25

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Implications of Long Term Irrigation with Wastewater on The Contents and Retention Kinetics of Potentially Toxic Elements in *Typic Torripsamment* Soils

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THE consequences of irrigation with wastewater (rich in organic matter) on the distribution of potentially toxic elements (PTEs) between the soluble and total forms as well as their distribution among the different soil layers of El-Gabal El-Asfar soils was the main target of this work. Eight soil locations were sampled at three different depths to represent different periods of irrigation with wastewater extended beyond 80 years. These samples were analyzed for their contents of SOM, cation exchange capacity (CEC), total and soluble concentrations of PTEs *i.e.* Ni, Pb, Cd, Co, Zn and Cu. Results revealed that both SOM and CEC increased steadily and significantly in the uppermost 030- cm layer with ageing. The corresponding increases within the subsequent soil depths seemed to be slight. Soluble and total concentrations of PTEs also increased progressively within the different soil depths with ageing; however, the depthwise increases seemed less obvious. Based on the Dutch system formula, the soil irrigated for a period extended up to 80 years could be considered slightly polluted with Co, moderately polluted with Pb, severely polluted with Ni, Cu and Zn and very severely polluted with Cd. Soluble PTEs concentrations were correlated significantly with their total concentrations in soil and both were correlated significantly with SOM and CEC. The relationships between amounts of retained PTEs and their corresponding soluble concentrations were best fitted to Langmuir isotherm model. The outcome relations between the amounts of retained PTEs and aging were fitted to five kinetic models, the power function and the parabolic diffusion ones seemed to be the best fitting models. In conclusion, although soil organic matter plays important role in distribution of the PTEs between the soluble and retained forms in soil irrigated with wastewater; yet ageing affects this distribution obviously especially in the uppermost soil layer.

Keywords: Retention kinetics, El-Gabal El-Asfar, Adsorption isotherms, Soil organic matter, Soil layers

Introduction

Potentially toxic elements PTEs can be brought to soils from different anthropogenic sources e.g. industrial and agricultural activities (Bolan and Duraisamy, 2003; Abdelhafez et al., 2012), metal smelter (Alloway, 2013), sewage sludge and livestock manures (Nicholson *et al*., 2003). Once they come in contact with a sandy soil, they become sorbed within the surface layers (Gustafsson et al., 2003) mainly by soil organic matter (Ellen et al., 2008). These elements persist in soils and do not undergo microbial degradation (Greger, 2005). Plants grown on contaminated soils absorb and accumulate PTEs within the different plant parts and this might possess potential health risks for man and animals feeding on these plants (Khan et al., 2008, Ibrahim et al., 2016; Abbas and Abdelhafez, 2014;−Abdelhafez et al., 2015; Ebong et al., 2018). Accordingly, monitoring the level of contaminants in soil periodically is essential to ensure safe environmental and ecological use of this natural resource.

Although, soil organic matter (SOM) plays important roles in increasing soil fertility, especially in low textured soils (Farid et al., 2014), beside of its positive effect on improving soil physical and chemical characteristics (Abdelhafez et al., 2018); yet, successive applications of organic matter can increase the levels of retained PTEs in soils (Guo et al., 2018), especially when soils are irrigated with wastewater for long time periods (Mapanda et al., 2005)**.** In this concern, sorption of PTEs by SOM is thought to be 613- fold higher than that occurred on soil mineral surfaces (Lair et al.,

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2007). Probably, the functional groups of soil organic matter account for specific adsorption of PTEs from soil solution (Wang et al., 2017; Wen et al., 2018); thus, reduce their mobility and phytotoxicity to the grown plants (Ciavatta et al., 1993; Clemente et al., 2006; Peng et al., 2009; Diagboya et al., 2015). On the other hand, these metals can be released again to the soil solution upon organic matter decomposition (Yue et al., 2017). Also, the fraction of the organic matter which dissolves in water can form soluble organo-metal complexes (Weng et al., 2002; Ren et al., 2015; Kunhikrishnan et al., 2017). Moreover, dissolved organic carbon can block the binding sites and this might in turn reduce further sorptivity of PTEs by soil (Refaey et al., 2017). Thus, light textured contaminated arid soils of low $CaCO_3$ content probably exhibit low affinity for PTEs retention.

In Egypt, 1,250 hectares at El-Gabal El-Asfar Farm are irrigated with wastewater (Abo el Abas, 2004) for a period extended over 80 years (Elgala et al., 2003). Successive irrigations with wastewater raised significantly the level of PTEs in soils (El-Motaium et al., 2009) and; at the same time, added appreciable amounts of organic matter to the irrigated soil (Su et al., 2010). This farm is located within the arid zone area and its soils are characterized by light texture (low in their silt and clay contents) (El-Hassanin et al., 1993). Therefore, the rate of decomposintion of soil organic matter at this arid zone area is high (Rodeghiero et al., 2009). In spite of that the soluble contents of PTEs in such soils are extremely low and did not exceed 5% of the total contents (Zaghlol et al., 2006). The mechanism of changing PTEs from a form to another seems to be not clearly documented. To what extent can SOM reduce the mobility and phytotoxicity of PTEs in a Typic Torripsamment soil irrigated with wastewater (rich in organic materials) for a period extended up to 80 years or more was the question upon which the current study tried to answer. Therefore, this investigation took into account the soluble and total concentrations of these metal ions within the different soil layers in a trial to through some light on the mechanism of PTEs sorption within the surface and subsurface soil layers since the mechanisms of PTEs sorption within the subsurface soil layers are not well identified according to Tiberg et al. (2018). Moreover, the kinetics of PTEs retained within the different soil layers were considered to identify the slowest step affecting the immobilization of PTEs under field conditions rather than the laboratory ones. Changes in SOM and consequently CEC of soil with ageing will be a matter of concern in this study to explore, to what extent; these variables might affect the amounts of the soluble and total contents of PTEs in soils.

Materials and Methods

Study Site

The current study was conducted on the soils of El-Gabal El-Asfar farm. This farm is located about 25 km northeast of Cairo governorate (Elbana et al., 2013) between longitude 31° 22′ 00″ E; latitude 30° 12′ 00″ N, at 15 meters above sea level (Abdel-Shafy and Abdel-Sabour, 2006). The climate of the study area is arid where the average temperature is from 13 °C (in January) to 28°C (in June), total rainfall is as low as 25 mm yr^{-1} and the annual evapotranspiration rate is high i.e. 1,600 mm (Abo el Abas, 2004). Mean annual relative humidity is 49% and average annual wind speed is 20 km h^{-1}. Direction of wind is generally north east. Irrigation of soils of this farm is mainly surface with wastewater. Main properties of the wastewater are shown in Table 1. According to

TABLE 1. Main properties of the wastewater used for irrigation of El-Gabal El-Asfar soils

Property	Unit	Value	Properties	Unit	Value
pH	-	8.12	Zn	mg L^{-1}	1.78
EC	dS m^{-1}	1.52	Cu	mg L^{-1}	0.169
TDS	mg L^{-1}	972.80	Pb	mg L^{-1}	0.39
TH	mg L^{-1}	368.50	Co	mg L^{-1}	0.17
SAR	-	3.44	Cd	mg L^{-1}	0.02
Mg ratio	%	52.23	Ni	mg L^{-1}	0.18
COD	mgO_2 L^{-1}	450.00	DOC	mgC L^{-1}	195.00
BOD	mgO_2 L^{-1}	262.00			

Note: EC is the electric conductivity, TDS is the total dissolved solids, TH is the total hardness, SAR is the sodium adsorption ration, COD is the chemical oxygen demand, BOD is the biological oxygen demand and DOC is the dissolved organic carbon.

Ayers and Westcot (1994), Co and Cd exceeded the permissible levels which are 0.05 and 0.01, respectively, whereas, Zn, Cu, Pb and Ni were within the acceptable levels in water (2, 0.2, 0.5 and 0.2, respectively).

Soil sampling

Eight locations were selected from El-Gabal El-As far area to comprise 0, 5, 10, 15, 25, 40, 60 and 80 years of the cropping history (Fig 1).

Soil samples were collected from each location at three different depths, *i.e.* 0-30, 30-60 and 60-120 cm, air dried, cursed, sieved to pass through a 2 mm sieve and analyzed for their chemical characteristics as well as particle size distribution as outlined by Sparks *et al*. (1996) and Klute (1986) (Table 2).

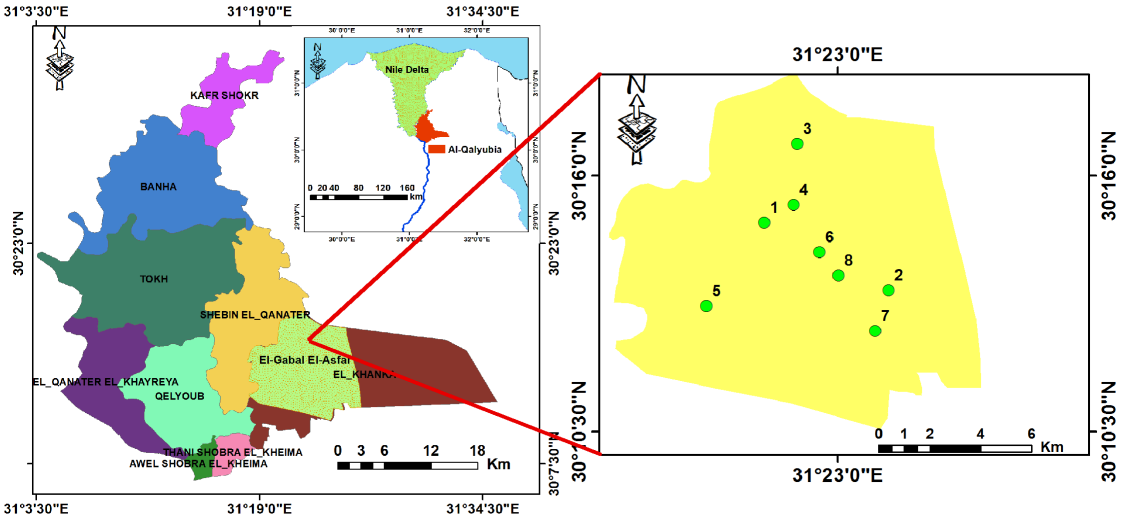

Fig. 1. Location map of the studied sites (numbers from 1 to 8 corresponding to 0, 5, 10, 15, 25, 40, 60 and 80 years cropping period .

TABLE 2. Chemical properties and particle size distribution of the soil surface layer (0-30 cm) of the studied locations

Soil location		L1	L2	L3	L4	L5	L6	L7	L8
Cropping period	**years**	**0**	**5**	**10**	**15**	**25**	**40**	**60**	**80**
pH*	-	7.63	7.34	7.23	7.17	7.01	6.83	6.69	6.53
EC**	dS m^{-1}	2.8	2.7	2.5	2.3	2.1	2.1	2.0	2.0
OM	g kg^{-1}	0.78	7.45	12.56	33.75	39.76	41.55	48.67	53.12
$CaCO_3$	g kg^{-1}	2.65	2.57	2.48	2.34	2.31	2.13	2.11	1.12
CEC	$cmol_c$ kg^{-1}	7.71	7.76	7.85	15.54	20.12	31.23	35.65	37.43
Sand	%	96.3	95.2	94.1	92.2	90.7	88.9	87.3	86.5
Silt	%	2.6	2.76	2.4	3.6	4.7	5.8	6.4	7.1
Clay	%	1.1	2.04	3.5	4.2	4.6	5.3	6.3	6.4
Texture	(USDA)	Sand	Sand	Sand	Sand	Sand	Sand	Loamy sand	Loamy sand

Note: * pH: in 1:2.5 soil: water suspension; ** EC: in saturated paste extract; L: location

Soil portions of the eight sampled locations at the three successive soil layers were analyzed for their soluble contents of Pb, Ni, Cd, Co, Zn and Cu after being extracted with deionized water (1:15 soil: water) for two hours according to Aikpokpodion (2013). Corresponding soil portions were digested using a tri-acid mixture (HNO3:H2SO4:HClO4, 10:4:1) according to Sahrawat et al. (2002), filtered through 0.45um-pore-diameter filter and acidified with nitric acid pH < 2. Both the total and soluble contents of PTEs were determined using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Model PERKIN ELMER Optima 3000. Soil organic matter (SOM) was determined using the modified Walkley and Black method (Nelson and Sommers, 1996). Cation exchange capacity (CEC) was determined using ammonium acetate method according to Roweli (1994). All chemicals used in this study were of analytical grade reagent.

Data analyses

The obtained data were statistically analyzed using PASW Statistics software through the analysis of variance (ANOVA) and Dunken Test at 0.05 probability level. The reference levels of PTEs in soil were calculated according to the Dutch system formula as mentioned by Lacatusu (2000) as follows: Ni (10+A), Pb (50+A+MO), Cd (0.4 + 0.007 (A* + 3MO**), Co (20), Zn (50 + 1.5 (2A + MO)), Cu (150.6+(A+MO), where A is the clay content (%) and MO is the organic matter content (%) in soil. The concentrations of retained PTEs in soil were calculated by subtracting the soluble concentrations of PTEs from the corresponding total contents and then the retained values of the investigated PTEs were plotted graphically versus the period of cultivation and these relations were fitted to the following five kinetic models as mentioned by Sparks (1999) and used by Reyhanitabar and Gilkes (2010) and Abbas and Salem (2011):

Zero order ($Q_t = Q_0 - k_0 t$) Eq 1

First order ($\ln Q_t = \ln Q_0 - k_1 t$) Eq. 2

Power function ($Q_t = \alpha t^{b}$) Eq. 3

Simple Elovich ($Q_t = \frac{1}{\beta}\ln(\alpha\beta) + (\frac{1}{\beta})\ln t$) Eq. 4

Parabolic diffusion ($Q_t = Q_0 + K_p t^{1/2}$). Eq 5

The used symbols Q_t and Q_0 refer to the retained values of PTEs calculated at time t (hour) and at t=zero, respectively. The standard error of estimation (S.E.) was calculated according to Reyhanitabar and Gilkes (2010) and Abbas (2013) as follows:

$$SE = [\sum (Q_t - Q_t')^2 / (n-2)]^{1/2}$$ Eq 6

Where Q_t' and Q_t' are the measured and predicted amounts of sorbed PTEs obtained at time t, respectively, and n is the number of measurements.

Retained heavy metals were calculated by subtracting the soluble concentrations of PTEs from the total contents in soil, plotted graphically versus the soluble concentrations of these metal ions in soil and then the obtained relations were fitted to the following adsorption isotherm models as described by Sposito (2008) and Loffredo and Senesi (2006).

Linear model $Q = k_p C$ Eq. 7

Langmuir isotherm $Q = \frac{abC}{1 + bC}$ Eq. 8

Van Bemmelen- Freundlich $Q = kC^{\frac{1}{n}}$ Eq. 9

Results and Discussion

Soil organic matter (SOM) and CEC in Typic Torripsamment soil as affected by successive irrigations with wastewater

Results shown in Fig. 2 reveal that SOM content increased steadily and significantly with ageing within the uppermost 030- cm layer. On the other hand, such increases seemed to be slight and insignificant within the subsequent soil layers with ageing until 60 years beyond which significant increases occurred. The decrease in the organic matter content in soil with depth was also observed by Jobbágy and Jackson (2000). Concurrent increases in soil CEC were also recorded within the top 030- cm layer; however, these increases seemed to be significant only after 15 years ageing. The slight increases in soil CEC within the first 10 years of cultivation probably occurred due to a corresponding slight variation in SOM within the same period. This finding supports a previous one attained by Machmuller et al. (2015) who showed that soil CEC increased significantly with the increase in soil organic matter content.

Soluble PTEs in Typic Torripsamment as affected by ageing

Figure 3 reveals that the concentrations of soluble PTEs increased progressively within the different soil layers with ageing; however, these concentrations did not exceed 8% of the corresponding total contents. Concentrations of soluble Ni, Pb, Zn, Cu, Cd and Co within the uppermost 0-30 cm layer of the soil, irrigated with sewage water for 80 years, were 9.02, 11.13, 31.52, 16.40, 10.39, 44.50 fold higher than those of the control one (zero time cropping) , respectively. The solubility

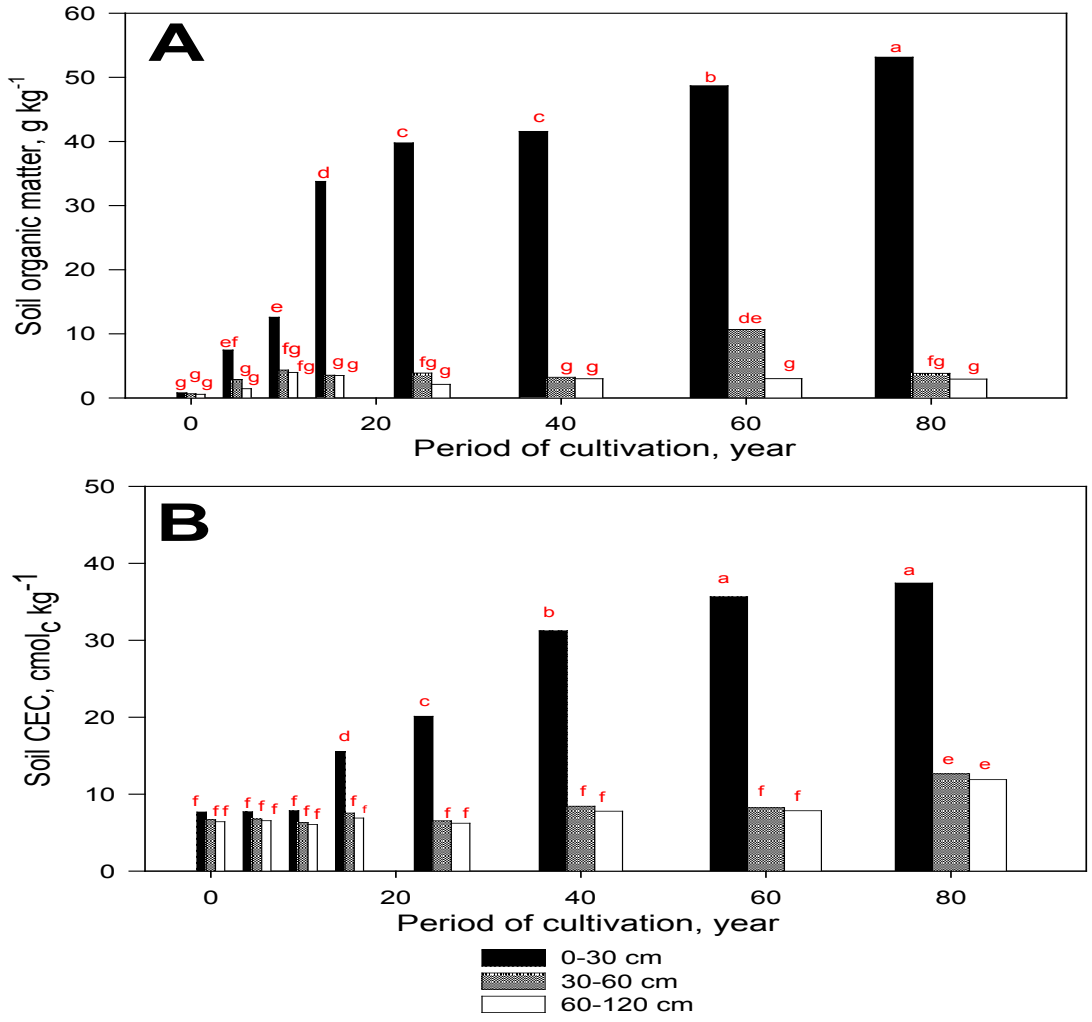

Fig. 2. Effect of ageing on soil organic matter (SOM) and CEC in Typic Torripsamment soil irrigated with wastewater

of PTEs in deeper soil layers also increased with ageing, but with a relatively lower trend. The successive irrigations and the different agricultural practices might account for the transfer of pollutants to deeper soil layers (Hashim et al., 2017). Also, SOM can chelate PTEs forming relatively soluble organo-metallic complexes (Kalbitz and Wennrich, 1998; Almås, 2000; Ren et al., 2015) and these complexes increase the mobility of heavy metals in soil (Ashworth and Alloway, 2008; Rikta et al., 2018). The reductions occurred in soil pH owing to organic matter decomposition (Abdelhafez et al., 2018), might, in turn, increase the solubility of minerals bearing heavy metals in soil (Blume and Brümmer, 1991). On the other hand, the low oluble content of lead within 60-120 cm soil layer might be attributed to formation of relatively stable complexes with the organic components; hence its mobility and desorption seemed to be relatively low (Strawn et al., 2000). The increase in concentrations of soluble PTEs fraction probably account for corresponding increases in total PTEs in soil with ageing.

Total contents of PTEs in the Typic Torripsamment soil as affected by ageing

Total concentrations of the investigated PTEs increased markedly within the different soil layers owing to the successive irrigations with wastewater (Fig 4). Total concentrations of Pb and Zn, within the different soil segments after 15 years of ageing, exceeded the permissible levels recommended by Kabata-Pendias and Pendias (2001), in the agricultural soils of Austria (100 mg Pb kg^{-1} and 300 mg Zn kg^{-1}), Likewise, the concentrations of total Ni and Cu within the surface 0-30 cm layer after 80 years of ageing exceeded their

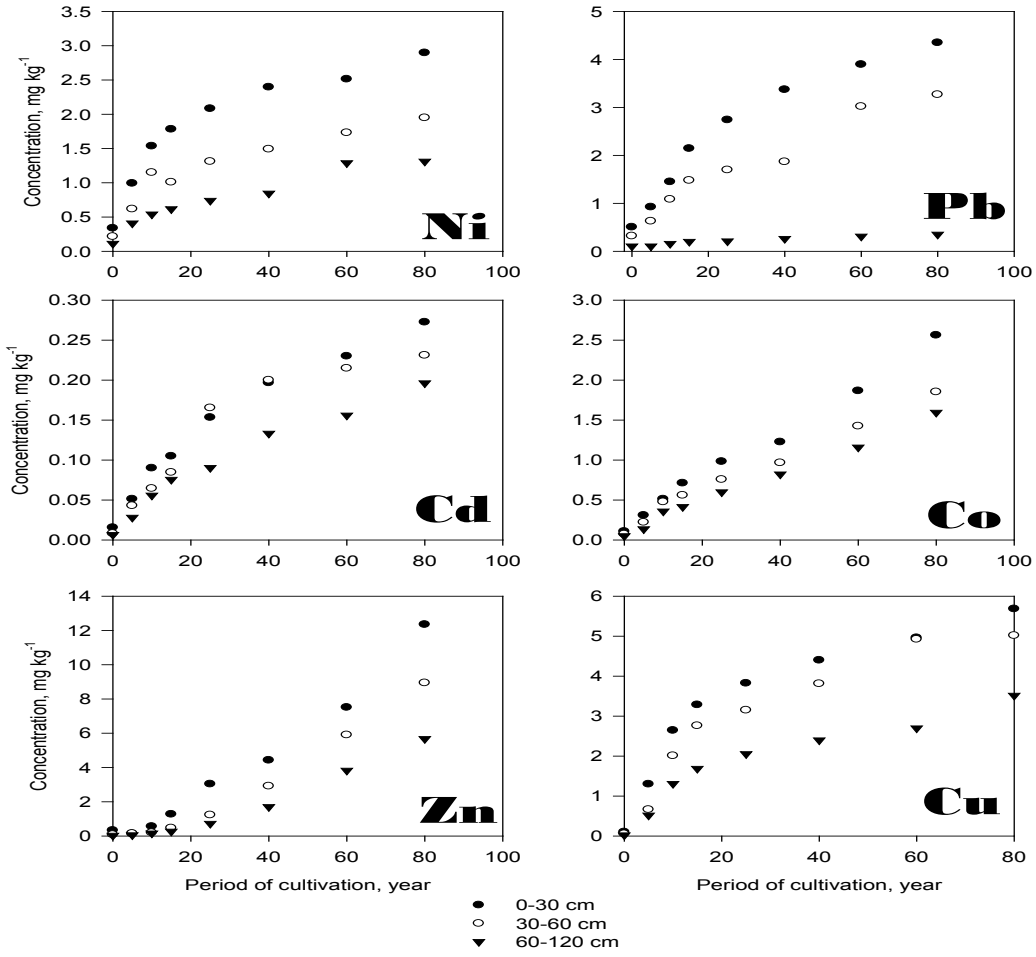

Fig. 3. Effect of ageing on concentrations of soluble PTEs in the different soil layers of the Typic Torriorthent soil (0-30 cm (●), 30-60 cm (○) and 60-120 cm (▼))

permissible levels recommended by Kabata-Pendias and Pendias (2001) (*i.e.* 100 mg Ni kg^{-1} and 100 mg Cu kg^{-1}). On the other hand, the concentrations of both Cd and Co were within the permissible levels (5 mg Cd kg^{-1} and 50 mg Co kg^{-1}, respectively); however, attention should be paid towards the potentially continuous increase in concentrations of these elements with ageing. Therefore, the ecological evaluations of El-Gabal El-Asfar project should take into account the present and the future concentrations of the potentially toxic elements in soil due to the pronounced effect of ageing on these PTEs.

Based on the Dutch system formula, the metal pollution index was calculated to investigate the increases that occurred in PTEs in soil with ageing as ratios to their natural background levels (A-value) adapted from Lacatusu (2000). Contamination/pollution indexes were evaluated then presented graphically versus ageing (Fig 5). Results show that the investigated soils were slightly polluted with Co, moderately polluted with Pb, severely polluted with Ni, Cu and Zn and very severely polluted with Cd.

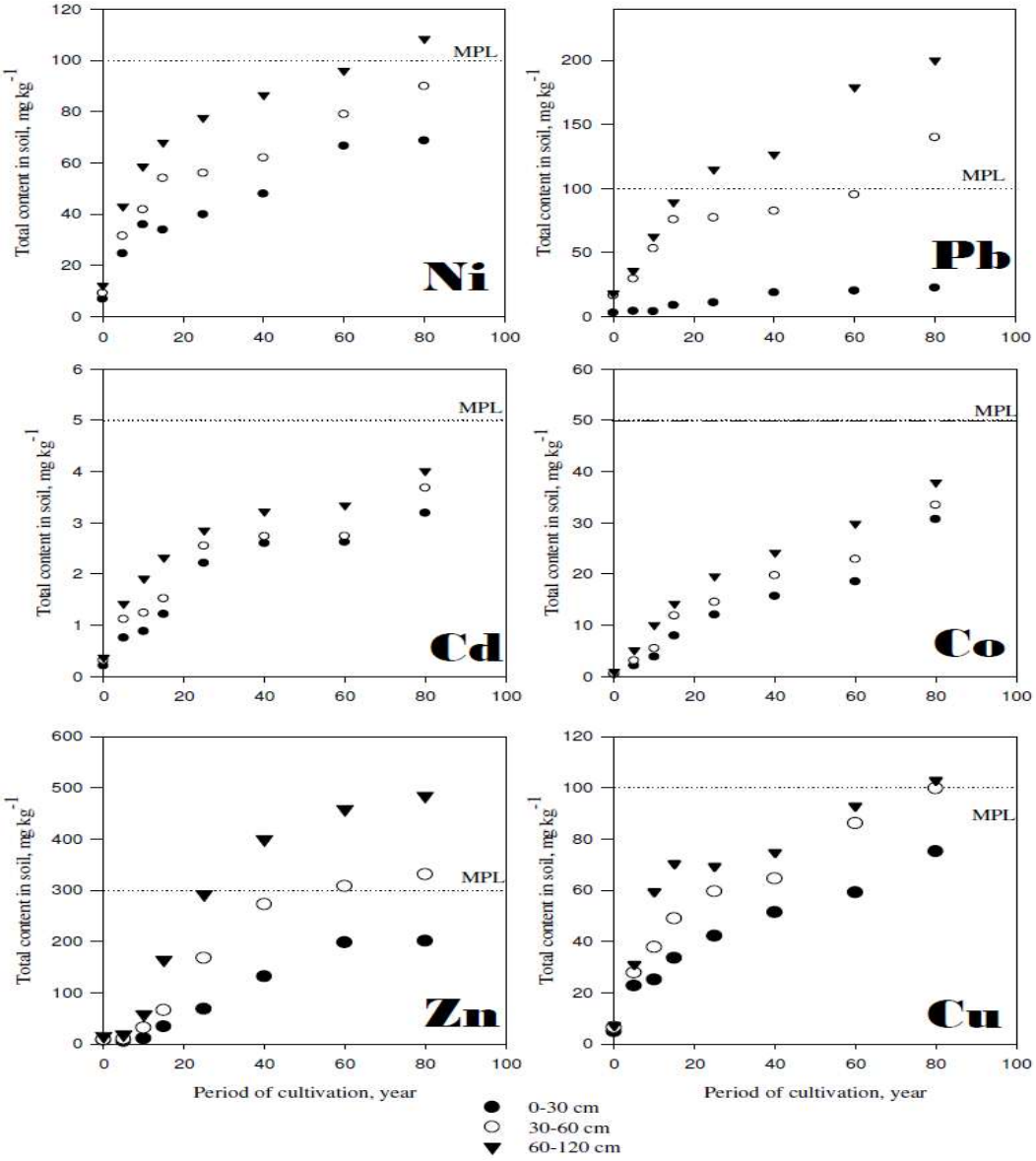

Fig 4. Total concentrations of heavy metals in the different soil layers of the Typic Torriorthent soil (0-30 cm (●), 30-60 cm (○) and 60-120 cm (▼)). (MPL: maximum permissible levels adapted from Kabata-Pendias and Pendias, 2001)

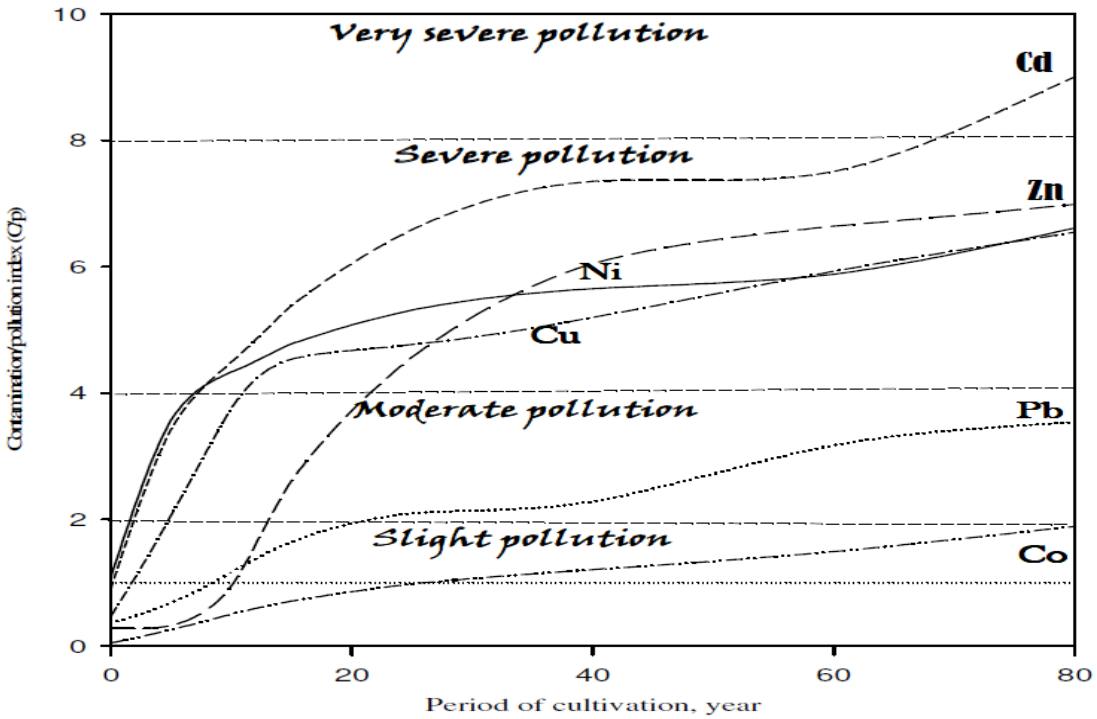

Fig. 5. Interpretation of contamination/pollution of heavy metals in a Typic Torripsamment soil (Based on the Dutch system formula, adapted from Lacatusu 2000)

Description of PTEs retention by Typic Torriorthent soil

Soluble PTEs were plotted graphically versus the corresponding retained concentrations of these metals in soil (Figs 6 and 7) and the obtained relations were fitted to three isotherm models, *i.e.* the linear, Langmuir and Freundlich ones. The calculated parameters as well as the "r^2" values are recorded in Table 3. Based on the highest "r^2" values. Langmuir isotherm seemed to be the best model fitting the retention of Pb, Zn, Co, and Cd within the different layers of the Typic Torriorthent soil which means that the retention process can be considered as adsorption. This model assumes that the thickness of the adsorbed PTEs is only one molecule (Chen, 2015). On the other hand, the retention of Ni and Cu within the subsequent soil layers seemed to follow a linear model. Although, the different functional groups of the organic molecules, added to the soils, might account for heterogeneous site sorptivity of PTEs (Zhou and Haynes, 2010); yet, this study illustrates that the long term sorptivity of PTEs in soil seemed to exist in the form of monolayer of adsorbed molecules. Probably, organic matter decreases the soluble and exchangeable forms of PTEs while increases the non-exchangeable ones (Mohamed et al., 2018). This might take place because of the transformation of PTEs within the organic fractions (Han and Banin, 1999). Moreover, the released CO2 , upon decomposition of soil organic matter (Lehmann and Kleber, 2015), dissolved in the soil solution forming insoluble carbonate salts of PTEs according to the equations adapted from Lindsay (1991)

$Pb^{2+} + CO_2\,(g) + H_2O \leftrightarrow PbCO_3\,(cerussite) + 2H^+$ log k0=-4.65

$Zn^{2+} + CO_2\,(g) + H_2O \leftrightarrow ZnCO_3\,(smithsonite) + 2H^+$ log K0=-7.91

$Cd^{2+} + CO_2\,(g) + H_2O \leftrightarrow CdCO_3\,(octavite) + 2H^+$ log K0=-6.16

$Cu^{2+} + CO_2\,(g) + H_2O \leftrightarrow CuCO_3\,(malachite) + 2H^+$ log K0=-12.99

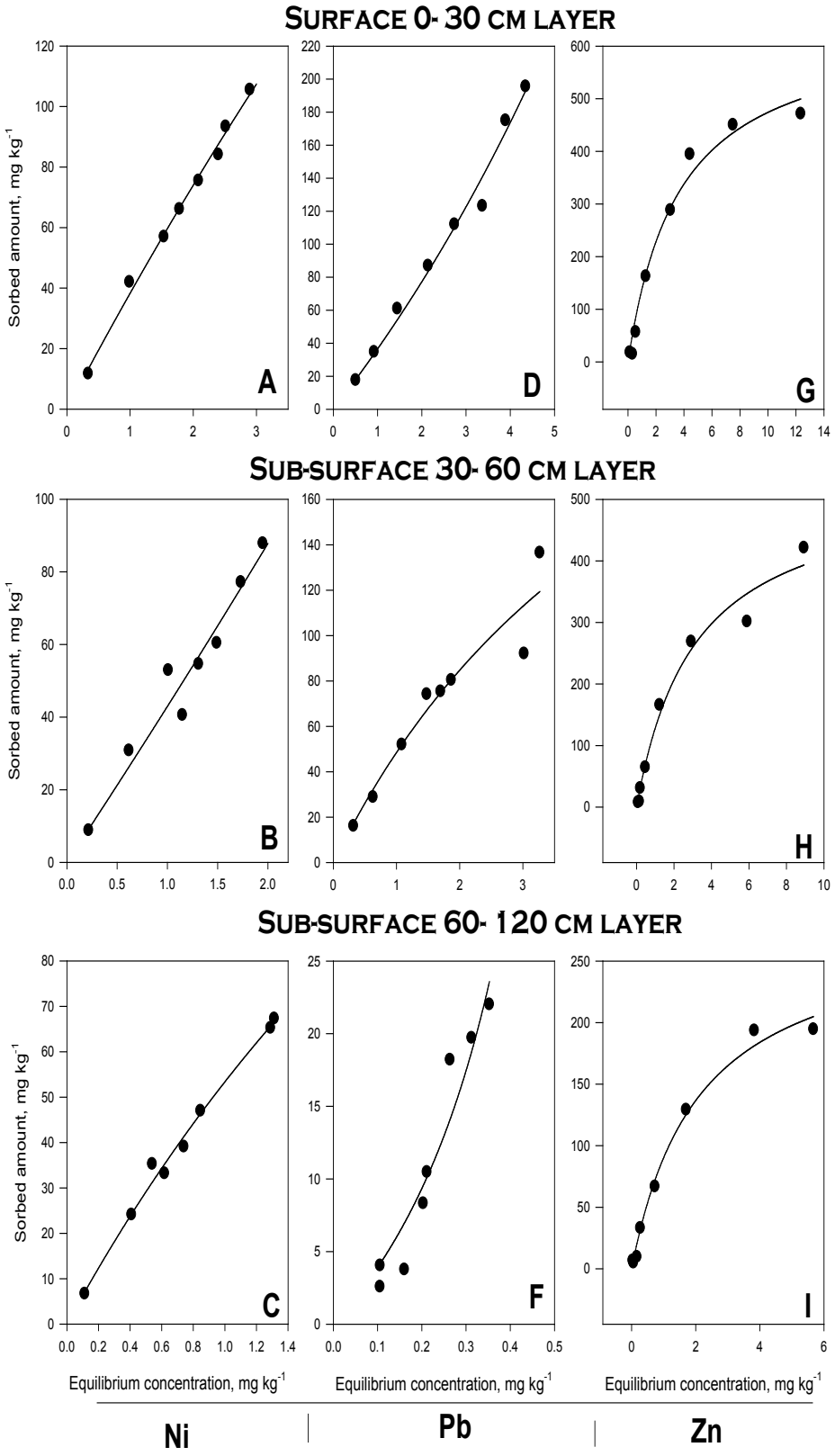

Fig. 6. Sorption of Ni, Pb and Zn on Typic Torriorthent soil as affected by their equilibrium concentrations

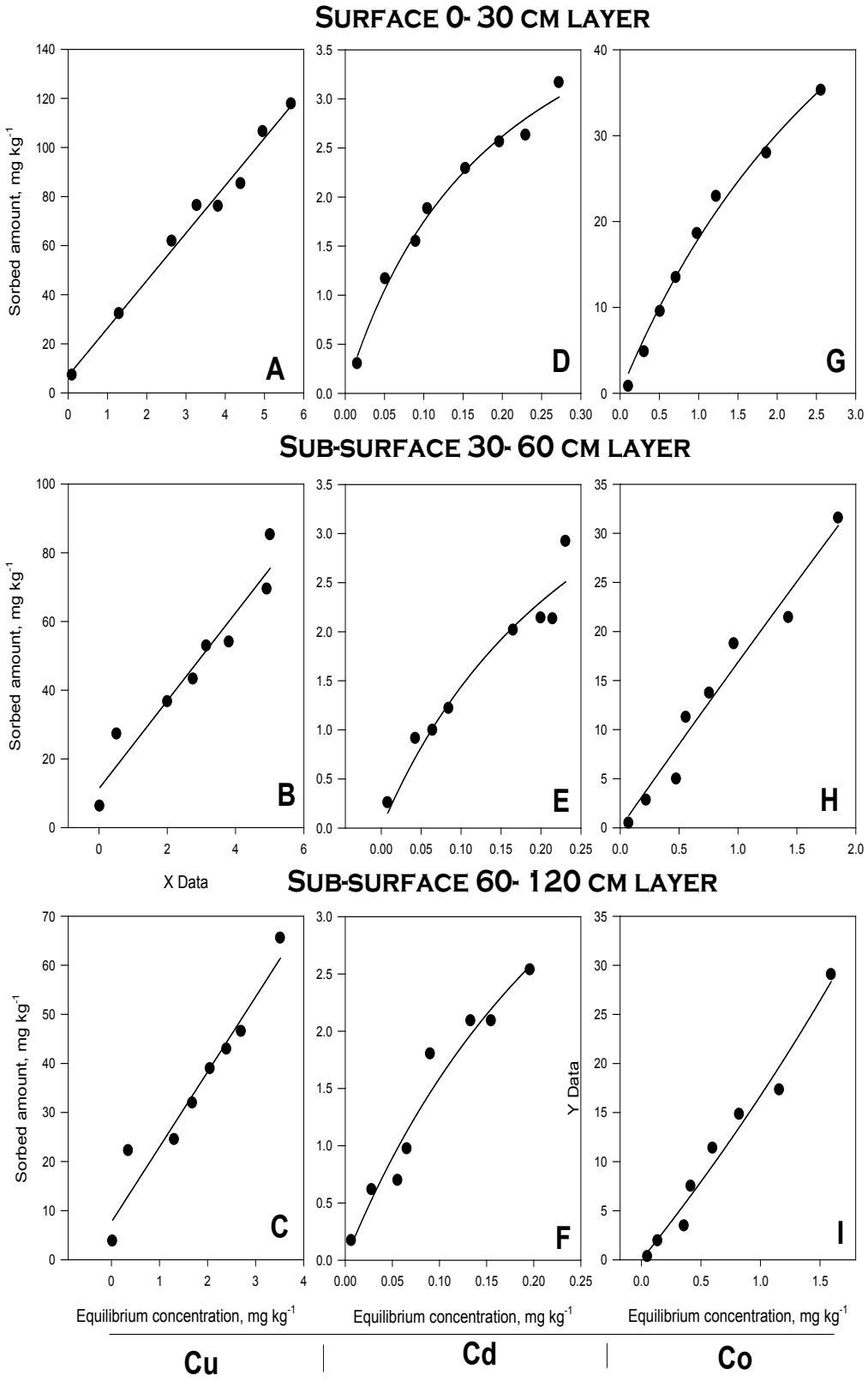

Fig. 7. Sorption of Cu, Cd and Co on Typic Torriorthent soil as affected by their equilibrium concentrations

TABLE 3. Calculated parameters and "r^2" values for the investigated adsorption isotherm models

		Linear		Langmuir			Van Bemmelen-Freundlich		
		K_d	r^2	a	b	r^2	k	1/n	r^2
Ni	0-30 cm	35.44	0.993	39.66	0.04	0.994	38.58	0.936	0.994
	30-60 cm	42.95	0.995	42.05	0.02	0.950	4353	0.997	0.949
	60-120 cm	48.53	0.986	64.07	0.20	0.991	52.92	0.860	0.990
Pb	0-30 cm	44.69	0.980	34.76	0.05	0.985	35.97	1.132	0.982
	30-60 cm	34.25	0.904	56.67	0.17	0.919	48.41	0.775	0.916
	60-120 cm	13.50	0.871	20.54	0.32	0.912	15.21	0.813	0.886
Zn	0-30 cm	39.95	0.789	176.30	0.27	0.981	144.90	0.521	0.921
	30-60 cm	45.18	0.898	169.50	0.32	0.979	121.10	0.569	0.965
	60-120 cm	36.49	0.8814	133.10	0.47	0.991	80.82	0.566	0960
Cu	0-30 cm	19.37	0.986	24.67	0.04	0.982	25.94	0.858	0.984
	30-60 cm	12.78	0.933	21.18	0.08	0.880	25.41	0.653	0.909
	60-120 cm	11.53	0.920	21.55	0.06	0.892	23.89	0.722	0.915
Cd	0-30 cm	9.947	0.938	26.30	5.05	0.987	6.985	0.619	0.979
	30-60 cm	9.77	0.947	19.16	3.31	0.939	7.094	0.702	0.949
	60-120 cm	12.75	0.935	20.36	2.83	0.951	9.376	0.783	0.946
Co	0-30 cm	13.88	0.958	22.37	0.24	0.990	17.35	0.788	0.980
	30-60 cm	17.11	0.964	17.16	0.09	0.964	16.75	0.997	0.963
	60-120 cm	17.96	0.973	15.18	0.09	0.974	16.92	1.089	0.973

Note: Kd: distribution coefficient, a: capacity and b affinity coefficients of Langmuir isotherm; k and n are constants related to the capacity and affinity coefficients of Van Bemmelen-Freundlich isotherm

Changes of the retained PTEs with ageing

Values of the PTEs retained in soil (total minus soluble contents) were calculated and then presented graphically versus soil ageing. The outcome relations were fitted to five kinetic models i.e zero order reaction, first order reaction, power function, simple Elovich and parabolic diffusion. The calculated "r^2" values and standard error of estimation (S.E.) are presented in Table 4. Based on the highest " r^2" and lowest "S.E." values, the power function and the parabolic diffusion seemed to be the best models fittings for the kinetics of PTEs retention in the studied Typic Torripsamment within the different soil layers. Such models probably indicate that the kinetics of PTEs retention is controlled by the diffusion process which affects strongly the redistribution and reactivity of PTEs in soil (Han et al., 2001) beside of the transformation of PTEs into the organic bound fractions (Han and Banin, 1999). Retention coefficient rates (calculated from the "Power function kinetic model) and diffusion rate constant (calculated from the "Parabolic diffusion kinetic model) are presented in Table 5 and Figs 8 and 9.

Results shown in Table 5 reveal that the values of the retention coefficient rates (calculated for the "Power function kinetic model") increased with increasing soil depth; whereas, the diffusion rate constant decreased with increasing the depth. Probably, soil compaction within the sub-surface soil layers brought soil particles close together (Gao et al., 2016), thus the water infiltration decreased (Epron et al., 2016) and consequently the diffusion rate constant of PTEs decreased. On the other hand, SOM decreased with soil depth (Fig. 2); therefore, the affinity of SOM to form organo-metal complexes decreased noticeably (Kleber et al., 2015). Generally, the retention coefficient rates among Ni, Cd and Cu seemed to be close to each other, while slightly varied among Co, Zn and Cu. In this concern, Cu has high affinity to form organo-metal complexes (Lookwood et al., 2015) mainly with low molecular weight organic matter (Calace et al., 2001) and this might result in formation of soluble complexes (Zhou and Wong, 2001; Clemente et al., 2006) whereas Cd is mainly adsorbed by high molecular weight organic matter (Calace et al., 2001). Moreover, Ni complexes are less labile than Cd or Zn complexes (Welikala et al, 2018). The lowest diffusion rate constant was recorded for Cd while the highest ones were recorded for Zn and Pb. This might be attributed to the relatively low concentrations of Cd in soil while those of Zn and Pb were the highest among the studied ones.

TABLE 4. Values of coefficient of determination (r^2) and standard error of estimation (S.E.) for the kinetic models

	Soil layer,	Zero Order Reaction		First Order Reaction		Power Function		Simple Elovich		Parabolic Diffusion	
	cm	r^2	S.E.	r^2	S.E.	r^2	S.E.	r^2	S.E.	r^2	S.E.
	0-30	0.795	14.965	0.518	0.529	0.952	4.770	0.807	14.281	0.966	5.980
Ni	30-60	0.862	10.124	0.573	0.512	0.963	5.202	0.732	14.092	0.973	4.184
	60-120	0.884	7.435	0.597	0.504	0.973	5.307	0.691	12.134	0.970	3.759
	0-30	0.944	16.215	0.736	0.459	0.933	2.082	0.547	46.117	0.971	11.626
Pb	30-60	0.867	14.909	0.678	0.423	0.889	13.587	0.577	26.551	0.913	12.066
	60-120	0.916	2.329	0.815	0.383	0.975	10.772	0.439	6.010	0.909	2.415
	0-30	0.797	0.448	0.520	0564	0.934	0.241	0.779	0.470	0.962	0.195
Cd	30-60	0.861	0.349	0.629	0.508	0.938	0.232	0.634	0.567	0.945	0.936
	60-120	0.859	0.350	0.653	0.579	0.939	0.174	0.579	0.604	0.939	0.230
	0-30	0.949	2.863	0.597	0.848	0.992	1.151	0.567	8.371	0.982	1.690
Co	30-60	0.956	0.948	0.635	0.905	0.972	1.913	0.489	8.132	0.943	2.719
	60-120	0.963	1.992	0.675	0.905	0.964	1.960	0.428	7.845	0.905	3.1911
	0-30	0.882	71.962	0.684	0.871	0.951	19.652	0.460	153.732	0.914	61.398
Zn	30-60	0.968	30.414	0.772	0.819	0.969	29.713	0.385	132.778	0.950	52.675
	60-120	0.950	19.661	0.807	0.723	0.927	56.731	0.353	71.019	0.936	30.983
	0-30	0.797	17.783	0.492	0.705	0.958	8.142	0.747	19.869	0.946	9.175
Cu	30-60	0.886	8.967	0.562	0.583	0.970	4.600	0.707	14.372	0.979	3.838
	60-120	0.871	7.194	0.528	0.651	0.954	4.295	0.702	10.917	0.960	3.998

TABLE 5. The calculated parameters of the best fitting kinetic models of PTEs sorption on Typic Torriorthent soil

Soil depth, cm	Ni	Pb	Cd	Co	Zn	Cu
	Power Function model "b" (sorption rate coefficient $(\mu g.g^{-1})^{-1}$					
0-30	0.299	0.435	0.322	0.607	0.688	0.355
30-60	0.356	0.551	0.428	0.731	0.942	0.395
60-120	0.387	0.632	0.501	0.877	0.950	0.397
	Parabolic diffusion "K_p" (diffusion rate constant $(\mu g.g^{-1})^{0.5}$)					
0-30	9.996	21.147	0.305	3.945	62.673	12.021
30-60	8.415	12.205	0.285	3.459	50.354	8.218
60-120	0.674	2.395	0.283	3.089	25.885	6.135

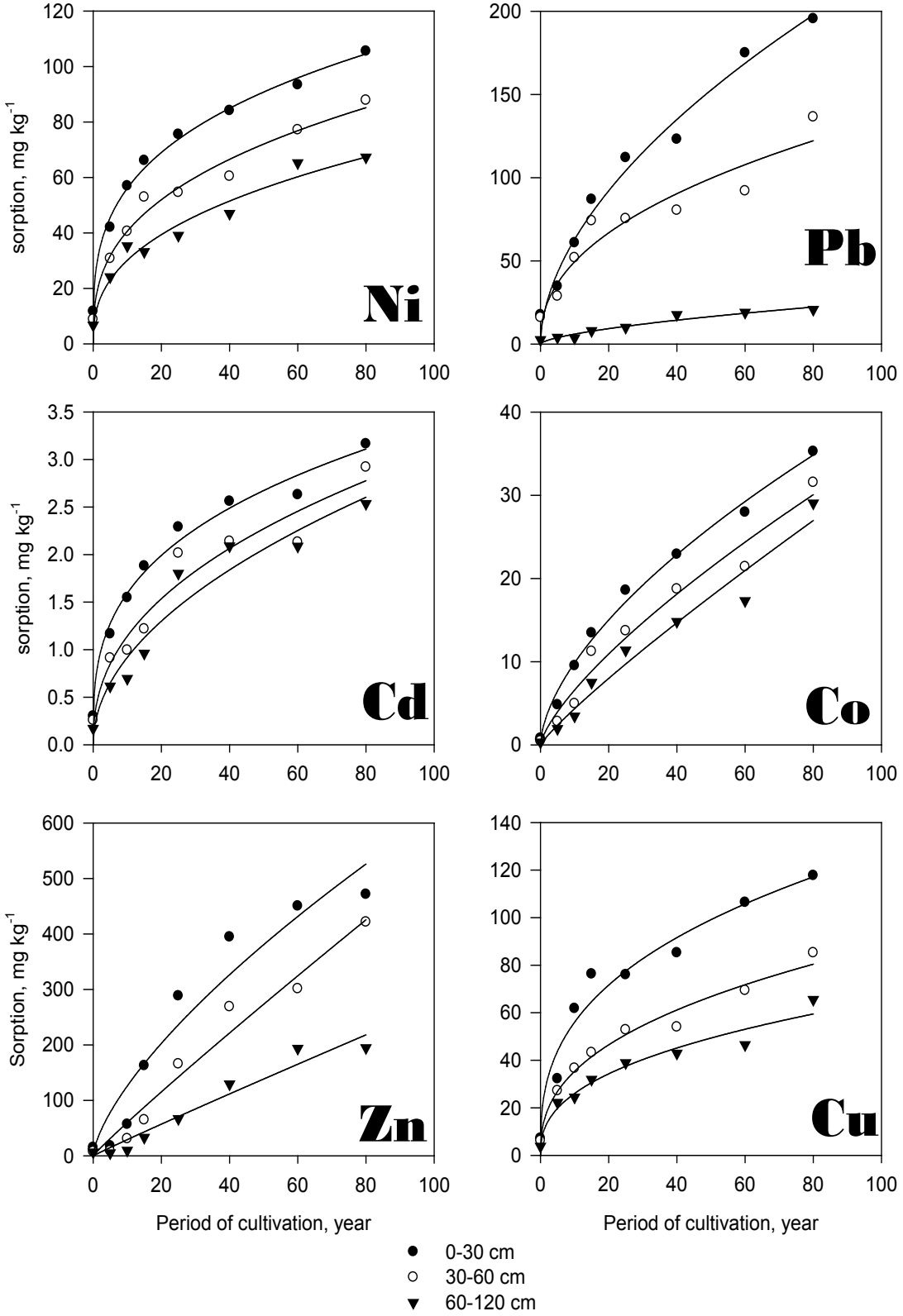

Fig. 8. The power function fittings for the kinetics of heavy metal sorption in Typic Torriorthent soil: 0-30 cm (●), 30-60 cm (○) and 60-120 cm (▼)

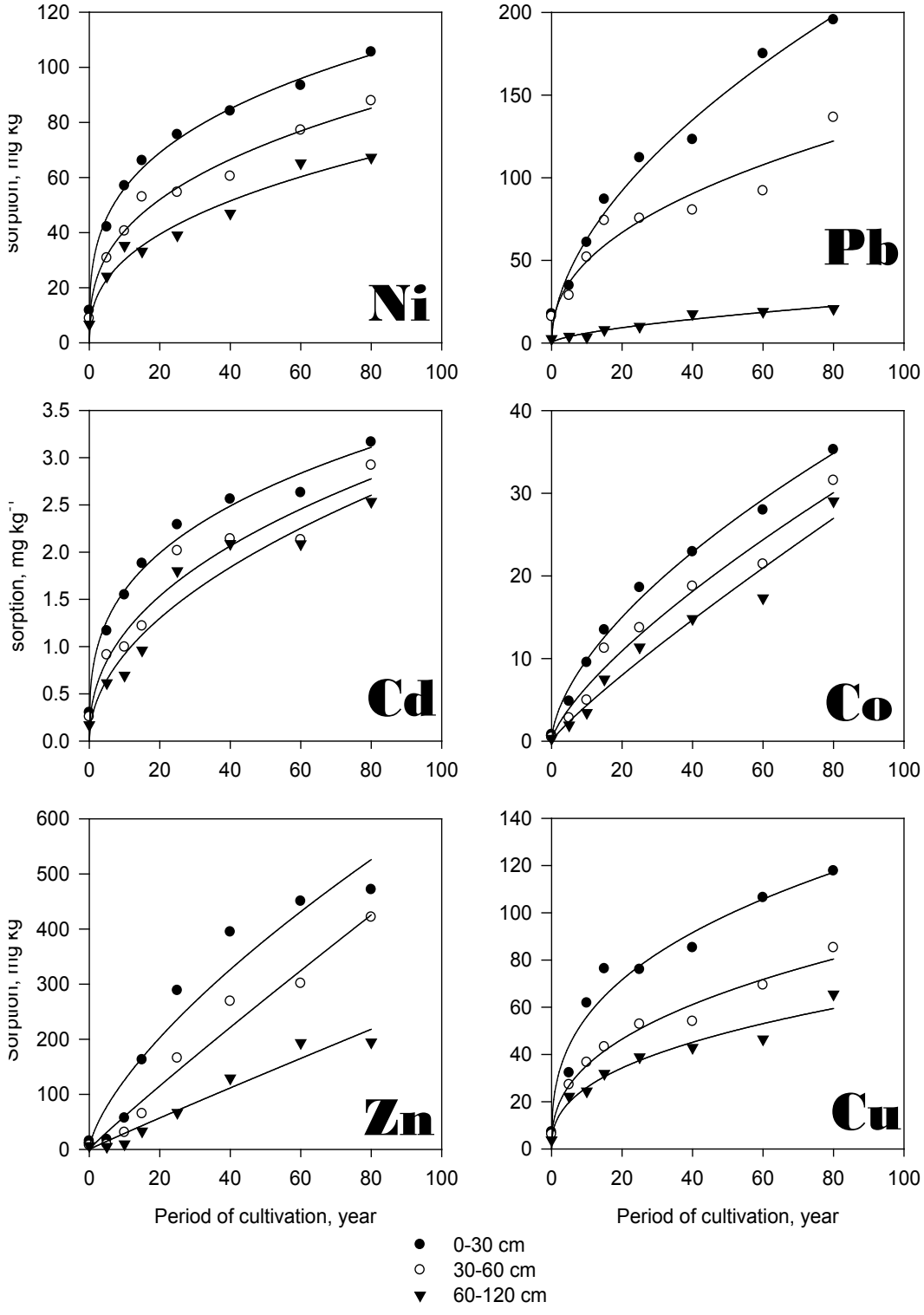

Fig. 9. The parabolic diffusion fittings for the kinetics of heavy metal retention by the Typic Torriorthent soil: 0-30 cm (●), 30-60 cm (○) and 60-120 cm (▼)

Results of the correlations presented in Table 6 indicate that both the soluble and total concentrations of PTEs were significantly correlated with each of the organic matter content in soil and soil CEC. This might take place because of the functional groups of SOM which bind preferentially PTEs e.g. Cu and Cd (Lo et al., 2008). Similar results indicate that Zn (Kidd et al., 2007), Cu, Ni (Yin et al., 2002; Ashworth and Alloway, 2004; Kahapanagiotis et al., 2008), Pb and Cd (Weng et al., 2002; Gondar et al., 2006) were closely related with the soil content of organic matter. The obtained results also reveal that the soluble contents of the studied metals were significantly correlated with their total contents in soil. These results agree with those of Gray and Mclaren (2006) who found that the solubility of PTEs in soil depends on each of SOM content and the total contents of PTEs themselves. It is worthy to mention that the soluble concentrations of PTEs were significantly correlated with each other. This probably occurred because the factors affecting the solubility of these PTEs are almost the same.

Conclusion

Soil organic matter plays significant roles in improving soil fertility; however it also increases the level of soil pollution with the potentially toxic elements (PTEs) especially in Typic Torriorthent soil. These organic residues stabilize PTEs in soil mainly within the surface soil layer (0-30 cm). Thus, there is no wonder to find out that the total and soluble concentrations of these metals in soil were significantly correlated with the SOM. It seems that the sorption of these metals took place via one molecule thickness and followed Langmuir isotherm model. The diffusion of PTEs in soil seemed to be a rate limiting step against PTEs retention versus soil ageing. Therefore, soil fertility and future use of sewage water in irrigation appears to be dependent on not only the PTEs contents of the irrigation water but also the effect of both PTE itself together with the soil properties specially the organic matter content and CEC on the transformations of the PTEs among the soluble and retained forms with ageing.

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TABLE 6. Soluble and totals contents of PTEs in the uppermost layer (0-30 cm) of the studied soils and their relations to both the soil organic matter (SOM) and CEC

		CEC	SOM	Soluble PTEs in soil, mg kg^{-1}					Total PTEs, mg kg^{-1}				
				Ni	Pb	Zn	Cu	Cd	Co	Ni	Fe	Cu	Mn	Pb	Zn
	CEC														
	SOM	0.910**													
Soluble PTE content in soil, mg kg^{-1}	Ni	0.900**	0.956**												
	Pb	0.973**	0.957**	0.973**											
	Zn	0.915**	0.789**	0.828*	0.903**										
	Cu	0.906**	0.954*	0.998**	0.977**	0.839**									
	Cd	0.966**	0.932**	0.971**	0.994**	0.925**	0.973**								
	Co	0.941**	0.931**	0.906**	0.954**	0.985**	0.915**	0.969**							
Total PTE content in soil, mg kg^{-1}	Ni	0.889**	0.940**	0.997**	0.965**	0.826*	0.995**	0.965**	0.907**						
	Pb	0.960**	0.918**	0.957**	1.00**	0.932**	0.967**	0.990**	0.977**	0.955**					
	Zn	0.990**	0.944**	0.932**	0.903**	0.983**	0.936**	0.977**	0.932**	0.918**	0.970**				
	Cu	0.882**	0.926**	0.988**	0.961**	0.831**	0.993**	0.957**	0.912**	0.989**	0.962**	0.908**			
	Cd	0.905**	0.958**	0.971**	0.958**	0. 842**	0.993**	0.997**	0.915**	0.996**	0.958**	0.935**	0.979**		
	Co	0.962**	0.931**	0.965**	0.994**	0.942**	0.970**	0.974**	0.982**	0.961**	0.994**	0.970**	0.958**	0.970**	

Note: **Significant $p < 0.01$ and *Significant $p < 0.05$

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تداعيات الري طويل الاجل باستخدام المياه العادمة علي محتوي وحركية ادمصاص ايونات العناصر الثقيلة في اراضي *Typic Torripsamment*

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يهدف هذا البحث إلي دراسة تداعيات الري باستخدام المياه العادمة (الغنية في محتواها من المادة العضوية) علي توزيع العناصر محتملة السمية (الذائبة والكلية) في طبقات التربة المختلفة في منطقة الجبل الاصفر، ولتحقيق هدف الدراسة فإنه تم اختيار 8 مواقع داخل مزرعة الجبل الاصفر، والتي تمثل اراضي مناطق تم زراعتها لفترات زمنية مختلفة باستخدام المياه العادمة في الري، حيث تم جمع العينات على ثلاثة أعماق ، وقد تم تحليل هذه العينات لمعرفة محتوياتها من المادة العضوية (SOM) ، والسعة التبادلية الكاتيونية للتربة (CEC) ، بجانب التركيزات الكلية والذائبة للعناصر محتملة السمية (Ni و Pb و Cd و Co و Zn و Cu) ، وقد اظهرت النتائج ازدياد كلا المادة العضوية في الارض، والسعة التبادلية الكاتيونية زيادة مضطردة مع زيادة فترات زراعة الارض، خصوصاً في الطبقات السطحية منها، بينما كانت الزيادات المقابلة خلال الطبقات التحت سطحية طفيفة، كما زاد محتوي الارض الكلي والذائب من العناصر محتملة السمية بشكل تدريجي خلال طبقات التربة المختلفة مع زيادة فترات زراعة الارض؛ ومع ذلك ، يبدو أن تلك الزيادات كانت أقل وضوحاً مع العمق، واستناداً إلى النظام الهولندي في تقييم مستوي تلوث الارض بالعناصر محتملة السمية، فإن النتائج اوضحت أن تلوث الارض التي تمت زراعتها لمدة 80 سنة كان منخفضاً بالنسبة للكوبلت ، بينما كانت نسبة التلوث بالرصاص معتدلة ، وكان التلوث بكل من النيكل والنحاس، والزنك شديداً، أما التلوث بالكادميوم فقد كان شديداً جداً ، هذا وقد ارتبطت التركيزات الكلية والذائبة من العناصر محتملة السمية في التربة ببعضها البعض، وكلاهما ارتبط بصورة معنوية مع مادة الارض العضوية، وكذلك السعة التبادلية الكاتيونية للتربة، وقد تم حساب الكمية المحتجزة من كل من هذه العناصر في التربة وتم تمثيل العلاقة بين الكمية المحتجزة في مقابل التركيز الذائب من تلك العناصر بيانيا، واستخدمت نماذج الادمصاص المختلفة لمحاكاة تلك العلاقات، وقد اكدت النتائج علي ان نموذج لانجمير Langmuir هو الامثل في وصف توزيع احتجاز العناصر المحتملة السمية في تلك الاراضي، كما تم تمثيل العلاقة بين الكمية المحتجزة مع الزمن بيانياً، واستخدمت خمس نماذج لدراسة حركية تلك العناصر في التربة ، وكان نموذجي الانتشار، والكسر الاسي، أفضل تلك النماذج، وبالتالي خلص البحث إلي أنه بالرغم من الدور الفعال للمادة العضوية في توزيع العناصر محتملة السمية ما بين الذائب، والمحتجز في التربة، إلا أن عامل الزمن يظل ذو اهمية ملحوظة في هذا التوزيع خاصة في الطبقة السطحية من التربة