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"Study of Cadmium chemistry in some Egyptian Soils"

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6. Summary

As demand for water hits the limits of finite supply, potential conflicts are brewing between nations that share Tran's boundary freshwater reserves. In Egypt, the acceleration of economic and demographic development, with rapid urbanization, growing industrialization and agriculture, has stepped up the pressures on the country's water resources.

Therefore, the main objective of the present study is to evaluate the influence of using sewage water effluent in irrigation consecutively for up to 100 years on Cd chemistry in soil. 1) Assessing the state of Cd in sewage effluents irrigated soils.2)Studying factors affecting Cd mobility in soil profiles. Fractionate Cd sequentially to its various pools and calculating mobility factor.3) Determining active portion (free) of Cd in soils.4)Determining the solid phase which controlling solubility of Cd in the soils.5Evaluating some of remedial techniques for Cd.6)Employing some of Ecological Risk Assessments.

This study was carried out on 3 sites from El-Gabal El-Asfarfarm(control,70yrs and100yrs) irrigated with sewage effluent.

The description of these experiments is as follow:-

The Egyptian Wastewater Treatment Plant namely Gabal El-Asfar (GAWWTP) in Cairo is one of the largest WWTPs in the world. It is located in the Eastern desert in the southeastern edge of Al Qaliobia governorate, this plant received sewage effluent from Great Cairo since 1911. The soils of this plant where selected for the present study because it represent long-term use of sewage effluent water in irrigation.

The sewage effluent water sample (4 separately liters) were carefully taken from the farm, mixed and were stored at less than 4°C and the Nile water sample. for until the following analysis carried.

Three soil profiles were dug to the depth 120 cm ;the first site reflected non cultivated soils (control), while the second and third profiles representing soils irrigated continuously with sewage effluent water for 70 and 100 years, respectively and denoted as 0-yrs(control), 70-yrs, and, 100-yrs soils respectively.

Each soil profile was sampled at 30 cm increments. At each depth, three disturbed sub – soil samples were collected to make a composite soil samples for (chemical analysis) and triplicate undisturbed soil samples were also collected for (physical analysis).

The obtained results show that:-

1-Wastewater and Nile water:-Data reported in Table (3) indicate that, the pH values for the tested sewage water (Ww) were (7.87) which were slightly basic. It was higher than that of Nile water by (0.57 unit), the obtained pH of Ww was within the permissible limit (PML) for irrigation, which cited between (7 to 9), (FAO, 1976).and also the Nile water. EC., of the Ww exceeded than that in Nile water by (246.15%), indicating that this effluent was saline in nature and was lower than the MPT which suggested as (FAO.1976).

The data referred in the filtered sewage water (Ww) that sodium was the dominant cation (6.38meq/l) followed by calcium (3.3meq/l),and magnesium (2.01meq/l), while the sequence (in meq/l) in Nile water was; calcium (2.095) > magnesium(0.68) and sodium (0.64). Furthermore, chloride was the dominant anions (8.44meq/l) in (Ww) followed by bicarbonate (3.00meq/l), while sulphate contributed small portion(2.05meq/l)

, whereas the sequence in Nile water sample(in meq/l) was ; SO_4^{-2}(2.17) > HCO_3^-(1.29) >Cl^-(0.40), besides the calculated Sodium adsorption ratio (SAR)for Ww accounted 5.55, meanwhile it was 0.76 in Nile water. SAR value of Ww was within the levels (6-9) which established by (FAO.1992).

The concentrations of some macro nutrients in Ww are listed in Table (3). N concentration in Ww as shown from the Table was more than 5.7folds that of Nile water. Moreover, that amounts of water nitrate concentration in Ww reached to (24.01ppm).Also, the concentration of NH_4Ww as exceeded than that in Nile water sample by more than 2.2 folds and higher than PMLcited by (5ppm), and also P and K values of Ww exceeded that Nile water By (16.1and 3.58 folds, respectively) .

Heavy metals in Ww (in ppm) were follow the sequence; Fe(1.116)>Zn (0.76)>Cu (0. 63)>Mn(0.42)>Cd (0.08) .While the sequence in Nile water was ; Fe (0.065ppm)>Cu=Zn=Mn(0.015 ppm) >Cd(n.d).

2-Effect of Long-term Sewage Irrigation on Soil Physico-chemical Properties:-

I-Texture Characteristics:-

The nature texture grade of 0-yrs soil is almost sandy, in all successive soil depths. Sand fraction is ranges from (84.15 to 87.22 %), followed by Silt (15.79 to 12.73 %), while clay fraction accounted small portion (0.06 to 0.05%).The texture after irrigated by 70- yrs and 100-yrs show in Table (4) that appreciable high content of clay fraction occurred only in the upper soil layer (0-30cm), it amounted (21.4%),(22.3%) respectively**,** Reflecting accumulation of fine particles carried by the disposal wastewater.

Ii-Bulk Density(BD):

Soil BD values in the top soil depth (0-30cm) of 100-yrs, 70-yrs, and 0-yrs soils were (1.45, 1.47, and 1.57g/cm^3), respectively. It is obvious from these data that as period of sewage water application increases, soil BD values decreased.

Iii-Hydraulic Conductivity (HC):-

The influences of sewage water irrigation on the tested soils are listed in Table (5). It is obvious from the data that HC values of 100-yrs soils(X= 53.36mm.h^{-1}) is less than in 70-yrs (X=58.44 mm.h^{-1}) and 0-yrs soil (X=136.5 mm.h^{-1}), especially in the surface layers, reflecting the effects of disposal of sewage water onto soils.

Iv- **Soil Moisture characteristic Curve (Available Water):**

Results of available water capacity (AWC) of the tested soils are presented in Fig.(1).The Figure refer that continuous application with sewage effluent greatly influenced on AWC, especially in the surface soil layers. The Average of AWC are (9.605, 9.605 and 6.29%) in 100-yrs, 70-yrs,and 0-yrs soils, respectively.

v- $CaCO_3$ (Calcium Carbonate Content) of Soils:-

$CaCO_3$ content of soil irrigated with Ww reduced as increasing period of application. $CaCO_3$ content ranges from 2.76 to 1.53 %after irrigated by 70-yrs and 100-yrs soil samples, respectively compare with 0yrs soil.

Vi- Organic Matter Content (OM):

The highest OM was recorded in 100-yrs soil (ranged from 3.4 to 2.00) followed by 70-yrs soil (ranged from 1.78 to 1.03). It is obvious from the data that Long-term use of Ww for irrigation results in increased in soil OM.

Vii-Soil pH:-

The pH values of 0-yrs soil are neutral to slightly alkaline in nature with an average pH value fluctuated around (7.31) increase to (7.63), (7.7) after irrigated by 70-yrs and 100-yrs soil samples, respectively.

These results confirmed that long – term application of Ww caused increasing on Soil pH. Such effect may be attributed to the high content of basic cations viz. Na^{+}, $Ca^{2+}$and Mg^{2+} in the Ww.

Viii-Soil Salinity and Sodicity :-

As a general shown from Table (4), 100 –yrs soil had the highest EC value (x = 1.39 dSm^{-1}), followed by 70 – yrs soil samples (x=1.027 dSm^{-1}), and 0-yrs soil (x= 0.337 dSm^{-1}).The increase in EC values could be attributed to the predominant irrigation by saline Ww.

Viii-Soluble salts:-

Indicate that the continuous use of sewage effluent in irrigation had only little effect on salt accumulation obviously, Na^{+} concentration was very high particularly, followed by Ca^{++}then Mg^{++} and K^{+} and anionic composition of salts in soils Cl^{-} was the dominant anion, followed by SO_4^{--} and HCO_3.

x- Exchangeable Sodium Percentage (ESP):-

The calculated Exchangeable sodium percentage (ESP) of the studied soils refer that only remarkably increase in ESP was occurred in the top soil layers of 100- and 70-yrs soil**.**

3-Soil Macronutrient concentrations in the tested soils:-

A-Total-N:-

Data of Total soil N in the studied soils are listed in Table (7). As shown from the data, in 0-yrs soil total nitrogen range between (45.5 to 2 4.8 ppm), also , on mean basis , available N values (NH_4 and NO_3) represent (4.9 and 76.92%) from its total. In 70-yrs soil NH_4 and NO_3were (21.8 and 217.6ppm).respectively, while they were (22.4and 239.2ppm) in 100-yrs soil, respectively

The average values of total soil N in 70-yrs and 100-yrs soil samples were (291.74 and 328.65ppm, respectively, as clearly obvious from the present results that total nitrogen increased with consistent use of sewage water effluent.

B-Available- P:-

Data of available P are presented in 0-yrs throughout soil profile is low. It ranges between (1.34 and 1.08ppm),While in disposal sewage water soils, the highest value is recorded for top depth of 100-yrs soil (10.75ppm), followed by the top soil depth of 70-yrs (3.53ppm).

C-available-K: -

Data of mean value of available K in 0-yrs, 70-yrs and 100-yrs soils are represented (34.91, 348.51, 628.95) respectively. It is clearly shown that sewage disposal soils exhibit the highest values of available k.

4-Heavy Metals (HM) in the Soils:-

1-Total contents of Fe, Mn, Zn, Cu, and Cd in different layers of the investigated soils profiles are shown in Table (8).

The mean values of the tested soils reveal that soil HM contents differ according to period of using sewage water for irrigation. The mean value of tested metal contents in 70-yrs soil and100-yr, the data reveal, that Fe concentrations increased from (10814.64 to 12465), Zn by (90.43 to 152.15), Cu by (32.6 to 99.06) Mn by (22.77 to 98.3), and Cd by (5.57 to 7.81), respectively, the elevated contents in sewage effluent soils compared to the control soil mainly due to repeating irrigation with sewage effluent water.

The average abundance order of heavy metal contents are: Fe>Zn>Cu>Mn>Cd(10814.64>90.43>32.6>22.8>5.57),(12465.00>152.15>99.06>98.3>7.81) mg/kg, in 70,100-yrs soils, respectively.

2- DTPA- heavy metals in the tested soils data presented in Tables (8) show the concentrations of DTPA-of Fe, Zn,Cu,Mn, and Cd.

The results show that the highest extractable concentrations of the tested metals are observed in the top layers, the extracted Fe, Zn,Cu,Mn and Cd (0-30 cm)by 3008.98 to 3078,53.37 to 124.5,18.8 to 55.8,8.9 to 50.8 and 0.923 to 1.26 ppm for 70-yrs and 100yrs respectively.

3-Zn – Equivalent calculation (soil quality criterion index):-

The calculated Zn – Equivalent of the different sewaged soil are presented in Table (9). The data show that means Zn-equivalent values varied between (70.70 to 139.19) in 70- and 100-yrs soils, respectively. It appears that the values of Zn equivalent are in the safe level.

4-Distribution of cadmium in soils:-

The present data show that Cd distribution in 0-yrs soil (control) was almost constant along soil depths. Its concentrations accounted (1.01, 0.97, 0.61 and 0.66 mg/kg) in the successive soil layers. The distribution of Cd in the sewaged soils in Fig.(3) reveals that the highest value of Cd recorded in the surface soil later (0-30 cm) and extent in subsurface (30-60) layer, then it sharply decreased with depth.

In 70-yrs soil Cd contents in the underlying soil layers accounted (79.90, 25.88 and 12.75%) compared with Cd contents in surface layer (0-30cm).Meanwhile in 100-yrs soil, it accounted(76.32, 26.39 and 20.04%) of Cd content in surface layer), respectively. It is obvious from the present data that most of Cd restricted in surface soil, that is may be associated to high pH of these layers as well as high contents of adsorptive materials in that layer and Clay contents.

5- Fractionation of Cd in the investigated soil samples:-

The results of Cd fractionation of the tested soils are shown in Table (10). Its indicate from the table that the sum of the various Cd factions accounted (on mean basis) 90.67, 88.71, and 89.51% of their corresponding totals. This indicates that the method used in this study is reliable and repeatable.

The data refer that the order of mean abundance of Cd factions in 0-yrs soil were residual F. (69.94%) followed in decreasing order by oxide F.(9.95%) > organic F.(9.33%) > carbonate F. (6.53%) >exchangeable F.(4.26%) ,of their totals.

In 70-yrs soil, the sequence (as shown from the Table10) was residual F. (59.38 %) followed in decreasing order by oxide F. (11.93 %)

>carbonateF.(11.43%)>Organic F. (10.87%) >exchangeable F.(6.40%), of their totals.

Whereas in 100-yrs soil ,residual F. (55.11%) followed in decreasing order by oxide F.(13.44%) ≈organic F.(13.21%) > carbonate F. (10.65%) >exchangeable F. (7.60%), of their totals, the percentages of all Cd fractions decreased sharply with increasing soil depth.

6-Mobility Factor:-

In the control soil (0-yrs), MF ranged from 18.64 to 21.27%, x=20.73%) , while it ranged from (27.78 to 31.33%, x=29.75%) and (26.8% to 39% , x=31.68%) in 70-yrs and 100-yrs soils, respectively.

These results confirmed that Cd mobility index (MF) increased with continued use of sewage effluent water for irrigation. Under these circumstances, it is suggested that Cd has high potentials to be mobile and consequently posing environmental hazards.

In all the tested soils , the observed values (Table10) referred that MF value of Cd was high in the surface layer and generally decreased with increasing depth that because this layer exposed directly to disposal sewage effluent water.

7-Influence of remediation materials on Cd fraction :-

As shown from the Figs(8,9) that the majority of Cd was associated with residual fraction the mean concentrations of that fraction accounted 63.26 % and 61.79% in ZVI – and RP- amended soil, respectively. While the second dominant fraction was organically bounded fraction. It constituted 14.17% in ZVI- and 13.8% in RP- amended soil.

Moreover, the other fractions in ZVI- amended could be ranked as follows; exchangeable (10.71%)> carbonate (7.22%) and oxide f (4.28%).

While the sequence in RP- amended soil was carbonate f (8.61%)≈ exchangeable f (8.46%) and oxide f (7.35%).

Furthermore , comparing the results of Cd fractionation prior and after amending , the present data indicate that in ZVI- amended soil residual and exchangeable fraction increased over untreated soil (0yrs-soil) by 38.2 % and 7.13% , respectively , While oxide , carbonate, and organic were less than its corresponding values in the untreated soil (C_0-soil) by 71.45,48.39 and 5.40% , respectively.

Meanwhile in RP- amended soil, only the residual fraction was increased over its corresponding value in untreated soil (0yrs-soil) by 34.24% due to amending, while the rest of fractions were less than that in the untreated soil. The magnitude reduction was associated by oxide F (51.02%) > carbonate F(38.49%) > exchangeable F(15.41%) and organic F (7.88%).

So, in general speaking, the data reveal that amending Cd-contaminated soil either by ZVI or RP lead to increase of residual Cd on the expense of the other Cd fractions.

The present data revealed that ZVI material was more effective than RP material since the Cd residual fraction increased in ZVI-amended soil by (38%) , over its corresponding value in untreated soil , while it increased by about (34%) in RF- amended soil.

8-Measurement Cd activities in the tested soils:-

The measured Cd^{2+}activities were negatively correlated with pH values. For example the activity of Cd in the uncontaminated soil sample was8.1548E-10 M/l (pCd =9.0885871) ,with a pH of 7.75 , and increased to 8.11333E-09M/l ((pCd^{2+}=8.090801) in the contaminated soil sample with pH 7.44.

The influences of soil contamination on the activities of Cd^{2+} in soils were also investigated in the present study. As shown from the Table (11), pCd^{2+} values were 9.08 and 8.09 in the control and contaminated soil sample, respectively, indicating that the continual use of sewage effluent water in irrigation increased Cd^{2+}activity by 9.94 folds than the control soil sample.

They also added that continual use of sewage effluent in irrigation decreased the activity of both of Pb and Cd than the control by (26% and 72%, respectively), meanwhile Cd^{2+} activity increased by about 8 times due to sewage effluent application.

Also, It is clearly obvious from the Table(11) that the tested remedial materials (Zero-iron and Rock phosphate) with the three rates of amending (1, 2,and 3% w/w) had great influences on the values of Cd activities. As shown from the Table , the values of log Cd^{2+} activities varies widely among the tested soil samples ;in the Zero valent iron– remediated soil samples , the activities of Cd being from(M/l); 4.65006E-09, 3.7353E-09 , and 4.61439E-09in C1 , C2, and C3 , respectively which represent about 57% , 46%, and 56 %, respectively compared with Cd^{2+} activity of the contaminated soil sample.

Meanwhile in rock phosphate– remediated soil samples, the Cd activities (M/l) were; 6.89868E-09, 6.00091E-09, and 5.93551E-09 for C1,C2, and C3 , soil sample, respectively, which represent only 85%, 73 % , and 73%, respectively, compared with Cd^{2+} activity of the contaminated soil sample.

From the previous results, it could be concluded that the Zero valent iron material was more effective in decreasing Cd^{2+} activities than that of rock phosphate material.

9-Predicted solid- phases which controlling the solubility of Cd in the soils:-

Plotting Fig.(18) the calculated values of Cd^{2+}on the Cd solubility mineral diagram indicated that Cd^{2+} value were lie below the constructing minerals. This suggested that other possible solid phase of cadmium may be controlling its activity in that soil.

10-Environmental Risk Assessment:-

The contamination factor (CF_s) values of the tested soils are listed in Table (12).Interpreting the CF_s values as suggested by (Hakanson 1980) indicate that the 0-yrs soil samples were categorized as low contaminated ($CF < 1$), except at (30-60 cm) depth, which was moderate contaminates ($1 \leq CF < 3$). This exception may be attributed to the effect of leaching of Cd from the top soil layer and accumulated in the subsoil layers.

In the contaminated soil samples the CF_s values of Cd ranged from (17.30 to 9.65), Thus it in the very high contaminated category in the surface and subsurface soil layers (0-30 and 30-60 cm),($CF \geq 6$), and in considerable contaminated category at both the (60-90 and 90-120 cm) soil layer, ($3 \leq CF < 6$). Also , it worth to mentioned that ,the present CFs values in the contaminated soil decreased with increasing soil depth.

The CF_s values in remediated soil sample (top layer of 100yrs soil) after remediation either by iron filling material or rock phosphate material, were almost equal to its CF corresponding values before remediation processes ($CF \approx 17$). That is because CF numerical formula relies mainly on total metal content which it not change appreciably by the employed remediation processes (precipitation and /or adsorption techniques). Corollary to that it may be concluded that CF index is not reliable and

suitable for characterizing precipitation technique of heavy metal remediation, however, it still effective for assessing pollution hazards.

The calculated geo-accumulation index (Igeo) values of Cd in of the studied soil samples are listed in Table (12). As indicated in the results, the Igeo values for the Cd metal in the 0-yrs soil samples (the control soil) were characterized as uncontaminated(Igeo less than 1) in all the tested soil depths. Meanwhile in contaminated soil samples , Igeo values ranged from 2.28 in the surface soil layer (0-30cm) to 0.46 in the last tested soil layer (90-120cm), consequence to that this soil could categorized as moderately to highly contaminated soil in the surface soil sample($2 < Igeo \leq 3$)to uncontaminated to moderately contaminated($0 < Igeo \leq 1$)in the last soil layer.

Irrespective the tested remedial materials or the used concentrations, the Igeo values in the remediated soil sample (Table12) were almost equal to that for the corresponding surface contaminated soil (about 2.25) , consequence to that it may be confirmed that Igeo index is not considered as convenient tool for evaluation of remediated soils but at the same time it is considered as effective tool for evaluating pollution intensity.

Single Pollution Index (PI) was also calculated to assess the pollution degree of Cd in the tested soils and it was classified according to Table (2).

As shown from the Table, PIs of Cd in the uncontaminated soil (0-Yrs) soil were ranged between (11.11 to 35.92, x=23.52), referring that this all soil depths classified according PI categorized as low risk ($PI< 40$). Meanwhile in the contaminated soil samples it was in very high risk in the surface and subsurface layer ($PI \geq 320$) , and considerable risk in the third and fourth soil layers($80 \leq PI< 160$).

As aforementioned in the previous employed indexes, the present data show that SPI not changed appreciably in the remediated soil, it was categorized as very high risk. (SPI $\geq$ 320) as well as in the polluted soil. Consequence to that it may be concluded that ecological indexes which total metal content involved in its calculated formula not able to assemble or evaluate precipitation or adsorption remedial techniques, but it could to quantified pollution hazards only.