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Effect of contamination sources on the rate of zinc, copper and nickel release from various soil ecosystems

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Abstract

Background and objective: Soil is a substantive component in biosphere habitually endangered to superfluity contaminants particularly potential toxic elements (PTEs). The source of soil contaminants is very critical in controlling both their release and expected hazards in the different soil ecosystems. This study aims to investigate the effect of low-quality irrigation water (LQW) on the extent of soil pollution through desorption of zinc (Zn), nickel (Ni) and copper (Cu) from different polluted soils, collected from LQW irrigated farms for more than 40–80 years at Giza and Kafr-Elsheikh Governorates, Egypt.

Results: Models incorporated modified Freundlich (MFE), Elovich, first order and parabolic diffusion (PDE) showed significant results in describing the kinetic data under Egyptian conditions. Results entailed that according to the coefficient of determination (R^2) and standard error, all used models well described the desorption of Cu, Ni and Zn, the most prevalent contaminants in the trailed soil ecosystems; for example, the R^2 values were higher than 0.96** for zinc desorption using MFE model. As far as the PTEs levels are considered, the highest contaminant desorption rates were recorded at Kafr-Elsheikh site, followed by Kombora, and the lowest ones were in Abo Rawash soil ecosystem. The succession of more than one model to describe the kinetic perspective confirmed that the different mechanisms take place in PTEs sorption, distribution and subsequently release from different soil ecosystems.

Conclusions: The numerical values indicated that the soil ecosystems contaminated with industrial effluents were higher than those irrigated with sewage effluents regardless of the type of land use. More attention should be paid to low-quality water application in agriculture irrigation and its environmental risks.

Keywords: Contaminated soil, Water contamination, Soil pollution, Land use, Kinetic models, Potential toxic elements, Sewage and industrial effluents, Heavy metals, PTEs, Desorption

Background

Mutually, behavior and reactions of the varied soil components with potential toxic elements (PTEs) and their distribution coefficients (K_d s) are key issues in assessing the mobility and retention of these contaminants (Shaheen et al. 2013). Soil physical, chemical and biological processes determine the

sorption, speciation, redistribution, mobility as well as the bioavailability of PTEs in a given soil ecosystem. The timescale at which the different processes occur in soil ecosystems varies between nanoseconds and centuries or even a millennium. Due to the wide range of reaction kinetics and since the soil ecosystem is continuously lay open to varied fluctuating settings in temperature, moisture etc., it would never reach a true chemical equilibrium. The distribution coefficient (K_d) is the ratio of a given PTE concentration in the solid phase to its ratio in an equilibrium solution after a specified reaction time. Braz et al. (2013) measured the

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distribution coefficient (K_d) and the affinity of PTEs with the soil colloids; it is found that the coefficient played a key role in defining PTEs in a given soil ecosystem and in assessing the environmental risks of the inorganic pollutants. In addition, K_d value depends on the climatic conditions of the soil ecosystems that exist. The K_d is a useful parameter for comparing the sorptive capacities of different inorganic pollutants in different soil ecosystems. The selectivity of sorption and the K_d parameter is affected by soil properties such as the percentage and type(s) of clay minerals in the system, the concentrations of Fe and Mn oxides, organic matter OM, roles of microorganism, phosphate concentration and the concentration of the basic cations. Also, the K_d parameter can be affected by sorbate properties such as ionic radius, polarity, aqueous radius, equivalent conductivity, hydration, enthalpy and entropy. Some chemical properties such as pH, especially in the arid region and amorphous hydroxides, have a significant impact on the formation of complexed compounds, reaction speed and stability (Shaheen et al. 2013). Sparks and Elzinga (2001) stated that predicting the movement of environmental contaminants requires understanding the mechanism(s) of their retention on the surface of soil particles. Sorption reactions at solid–water interfaces decrease solute mobility and often control the fate of their bioavailability.

Sukreeyapongse et al. (2002) mentioned that losses due to leaching and assimilation by plants and microorganisms are key issues in assessing the environmental risk of PTEs in terrestrial ecosystems. Mansour et al. (2019) noted that the mass balances of PTEs in a given soil ecosystem are strongly dependent on varied biogeochemical processes such as sorption and dissolution. These processes are mainly exaggerated by the type of sorbents and existing PTEs pools, pH, redox potential, concentrations of co-adsorbates and concentration of complexing ligands in solution. Several studies confirmed that soil pH is the most influential factor controlling sorption–desorption of PTEs in soil ecosystems (Mansour et al. 2019). Guala et al. (2010) inverted that PTEs retention (or sorption) on the surface of soil particles decreased the ability of a contaminants to move through soil and aquatic ecosystems. Kim et al. (2010) stated that PTEs solubility and speciation in soil solution are the most imperative factors controlling phytoextraction and inorganic pollutants accumulating capacity in plants.

Accordingly, the primary objectives of this study are to investigate the effect of quality of irrigation water on soil pollution and soil properties on Zn, Ni and Cu desorption from some Egyptian contaminated soils collected from different farms irrigated with LQW for

more than 40–80 years. The results of this study may be declared the best remediation management(s) practices should be applied under varied conditions.

Methods

Soil sampling

From Giza and Kafr-Elsheikh Governorates (Fig. 1), soil and water samples were collected as follows:

Soils irrigated with sewage effluent

- Surface (0–30 cm) soil samples from both cultivated (C) and uncultivated (UC) soil ecosystems were collected from Abo Rawash farmland at (Giza Governorate S1), (30° 4 6" N; 31° 3 38" E). The main source of irrigation of these soils is sewage effluent from El-Lebeny drain for more than 40 years and is cultivated with citrus trees at the time being. The uncultivated soil samples were previously cultivated with artichoke and are now left without cultivation for the last 3 years ago for unsuitability of this soil to be cultivated with edible crops.
- A surface soil sample was collected from Kombora farmland (Giza Governorate S2), (30° 4 62" N; 31° 7 6" E). The soil was irrigated with sewage effluent from El-Lebeny drain for more than 35 years and is now cultivated with corn.

Soils irrigated with a mixture of industrial effluents, agricultural drainage and Nile water

- A surface soil sample was collected from Northern Delta (Kafr-Elsheikh Governorate S3), (31° 05.584 N; 031° 03.557 E). The main source of irrigation of these soils is Branch 62-main canal pronged from Kitchener drain for not less than 80 years. The selected farm was cultivated with different types of vegetables.

Low-quality water samples were used in the irrigation of selected farms; that is, in addition, Nile water sample from El-Kalubia Governorate was collected and analyzed for their heavy metals concentrations.

Soil chemical characteristics were determined in triplicate as given in Jackson (1958) as follows:

- Soil reaction pH values were measured using glass electrode in soil paste.
- The electrical conductivity (ECe) in dS m^{-1} at 25 °C was determined in soil paste extract.

Fig. 1 Map representing the location of soil samples in the different investigated Governorates

- Soluble cations and anions were measured in soil paste extracts. The extracts were analyzed for sodium and potassium using flame photometer, calcium and magnesium by titration with (EDTA-Na), chloride by titration with silver nitrate and soluble carbonate by titration with standardized sulfuric acid.
- Exchangeable cations were extracted by ammonium acetate solution (Cottenie et al. 1982). The extracts were analyzed for exchangeable Ca, Mg, Na and K using the standard methods.
- Cation exchange capacity (CEC) was determined by ammonium acetate method described by Cottenie et al. (1982).
- Mechanical analysis was performed according to the International Pipette Method using sodium hexametaphosphate as a dispersing agent as given in Piper (1950).
- Total concentration of PTEs was determined using atomic absorption spectrophotometry (AAS) (Cottenie et al. 1982).
- Some chemical properties, particle size distribution and total concentrations of heavy metals in the studied soil ecosystems as well as some chemical characteristics of the irrigation water are presented in Tables 1, 2, 3, and 4.

Kinetic studies

Kinetic experiments on the trailed soil ecosystems were done using an Electrical Stirred Flow Unit (ESFU) (Zaghloul 2002). Triplicate of soil (two-gram portions) was placed in a falcon plastic tube, and 25 ml of ammonium bicarbonate-DTPA was added; the tubes were thereafter put in the ESFU shaken rapidly before sampling at varied times between 1s and 120 min. or at specified time according to stability of the ion(s) released from the studied soil samples at $25 \pm 2^\circ\text{C}$. The concentrations of PTEs (Zn, Cu and Ni) were determined using atomic absorption spectrophotometry (AAS) (Cottenie et al. 1982).

The following four kinetic models signifying both empirical and theoretical calculations were used to test data according to the coefficient of determination (R^2) and standard error (SE) values, to describe the release of PTEs from the trailed soil ecosystems and their bioavailability to the different plants grown in studied contaminated soil ecosystems:

First-order equation

$$\text{Log}(q_\phi - q_t) = \text{Log} q_0 - k_1 t$$

where q_ϕ = maximum amounts of PTEs released, q_0 = initial amounts of PTEs at the time of added resin, q_t = amounts of PTEs released at time t , t = time in minute, and k_1 = the rate constant of reaction (n) in min^{-1} .

Table 1 Some chemical properties of the studied soils

Treat. soil	pH	EC _e dS m ⁻¹	Soluble cations and anions (meq/l)							SAR
			Cations				Anions			
			Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	HCO ₃ ⁻ + CO ₃ ⁻⁻	SO ₄ ⁻⁻	
Kombora										
UC*	8.50	2.32	6.56	0.40	11.36	4.64	9.44	10.96	2.56	2.32
C*	8.49	2.16	5.20	0.40	11.20	4.16	9.28	10.72	0.96	1.88
Abo Rawash										
UC*	8.35	3.30	15.62	0.66	10.56	5.60	18.22	10.44	3.78	5.50
C*	8.27	3.30	13.56	0.66	12.74	4.83	16.24	9.18	6.37	4.57
Kafr-Elsheikh										
UC*	8.65	6.39	30.74	0.54	14.50	16.03	32.22	20.97	8.62	7.87
C*	8.52	5.04	24.39	0.18	11.25	13.50	28.53	16.47	4.32	6.93

UC uncultivated soil, C cultivated soil

Table 2 Particle size distribution (%) of the studied soil samples

Treat. soil	Coarse sand	Fine sand	Total sand	Silt	Clay	Texture
Abo Rawash						
UC*	31.5	56	87.5	3.3	9.2	Loamy sand
C*	21.8	67	88.8	9.2	2	Sandy
Kombora						
UC*	5.4	12.0	17.4	32.2	50.4	Clay
C*	8.7	34.3	43.0	19.4	37.6	Clay loam
Kafr-Elsheikh						
UC*	2.4	14.2	16.6	33	50.4	Clay
C*	1.2	14.3	15.5	32.1	52.4	Clay

UC uncultivated soil, C cultivated soil

Table 3 Total concentrations of potential toxic elements (PTEs) in the studied soils in (mg kg⁻¹)

Soil sample	Cu	Ni	Zn	Co	Cr	As	Mn	Mg	Fe	Pb	Cd
Kombora											
UC*	90.26	40.50	400	28.9	573.90	170.33	115.13	377.40	1459.73	44.00	12.43
C*	46.68	18.60	350	31.45	402.15	113.12	98.12	322.16	1365.75	38.02	13.05
Abo Rawash											
UC*	86.464	73.79	89.50	38.53	263.30	430.33	193.83	413.13	1615.40	62.80	15.53
C*	53.06	77.15	111.93	56.13	365.53	304.33	509.30	548.93	2127.40	66.96	14.73
Kafr-Elsheikh											
UC*	31.20	115.73	112.93	58.20	386.80	432.00	601.43	534.26	2162.40	47.43	14.40
C*	29.83	90.83	80.13	60.30	413.50	63.00	498.26	507.40	2181.40	31.30	11.93

UC uncultivated soil, C cultivated soil

Elovich's equation

$$q = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t$$

where q = amount of PTEs desorbed at time t , α = constant of PTEs in mg PTEs kg⁻¹ soil.min⁻¹, β = constant of PTEs in mg PTE kg⁻¹ soil, and t = time in minute.

Parabolic diffusion's equation

$$q = b + Rt^{1/2}$$

where q = amount of PTEs desorbed in time t , R = apparent diffusion rate coefficient in mg PTEs kg⁻¹ soil min⁻¹, and b = constant in mg PTEs kg⁻¹ soil.

Table 4 Concentrations of some heavy metals in the studied water samples used in irrigation in (mg L⁻¹)

Location	Cd	Pb	Mn	As	Cr	Zn	Ni	Cu
Safe level ^a	0.01	5.00	0.20	0.05	0.01	2.00	0.20	0.20
NW(El-Kalubia)	–	–	–	–	–	0.01	0.02	0.01
Kombora	0.33	–	0.46	9.51	–	0.7	2.49	0.12
Abo Rawash	0.35	–	0.43	12.85	–	1.08	2.35	0.12
Kafr-Elsheikh	0.35	–	0.43	12.85	–	1.08	2.35	0.12

^a According to ATSDR (1993)**Modified Freundlich's equation**

$$q = k_d t^{b^1}$$

where q = amount of PTEs desorbed in time t , k_d = desorption rate coefficient in mg PTEs kg⁻¹ soil min⁻¹, and b^1 = constant in mg PTEs kg⁻¹ soil.

The constants of the best-fitted models are documented in tables to compare desorption of Zn, Cu and Ni, the most dominant pollutants from the different soils.

Results
Kinetics of some potential toxic elements (PTEs) desorption from the studied samples as affected by irrigation with low-quality water (LQW) for extended periods
Zinc

A kinetic study was carried out to dominate PTEs desorption and explore the highest affected soil ecosystem irrigated with low-quality water. Results given in Table 5 represent the rate constants of Zn desorption from the varied trailed soil ecosystems. The best-fitted model(s)

was selected on the basis of the fact that the higher the R^2 , and the lower the SE values; the best-fitted model described the kinetic results. According to the R^2 values, modified Freundlich equation (MFE), Elovich and in some cases first order were the best-fitted models in describing the kinetic results. The numerical values of R^2 of these models ranged between 0.88**–0.98**, 0.93**–0.97** and 0.81**–0.87**, respectively. According to SE values, the decreasing order arranged as MFE (0.17–0.31), Elovich (2.46–4.23) and PDE model (0.30–8.91), pointed to the priority of MFE to describe the kinetic results compared to other models.

The rate constants of MFE always exhibited the actions of LQW on PTEs release from the trailed soil ecosystems. The constant (a) that describes the rate of PTEs desorption (Wahba et al. 2010) showed a wide variation in cultivated (C) and uncultivated (UC) soil ecosystems. For example, in Kombora the rate constant (a) being 0.31 mg kg⁻¹ min⁻¹ in uncultivated soil ecosystem (UC) decreased to 0.26 mg kg⁻¹ min⁻¹ in cultivated (C). This result was expected due to absorbing the contaminant by the growing plants. The respective values were 0.35

Table 5 Rate constants describing Zn desorption release from the soils

Soil	Kombora				Abo Rawash				Kafr-Elsheikh			
	a	b	R^2	SE	a	b	R^2	SE	a	b	R^2	SE
Modified Freundlich equation												
UC*	0.31	0.77	0.93**	0.31	0.21	0.76	0.88**	0.18	0.35	0.79	0.96**	0.17
C*	0.26	0.39	0.90**	0.26	0.26	0.85	0.88**	0.15	0.24	0.61	0.98**	0.23
Elovich equation												
UC*	3.89	7.02	0.93**	3.89	2.27	5.10	0.94	4.23	3.95	6.37	0.94**	3.16
C*	2.62	5.86	0.93**	3.62	3.96	6.81	0.94	3.63	2.99	1.57	0.97**	2.46
Parabolic diffusion equation												
UC*	0.32	18.02	0.75*	0.32	0.33	16.06	0.71*	8.91	0.26	14.63	0.70*	6.77
C*	0.30	16.07	0.74*	0.30	0.27	16.00	0.70*	7.59	0.24	9.62	0.76*	6.11
First-order equation												
UC*	–0.42	–0.47	0.81**	–0.42	–0.45	–0.43	0.82**	0.33	–0.49	–0.45	0.87**	0.30
C*	–0.53	–0.44	0.83**	–0.43	–0.52	–0.50	0.82**	0.38	–0.52	–0.35	0.87**	0.30

UC uncultivated soil, C cultivated soil

and $0.24 \text{ mg kg}^{-1} \text{ min}^{-1}$ in Kafr-Elsheikh, while values reached 0.21 and $0.26 \text{ mg kg}^{-1} \text{ min}^{-1}$ in Abo Rawash soil ecosystem. Variations in the numerical values in Abo Rawash and other soil ecosystems might mainly be ascribed to the light texture of Abo Rawash soil ecosystem compared to other sites as shown in Table 2, and this variation directly increased the contaminant uptake by grown plants.

The difference between the different soil ecosystems trailed in this work in their ability to release of Zn was more pronounced using Elovich model. Results in Table 5 showed an increase in a constant of Zn release reaching $3.89 \text{ mg kg}^{-1} \text{ min}^{-1}$ in uncultivated soil ecosystem (UC); meanwhile, it was $2.62 \text{ mg kg}^{-1} \text{ min}^{-1}$ in the cultivated one (C).

The numerical values of capacity factor (b) revealed the same trend in raising this constant in the uncultivated soil ecosystem compared to the cultivated one; however, some exclusion was recorded in Zn release in both soil samples. The capacity factors of Zn in uncultivated soil equaled 0.77 and $0.39 \text{ mg kg}^{-1} \text{ min}^{-1}$ soil in uncultivated (UC) and cultivated (C) of Kombora soil ecosystems, the corresponding values were increased to 0.79 and $0.61 \text{ mg kg}^{-1} \text{ min}^{-1}$ in uncultivated (UC) and cultivated (C) soil of Kafr-Elsheikh soil ecosystems, and the corresponding values of Abo Rawash soil were 0.76 and $0.85 \text{ mg kg}^{-1} \text{ min}^{-1}$. This result might be due to the renewable source of contaminants daily added in Abo Rawash soil ecosystem. The variations in the capacity factors between different soil ecosystems might be linked with the variation in the soil properties in these sites.

The significant recorded values of R^2 and low SE values of first-order and diffusion models given in

Table 5 indicated the suitability of using such model in describing the kinetic results. The rate constants of both models showed the same trends of MFE and Elovich models. Furthermore, it should be said that in most cases, the diffusion phenomena did not take place in Zn desorption. The succession of more than one model in describing Zn release might indicate that more than one mechanism took place in Zn adsorption in the trailed soil ecosystems.

Copper

Results given in Table 6 represent the rate constants of Cu release from the studied soil ecosystems. According to the higher R^2 and lower SE values, the best-fitted model describing the kinetic results was MFE and Elovich equations and to a less extent first-order and diffusion models. The numerical values ranged between 0.91^{**} – 0.98^{**} and 0.96^{**} – 0.98^{**} in the above-mentioned best-fitted models, respectively. According to the SE values, the decreasing order arranged as MFE (0.11 – 0.24) and Elovich (0.98 – 2.71) means the priority of MFE compared to other models. Nevertheless, it should be mentioned that other models might also contribute in explaining the different mechanisms controlled the release phenomena.

Rate constants of MFE clearly explained the action of LQW on the rate of PTEs release. The constant (a) that is convenient to describe the rate of PTEs desorption showed significant variations between cultivated (C) and uncultivated (UC) soil ecosystems. The (a) values of Cu desorption decreased from 0.20 to $0.18 \text{ mg kg}^{-1} \text{ min}^{-1}$ in both uncultivated (UC) and cultivated (C) soil ecosystems of Kombora, respectively. This trend represents the variation in retention of this contaminant in trailed soil

Table 6 Rate constants describing Cu desorption release from the soils

Soil	Kombora				Abo Rawash				Kafr-Elsheikh			
	a	b	R^2	SE	A	b	R^2	SE	a	b	R^2	SE
Modified Freundlich equation												
UC*	0.20	0.79	0.91^{**}	0.12	0.24	0.52	0.93^{**}	0.24	0.25	0.77	0.98^{**}	0.16
C*	0.18	0.71	0.92^{**}	0.11	0.23	0.67	0.96^{**}	0.18	0.23	0.67	0.95^{**}	0.18
Elovich equation												
UC*	2.37	4.58	0.98^{**}	0.98	3.43	3.61	0.97^{**}	1.87	4.27	5.58	0.96^{**}	2.71
C*	2.14	5.55	0.97^{**}	1.71	2.16	4.69	0.97^{**}	1.81	2.34	4.85	0.96^{**}	2.16
Parabolic diffusion equation												
UC*	0.29	10.35	0.78^*	4.19	0.37	11.89	0.62 ns	5.72	0.27	14.24	0.74^*	6.68
C*	0.21	11.83	0.77^*	4.65	0.39	13.46	0.62 ns	6.01	0.20	11.28	0.73^*	5.05
First-order equation												
UC*	−0.36	−0.37	0.87^{**}	0.22	−0.42	−0.36	0.85^{**}	0.24	−0.29	−0.40	0.85^{**}	0.28
C*	−0.38	−0.41	0.85^{**}	0.25	−0.37	−0.39	0.86^{**}	0.25	−0.31	−0.41	0.83^{**}	0.26

UC uncultivated soil, C cultivated soil

ecosystems. Although the same trend was recorded in other soil ecosystems, the desorption rate of Cu in Kafr-Elsheikh soil ecosystem was the highest reaching $0.25 \text{ mg kg}^{-1} \text{ min}^{-1}$ yet decreased to $0.23 \text{ mg kg}^{-1} \text{ min}^{-1}$ in both uncultivated and cultivated soil ecosystems, respectively.

The variations between the different ecosystems in their ability to release Cu were more pronounced when using Elovich model. Results in the same table showed an increase in (a) constant in Cu reaching $4.27 \text{ mg kg}^{-1} \text{ min}^{-1}$ in uncultivated soil ecosystem; this value, however, decreased to $2.34 \text{ mg kg}^{-1} \text{ min}^{-1}$ in the cultivated one. The same trend was recorded in the other studied ecosystems.

Although the capacity factor (b) given in the same table showed the same trend in increasing this constant in Kafr-Elsheikh uncultivated soil ecosystem compared to the cultivated one, other ecosystems showed signs of a reverse trend in increasing the release of Cu in cultivated soil ecosystems. Results in the same table showed that the capacity factor values of Cu were 4.58 and $3.61 \text{ mg kg}^{-1} \text{ min}^{-1}$ in Kombora and Abo Rawash uncultivated soil ecosystems; these values, however, increased to 5.58 and $4.69 \text{ mg kg}^{-1} \text{ min}^{-1}$ in Kafr-Elsheikh soil ecosystems. Constants of Elovich equation were highly correlated with readily available forms of contaminants (Saber et al. 2015); consequently, the capacity factor is expected to be higher in heavily texture soils like Kafr-Elsheikh and Kombora and lower in light texture one (Abo Rawash).

The first-order kinetic success to describe the results of Cu with significant R^2 ranged between 0.83** and 0.87** in the different soil ecosystems; however, increasing of SE values in all soils decreased the validity of this model to describe the kinetic results. Like first order, results

showed that the diffusion process for Cu desorption from different soil ecosystems showed low significant R^2 or insignificance in some cases and hence unvalued to be use in describing the kinetic data.

Nickel

Analogous to other studied contaminants, results given in Table 7 showed according to coefficient of determination R^2 , MFE was the best-fitted model to describe the kinetic results. Numerically, the R^2 values in cultivated and uncultivated soil ecosystems were 0.95**–0.98**, 0.97**–0.98** and 0.98**–0.99** in Kombora, Abo Rawash and Kafr-Elsheikh, respectively. Although the same trend was recorded in Elovich and first-order models, results confirmed that MFE was the best since the SE values were the lowest compared to other models trailed. The values of SE in MFE ranged between 0.03 and 0.12; meanwhile, they were 0.24–0.34 in the first-order model as an example that gives preference to use this model to describe the kinetic data.

The rate constant of MFE (a) given in Table 7 showed wide variations between cultivated and uncultivated soil ecosystems in the release of studied contaminant. The (a) constant values defining the rate of Ni release were 0.39, 0.30, 0.42 and $0.32 \text{ mg kg}^{-1} \text{ min}^{-1}$ in both Kombora and Kafr-Elsheikh soil ecosystems in uncultivated and cultivated soils, respectively. The corresponding values of Abo Rawash soil were 0.22 and $0.30 \text{ mg kg}^{-1} \text{ min}^{-1}$, respectively.

Kafr-Elsheikh soil ecosystems exposed to the irrigation with low-quality water containing industrial effluents together with sewage and drainage effluents

Table 7 Rate constants describing Ni desorption release from the soils

Soil	Kombora				Abo Rawash				Kafr-Elsheikh			
	a	b	R^2	SE	A	b	R^2	SE	a	b	R^2	SE
Modified Freundlich equation												
UC*	0.39	0.39	0.95**	0.03	0.22	0.58	0.97**	0.06	0.42	0.67	0.98**	0.03
C*	0.30	0.29	0.98**	0.12	0.30	0.30	0.98**	0.12	0.32	0.45	0.99**	0.11
Elovich equation												
UC*	2.11	2.53	0.94**	2.22	1.90	3.76	0.94**	2.13	3.30	0.86	0.96**	1.21
C*	1.99	1.50	0.96**	1.87	1.94	1.64	0.95**	1.96	2.13	0.51	0.97**	0.87
Parabolic diffusion equation												
UC*	0.18	8.34	0.72**	4.69	0.17	9.09	0.70*	4.42	0.11	4.39	0.75*	0.78
C*	0.17	6.88	0.75**	4.18	0.16	6.94	0.73*	4.22	0.10	3.50	0.75*	2.21
First-order equation												
UC*	−0.34	−0.33	0.81**	0.27	−0.43	−0.47	0.90**	0.34	−0.26	−0.30	0.83**	0.28
C*	−0.45	−0.38	0.89**	0.24	−0.45	−0.36	0.87**	0.28	−0.28	−0.35	0.86**	0.24

UC uncultivated soil, C cultivated soil

for more than eighty years and having hardpans at about 40–50 cm deep, led to increase both capacity and intensity factors for the studied different contaminants that might be confirmed by the capacity factor which emphasized such finding. Results in the same table showed that (b) constant values being 0.67 and 0.45 mg kg⁻¹ min⁻¹ for Kafr-Elsheikh soil decreased to 0.39, 0.29, 0.58 and 0.30 mg kg⁻¹ min⁻¹ in uncultivated and cultivated soil ecosystems of Kombora and Abo Rawash, respectively.

Elovich equation represents in the same table exhibited a significant trend in describing PTEs release from the studied soil ecosystems. The numerical values of the model showed that the constant *a* value pointed to the same trend in declaring the variations between Ni release in uncultivated and cultivated soil ecosystems. According to the values given in Table 7, the rates of Ni release were 3.30 and 2.13 mg kg⁻¹ min⁻¹ in uncultivated and cultivated soil ecosystems in Kafr-Elsheikh; meanwhile, it was 2.11 and 1.99 mg kg⁻¹ min⁻¹ in Kombora soil ecosystem. In Abo Rawash soil ecosystem, however, results showed that their rate values were 1.90 and 1.94 mg kg⁻¹ min⁻¹. In other words, the rate of release in uncultivated (UC) soil was less than in the cultivated (C) one.

Although the same trend was observed in first-order models that showed the variation between the two soil ecosystems, it should be mentioned that the presence of Ni in Egyptian soil ecosystems was more distinct compared to Cu and Zn according to the type of industrial activities neighboring the studied site. Results confirmed that the absence of Ni in Nile alluvial soils means that it is directly originating from several human activities.

Impacts of certain inorganic contaminants on soil properties

It is well known that the clay minerals in all soil ecosystems sustain negatively charged particle surfaces holding the exchangeable cations that significantly impacts the physical and chemical behavior of a given soil ecosystem referred to as cation exchange capacity (CEC).

In non-contaminated soil ecosystems, it was repeatedly noticed that the sum of exchangeable cations more or less equals CEC. Results given in Table 8 showed significant variations between CEC and sum of dominant exchangeable cations in all trails and even between cultivated and uncultivated soil ecosystems. Figure 2 exhibits that the calculated exchangeable PTEs represented 27.71% in light texture uncultivated soils at Abo Rawash, and that value increased up to 53.76% in the cultivated soil, while the sum of the dominant cations, i.e., Na, Ca, Mg and K, decreased from 72 to 51% in uncultivated and cultivated soil ecosystems, respectively. Such finding, however,

Table 8 Exchangeable cations and exchangeable sodium percent in the soil profile as influenced by irrigation water quality

Soil	Exchangeable cations (meq/100 g soil)				ESP	CEC meq/100 g
	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺		
Kombora						
UC*	6.64	1.17	8.80	5.69	15.06	44.09
C*	7.61	2.23	7.50	4.27	15.45	49.24
Abo Rawash						
UC*	3.35	0.56	5.61	3.56	18.62	17.99
C*	2.74	0.42	3.88	1.48	20.28	13.51
Kafr-Elsheikh						
UC*	13.81	1.47	3.22	3.35	35.59	38.8
C*	14.60	1.58	3.11	4.16	40.19	36.33

UC uncultivated soil, C cultivated soil

confirms the significance of CEC value in contaminated soil ecosystem as done in the current work.

Gained results endorsed that the sum of pollutant cations in uncultivated heavy textured soil ecosystem at Kombora site was slightly lower than that in the cultivated one reaching 21.78 and 21.79%, respectively, as given in Table 9. Expressed as percentages, the sum of contaminant cations equaled the sum of all contaminants in the uncultivated soil ecosystem achieving 50% of total exchangeable cations in uncultivated one being only 49% of total cations. The corresponding values in cultivated soil ecosystem were 49 and 51%, respectively.

Furthermore, gained results indicated that the sum of exchangeable contaminants in the uncultivated soil ecosystem in Kafr-Elsheikh was higher than that in the cultivated one with numerical percentage values equaling about 42 and 38% of total exchangeable cations. In the uncultivated soils ecosystem of the same site, however, the sum of dominant cations was almost equal in both uncultivated ones yet with a little priority to cultivated soil.

As given in Table 9, exchangeable cations concentrations for both exchangeable pollutant cations (EPC) and dominant cations (EDC) as well as for exchangeable Zn in

the uncultivated soil ecosystem in Kombora represented 14% of all exchangeable cations surprising the values of K and Mg, about 5 and 10% of total. Such findings point to the significance of calculated exchangeable cations in contaminated soil ecosystems as far as the same trends were also realized in Kombora cultivated soil ecosystem. Results in the same table also revealed that exchangeable Na values in Kafr-Elsheikh site were higher than all other studied cations that verify the cumulative value of soil pH in both cultivated and uncultivated soil ecosystems.

Results given in Table 9 indicate that some contaminants such as Cr existed at significantly high levels in both cultivated and uncultivated soil ecosystems, with numerical values higher than the EDC reaching up to 7–17% in all sites. The US-trivalent chromium agency considered Cr(III) ion an essential nutrient in insulin, sugar and lipid metabolism in human body. Furthermore, the European Food Safety Authority (EFSA) evidenced in 2014 that Cr might be recognized as an essential nutrient. According to EFSA, the human toxicity of Cr(VI) is due to its strong oxidizing properties. The toxic concentration of chromium(VI) within the human body ranges between 1.5 and 3.3 mg/kg (ATSDR 2000). Through blood transfusion, it causes damage to the liver, kidneys and

Table 9 Cation exchange capacity CEC and exchangeable cations in selected soil samples (meq/100 g)

Soil	Dominant cations (EDC)				Pollutant cations (EPC)									ΣEDC	ΣEPC	CEC*
	Na	K	Ca	Mg	Cd	Pb	Mn	As	Cr	Co	Zn	Ni	Cu			
Kombora																
UC*	7.61	2.23	7.50	4.27	0.21	0.65	1.74	2.61	7.41	0.44	6.32	0.87	1.53	21.61	21.78	43.39
% exp	17.54	5.14	17.28	9.84	0.48	1.51	4.02	6.03	17.07	1.00	14.56	2.01	3.52			
Sum%	49.80				50.20											
C*	6.64	1.17	8.80	5.69	0.22	0.65	1.74	2.61	7.41	0.44	6.32	0.87	1.53	22.30	21.79	44.09
% exp	15.06	2.65	19.96	12.91	0.49	1.48	3.95	5.93	16.80	0.99	14.33	1.98	3.46			
Sum%	50.60				49.40											
Abo Rawash																
UC*	3.35	0.56	5.61	3.56	0.07	0.29	0.69	1.33	1.21	0.18	0.41	0.34	0.40	13.08	4.92	18.00
% exp	18.62	3.11	31.19	19.79	0.40	1.60	3.82	7.37	6.73	0.98	2.29	1.89	2.21			
Sum%	72.67				27.33											
C*	2.74	0.42	3.88	1.48	0.05	0.22	1.50	1.01	1.21	0.19	0.37	0.26	0.18	8.52	4.98	13.51
% exp	0.04	3.90	36.06	13.75	0.45	2.06	13.91	9.37	11.26	1.73	3.45	2.38	1.63			
Sum%	63.10				36.90											
Kafr-Elsheikh																
UC*	14.60	1.58	3.11	4.16	0.14	0.45	5.76	4.14	3.71	0.56	1.08	1.11	0.30	23.45	17.25	40.70
% exp	35.87	3.88	7.64	10.22	0.34	1.12	14.16	10.17	9.11	1.37	2.66	2.72	0.73			
Sum%	57.62				42.38											
C*	13.81	1.47	3.22	3.35	0.12	0.32	5.14	0.65	4.26	0.62	0.83	0.94	0.31	21.85	13.19	35.04
% exp	39.45	4.20	9.20	9.57	0.35	0.92	14.68	1.86	12.18	1.78	2.36	2.68	0.88			
Sum%	62.36				83.64											

* UC uncultivated soil, *C cultivated soil, *CEC calculated cation exchange capacity (meq/100 g), *EDC exchangeable dominant cations (meq/100 g), *EPC exchangeable polluted cations (meq/100 g)

blood cells through oxidation reactions that lead to liver failure and hemolysis and may also lead to the need for aggressive dialysis. It should be mentioned that the same finding of increasing exchangeable contaminants over some dominant cations was recorded for arsenic (As) in Kombora and Kafr-Elsheikh sites.

Discussion

From an environmental perspective point of view, many human activities globally degrade earth as, for instance, PTEs accumulation in different ecosystems associated with irrigation with LQW for extended periods. Numerous organic and inorganic contaminants accumulate and perhaps run off from the soil ecosystems into drinking water sources causing innumerable problems of contamination. Mobility and destiny of PTEs in traileed soils are overseen to a great extent by both adsorption and desorption reactions at the solid–water interfaces of soil organic matter and minerals fraction (McBride and Holland 1989; Alloway 1995; Sparks 1995). Furthermore, leisureier activities such as diffusion process and PTEs formation could result in significant changes in metal speciation and solubility by the time (Barrow et al. 1989; Axe and Anderson 1997; Scheidegger et al. 1998; Elzinga and Sparks 1999; Roberts et al. 1999; Thompson et al. 2000). Soils are by nature very complex multi-component systems, in which many different ionic species in solution and solid phases with dissimilar surface properties are present (Temminghoff et al. 1995; Lee et al. 1996; Elzinga and Sparks 1999; Paulson and Balistrieri 1999; Roberts et al. 1999; Thompson et al. 2000; Voegelin 2001).

The comparison between soils collected from different sites through the kinetic study was conducted to understand the effect of the contamination source, i.e., mixture of sewage, drainage and industrial effluents used in irrigation of Kafr-Elsheikh selected farm; sewage effluents irrigation water used in Kombora selected farm and sewage effluents irrigation water used in Abo Rawash selected farm on the fate of contaminants could be found in such varied soil ecosystems. The capacity factor of the model represents the reserve of these contaminants in soil system as affected by source and the residence time of application of such contaminants in used soil. The intensity factor, however, represents the rate of contaminants desorption from the studied different sites as affected by both LQW applied and variations of soil properties of selected sites.

Kinetic models were extensively used in PTEs desorption from contaminated soils. For example, lead (Pb) release kinetically was studied by Zaghloul and Abou-Seeda (2003), cobalt desorption by Zaghloul and Gad (2006) and fluorine release by El-Dewany and

Zaghloul (2007). As shown in Tables 5, 6 and 7, according to R^2 and SE values, all the used models successfully well described Zn, Cu and Ni desorption with variation in significance. In general, all R^2 values are over 0.94** except the parabolic diffusion model for Zn release; this result means the succession of used models in describing desorption phenomena from varied ecosystems used in this work. Subsequently, the choice of the best model used as a guide for describing the kinetic results will be depended on the lower SE of used models. According to the values represented in the same tables, MFE was the best; this model showed the lowest SE values followed by Elovich and then the first-order equation. Successions of more than a model in describing the kinetic results mean different mechanisms take place in sorption of these contaminants and their distribution in soil system and subsequently their release from the system as well as the type of completion between the different contaminants in these studied soils.

The a constant of MFE indicated that higher desorption was observed in Kafr-Elsheikh soil, followed by Kombora, and the lowest values was observed in Abo Rawash soil. This result implies industrial contamination is more effective as a contamination source compared to the contamination of sewage effluents (Saber et al. 2012).

Desorption of PTEs from the contaminated soil ecosystems is a reverse phenomenon of sorption. The fate of desorption depends on the many factors such as mechanisms of contaminants retention in different soil systems, their concentrations, soil properties, etc. Generally, many factors affect these mechanisms, some related to the sorbates like electronegativity, concentrations of PTEs, valance charge, ionic radius, surface type and ionic strength, others related to the characters of the sorbents or soil ecosystem like amorphous materials, organic matter content, type and clay minerals content, pH and Eh of the soil.

It might be stated that the clay fraction in the soil could be a very good indicator for environmental contamination related to sorption/desorption and metal exchange; these results perhaps are emphasized through the data obtained from Kombora and Kafr-Elsheikh soils compared to Abo Rawash one. In addition, the time of soil exposed to contaminants is directly influencing the concentrations of these contaminants especially in high texture soils as those in Kafr-Elsheikh, Kombora compared to Abo Rawash soil.

In the present work, gained results refer to declare that the successions of more than one mechanism are controlling the release of contaminants. In Ni desorption from different ecosystems, for example, this pollutant could be bound mainly as hydroxy complex on the external basic surfaces of the clay minerals (hydrolytic

condensation). These sorption sites are available for competitive H^+ ions and could rapidly exchange the Ni or Cu ions. Although Zn undergoes to different mechanisms in its sorption reactions in used soils, Ni was exposed to specific sorption since it depends on reaction time. Therefore, the use of a kinetic rather than an equilibrium sorption mechanism could be more optional.

Conclusions

The results revealed that low-quality water (LQW) increased soil contamination with inorganic pollutants. From the rate constants of the traileed models, pollutants desorption from cultivated soils are less than uncultivated ones which mean that the uptake of pollutants takes place. Soils irrigated with mixture of industrial effluents mixed with any other types of water(s) even Nile water, potential toxic elements (PTEs) accumulation in these soils are higher than soils irrigated with sewage effluents regardless the land use of these soils. Also, only in polluted soils, exchangeable pollutant cations play a significant role in the changing our background related to relationship between CEC and exchangeable Ca, Mg, Na and K.

Abbreviations

AAS: Atomic absorption spectrophotometry; C: Cultivated soil; CEC: Cation exchange capacity; EDC: Exchangeable dominant cations; EPC: Exchangeable polluted cations; Kds: Distribution coefficients; LQW: Low-quality water; meq/100 g: Milliequivalent per 100 g soil; $mg\ kg^{-1}\ min^{-1}$: Milligram heavy metals per kilogram soil per minute; MFE: Modified Freundlich equation; PDE: Parabolic diffusion equation; PTEs: Potential toxic elements; R^2 : The coefficient of determination; SE: Standard error; UC: Uncultivated soil.

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Authors' contributions

HM helped in collecting the soil samples from the different sites, determining PTE contaminants in soils, making the kinetic models to the soil ecosystems and writing the manuscript. AZ and FA helped in finding the relationship between the fates of pollutants in relation to soil properties, discussing the obtained results and revising the manuscript. MS helped in clearing the objective of the study, writing the manuscript and revising the whole manuscript after it was written by Hesham. All authors contributed equally in the all article steps, writing the manuscript, and approved the final manuscript. All authors read and approved the final manuscript.

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Availability of data and materials

The data used for this study were obtained from determining the heavy metals and making kinetic studies in soil samples collected from three locations, Abo Rawash, Kombora farmlands (Giza Governorate) and El-Khasha site (Kafr-Elsheikh Governorate), Egypt, which are varied in the source of soil contaminants. The data are available from the corresponding author upon reasonable request.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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