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Total Iron and Manganese Status and Availability under Various Land Use

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Abstract: Current research has been focused on the influence of land use on Fe and Mn status in Sohag governorate soils, South Egypt. Soils were sampled from sites including the cultivated floodplain, reclaimed lands, Wadi deposits and the wastewater farmlands at El-Dair, and El-Kola. For these samples total and DTPA-extractable Fe and Mn were determined. Total Fe ranges 3.7-9.3%, 1.3-12.3%, 2.5-5.9% and 1.9-7.0% in cultivated floodplain, reclaimed, wadi deposits and wastewater farmland at El-Kola, respectively. Total Mn in the cultivated floodplain and reclaimed lands ranged from 604 to 2193 mg kg^{-1} and from 275 to 3505 mg kg^{-1} respectively, while, in wadi deposits is oscillating in the range 449-1181 mg $kg^{-1.}$ Fe and Mn exhibits positive correlation with clay and organic matter content while it is negatively correlated with the carbonate content. The wastewater disposal practice leads to abnormally elevated values of the available Fe in the reclaimed lands. In the lands applied for wastewater disposal at El-Kola and El-Dair, available Fe ranges from 3.5 to 526.0 mg kg^{-1} and 25.4-878.3 mg kg^{-1} respectively. This suggests wastewater disposal increased the risk of Fe loss to under ground water. Available Mn in cultivated floodplain soils ranges from 17.9 to 142.3 mg kg^{-1}, but in the reclaimed lands and wadi deposit range from 4.3 to 269.0 and from 1.66 to 144.7 mg kg^{-1} respectively. The wastewater disposal practice has no marked effect on the soil content of available Mn.

Key words: Iron and manganese availability, land use.

INTRODUCTION

The soils distributed in Sohag area were differentiated into four main sectors of various land uses. These are: cultivated floodplain, reclaimed lands, wadi deposits, and lands used for wastewater disposal. Chemical analysis of soils is considered to be an important tool within the framework of fertility forensic investigations (Meiggs, 1980; Forstner and Salomons, 1980; Alderton, 1985).

Iron in soils is mostly presented either as a component of various minerals (pyroxenes, amphiboles, biotite and olivine), or in the form of amorphous oxides and hydroxides, (Lindsay, 1972). Several investigators studied the total iron content of Egyptian soils. Among them, Holah (1977) found that the total iron ranged from 1.09 to 8.30% with a median of 5.95%; the highest content recorded in the alluvial soils while the lowest characterizes the sandy and calcareous soils. However, a wide range of total iron content was found by Metwally and Abdellah (1978), where the total iron content varied from 1.7 to 12.9% and 2.8-13.8%, respectively. Also, they found that there was significant positive correlation between clay and total iron and a significant negative correlation between total carbonate and iron content. Total iron in the soils of Sohag Governorate falls in the range 1.16 to 5.83% (Abd El-Razek *et al.,* 1984a). They also found that the content of total iron was highly correlated with soil texture. Similar results were obtained by El-Sebaay (1995) and Ibrahim *et al.* (2001). Manganese in soils originates primarily from the decomposition of ferromagnesian minerals. Soils derive all their manganese content from the parent materials, and the concentrations found in mineral soils reflect the composition of these parent materials. Regarding the total content of manganese in different soils. Berrow and Reaves (1984) reported an average of soil manganese as 450 mg kg^{-1}. They considered this value to be as a background content in uncontaminated soils. In the Egyptian soils, a study on soils of Middle and Upper Egypt, Kishk *et al.* (1980) found that total manganese ranged between 111 to 1187 mg kg^{-1}, the highest values were found in the fine textured alluvial soils and the lowest values in the sandy and calcareous ones. Rashad *et al.* (1995) found that the content of total manganese in the normal alluvial soils

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of Delta ranged between 720 and 1080 mg kg^{-1}, with an average of 926 mg kg^{-1}.

The aimed of the current research is to find out the reserve and available Fe and Mn in the selected soils and their relationships to land use in Sohag soils, Egypt.

MATERIALS AND METHODS

The study area is represented by the Nile basin stretch extending between latitudes 26° 24 16 and 26 ° 36 16 and bordered from both the east and west by the higher relief Eocene limestone plateau; Sohag city is situated in the middle of the area (Fig. 1). Sampling sites were proportionally distributed representing the main land uses in the study area with respect to their geographical distribution. Accordingly, a semisystematic sampling scenario, with an interval of about 5 km, was followed to cover the whole area. A well-constrained Global Positioning System (GPS) was used for navigation to record the sampling sites accurately. Two hundred twenty six samples distributed through 144 sampling sites were collected from the concerned land uses. Regarding the cultivated floodplain, the reclaimed lands and the wastewater farmlands at El-Dair, both the surface (0-20 cm) and sub-surface layer (20-40 cm) were considered. On the other hand, soil samples were collected from the surface layers of the wadi deposits and wastewater ponds at El-Dair and El-Kola. The sampling procedure described by USDA (1996) was followed. The collected soil samples (n = 226) were air-dried, then crushed to pass through a 2mm sieve. A portion was kept as bulk sample. The other portion was ground by the plastic mortar to pass through 63 µm sieve and designated as fine fraction. The bulk samples (2mm) were used to determined: Particle size analysis of the soil samples using pipette method as described by USDA (1996). Soil pH, Calcium carbonate content (CaCO3), organic carbon content, cation exchange capacity (CEC) and soil texture were also measured (Table 1).

Table 1: Physical and chemical properties of the selected soils as per their occurrence in land use.

Property	Cultivated floodplain	Reclaimed lands (n=65)	Wadi deposits (n=17)	Waste water disposal	
				El-Kola (n=29)	El-Dair (n=45)
Sand (%)	3.0 -67.0	12.0 - 97.0	35.0 - 95.0	15.0 - 94.0	5.0 - 95.0
Silt (%)	14.0 -84.0	1.0 - 82.0	3.0 - 55.0	5.0 - 81.0	1.0 - 90.0
Clay (%)	7.0 -54.0	1.0 - 35.0	1.0 - 10.0	1.0 -14.0	1.0 - 20.0
CEC cmol	35.0 -73.0	11.0 -50.0	7.0 - 33.0	8.0 - 95.0	5.0 - 61.0
pH (1.25)	7.4 -9.0	7.0 - 9.1	7.8 - 8.7	6.9 - 8.5	5.5 8.1
OM (%)	0.5 -2.5	0.03 - 8.6	0.02 - 2.4	0.01 - 13.7	0.10 - 53.7
Ca CO_3 (%)	1.1 -10.3	3.3 - 67.4	6.3 - 58.4	1.1 - 59.5	0.6 - 15.2

Total Fe and Mn was determined by digesting 0.5g air-dried sample (<63µm) in Teflon beakers using a concentrated acid mixture of 3ml HNO_3 (69%), 2ml $HClO_4$ (40%) and 10 ml HF (40%). The diethylenetriamine penta-acetic acid (DTPA) extractions were performed following Lindsay and Norwell (1978), where 10g of ground air-dried soil sample (<63µm) was mixed with 20 ml of 0.005M DTPA (pH = 7.3). The suspension was orbitally shaken for 2 hours and then filtered through a 0.45µm filter. Atomic Absorption Spectrophotometer (AAS) was utilized for the determination of Fe and Mn concentrations in both the digests for total and DTPA- extracts.Geochemical maps have been constructed by means of the SURFER 8 program (2002) distributed by Golden Software Inc. However, analysis of variance (ANOVA) was performed to quantify the similarity and dissimilarity of variables among the sample groups.

RESULTS AND DISCUSSIONS

Total Fe in cultivated floodplain ranges from 3.7 to 8.2% and from 5.0 to 9.3% in surface and sub-surface layers respectively (Table 2) and figure (2). Although the low variability of iron in both the surface and subsurface (sd.= 0.94 and 0.78, respectively), a significant difference was found among the two layers (p=0.003). Although Fe content of the cultivated floodplain is significantly higher than that of the average shale (4.7%, Turekian and Wedepohl, 1961) it is strongly similar to that of the PAAS (6.3%, Taylor and McLennan, 1985). The relative enrichment of iron in the soils of the Nile floodplain is controlled by the source rock composition, where they are derived principally from the Ethiopian basaltic plateau (Omer, 1996). In addition, the relative higher content of clay in these soils is another factor. Iron content in the reclaimed lands range from 1.8 to 12.3% and from 1.3 to 7.8% in surface and subsurface layers respectively. Total Fe of the surface layers is very close to that of the cultivated floodplain, whereas its level in the sub-surface layers is very akin

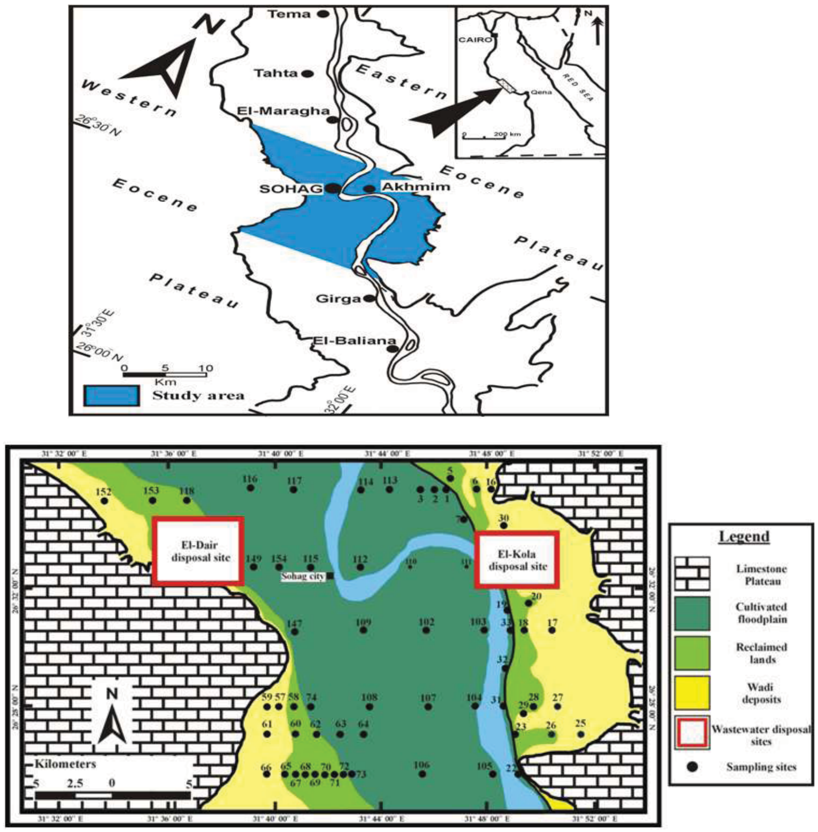

Fig. 1: Maps of the study area showing the soil sampling sites.

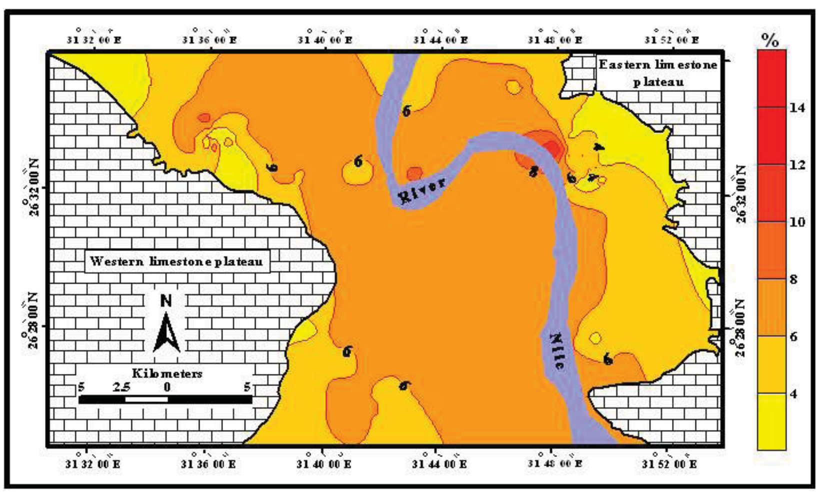

Fig. 2: Geochemical contour map showing distribution of the total iron content in the studied soils.

to that of the adjacent wadi deposits. The elevated level of iron in the surface layers follow the clay fraction content, whereas its lower concentration in the sub-surface layer is governed by the higher content of carbonate fraction. Wadi deposits exhibit significantly lower iron content (2.5 to 5.9%.) than the cultivated floodplain ($p<0.001$); and negatively correlated with the carbonate content (El-Gala and Hendawy, 1972). The total Fe content of soils used for wastewater disposal at El-Kola (ponds and wetlands), it ranges from 1.9 to

7.0% with a mean value of 4.6%. Such level of iron, on the average, is considerably lower than that of the cultivated floodplain whereas it is very close to that of the nearby Wadi deposits ($p = 0.235$). Total content of iron in the lands applied for wastewater disposal at El-Dair, varies between 2.3 and 4.7% in the surface layers of the wastewater farmlands, whereas it ranges from 1.2 to 6.7% in the sub-surface layers. The total Fe content exhibits insignificant difference between the surface and sub-surface layers ($p = 0.193$), whereas a negative correlation ($r = 0.44$) was found with organic matter. The mentioned results confirm the natural geogenic source of Fe and reflect the dilution effect of organic matter in the surface layer and the carbonate in the subsurface one. The total Fe measured in the surface soil layers of the wastewater ponds at El-Dair displays a wide range varying from 1.4 to 13.9% as indicated from the higher value of standard deviation (sd.= 3.3). Fe is positively correlated with clay content ($r=0.52$), while it is negatively correlated with the carbonate and organic matter content ($r = 0.44$ and -0.23, respectively). The exceptional abnormally elevated level of Fe recorded in some samples might be attributed to the corrosion of the transporting pipes by the chemically reactive wastewater, (Abd El-Razek *et al.,* 1984a ; Attia, 1988; El-Sebaay, 1995 and Ibrahim *et al.,* 2001).

Table 2: Summary of descriptive statistics for the total Fe (%) and Mn (ppm).

	Depth	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
	(cm)	Cultivated		Reclaimed		Wadi deposits		Wastewater		Wastewater	
	00-20	6.66	1312	6.04	1293	4.12	895	4.56	1058	3.45	1121
Mean	20-40	7.4	1378	4.24	968	4.14	923	4.77	850	4.04	1065
	00-20	6.81	1305	6.16	1299	2.54	449	1.87	258	3.59	884
Median	20-40	7.45	1365	3.95	1035	5.94	1181	7	5418	3.87	1074
	00-20	3.71	604	1.75	694	0.99	209	1.32	906	2.26	583
Minimum	20-40	4.95	1055	1.29	275	3.4	771	3.53	773	1.15	482
	00-20	8.16	2193	12.3	3205	4.8	1043	5.7	946	4.69	4213
Maximum	20-40	9.26	1885	7.84	1355	4.12	895	4.56	1058	6.69	1421
	00-20	0.94	246	1.82	413	4.14	923	4.77	850	0.78	873
Sd.	20-40	0.78	150	1.55	277	2.54	449	1.87	258	1.5	274

Data presented in (Table 2) and (Fig. 3) illustrate that, the total Mn in cultivated floodplain ranged from 604 to 2193 mg kg^{-1} and from 1055 to 1885 mg kg^{-1} in surface and sub-surface layers respectively. Insignificant statistical difference was reported in Mn content through the two layers ($p=0.182$), (Ghanem *et al.,* 1971; Abd El-Razek *et al.*,1984b). Such relative higher content of Mn in the floodplain is attributed to its elevated level in the parent source rocks particularly the basaltic rocks of the Ethiopian plateau, where Mn is mainly present substituting iron in the structure of ferromagnesian silicate minerals (Gilkes and McKenzie, 1988).

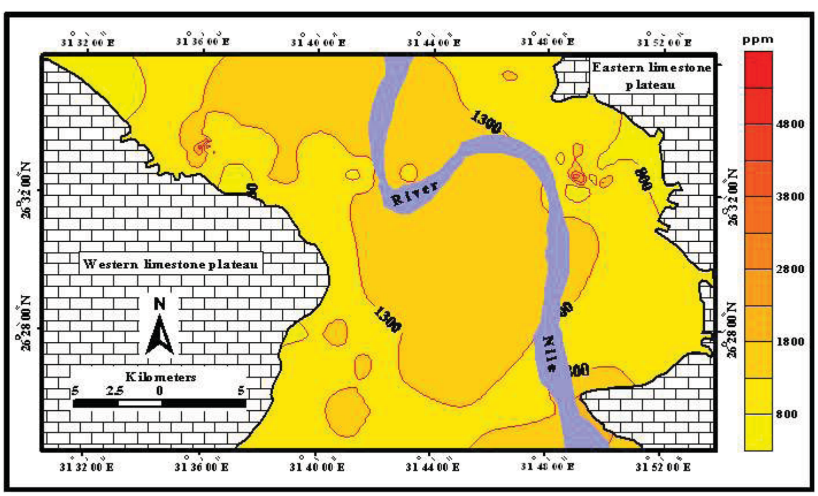

Fig. 3: Geochemical contour map showing distribution of the total manganese content in the soils of the study area.

In the surface layer of the cultivated floodplain, Mn shows significant positive correlation with Fe (r = 0.52). This behavior may reflect the natural association of Mn with the former metals and point to the occasional anthropogenic impact on the later ones. However, Mn content of the reclaimed lands range from 694 to 3505 mg kg^{-1}, and from 275 to 1355 mg kg^{-1} in surface and sub-surface layers respectively. Although no significant difference was found in Mn content through the surface layers of the reclaimed lands and the cultivated floodplain (p = 0.810), Mn shows a diverse behavior among the two layers. In the surface layer of the reclaimed lands, Mn shows a significant positive correlation with the organic matter (r = 0.71). On the other side, Mn has a significant negative correlation with the carbonate (r = -0.39) whereas it displays a very weak relation with iron. This behavior reveals that Mn is substantially influenced by the reclamation practice, particularly the addition of agricultural amendments. In the sub-surface of the reclaimed lands, Mn possesses a significant positive correlation with Fe (r=0.83) while it is negatively correlated with carbonate (r=- 0.80). Such behavior of Mn reflects its geogenic generation in the sub-surface layer and that it is incorporated principally in the argillaceous fraction transported from the Pliocene clays. So, the carbonate fraction has a dilution effect on the Mn distribution. Total Mn content in Wadi deposits is oscillating in the range 449-1181 mg kg^{-1}. No significant difference was reported in the Mn concentration through the eastern and western sides of the Nile Valley (p=0.741). Concerning the total Mn in the lands under wastewater disposal at El-Kola varies from 258 to 5418 mg kg^{-1}. The average content of Mn in these soils is relatively lower than its level in soils of the Nile floodplain, but there is a considerable resemblance with its content in the wadi deposits. In addition, Mn shows no significant correlation with any of the other variables suggesting its independent and complicated behavior in the considered soils. The total Mn content estimated in wastewater farmlands at El-Dair fluctuates between 583- 4213 and 482-1421 mg kg^{-1} in surface and sub-surface layers respectively. The stated behavior of Mn in soil of the wastewater farmlands reveals that it is significantly affected by the farming practice in the surface layer where a considerable part is incorporated in the organic matter fraction. Contrarily, the major part of Mn in sub-surface layer is included in the lithogenic fraction particularly the argillaceous portion. Such conclusion can be confirmed by the dilution effect of the carbonate fraction in both of the two layers. The total Mn estimated in soils of the wastewater ponds at El-Dair ranges between 557 and 2434 mg kg^{-1}. The average Mn content in these soils is comparatively lower than that of the cultivated floodplain whereas it is extremely similar to that of the wadi deposits. Mn exhibits positive correlation with the clay fraction and organic matter content (r = 0.42 and 0.36, respectively), while it is negatively correlated with the carbonate content (r = -0.35). Therefore, it can be concluded that although the major part of Mn is associated with the lithogenic clay fraction, a significant portion is incorporated with organic matter.

Dtpa-extractable Metals:

Although the elevated level of total Fe in soils of the floodplain, the DTPA-extractable fraction is relatively low (Table 3). This indicates that the major part of Fe is firmly incorporated in the crystal lattice of Fe-bearing mineral phases (e.g. ferromagnesian minerals and Fe oxides). The estimated DTPA-extractable Fe in the reclaimed lands range from 5.4 to 463.8 mg kg^{-1} with the elevated mean value which is twice higher than the median, reflects the presence of abnormally elevated values of the DTPA-extractable Fe in some sites. Extremely elevated level of DTPA-extractable Fe was found in sites Nos. 71 and 124 (197.5 and 463.8 mg kg^{-1}, respectively). As stated above, site No.71 is frequently used for manual wastewater disposal, while site No.124 is situated very close to El-Dair and located in lands often irrigated with wastewater (Fig. 4) So, the elevated DTPA-extractable fraction of Fe is evidently related to the wastewater disposal practice. Available Fe in normal alluvial soils of Upper Egypt, ranged from 0.35 to 26.6 mg kg^{-1} with an average of 8.0 mg kg^{-1}(Abd El-Razik *et al.,* 1984b). Rabie *et al.* (1996) reported that available Fe increased very much especially in the surface layer (66.2-75.1 mg kg^{-1}) due to irrigation with liquid wastes. El-Nashar (1985) found that available Fe increased 17 folds due to irrigation with sewage effluents. Levels of the DTPA-extractable Fe in the Wadi deposits of the study area range from 5.4 to 15.7 mg kg^{-1}. Wadi deposits exhibit significantly lower Fe content than the cultivated floodplain (p<0.001). With respect to the distribution manner of DTPA-extractable Fe in the lands applied for wastewater disposal at El-Kola, it ranges from 3.5 to 526.0 mg kg^{-1} with a mean value of 120.8 mg kg^{-1}. The higsh value of standard deviation reflects the very wide range and the extreme variability of Fe bioavailability in these soils. The average content of DTPA-extractable Fe in these soils is considerably higher than its level in soils of the cultivated floodplain (p<0.001) and the nearby Wadi deposits (p=0.007). The stated behavior of DTPA-extractable Fe reveals that it is significantly and positively affected by the wastewater disposal practice in this site. Regarding the distribution pattern of DTPA-extractable Fe in the lands applied for wastewater disposal at El-Dair, it varies between 25.4 and 878.3 mg kg^{-1} in the wastewater farmlands. The estimated DTPA-extractable Fe content, in average, is markedly higher than that reported for the cultivated floodplain ($p<0.001$) and Wadi deposits ($p<0.001$). The DTPA-extractable Fe content measured in the surface soils of the wastewater ponds at El-Dair displays a wide range varying from 99.9 to 918.3 mg kg^{-1} as indicated from the higher value of standard deviation (sd.=249.4). The average content of DTPA-extractable Fe in these soils is significantly higher than that of the adjacent Wadi deposits whereas it is very close to that of the wastewater farmlands ($p=0.992$). The abnormally elevated content of DTPA-extractable Fe in the lands applied for wastewater disposal at El-Kola and El-Dair indicates that a considerable content of the mobile Fe is carried by the wastewater; corrosion of the household and transporting Fe pipes may be the main source. The wide range of the DTPA-extractable Fe content in these sites reflects the variable grade of Fe content as a results of disposed wastewater.

Table 3: Summary of descriptive statistics for the DTPA-extractable Fe (%) and Mn (ppm) content.

	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
	Cultivated		Reclaimed		Wadi deposits		Wastewater		Wastewater	
Mean	19.8	67	37.9	64.9	9.3	20.5	120.8	41.2	334.3	38.8
Median	19.6	56	18.5	53.3	9	5.9	41.4	29.4	283.9	42.4
Minimum	3.2	17.9	5.4	4.3	5.4	1.7	3.5	0.56	25.4	9.9
Maximum		32.3	142.3	463.8	269	15.7	144.7	526	184.8	878.367.2
sd.	6.1	35.5	82.9	54.1	2.8	34.3	162.6	38.6	287.6	17.1

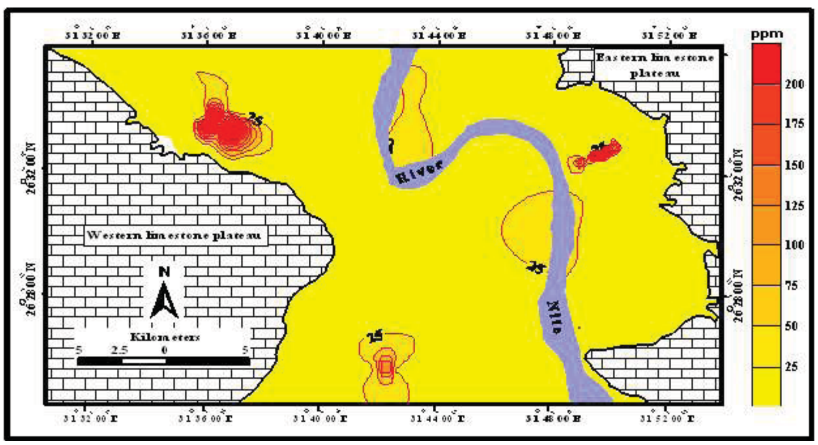

Fig. 4: Distribution of the DTPA-extractable iron content in soils of the study area.

DTPA-extractable Mn through the studied soils are given in (Table 3) and illustrated in the geochemical contour map (fig. 5). The DTPA-extractable Mn in cultivated floodplain soils ranges from 17.9 to 142.3 mg kg^{-1}. Although the total Mn content in soils of the floodplain is extremely lower than that of Fe, its DTPA-extractable fraction is considerably higher; this reflects the more mobility of Mn under the surficial conditions. The estimated concentrations of DTPA-extractable Mn in the reclaimed lands range from 4.3 to 269.0 mg kg^{-1}. Generally, the DTPA-extractable Mn content of this land use, in average, is very close to that reported for the cultivated floodplain ($p=0.851$). Levels of the DTPA-extractable Mn in the Wadi deposits of the study area ranges from 1.66 to 144.7. Wadi deposits exhibit significantly lower Mn content than the cultivated floodplain ($p<0.001$) reflecting the effect of carbonate immobilization. Concerning the DTPA-extractable Mn concentration in the lands applied for wastewater disposal at El-Kola it varies from 0.56 to 184.8 mg kg^{-1}. The average content of the DTPA-extractable Mn in these soils is relatively lower than its level in soils of the Nile floodplain ($p=0.007$), but there is no significant difference with its content in the wadi deposits ($p=0.074$). The DTPA-extractable Mn content estimated in the wastewater farmlands at El-Dair fluctuates between 9.9 and 67.2 mg kg^{-1}. The DTPA-extractable Mn content, on the average, is relatively lower than that reported for the cultivated floodplain ($p=0.005$), whereas there is insignificant difference compared with that of the nearby wadi deposits ($p=0.072$). The DTPA-extractable Mn level estimated in soils of the wastewater ponds at El-Dair ranges between 12.1 and 89.7 mg kg^{-1}. The average Mn content in these soils is extremely similar to that of lands applied for wastewater disposal at El-Kola ($p=0.933$) and El-Dair farmlands ($p=0.854$). The distribution pattern of the DTPA-extractable Mn content in the lands applied for wastewater disposal at El-Kola and El-

Dair is markedly similar to that of the nearby wadi deposits. This matter indicates that the wastewater disposal practice has no marked effect on the Mn bioavailability. The obtained results in agreement with others such: Sedberry *et al.* (1978); Kishk *et al.* (1980); Abou El-Khir (2000).

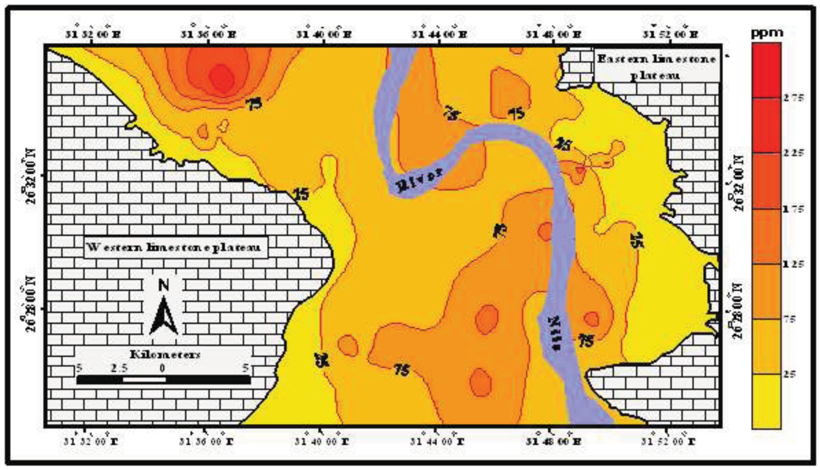

Fig. 5: Distribution of the DTPA-extractable manganese content in soils of the study area.

It can be concluded that, the Fe and Mn status in Sohag soils were governed by land use of the soils. The variation of Fe and Mn distribution with depth indicates that effect pedogenic processes and parent materials. It was expected that Fe availability was strongly greater in wastewater disposal area than the other areas, but the wastewater disposal practice has no marked effect on the Mn availability. This suggests wastewater disposal increased the risk of Fe loss to under ground water; however, it is important to note that the wastewater disposal areas started to be cultivated by woody trees received no fertilizers and thus were expected to decreasing Fe content of these soils.

Abbreviations: DTPA, diethylenetriamine penta-acetic acid; GPS, Global Positioning System. PAAS, Post Archean Australian Shale.

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