 18 top peri-urban soil samples with 18 edible portions from okra and eggplant were collected from peri-urban area of Alexandria city, Egypt. Results showed that all studied heavy metals concentrations in soils were in the safe limits and followed the order of $Cu > Pb > Ni > Cd$. Sequential extraction procedure (SEP) showed that metals were identified as hosted by Fe-Mn oxides and residual fractions for Ni, Cu and Pb and by carbonate and residual fractions for Cd. The plant metal concentrations showed lower values than those reported by WHO/FAO, implying that studied vegetables were safer to consume. Translocation factor (TF) values of heavy metals differed between different locations and plant species; TF followed the order of $Cu > Pb > Ni > Cd$ and $Cu > Cd > Ni > Pb$ for okra and eggplant edible portions, respectively. The plant metal concentration showed no corresponding values with any single extraction of SEP or summation of extractions (F1-F2, F1-F3 and F1-F4). Lack of such relationship with plant metal concentrations indicated that the availability of Ni, Cu, Cd and Pb is controlled to a great degree by soil properties' interactions. Therefore, multi-regression model that used to predict metal concentrations in plant showed a relative high performance when the sum F1-F2 of SEP used as input variable instead of total metal concentrations. Undoubtedly prediction model could be improved by including more soil features in the regression model but from pragmatic view of point simple soil characteristics has gained a favor to predict metal plant concentration. The predicted metal concentration in plant follows the order $Pb > Cu > Ni > Cd$.

Keywords: Heavy metal concentrations; Sequential extraction procedure; Vegetables

INTRODUCTION

The peri-urban areas could be generally considered as a variety of different land uses populated by different standard level communities, in rapid change manner with an infrastructure deficiency and a serious deteriorating environment actions. Simply, it could be identified as a vague boarder between rural and urban areas (Birley and Lock, 1998). Contaminants are being released into the environment with the quick development of industry and the economy in such peri-urban areas. In peri-urban soils, heavy metals (HMs) pollution has become an important issue (Sun *et al.*, 2013 and Leclerc and Laurent, 2017). Moreover, potential sources of HMs could be anthropogenic activities such as industrial and energy production, vehicle exhaust and waste disposal (Jiang *et al.*, 2017). The increasing dependency on chemical fertilizers and pesticides for crop productions, especially in developing countries, is another important source of HMs in agricultural soils (Jiang *et al.*, 2017). Vegetables take up HMs from soils. Therefore, HM contamination in agricultural soil has serious negative impact on food chain and consequently on human health (Liu *et al.*, 2011). Approximately, half of the world's population lives in urban areas. Extensive relocation from rural to urban areas in developing countries is producing a rapid growth of the peri-urban boundary, where invading the environment affect agricultural sector (Taghipour *et al.*, 2013). Therefore there is increasing issues about the contamination of agricultural production due to rapidly urbanization.

On the other hand, the sound regarding the high level of HMs in the environment has created a certain worry and fear to the communities as to the existence of HM deposits in their daily food. The public is disordered and alarmed about their food safety. Due to the potential toxicity, undegradable nature and

cumulative behavior of HMs as well as the consumption of vegetables, there is necessary to test and investigate the soil and plant grown on it to ensure that the levels of these contaminants meet the international safe limits. Moreover, developing an empirical model to predict HMs concentrations in plant is needed. In developing countries such as Egypt, there is no sufficient data on HMs concentrations in vegetables (Radwan and Salama, 2006). Therefore, it is crucial to screen HMs concentrations in vegetables. Moreover, determination of HMs in agricultural soil might help to better understand sources of contamination and subsequently develop an effective management strategy (Maleki *et al.*, 2014).

The binding forms of HMs in soils determine the intensity of the release to the soil solution and hence the likelihood of mobilization and absorb by vegetables (Tack and Verloo, 1995). From nutrition or eco-toxicity viewpoints the release of HM is important, while their retention is also important in designing specific physicochemical treatments for binding them into immobile fractions. With the aim of releasing HM from specific soil phases, a range of extraction methods is used to assess the solubility and mobility of metal fractions in the soil solid phase. The forms of a metal, which determines its mobility, toxicity and behavior in the environment (Gupta and Aten, 1993), can be examined by the sequential extraction method proposed by Tessier *et al.*, (1979). Sequential extractions include chemical fractionation procedures, is considered as a valuable tool to distinguish between heavy metal fractions which are empirically related to plant uptake, despite their limitations. Moreover, the binding behavior of HMs depends on the soil characteristics, which play an important role for the accumulation factor of HMs in plants. According to available knowledge, up to now, the chemical fractions of HMs, particularly their relations to soil characteristics and vegetable plants

grown in peri-urban soils on Egypt have seldom been deliberated. Therefore, the objectives of this study are to: (i) investigate the chemical partition of heavy metals (Ni, Cu, Cd and Pb) of peri-urban soil samples using sequential extraction precoders (SEP), (ii) evaluate the translocation factor of HMs from soil to edible portions of some vegetable plants, (iii) determine whether metal plant concentration will equate to any single fraction of SEP, and (iv) develop a simple empirical model to predict metal concentrations in vegetable depending on different soil properties.

MATERIALS AND METHODS

1. Soil and plant sampling, preparation and chemical analysis

Eighteen cultivated 'peri-urban' topsoil samples (0-30 cm) were collected from chosen locations around the international road between Alexandria and Rosetta cities, Egypt (between coordinates of 29° 58' 05.82" E, 31° 09' 03.69" N and 30° 12' 01.20" E, 31° 16' 01.53" N Fig. 1) in summer season, 2015. Soil samples were air-dried and sieved to < 2 mm. Soil pH was determined in soil : water suspensions (1:2.5 ratio) using pH meter (Model pH 209, HANNA Instruments, Bedford, UK). Calcium carbonate (CaCO₃, %) was measured using the Collins' Calcimeter method (Piper, 1954). Hydrometer method was used to determine the particle size distributions of the tested soil samples according to Gee and Bauder (1986). The general average of clay, silt, and sand fractions were 41.3 ± 9.02, 47.2 ± 9.26 and 12.6 ± 5.14 %, respectively. Accordingly, the textures of studied soils were categorized (% from the total soil number, n = 18) as 55.6% silty loam, 22.2 % sandy loam and 22.2 % loam. Ground soil samples of 200 mg was digested using 2.5 ml HF (40 %), 2.0 ml HNO₃, 1.0 ml HClO₄ and 2.5 ml H₂O and stored for multi-element analysis. For vegetable plant samples, two species of plant samples were collected from the dominant plant types in the studied area; okra (*Abelmoschus esculentus* L.) and eggplant (*Solanum melongena* L.). Nine samples from each okra and eggplant edible portions were collected from fields at the same points used for soil sampling with a total number of 18 plant samples. The edible portions of okra and eggplant were washed with distilled water and then oven dried at 70 °C for 72 hours. Fine ground plant samples of 200 mg was digested in pressurized PFA vessels in 6.0 ml of HNO₃ with microwave heating (Anton Paar 'Multivalve' fitted with 48 - place carousel). Multielement analysis of Ni, Cu, Cd and Pb were carried out by ICP-MS (Model X-SeriesII, Thermo-Fisher Scientific, Bremen, Germany)

on appropriate diluted soil and plant digests. The certified reference materials of NIST 2711 (Montana soil) and NIST 1573a (tomato leaves) were used for quality assurance (average recoveries for all measured metals were 94 ± 4% and 92 ± 2 for soil and plant samples, respectively); Analyses were run in triplicate and duplicate for soil and plant samples, respectively.



Figure 1. Map of soil and vegetable plant sample locations from Alexandria's peri-urban areas. Samples from 1 to 18 represent sample codes from A01 to A18, respectively.

2. Sequential extraction procedures, SEP

Sequential chemical extraction was carried out following the method described by Li and Thornton (2001) which is modified from Tessier *et al.*, (1979). This is a five step sequential extractions and it has been widely applied as a robust precoders (Atkinson *et al.*, 2011); The sequence of extraction was as follows: (i) Fraction 1 – 'Soluble and Exchangeable': 1 g soil was extracted for 20 min with 8 ml 0.5 M MgCl₂, (ii) Fraction 2 – 'Carbonate bound': residual soil from step 1 was extracted with 8 ml 1 M Na-acetate (NaOAc; adjusted to pH 5 with HOAc), (iii) Fraction 3 – 'Bound to Fe/Mn oxides': the residue from step 2 was extracted with 20 ml 0.04 M NH₂.OH.HCl in 25% (v/v) HOAc, (iv) Fraction 4 – 'Bound to organic matter': the residue from step 3 was extracted with 3 ml 0.02 M HNO₃, 5 ml 30% H₂O₂, 3 ml H₂O₂ and 5 ml 3.2 M NH₄OAc, and (v) Fraction 5 – 'Residual': the residual fraction was calculated by differences from the total metal concentration.

3. Translocation factor, TF

Translocation factors (TF) of HMs from soil to vegetables' edible portion were calculated according to Li *et al.*, (2012) as follows:

$$TF = \frac{C_{plant}}{C_{soil}} \quad (1)$$

Where C_{plant} and C_{soil} represents HM concentration (mg kg⁻¹) in plants and soil on dry basis, respectively.

4. Multi-regression model for predicting metal plant concentration from different soil properties

Multiple regression models were used to predict the metal concentration in plant (mg kg⁻¹) from soil pH,

% CaCO₃ and either total metal content (M_T) or extracted by the summation of F1 and F2 (M_F) of SEP (Eq 2).

$$M_{\text{Plant}} = k_1 + k_2(\text{pH}) + k_3(\% \text{CaCO}_3) + k_4(M_{\text{T or F}}) \tag{2}$$

Where the regression coefficients (k1, k2, k3 and k4; can be positive or negative), were optimized using Minitab statistical software (Minitab® 17.1.0). The overall goodness fit for all measured and modelled values was determined based on determination coefficient (R²), Pearson coefficient (r) and the residual standard deviation (RSD) (Eq 3):

$$\text{RSD} = \sqrt{\frac{1}{n-c} \sum_{i=1}^n (M_i - P_i)^2} \tag{3}$$

Where M_i and P_i are the measured and predicted values of metal plant concentration (mg kg⁻¹), n is the number of the observed values (n = 18) and c is the number of regression coefficients in equation 2 (typically 4).

RESULTS AND DISCUSSION

1. General soil characteristics

Mean, median, standard deviation, and minimum and maximum values of soil Ni, Cu, Cd, Pb concentrations, pH and CaCO₃ for samples collected from okra and eggplant fields are summarized in Table 1. Soils reaction (pH) values ranged from 7.25 to 8.64 with a mean value of 7.91 ± 0.45 and 7.62 to 8.11 with a mean value of 7.81 ± 0.15 for from okra and eggplant growing soils, respectively. This may be associated with a relatively high soil content of CaCO₃ (average = 26.1 ± 12.8 and 15.4 ± 4.82 % for okra and eggplant growing soil samples, respectively). The closeness of pH median value to mean value implies the narrow range of soil pH in the whole dataset.

Soil metal concentrations ranged from 17.9 to 54.9, 24.1 to 149, 0.594 to 1.012 and 21.9 to 88.4 mg kg⁻¹ for Ni (mean concentration, mg kg⁻¹ = 37.8), Cu (50.6), Cd (0.692) and Pb (39.4), respectively, in okra growing soil samples. However, the eggplant growing soil metal concentrations ranged from 21.7 to 50.5, 21.0 to 52.8, 0.607 to 0.825 and 24.2 to 84.0 mg kg⁻¹ for Ni (mean concentration, mg kg⁻¹ = 34.9), Cu (38.1), Cd

(0.668) and Pb (43.9), respectively. The T-paired test showed that there is no significant difference between all soil characteristics collected from okra and eggplant growing soils (p > 0.05). Although average % CaCO₃ showed a relative high value in okra growing soil samples (26.1%) compare with eggplant growing soil samples (15.4%), this was statistically insignificant (T value = 2.14; p = 0.065).

Significant correlation coefficient has been found between Ni and Cu (r = 0.56; p = 0.015) suggesting their probable common origin such as co-association with calcareous minerals CaCO₃ or apatites (Ca₁₀(PO₄)₂(OH)₂) or possibly partly an anthropogenic source, Cu and Cd (r = 0.75; p = 0.0001), Cu and Pb (r = 0.67; p = 0.03) suggesting their geochemical association with common soil component (e.g. organic matter or oxy-hydroxides phase) (Narwal *et al.*, 1999). The result of the present study stated that the level of HMs in soil was much lower than those reported by Kabata-Pendias and Pendias (1992). The general sequence of HMs in the whole dataset was found in the order of Cu > Pb > Ni > Cd.

Table 1. Descriptive statistical analysis for soil metal concentrations (mg kg⁻¹), soil pH and % CaCO₃ (n = 18) in okra and eggplant growing soils.

	Okra growing soils						Eggplant growing soils					
	Ni	Cu	Cd	Pb	pH	CaCO ₃	Ni	Cu	Cd	Pb	pH	CaCO ₃
Mean	37.8	50.6	0.692	39.4	7.91	26.1	34.9	38.1	0.668	43.9	7.81	15.4
Median	45.0	37.7	0.657	37.7	7.92	23.3	37.2	39.3	0.642	41.2	7.79	15.9
Standard Deviation	15.1	38.1	0.128	20.2	0.45	12.8	8.82	9.96	0.065	17.1	0.15	4.82
Minimum	17.9	24.1	0.594	21.9	7.25	8.54	21.7	21.0	0.607	24.2	7.62	9.18
Maximum	54.9	149	1.012	88.4	8.64	50.5	50.5	52.8	0.825	84.0	8.11	24.9

2. Metal speciation by sequential extraction procedures

Figure 2 shows metal speciation by SEP classified according to grown vegetable plants. The general pattern of all metals distribution in different soil fractions (F1-F5) were similar for most soil samples with few exceptions such as Cu in sample A04 and Pb in samples A09 and A11 (Fig 2). The general average results showed that Ni was mainly associated with residual (F5) and Fe-Mn oxide (F3) fractions making up 72.8 % and 17.0 %, respectively. Exchangeable (F1) was the lowest, only accounting for 0.46 %. The percentage of organic (F4) and carbonate (F2) are 8.01 % and 1.66 %, respectively. The proportion of Ni fractions follows the order: residual > Fe-Mn oxides > organic > carbonate > exchangeable. The percentage of the soil Cu in exchangeable (F1), carbonate (F2), Fe-Mn oxides (F3) and organic (F4) fractions were 0.139, 1.38, 10.9 and 8.78 %, respectively. Most of the Cu which is

87.8 % was associated with the residual fraction. The amount of Cu in each fraction follows the order: residual > Fe-Mn oxide > organic > carbonate > exchangeable. Cadmium is mainly associated with residual (F5) and carbonate fraction (F2) fraction making up 77.1 % and 12.5 %, respectively. Exchangeable (F1) is the lowest, only accounting for 1.17 %. The percentage of Fe-Mn oxide (F3) and organic (F4) are 5.82 % and 3.39 %, respectively. The proportion of Cd fractions follows the order: residual > carbonate > Fe-Mn oxide > organic > exchangeable. The percentage of the soil Pb in exchangeable (F1), carbonate (F2), Fe-Mn oxides (F3) and organic (F4) fractions are 0.07 %, 7.77 %, 21.9 and 3.62 %, respectively. Most of the Pb 66.6 % is present in the residual fraction. The amount of Pb in each fraction follows the order: residual > Fe-Mn oxide > carbonate > organic > exchangeable.

It is well known that the concentration of total metals does not provide sufficient information into their bioavailability. Therefore, availability of metals strongly depend on their different binding forms or specific chemical speciation (Marzouk *et al.*, 2011). Accordingly, knowledge gained from SEP for the studied metals was necessary to assess their bio-

available fractions. Exchangeable, carbonate bound, Fe and Mn oxide-bound, organic-bound, and residual forms were usually distinguished as the chemical species of soil HMs (Lu *et al.*, 2003). Generally, the solubility and bioavailability decreases in the first fraction to the last one (F1 > F2 > F3 > F4 > F5) (Lu *et al.*, 2003).

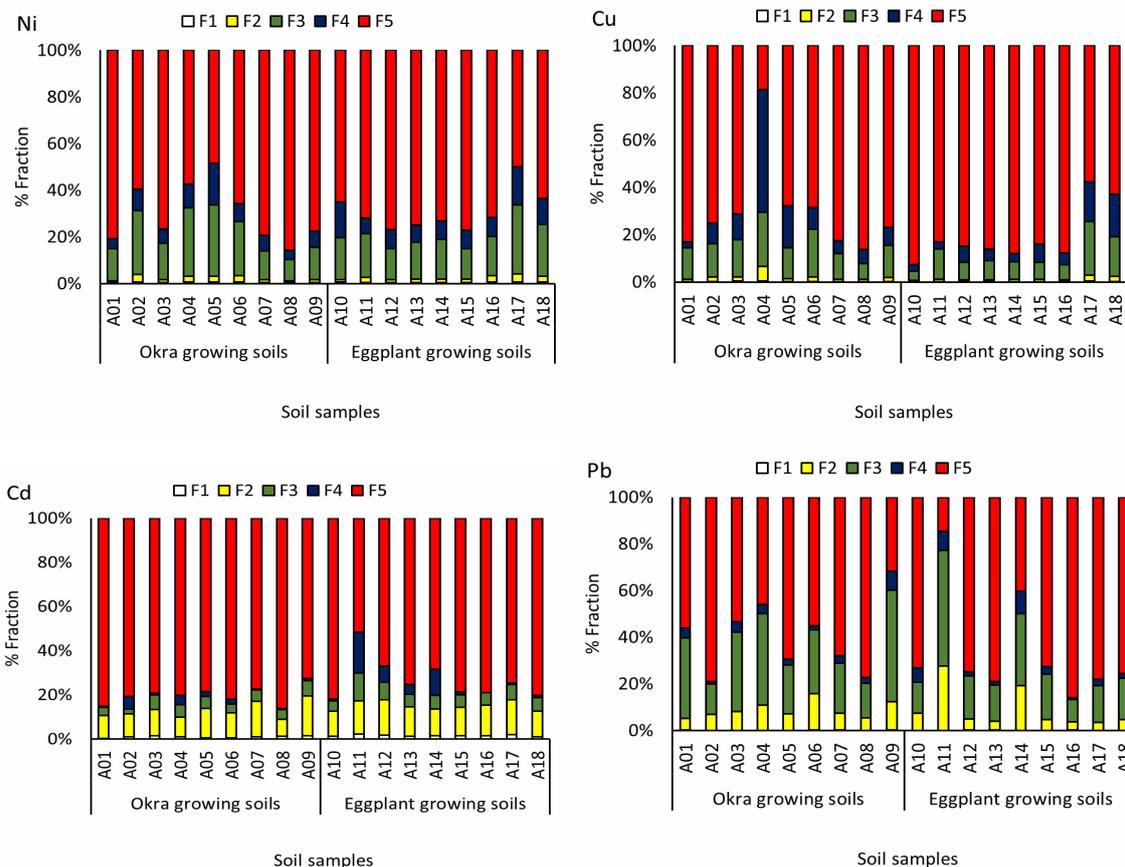


Figure 2. Proportion (%) of different fractions of soil Ni, Cu, Cd and Pb classified according to the grown plants (Okra and Eggplant) extracted by SEP; exchangeable (F1), carbonate (F2), Fe-Mn oxides (F3), organic (F4) and residual (F5).

3. Total metal concentration in plant edible parts

Descriptive statistical analyses data were presented in Table 2. Mean Ni concentration showed higher concentration in okra fruit ($0.547 \pm 0.433 \text{ mg kg}^{-1} \text{ DM}$ (dry matter)) than that of eggplant one ($0.248 \pm 0.143 \text{ mg kg}^{-1} \text{ DM}$). The Ni concentrations ranged from 0.161 to 1.39 and 0.104 to 0.545 $\text{mg kg}^{-1} \text{ DM}$ for okra and eggplant, respectively. The mean value of Cu concentrations were 1.46 ± 1.16 and $0.876 \pm 0.433 \text{ mg kg}^{-1} \text{ DM}$ for okra and eggplant, respectively. Copper concentrations ranged from 0.241 to 3.70 and 0.432 to 1.77 $\text{mg kg}^{-1} \text{ DM}$ for okra and eggplant, respectively. Regarding Cd and Pb, they pose higher concentrations in okra than eggplant as mentioned for Ni and Cu. The mean concentrations of Cd were 0.0148 ± 0.00785 and $0.0139 \pm 0.0034 \text{ mg kg}^{-1} \text{ DM}$ for okra and eggplant, respectively. However, mean Pb concentrations were 1.16 ± 1.02 and $0.262 \pm 0.218 \text{ mg kg}^{-1} \text{ DM}$ for okra and eggplant, respectively (one outlier value was removed from okra plant). Cadmium concentrations ranged from 0.00365 to 0.269 and 0.0101 to 0.022 $\text{mg kg}^{-1} \text{ DM}$ for

okra and eggplant, respectively. Lead concentrations ranged from 0.265 to 3.27 and 0.059 to 0.766 $\text{mg kg}^{-1} \text{ DM}$ for okra and eggplant, respectively.

Table 2. Descriptive statistical analyses for metal concentrations ($\text{mg kg}^{-1} \text{ DM}$) in edible parts of okra and eggplant collected from studied soils.

	Okra				Eggplant			
	Ni	Cu	Cd	Pb	Ni	Cu	Cd	Pb
Mean	0.547	1.46	0.0148	1.16	0.248	0.876	0.0139	0.262
Median	0.430	1.42	0.0165	0.91	0.285	0.674	0.0135	0.190
Standard Deviation	0.433	1.16	0.00785	1.02	0.143	0.433	0.0034	0.218
Minimum	0.161	0.241	0.00365	0.265	0.104	0.432	0.0101	0.059
Maximum	1.39	3.70	0.0269	3.27	0.545	1.77	0.022	0.766

Generally speaking, it was found that the overall concentrations of Ni, Cu, Cd and Pb in okra and eggplant edible portions were below the permissible limits according to World Health Organization (WHO)/Food and Agricultural Organization (FAO) and European Union (EU) safe limits (European Union,

2006 and WHO/FAO, 2007). The permissible limits reported by WHO/FAO and EU, in mg kg⁻¹ DM, are: Cu (40.0), Cd (0.2) and Pb (5.0) as reported by WHO/FAO and Ni (2.3) as reported by EU. The results indicated that no risk exists from consumption of okra and eggplant edible portions. The present results were in agreement with Radwan and Salama (2006). The authors undertook a market basket survey with the aim to assess the levels of Pb, Cd, Cu and Zn in various fruits and vegetables sold in Egyptian markets. They found that HMs in plants were below the safe levels and safe for consumers.

Many studies have demonstrated the importance of soil pH (Thakur *et al.*, 2016 and Zaki *et al.*, 2017) in determining metal bioavailable in soil. Correlation coefficient showed no significant relationship between plant metal concentrations and soil pH. This was probably because of the narrow range of soil pH values (7.25 -8.64). However, CaCO₃ showed a significant negative ($p < 0.05$) relationship with metal plant concentration of Ni ($r = - 0.46$). Different soil characteristics may affect metal plant concentration instead of a single parameter (Marzouk *et al.*, 2013).

All metal concentrations in plants showed no corresponding value or significant relationship with any single extraction of SEP even exchangeable one. The obtained data are in agreement with the results of Roy and McDonald (2015). This finding suggests that some of the bound (non-residual; F1 to F4) phases are sufficiently occluded in all SEP fractions where the available metal pool to plant could be distributed among different fractions. In this context, the summation of F1-F2, F1-F3 and F1-F4 (non-residual fraction) showed a poor correlation with plant metal concentration. This might suggest that the metals availability are more likely controlled by the source of metal rather than soil properties, particularly in such studied peri-urban area as it considered a sink for contamination produced from the activities of population of Alexandria city (the second highest populated city in Egypt).

4. Translocation factor (TF) of metals from soil to plant

Variations in TF among different vegetables may refer to variation of metals concentrations in soils and their concentrations in different vegetables (Cui *et al.*, 2004). The metal TF in plants (dry weight basis) is used to describe the extent of accumulation of a compound in an identified biological system. Figure 3 presents the TF values of the metals in the consumed parts of the studied plants. The values (with mean) of TF for heavy metals including Ni, Cu, Cd and Pb for vegetables were ranged from 0.0035 to 0.0534 (0.019), 0.036 to 0.13 (0.045), 0.005 to 0.032 (0.022) and 0.007 to 0.16 (0.047) for okra, respectively. However for eggplant, the TF values for HMs (Ni, Cu, Cd and Pb) were ranged (with mean) from 0.0028 to 0.015 (0.007), 0.0097 to 0.038 (0.023), 0.016 to 0.032 (0.021) and 0.0012 to 0.016 (0.006), respectively. It seems that okra plant absorb higher HMs concentrations than that of eggplant (Fig 3). The trend of TF for the studied heavy metals in okra edible portion were in the order of Cu > Pb > Ni > Cd while the trend

of TF for studied heavy metals in eggplant edible portion were in the order of Cu > Cd > Ni > Pb.

Correlation coefficient between TF values for all metals and soil pH showed positive but very poor correlation for Ni ($r = 0.27$; $p = 0.27$), Cd ($r = 0.35$; $p = 0.16$) and Pb ($r = 0.05$; $p = 0.83$). However, a significant positive value has been observed with Cu ($r = 0.59$; $p = 0.01$). The soil-to-plant transfer factor is the probably the product of two conflicting processes. On the one hand, metal solubility decrease as under higher pH values and so one might expect the transfer to decrease as pH value rises. On the other hand, as pH increases proton competition for uptake decreases and so it might be expected that metal uptake would increase. Therefore, the overall soil-to-plant transfer factor should show a fairly conservative, and unpredictable, relationship with soil pH (Sparks, 2003).

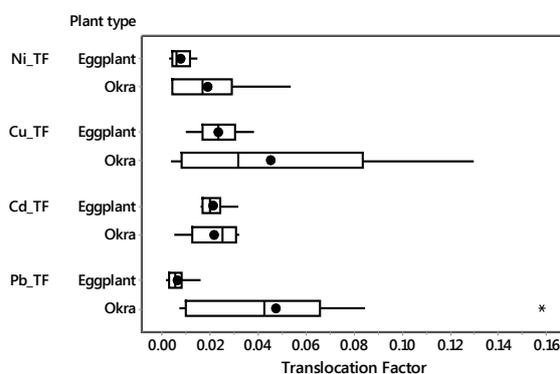


Figure 3. Boxplot of translocation factors of Ni, Cu, Cd and Pb. The ‘Box and Whisker’ plot shows median (vertical lines) and mean (circle black symbols) for the studied heavy metals.

5. Multiple regression model to predict metal concentrations in plants

Most studies focus on trying to quantify the solid-phase reservoir of available metal. For example, total metal concentration still be used in defining the regulations in most countries as a simple proxy of hazard in contaminated soils. However, total metal load takes no account of the soil characteristics that modify the bio-availability of metal pollutants in contaminated soils such as pH, for example. The total metal content of soil, defiantly, will include metal species that are not directly available to plants (Zhang *et al.*, 2001) although good correlations between total metal content and bioavailability was reported (Marzouk, 2012).

It has been suggested that the sum of the first two SEP fractions (F1-F2), may be considered ‘available to plants’ or ‘potentially labile’ (see Ahnstrom and Parker, 2001 and references therein). Therefore, predicting metal concentrations in plant utilizing both total metal content or the sum of F1-F2 was performed including simple soil characteristic such as soil pH and CaCO₃ content.

Multiple regression models were used to predict metal concentration in plants from soil properties (Equation 2). Approximately 16 %, 38 %, 32% and 70 % of the variability in metal plant concentration values for Ni, Cu, Cd and Pb, respectively, were explained by

the differences in soil pH, % CaCO₃ and total metal (M_T) content (see R² in Table 2). However, the summation of F1-F2 from SEP was substitute the total metal concentrations. Approximately 26%, 39%, 37% and 73% of the variability in metal plant concentration values for Ni, Cu, Cd and Pb, respectively, were explained by the differences in soil pH, % CaCO₃ and F1-F2 (M_F) concentrations (see R² in Table 3). This substitution relatively improved the prediction model for all metal concentrations in plant. Lead prediction model showed the highest significant (p < 0.01) correlation coefficient between measured and modeled values using Pb_T (r = 0.67) and Pb_F (r = 0.64) in the regression model. Figure 4 shows the closeness of

measured to predicted Pb concentration to 1:1 line; this model was plotted in Figure 4 to demonstrate the good agreement between measured and modeled values. Poor prediction performance for Ni and to some extent for Cu and Cd may imply anthropogenic sources of these metals. Previous researchers have mainly focused on prediction of metal solubility as a proxy of available metal pool. For example, Gray and McLaren (2006) used basic soil properties (pH, total carbon and total metal content) to predict 50% of Cd ‘solubility’ in a wide range of soils according to the variation of pH, total carbon and total Cd content.

Table 3. Multiple regression coefficients (k1, k2, k3 and k4; Eq. 2), RSD values, determination coefficient (R²) and correlation coefficients (Pearson r value, predicted vs measured), for multiple regression of either total metal concentration (e.g. Ni_T) or F1+F2 (e.g. Ni_F) of SEP against plant metal concentration, (n = 18). Equations were applied to a single dataset (all data regardless the plant species). Figures in the brackets represent probability.

Parameters	Regression coefficients and goodness of fit parameters (RSD, R ² and r value)							
	Ni _T	Ni _F	Cu _T	Cu _F	Cd _T	Cd _F	Pb _T	Pb _F
K1 (intercept)	-2.92 (0.201)	-2.64 (0.199)	-7.03 (0.201)	-6.51 (0.243)	-0.0869 (0.075)	-0.0032 (0.942)	6.070 (0.508)	2.24 (0.803)
K2 (pH)	0.384 (0.166)	0.457 (0.092)	0.94 (0.161)	0.873 (0.205)	0.00955 (0.067)	0.0026 (0.606)	-0.810 (0.469)	-0.40 (0.717)
K3 (CaCO ₃ , %)	0.01 (0.98)	0.0036 (0.648)	0.0436 (0.028)	0.0464 (0.021)	-0.00001 (0.930)	-0.0001 (0.794)	0.0942 (0.007)	0.0913 (0.009)
K4 (Metal, mg kg ⁻¹)	0.0031 (0.714)	-0.817 (0.182)	-0.0023 (0.765)	-0.220 (0.647)	0.0388 (0.028)	-0.023 (0.794)	-0.0165 (0.413)	0.004 (0.984)
RSD	0.351	0.330	0.781	0.778	0.0053	0.0064	1.308	1.341
R ²	0.163	0.259	0.380	0.386	0.323	0.356	0.703	0.729
Correlation (r)	0.404 (0.097)	0.510 (0.031)	0.617 (0.006)	0.621 (0.006)	0.568 (0.014)	0.189 (0.453)	0.665 (0.003)	0.644 (0.004)

Soil carbonate content (as % CaCO₃) was a significant parameter in the prediction model in case of predicting Cu and Pb concentrations in plants (see bold values in Table 3). This finding suggests that portion of sorbed Cu and Pb into CaCO₃ is labile. In general, the levels of bioavailable metal in soil is controlled by

several interactive complex factors, such as pH, organic matter (OM), cation exchange capacity (CEC), etc (Hernandez *et al.*, 2003). More importantly pH, would be the most dominant factor that affect metal lability to plants (Maleki *et al.*, 2014).

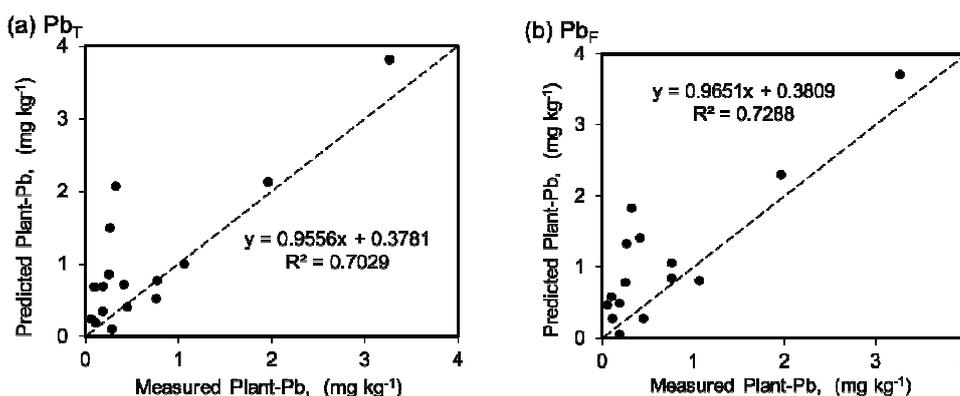


Figure 4. Modeled against measured values of Pb concentration in vegetable; (a) using total Pb (Pb_T) and (b) the sum of F1-F2 of SEP (Pb_F) as input variables to the regression model (Equation 2). Dash line represents 1:1 relationship.

However, it was unexpected to find no significant effects of soil pH on metal plant concentration. This might be explained by a very narrow range of the soil pH as mentioned before. It is believable to improve the prediction model by including more soil properties

(such as clay fraction, OM, CEC, soluble metals in soil pore water) in the regression equation but we intend to use a very simple parameters to predict metal plant concentrations. The predicted metal concentrations in plant follows the order Pb > Cu > Ni > Cd.

CONCLUSION

Interactions between soil, plant and HMs require sufficient information to understand the factors that govern this relationship. The peri-urban soils in the current study are not contaminated by HMs (Ni, Cu, Cd and Pb) and thereby the vegetable plants grown in. The major proportion of HMs in the studied soils was associated by residual, non-available, fraction followed by Fe-Mn oxides for Ni, Cu and Pb and by carbonate phase for Cd. Although TF values showed higher levels in okra plant comparing with eggplant, the estimated TF values were in the safe levels. This finding implies that okra plants have the potential ability to absorb HMs in their edible portion. Moreover, no single or sum of SEP's fraction was correlated with metal concentration in plants. This might be suggested that the metals availability are more likely controlled by the source of metal rather than soil properties or by a complex combination of soil properties. Therefore, the first two fractions of SEP (F1+F2) was used as a proxy of potential available metal pool in predicting metal plant concentration in combination with soil pH and CaCO₃ content (%). The prediction results demonstrated that model based on total metal content are relatively less successful than those based on F1+F2. Better predictions for Pb (R² = 0.73) were obtained. It is possible that such multiple regression models used to predict metal plant concentration could be improved by including more soil variables. However, from a pragmatic point of view, it is perhaps preferable that prediction should involve only fairly simple soil properties that are performed in a soil laboratory routine work.

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تقييم تجزئة العناصر الثقيلة و تركيزاتها بالخضروات النامية بالاراضي شبة الحضرية

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في هذه الدراسة، تم جمع 18 عينة سطحية من الترب شبه الحضرية مع 18 عينة نباتية من الاجزاء المأكولة من نباتي البامية والباذنجان من منطقة محاطة بمدينة الإسكندرية بمصر. أظهرت النتائج أن جميع تركيزات العناصر الثقيلة في التربة كانت في الحدود الآمنة واتبعت الترتيب: النحاس < الرصاص < النيكل < الكاديوم. أظهرت عملية الاستخلاص المتتابع أن العناصر تم تحديدها على أنها أكثر ترابطاً بأكاسيد الحديد والمنجنيز و الجزء المتبقى في الشكل المعدني وذلك بالنسبة للنحاس و الرصاص و النيكل و جزء الكربونات للكاديوم. وأظهرت النتائج أيضاً ان تركيزات العناصر الثقيلة في العينات النباتية التي تنمو في نفس الاراضى ذات قيم أقل من تلك الحدود المسموح بها من منظمة الصحة العالمية و منظمة الأغذية والزراعة، مما يعني أن الخضروات آمنة للاستهلاك الأدمى. وتختلف قيم معامل الانتقال للعناصر الثقيلة من التربة للنبات طبقاً لاختلاف المواقع والأنواع النباتية المدروسة؛ وتتبع الترتيب: النحاس < الرصاص < النيكل < الكاديوم لنبات البامية و النحاس < الكاديوم < النيكل < الرصاص لنبات الباذنجان بالاجزاء المأكولة منهما. لم يظهر تركيز العناصر الثقيلة بالعينات النباتية أي قيم مقابلة لها مع أي مستخلص فردي من الاستخلاص المتتابع أو مجموع تلك المستخلصات معاً (F1-F2)، (F1-F3 و F1-F4). وأشار عدم وجود علاقات ارتباط معنوية مع تركيزات العناصر الثقيلة بالعينات النباتية و الاستخلاص المتتابع إلى أن صلاحية كلا من النيكل، النحاس، الكاديوم و الرصاص يتم التحكم فيهم بدرجة كبيرة بالتفاعلات المعقدة لخصائص التربة المختلفة. ولذلك، فإن نموذج الانحدار المتعدد الذي استخدم للتنبؤ بامتصاص العناصر الثقيلة بواسطة النبات أظهر أداءً عالياً نسبياً عندما استخدم مجموع العناصر المستخلصة من المستخلص الأول و الثاني F1-F2 من الاستخلاص المتتابع كمتغير في المدخلات بدلاً من التركيزات الكلية لتلك العناصر. اضع الى ذلك انه يمكن تحسين نموذج التنبؤ بلا شك من خلال تضمين المزيد من خصائص التربة في نموذج الانحدار ولكن من وجهة نظر عملية فإن استخدام خصائص التربة سهلة التقدير في نموذج الانحدار له الاولوية. و اظهرت جودة نموذج التنبؤ للعناصر الثقيلة الممتصة من النباتين الترتيب: الرصاص < النحاس < النيكل < الكاديوم.