4. RESULTS AND DISCUSSION

As it was mentioned in the chapter of materials and methods, the incubation experiments of this investigation were conducted under cycles of alternate wetting and drying in order to simulate what may actually occurs in soils upon irrigation. Thus, at the beginning of wetting stage of each cycle, moisture contents of the studied soils were brought to saturation. On the other hand, decrease in available water content of the studied soils to about one half the whole corresponding available water was considered as an end of the drying stage of each cycle.

Effect of application of organic matter on redox parameters and consequently on availability of Fe and Mn in soils is thought to be different from that of elemental sulfur. Also response of the Nile alluvial non-calcareous soil of Moshtohor to these amendments is expected to be different from the corresponding one of the calcareous soil of Borg El-Arab. Therefore, the following discussion meant by studying the effect of the organic matter unattached to that of the elemental sulfur in each of the studied soils unattached to the other one.

4.1. Effect of compost application on Moshtohor soil under alternate wetting and drying cycles:

4.1.1. Effect on pH, Eh and redox parameter *(pH+pe)*:

Data presented in Table (3) and illustrated graphically in Figs. (1 and 2) show the changes that had taken place in values of pH, Eh and the redox parameter *(pH+pe)* of Moshtohor soil at the time zero and over four cycles of alternate wetting and drying i.e. the first, third, fifth and seventh ones.

Table (3): Effect of application of different rates of bagasse compost on pH, Eh, *pe* and the redox parameter (*pH+pe*) of Moshtohor soil under alternate cycles of wetting and drying.

Rate of applied bagasse compost % [R]	Soil parameter	Cycles of wetting and drying [C]					Mean
		Time zero	1st	3rd	5th	7th	
0	pH	8.18	8.00	8.06	8.07	7.99	8.06
	Eh (mV)	257	158	157	154	159	177.0
	pe	4.34	2.67	2.65	2.60	2.69	2.99
	pH+pe	12.52	10.67	10.71	10.67	10.68	11.05
2	pH	8.18	7.86	7.90	7.98	7.93	7.97
	Eh (mV)	257	156	154	149	152	173.6
	pe	4.34	2.64	2.60	2.52	2.57	2.93
	pH+pe	12.52	10.50	10.50	10.50	10.50	10.90
4	pH	8.15	7.82	7.84	7.92	7.85	7.92
	Eh (mV)	254	150	149	145	148	169.2
	pe	4.29	2.53	2.52	2.45	2.50	2.86
	pH+pe	12.44	10.35	10.36	10.37	10.35	10.77
		Means of the rates of applied compost					
	pH	8.17	7.89	7.93	7.99	7.92	7.98
	Eh (mV)	256.0	154.7	153.3	149.3	153.0	173.3
	pe	4.32	2.61	2.59	2.52	2.59	2.93
	pH+pe	12.49	10.51	10.52	10.51	10.51	10.91

LSD (0.05):	[R]	[C]	[R × C]
pH	0.06	0.07	NS
Eh (mV)	3.57	4.6	NS
pH+pe	0.18	0.23	NS

NS: not significant

4.1.1.1. Effect on pH:

pH values seemed to be reduced as compared with zero time due to exposing soil to alternate cycles of wetting and drying. Such a finding could be attributed to depletion of oxygen and build up of carbon dioxide from microbial respiration processes. **Sposito (1989)** referred that the content of O_2 in soil inundated by water dropped to a negligible value during the first day. Oxygen depletion must regulate the proton activity in the soil solution according to the following equation:

$$CO_2\,(g) + H_2O\,(l) \longrightarrow H_2CO_3$$

$$H_2CO_3 \longrightarrow H^+\,(aq) + HCO_3^-$$

and therefore, the pH of the soil decreases. **Russell (1973)** declaired that soil micro-organisms, in decomposing the organic matter, will use up any free oxygen dissolved in the soil much faster than atmospheric oxygen can diffuse into the wet soil.

The reducing effect of saturating soil with water on its pH value was reported also by **Russell (1973); Tian-ren (1985); Holah (1990)** and **Eskandar (2001).**

It is obvious also from Table (3) and Fig.(1) that application of organic matter contributed to more reduction in pH values of Moshtohor soil. This reduction in soil pH is probably due organic matter upon decomposition results in some organic acids which slow down soil pH. Besides, the organic matter decomposers give out carbon dioxide upon exhalation which dissolves in soil moisture forming carbonic acid (H_2CO_3) that leads also to further decrease in soil pH. The reducing effect of organic matter on soil pH was reported by many investigators

(Russell, 1973; Abou El-Fadl et al., 1990; Fahmy, 1995; Holah, 1990; Awad, 1998 and **Eskandar, 2001).**

Increasing the rate of applied bagasse compost, led to relatively higher effects on reducing soil pH. Similar results were reported by **Xie-ming (1985)** and **Holah (1990).**

Reduction of soil pH whether due to alternate wetting and drying cycling or application of the organic matter (bagasse compost) seemed, generally, to be highest at the first cycle of wetting and drying beyond which a case of stability almost had been achieved, though limited fluctuation in pH values could be noticed.

4.1.1.2. Effect on the redox potential (Eh) and the redox parameter *(pH+pe)*:

Incubation of Moshtohor soil without applied bagasse compost resulted in decrease in Eh and consequently in the redox parameter *(pH+pe)*. At the time zero, the *(pH+pe)* value was as high as 12.52 decreased to 10.67 after one cycle of wetting and drying, however, it tended to be almost constant within the rest cycles.

As shown from Fig. (2), application of the compost at a rate of 2 % was associated with further decreases in Eh and *(pH+pe)* values. This occurred at all the cycles with a very narrow range of fluctuation. Increasing the rate of the applied compost enlarged slightly the values decrease. The applied compost achieved its highest effect on reducing value of the redox parameter at the first cycle beyond which this parameter tended to be nearly constant. The results obtained herein agreed with those of **Holah (1990)** and **Eskandar (2001).**

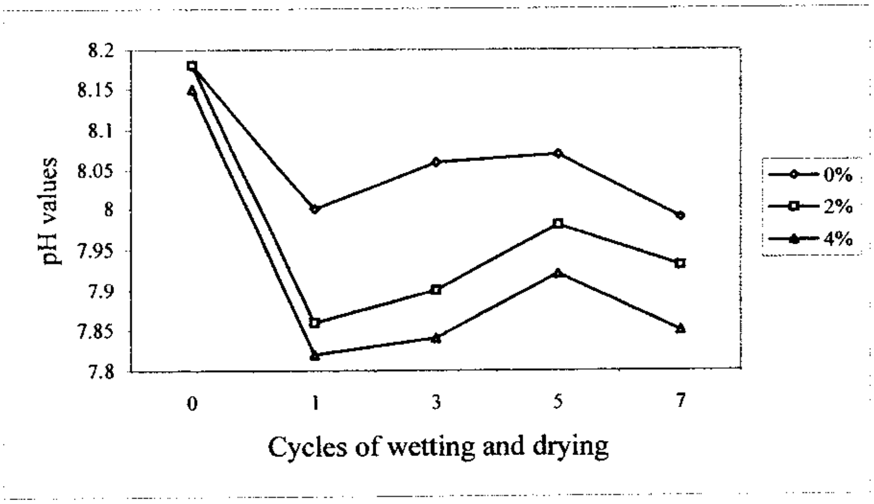

Fig. (1): Effect of compost application on pH values of Moshtohor soil under alternate cycles of wetting and drying.

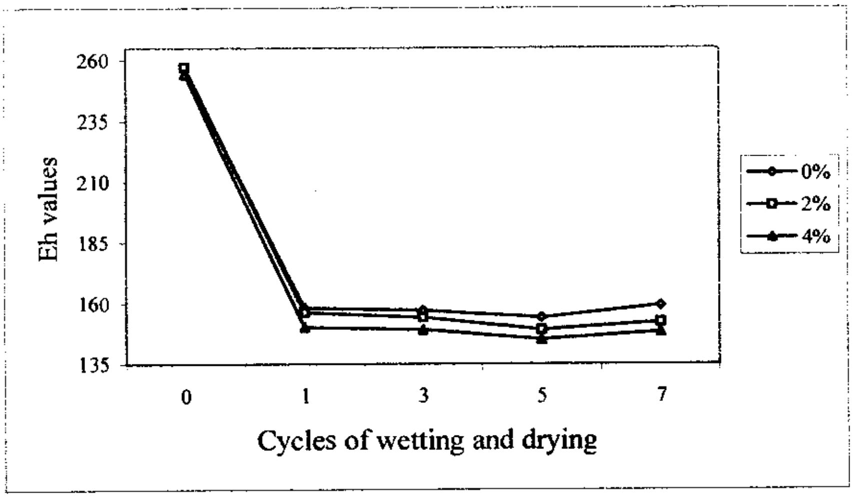

Fig. (2): Effect of compost application on Eh values of Moshtohor soil under alternate cycles of wetting and drying.

Tian-ren (1985) indicated that organic matter is the principal source of electrons. Release of electrons during organic matter decomposition lowers the Eh or the *pe* of the soil. This indication assured a previous one of **Bloom (1981)** who referred that organic matter is an energy substrate for microorganisms and acts as an electron donor in redox reactions thus reduces the soil Eh. **Mc Bride (1994)** pointed out that the decrease in the Eh (or soil redox parameter *pH+pe*) depends on the quantity of reactive electron acceptors in the soil compared with the quantity of electrons generated by biological reactions, particularly organic matter oxidation. She added that a large reserve of electron acceptors such as Mn^{4+} or Fe^{3+} in the form of oxides means that the redox potential tends to maintain a nearly constant value as reduction of acceptors continues. Even so, a high organic matter level in soils usually means that the electron acceptors are overwhelmed by microbial activity and the Eh decreases rapidly.

4.1.1.3. Sequence of reduction in soil of Moshtohor:

At the beginning of each cycle, where soil organisms respire aerobically, the final electron sink would be oxygen which accepts electrons and combines with hydrogen ions to give water.

$$O_2 + 4H + 4e^- \longrightarrow 2H_2O$$

Russell (1973) pointed that in the absence of free oxygen a number of other substances such as nitrates and sulfates can accept electrons and take part in a reduction reaction.

$$NO_3^- + 2H^+ + 2e^- \longrightarrow NO_2^- + H_2O$$

$2NO_2^- + 8H^+ + 6e^- \longrightarrow N_2 + 4H_2O$

He added that a second sequence of bacterial activity under conditions of oxygen deficiency is that the organic materials are no longer fully oxidized to carbon dioxide and water, but instead intermediate products are excreted such as simple fatty acids, hydroxy-carboxylic and polycarboxylic acids.

Sposito (1989) declared that when the pe of the soil solution drops below +11, enough electrons become available to reduce O_2 (g) to water. He added that as the pe decreases below +8, electrons become available to reduce NO_3^- and as the soil pe value drops into the range 7 to 5, electrons become plentiful enough to support the reduction of Fe and Mn in solid phases.

pe values of Moshtohor soil were usually within the range of 2 to 3 (except for the time zero) whether the soil did not receive bagasse compost or received it at a rate of 2 or 4 % .Thus, it was expected that in Moshtohor soil, there were electrons enough to reduce both Mn and Fe.

4.1.2. Effect on availability of Fe and Mn and their relation to the redox parameters:

4.1.2.1. Effect on Fe:

Values of available Fe content as extracted by DTPA from Moshtohor soil are presented in Table (4) and illustrated graphically in Fig. (3). These values were generally lowest at the time zero, highest at first cycle of the alternate wetting and drying. Application of the bagasse was associated with increase in values of DTPA extractable Fe. Except for the first and third cycles further increase in rate of the applied organic matter from 2 to 4 % seemed of no detectable effect on values of extractable

Table (4): Effect of application of different rates of bagasse compost on DTPA-extractable Fe Moshtohor soil under alternate cycles of wetting and drying.

Rate of applied bagasse compost % [R]	DTPA-extractable Fe (mg kg^{-1})					
	Time zero	Cycles of wetting and drying [C]				Mean
		1st	3rd	5th	7th	
0	15.98	41.21	39.58	36.66	36.05	33.90
2	16.05	43.80	41.25	38.50	42.17	36.35
4	16.15	44.91	42.05	38.66	42.01	36.76
Mean	16.06	43.31	40.96	37.94	40.08	35.67
<u>LSD (0.05):</u>	[R] = 0.45		[C] = 0.58		[R×C] = 1.00	

Table (5): Regression equations and simple correlation coefficients between the redox parameter *(pH+pe)* and DTPA extractable Fe from Moshtohor soil under different rates of applied bagasse compost.

Rate of applied bagasse compost %	Regression equation	Simple correlation coefficient (r)
0	Y= -12.174x + 168.42	0.97755
2	Y= -12.564x + 173.36	0.98595
4	Y= -12.386x + 170.20	0.98346

x: Values of DTPA-extractable Fe
Y: Values of the redox parameter *(pH+pe)*

Fe. Such a finding might be due to formation of insoluble chelates upon application of the higher rate of the compost. On the other hand, the increase in availability of Fe due to application of the compost seemed to be inversely and significantly related to values of soil *pH+pe* which were generally lowest at the first cycle of alternate wetting and drying cycles whether in absence or in presence of applied compost (Table, 5).

This finding stands in well agreement with Lindsay (1979) who stated that the activity of Fe^{3+} maintained by Fe(III) oxides increases 1000-folds per unit decrease in pH

$$Fe(OH)_{3\,(soil)} + 3\,H^{+} \longrightarrow Fe^{3+} + 3H_2O \qquad \log K^{\circ} = 2.7$$

$$\text{Log}\, Fe^{3+} = 2.7 - 3pH$$

Besides, bagasse compost itself is a source of enriching soil with Fe due to its high content of Fe (see Table 2).

It is worthy to note that availability of Fe seemed to be negatively correlated with the redox parameter *(pH+pe)*. This finding stands in well agreement with that of **Bloom (1981)** who revealed that the parameter *(pH+pe)* decreases and the reduction of Fe occurs and its availability increases when organic matter was applied because it acts as an electron donor reducing soil Eh (or soil *pe*).

4.1.2.2. Effect on Mn:

Data presented in Tables (3) and (6) reveal that availability of Mn (DTPA extractable content) seemed not to be significantly dependent on soil pH. However, negative relation between available Mn content and soil pH was reported by many

Table (6): Effect of application of different rates of bagasse compost on DTPA-extractable Mn Moshtohor soil under alternate cycles of wetting and drying cycles.

Rate of applied bagasse compost % [R]	DTPA-extractable Mn (mg kg^{-1})					
	Time zero	Cycles of wetting and drying [C]				Mean
		1st	3rd	5th	7th	
0	25.05	88.18	97.61	98.89	97.38	81.42
2	25.09	68.89	118.20	117.41	113.99	88.72
4	25.08	69.51	127.29	126.09	125.78	94.75
Mean	25.07	75.53	114.37	114.13	112.38	88.30
LSD (0.05):	[R] = 2.19		[C] = 2.82		[R×C] = 4.89	

Table (7): Regression equations and simple correlation coefficients between the redox parameter *(pH+pe)* and DTPA extractable Mn from Moshtohor soil under different rates of applied bagasse compost.

Rate of applied bagasse compost %	Regression equation	Simple correlation coefficient (r)
0	$Y = -38.295x + 504.58$	0.98975
2	$Y = -39.373x + 518.03$	0.86441
4	$Y = -41.692x + 543.94$	0.84262

x: Values of DTPA-extractable Mn
Y: Values of the redox parameter *(pH+pe)*

investigators **(Foy, 1973; Abd El- Hameed, 1984; Hassan, 1995 and Eskandar, 2001).** The insignificancy of the relation obtained herein means that the soil pH is not the only factor that affects Mn availability but also some other ones contribute to its availability. However the total Mn content, organic matter level and microbial activity are among these factors **(Foy, 1973 and Stahlberg et al., 1976).**

Application of the compost resulted in pronounced increases in soil content of DTPA-extractable Mn whose average value increased from 81.42 mg kg^{-1} when the soil did not receive organic matter additions to 88.71 mg kg^{-1} when organic matter was applied at a rate of 2 % to 94.75 mg kg^{-1} when rate of application of organic matter was raised to 4 %. Microbial effects such as catalysis and chelation may play a large role in the reduction of Mn oxides **(Gotoh and Patrick, 1972 and Lovley, 1995). Bartlett and James (1980)** reported that a flush of microbially available C released when soil was dried and remoistend may have to contribute a marked increase in soluble and exchangeable Mn. They suggested that some microbes may be capable of coupling oxidation of organic C to reduction of Mn oxides. The decrease in values of the redox parameter *(pH+pe)* due to moisture cycling and /or application of the bagasse compost induced availability of Mn (Table, 7). **Weil et al. (1997)** stated that a combination of low pH and low Eh (or *pe*) causes a higher percentage of soil total Mn to occur in the soluble form. However, **Paranasasivan (1973)** claimed that exchange process in the soil is more important than redox process in determining available content of Mn in soil.

It is worthy, however, to indicate that application of the compost resulted in adverse effect on availability of Mn at the first cycle where values of DTPA extractable Mn attained upon application of the compost at the rate of 2 % or 4 % were obviously lower than that of the control (0 % rate). This may be because the simple organic compounds upon decomposition, the microbial population increases and this leads to immobilize some of the available (reduced) Mn and consequently decreases its content in soil.

Average values of DTPA extractable Mn of the different alternating wetting and drying cycles reveal that DTPA-extractable Mn attained its highest values after 3 cycles thereafter tended to decrease very slightly. This result agrees, to some extent, with what had been reported by **Russell (1973)** who stated that the severe reducing conditions raise the concentration of Fe and Mn ions in the soil solution very rapidly, reaching a maximum in about four weeks.

The aforementioned results (Tables 4 & 6) reveal obviously higher increase in available content of DTPA-extractable Mn than Fe. This is because (as stated by **Xie-ming, 1985**) Mn compounds possess a strong oxidizing property as compared with Fe compounds. It is for this reason that at ordinary soil pH ferrous iron (Fe^{2+}) can exist only at low Eh whereas manganous manganese (Mn^{2+}) can exist even in well aerated soils. Moreover, the pK_{sp} of $Mn(OH)_2$ in water is about 13, much smaller than that of $Fe(OH)_3$ or $Fe(OH)_2$. It is for this reason, Fe is more easily precipitated than Mn.

Another explanation for the aforementioned phenomenon is that Fe and Mn respond to the oxidation-reduction conditions differently. According to the sequential reduction, Mn compounds in soils should be more easily reducible than Fe compounds. Actually, this is just the case. It can be seen that although the amount of reduced Fe increased slightly with the increase in concentration of the reducing agent, it accounts for the total iron by not more than several thousandths. On the contrary, the amount of Mn accounts for a large proportion of the total Mn content of the soil.

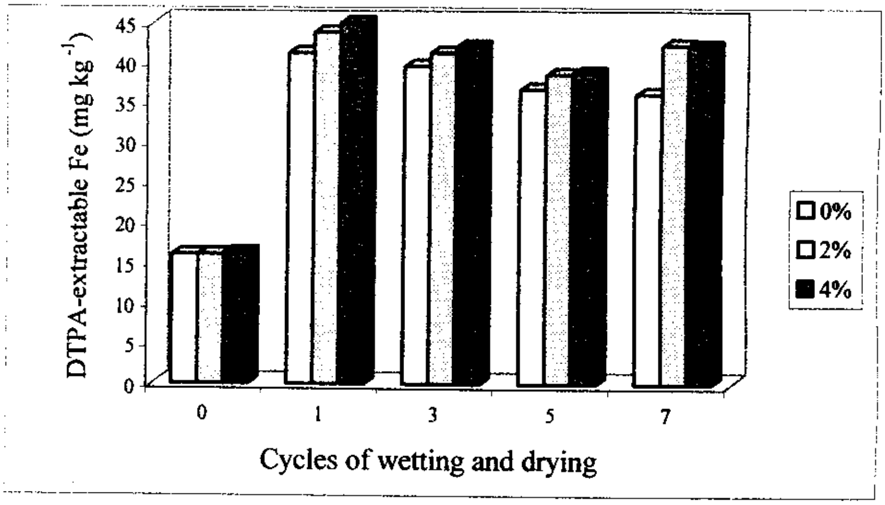

Fig. (3): Effect of compost application on DTPA-extractable Fe from Moshtohor soil under alternate cycles of wetting and drying

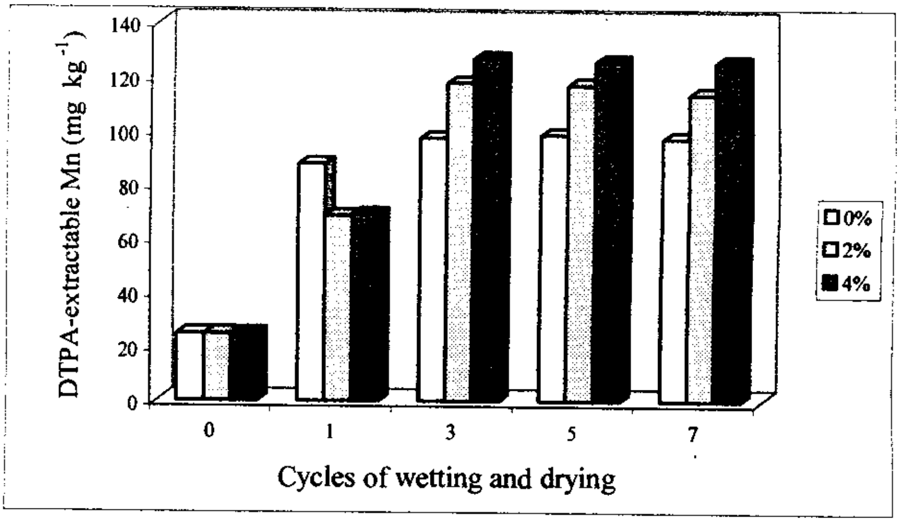

Fig. (4): Effect of compost application on DTPA-extractable Mn from Moshtohor soil under alternate cycles of wetting and drying

4.2. Effect of application of elemental sulfur (S) on Moshtohor soil under alternate cycles of wetting and drying:

4.2.1. Effect on pH, Eh, pe and the parameter *(pH+pe)*:

Data presented in Table (8) reveal values of the pH, Eh, *pe* and *(pH+pe)* parameters as influenced by alternate wetting and drying cycles and application of different rates of elemental sulfur (S) to Moshtohor.

4.2.1.1. Effect on soil pH:

Application of elemental sulfur (S) enhanced the effect of alternate wetting and drying cycles on reducing pH values of soil to be slightly more obvious. However, increasing the rate of the applied sulfur from 0.2 to 0.4 % resulted in an only hardly noticeable reduction in soil pH. This slight reduction in soil pH may be attributed to oxidation rather than reduction of S under the alternate wetting and drying cycles. Reduction of sulfur only occurs under strongly reducing conditions. On the other hand, the aerobic conditions that exist between each successive wetting cycles would permit chemical as well as biological oxidation of sulfur leading to formation of SO_4^{2-} and consequently sulfuric acid and thus pH decreases. This finding agree with **Wassif et al. (1995), El-Fayoumy and El-Gamal (1998) and Elsikhry (2000).**

Effect of cycles of alternate wetting and drying on reducing soil pH seemed to be highest at the third cycle probably because most of the applied elemental sulfur had been converted

Table (8): Effect of application of different rates of elemental sulfur on pH, Eh, *pe* and the redox parameter *(pH+pe)* of Moshtohor soil under alternate cycles of wetting and drying.

Rate of applied elemental sulfur % [R]	Soil parameter	Cycles of wetting and drying [C]					Mean
		Time zero	1st	3rd	5th	7th	
0	pH	8.18	8.00	8.06	8.07	7.99	8.06
	Eh (mV)	257	158	157	154	159	177.0
	pe	4.34	2.67	2.65	2.60	2.69	2.99
	pH+pe	12.52	10.67	10.71	10.67	10.68	11.05
0.2	pH	8.18	7.93	7.85	8.01	8.03	8.00
	Eh (mV)	257	138	128	132	133	157.6
	pe	4.34	2.33	2.16	2.23	2.25	2.66
	pH+pe	12.52	10.26	10.01	10.24	10.28	10.66
0.4	pH	8.18	7.86	7.76	7.99	8.01	7.96
	Eh (mV)	257	128	114	117	119	147.0
	pe	4.34	2.16	1.93	1.98	2.01	2.48
	pH+pe	12.52	10.02	9.69	9.97	10.02	10.44
		Means of the applied elemental sulfur					
	pH	8.18	7.93	7.89	8.02	8.01	8.01
	Eh (mV)	257.0	141.3	133.0	134.3	137.0	160.5
	pe	4.34	2.39	2.25	2.27	2.32	2.71
	pH+pe	12.52	10.32	10.14	10.29	10.33	10.72
LSD (0.05):		[R]		[C]		[R × C]	
	pH	0.06		0.07		NS	
	Eh (mV)	3.57		4.6		7.97	
	pH+pe	0.13		0.16		0.28	

NS = not significant

into sulfuric acid due to the oxidation of sulfur that might take place as follows:

Alexander (1977) indicated that the oxidation of S° can occur chemically as well as biologically. The chemical oxidation could be as follows:

$$2S^\circ + 2\,H_2O + 3\,O_2 \longrightarrow 4\,H^+ + 2\,SO_4^{2-}$$

The biological oxidation of S° by microorganisms (bacillus) is faster and more important in amount than the chemical one **(Wiklander et al., 1950).** The biological oxidation could be as follows:

$$S^\circ + 4\,H_2O \xrightarrow{\text{bacteria}} SO_4^{2-} + 8\,H^+ + 6\,e^-$$

Balba (1995) indicated that oxidation of elemental S° to sulfate (SO_4^{2-}) would require about 3 weeks. This finding may explain the higher reducing effect of the applied S on soil pH at the third cycle which is equivalent to a period of about or slightly exceeds 3 weeks. Increases in pH values after the third cycle may be attributed to the high buffering capacity of Moshtohor soil through which the soil tries to regain its original pH value.

4.2.1.2. Effect on the soil redox potential (Eh) and the redox parameter *(pH+pe)*:

Value of the redox potential was rapidly decreased from 257 mV one hour after saturating soil with water to values ranging from 154 to 159 mV for cycles of alternate wetting and drying.

Application of sulfur seemed to maximize the reducing effect of the cycles of wetting and drying on the Eh values which were decreased to values ranged from 128 to 138 mV upon

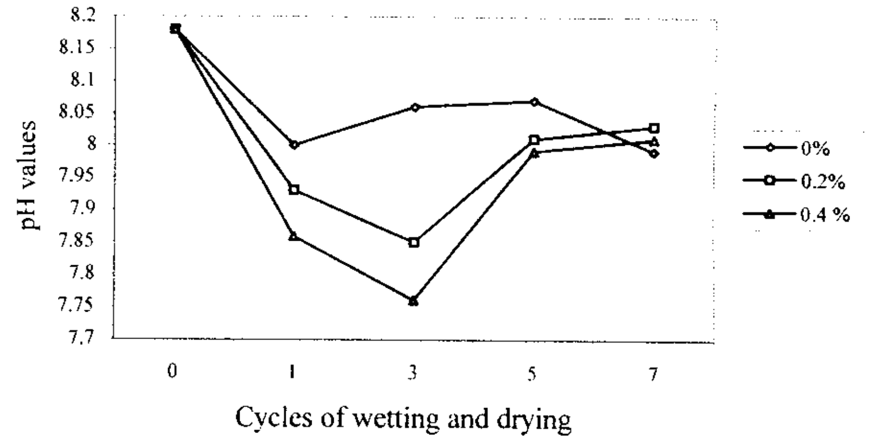

Fig. (5): Effect of sulfur application on pH values of Moshtohor soil under alternate cycles of wetting and drying.

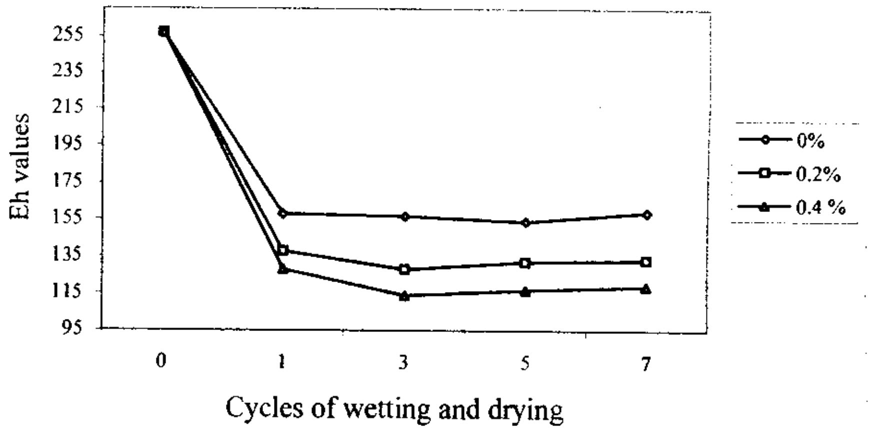

Fig. (6): Effect of sulfur application on Eh values of Moshtohor soil under alternate cycles of wetting and drying.

application of sulfur at a rate of 0.2 %. Further decreases occurred in the Eh values when rate of the applied sulfur was raised up to 0.4 %.

As a result of the reducing effect of the applied elemental sulfur on soil pH and also its redox potential Eh, the redox parameter *(pH+pe)* was also reduced and the reduction was more obvious with increasing rate of the applied elemental sulfur due to sulfur oxidation and as a result, the activity of protons and aqueous electrons increased and thereby; the redox parameter decreases to values lower than of the control (the time zero). Thus, it could be concluded from the aforementioned results and discussion that the greater the amount of the applied elemental S° to the soil, the lesser the redox parameters.

Regarding the effect of moisture cycling on the redox parameter *(pH+pe)*, the obtained results indicated that it decreased with time of incubation until it reached the lowest value after three cycles thereafter tended to be nearly stable. Yet, it is worthy to indicate that the reductions in the pH, Eh and consequently the redox parameter *(pH+pe)* were very limited due to the high buffering capacity of Moshtohor soil which is characterized by a high content of clay and a high cation exchange capacity. On the other hand, the overall redox parameters achieved their lowest values after three cycles of wetting and drying which means that the highest reduction in all redox parameters occurred at the same time at which oxidation of the elemental sulfur (S°) achieved the maximum.

4.2.2. Effect on availability of Fe and Mn and their relation to the redox parameters:

4.2.2.1. Effect on Fe:

Data presented in Table (9) reveal that application of the elemental sulfur to the soil enhanced the soil effect of the alternate wetting and drying cycles on DTPA-extractable Fe. Increasing rate of the applied elemental sulfur from 0.2 to 0.4 % resulted in further increase in DTPA-extractable Fe. Similar results were reported by **Elsikhry(2000)** and **Khalefa (2002).**

The increase in DTPA-extractable Fe was associated with the decrease in the pH and the redox parameters Eh, *pe* and *(pH+pe)* (Table, 10). The increase in DTPA-extractable Fe due to a corresponding decrease in the redox parameters can be explained by the following reaction as reported by **Lindsay (1979)**:

$$Fe(OH)_3\,(soil) + 3\,H^+ + e^- \longrightarrow Fe^{2+} + 3\,H_2O \qquad \log K^\circ = 15.74$$

$$\text{Log}\,Fe^{2+} = 15.74 - (pe + pH) - 2\,pH.$$

4.2.2.2. Effect on Mn:

Data presented in Table (11) show values of DTPA-extractable Mn from Moshtohor soil. Application of elemental sulfur (S°) to the soil was associated with increase in amounts of DTPA-extractable Mn. Moreover, excessive application of elemental sulfur led to a descending increase in Mn availability. This finding agrees with those of **Elsikhry and Ali (1991), Hilal and Shata (1997), Elsikhry (2000) and Khalefa (2002).**

Tisdale and Bertramson (1949) concluded that the increased acidity due to oxidation of sulfur was the cause of

Table (9): Effect of application of different rates of elemental sulfur on DTPA-extractable Fe from Moshtohor soil under alternate cycles of wetting and drying.

Rate of applied elemental sulfur % [R]	DTPA-extractable Fe (mg kg^{-1})					
	Time zero	Cycles of wetting and drying [C]				Mean
		1st	3rd	5th	7th	
0	15.98	41.21	39.58	36.66	36.05	33.90
0.2	16.00	42.20	46.50	40.59	39.35	36.93
0.4	16.04	43.02	48.60	41.14	40.50	37.86
Mean	16.01	42.14	44.89	39.46	38.63	36.23
LSD (0.05):	[R] = 0.49		[C] = 0.63		[R×C] = 1.10	

Table (10): Regression equations and simple correlation coefficients between the redox parameter *(pH+pe)* and DTPA extractable Fe from Moshtohor soil under different rates of applied elemental sulfur.

Rate of applied elemental sulfur %	Regression equation	Simple correlation coefficient (r)
0	Y= - 12.174x + 168.42	0.97755
0.2	Y= - 11.395x + 158.42	0.99116
0.4	Y= - 10.665x + 149.25	0.98853

x: Values of DTPA-extractable Fe
Y: Values of the redox parameter *(pH+pe)*

Table (11): Effect of application of different rates of elemental sulfur on DTPA-extractable Moshtohor soil under alternate cycles of wetting and drying.

Rate of applied elemental sulfur % [R]	DTPA-extractable Mn (mg kg^{-1})					
	Time zero	Cycles of wetting and drying [C]				Mean
		1st	3rd	5th	7th	
0	25.05	88.18	97.61	98.89	97.38	81.42
0.2	25.09	89.89	137.58	105.01	98.36	91.19
0.4	25.08	90.93	143.79	117.99	106.02	96.76
Mean	25.07	89.67	126.33	107.30	100.59	89.79
LSD (0.05):	[R] = 1.83		[C] = 2.36		[R×C] = 4.08	

Table (12): Regression equations and simple correlation coefficients between the redox parameter *(pH+pe)* and DTPA extractable Mn from Moshtohor soil under different rates of applied elemental sulfur.

Rate of applied elemental sulfur %	Regression equation	Simple correlation coefficient (r)
0	$Y= - 38.295x + 504.58$	0.98975
0.2	$Y= - 36.9275x + 484.9$	0.93776
0.4	$Y= - 35.842x + 471.09$	0.94128

x: Values of DTPA-extractable Mn
Y: Values of the redox parameter *(pH+pe)*

increased availability of Mn. However they suggested that acidity is not the only factor affecting the availability of Mn. They proposed that an oxidation- reduction reaction may take place in soil as shown by following half reactions:

$$3\ MnO_2 + 12\ H^+ + 6\ e^- \longrightarrow 3\ Mn^{2+} + 6\ H_2O$$

$$S^\circ + 4\ H_2O \longrightarrow SO_4^{2-} + 8\ H^+ + 6\ e^-$$

$$3\ MnO_2 + 4\ H^+ + S^\circ \longrightarrow 3\ Mn_2+ + 2\ H_2O + SO_4^{2-}$$

Norvell (1988) reported that Mn^{2+} oxidation state is the only species expected in the soil solution across the range of *pe* (-5 to 12) and pH (3 to 9) of most soils. Both the pH and pe values recorded herein are within the above mentioned ranges which means that Mn^{2+} ions which are readily available for plants are the dominant Mn species in Moshtohor soil.

Nazrul-Islam (1990) reported that a combination of low pH and low Eh caused a higher percentage of total soil Mn to occur in the water-soluble form than in the exchangeable form.

Mn availability seemed to increase with incubation period until it reaches its highest values at the third cycle of alternate wetting and drying beyond which it underwent gradual decrease. The decrease in pH, Eh and the overall redox parameter to achieve lowest values at the 3rd cycle of alternate wetting and drying may give account for the corresponding increases in available content of Mn. The decrease in available content of Mn after the third cycle can be attributed, on the other hand, to the relative increase in values of the redox parameters at the fifth and seventh cycle. It could also be concluded from Table (12) that values of DTPA extractable Mn were significantly and negatively affected by the redox parameter *(pH+pe)*.

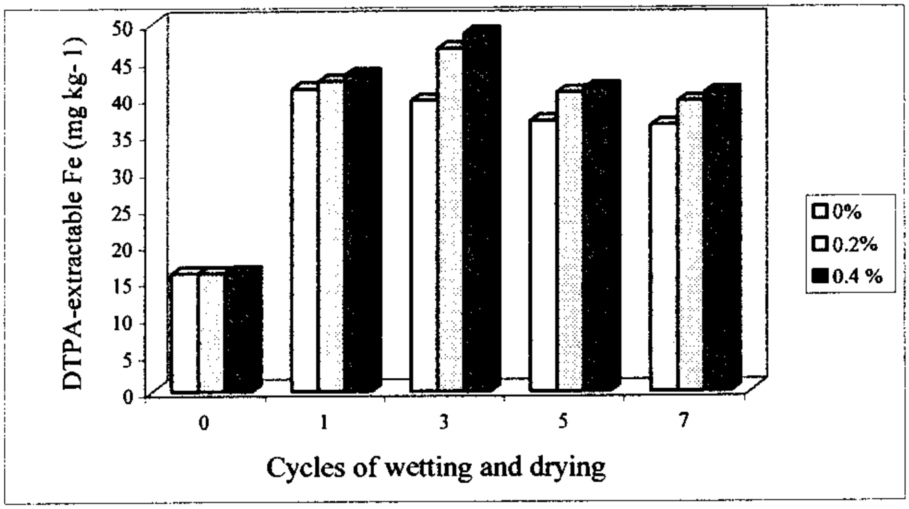

Fig. (7): Effect of application of sulfur on DTPA-extractable Fe from Moshtohor soil under alternate cycles of wetting and drying

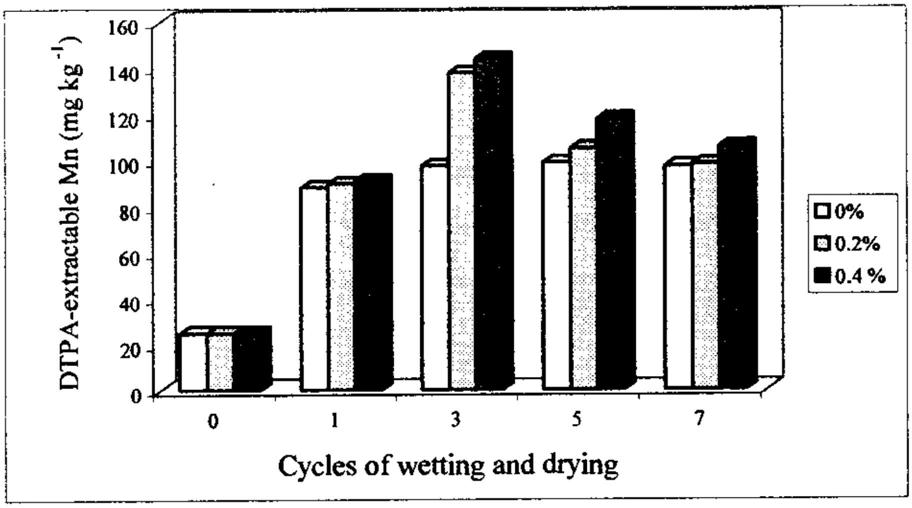

Fig. (8): Effect of application of sulfur on DTPA-extractable Mn from Moshtohor soil under alternate cycles of wetting and drying.

4.3. Effect of application of bagasse compost on Borg El-Arab soil under alternate cycles of wetting and drying:

4.3.1. Effect on pH, Eh, *pe* and the redox parameter *(pH+pe)*:

Data presented in Table (13) and illustrated graphically in Figs. (9 and 10) reveal the changes in soil pH, the redox potential Eh *(pe)* and the redox parameter *(pH+pe)* that occurred in Borg El-Arab soil due to application of bagasse compost to this soil at different rates i.e. 0, 2 and 4 % under cycles of alternate wetting and drying.

The calcareous soil under investigation is characterized by a high content of $CaCO_3$ (41 %) and relatively initial high pH value (8.2).

In absence of applied compost, when this soil was initially saturated with water, the diffusion of O_2 (g) into the soil and CO_2 (g) out of the soil was greatly restricted. The reduction in pH value of the calcareous soil due to the increase in partial pressure of CO_2 upon wetting could be explained by **Sajwan and Lindsay (1986)** as follows:

$$CO_{2\,(g)} + H_2O_{(l)} \longrightarrow H_2CO_3^{\circ}$$

$$H_2CO_3^{\circ} \longrightarrow H^+ + HCO_3^-$$

$$HCO_3^- + Ca^{2+} \longrightarrow CaCO_3\ \text{(calcite)} + H^+$$

However, upon drying (depletion of 50 % of the available water), partial aeration of the soil permits O_2 (g) to diffuse into soil and CO_2 (g) to diffuse out of it.

Table (13): Effect of application of different rates of compost on pH, Eh, *pe* and the redox parameter *(pH+pe)* of Borg El-Arab soil under alternate cycles of wetting and drying.

Rate of applied bagasse compost % [R]	Soil parameter	Cycles of wetting and drying [C]					Mean
		Time zero	1st	3rd	5th	7th	
0	pH	8.28	7.96	7.88	8.11	8.20	8.09
	Eh (mV)	287	173	168	177	171	195.2
	pe	4.85	2.92	2.84	2.99	2.89	3.30
	pH+pe	13.13	10.88	10.72	11.10	11.09	11.36
2	pH	8.28	7.93	7.80	8.04	8.11	8.03
	Eh(mV)	287	158	161	157	158	184.2
	pe	4.85	2.67	2.72	2.65	2.67	3.11
	pH+pe	13.13	10.60	10.52	10.69	10.78	11.14
4	pH	8.28	7.90	7.73	7.99	7.95	7.97
	Eh (mV)	287	150	139	148	141	173.0
	pe	4.85	2.53	2.35	2.5	2.38	2.92
	pH+pe	13.13	10.43	10.08	10.49	10.33	10.89
		Means of the rates of applied compost					
	pH	8.28	7.93	7.80	8.05	8.09	8.03
	Eh (mV)	287.0	160.3	156.0	160.7	156.7	184.1
	pe	4.85	2.71	2.64	2.71	2.65	3.11
	pH+pe	13.13	10.64	10.44	10.76	10.73	11.14
LSD (0.05):			[R]		[C]		[R×C]
	pH		0.05		0.07		NS
	Eh		2.49		3.21		5.56
	pH+pe		0.09		0.12		0.20

NS = not significant

Thus, no further reduction occurs in soil pH, *pe* or the overall redox parameter *(pH+pe)*. Also, the pH reduction during wetting is supposed to be reserved during drying.

4.3.1.1. Effect on pH:

Data in Table (13) show that very slight changes occurred in pH value of calcareous soil of Borg El-Arab due to application of the compost to this soil. The reducing effect of the applied compost was more obvious when the rate of the applied compost was raised from 2 % to 4 %. The high capacity of the investigated soil to buffer its pH can be explained according to **McBride (1994)** who pointed out that free carbonate minerals in the calcareous soil, most commonly Ca and Mg carbonates, are a reserve of soil alkalinity that can neutralize natural soil acidity (carbonic acids and organic acids). Acid neutralization reactions generate bicarbonate salts, for example:

$$H^+ + CaCO_3 \longrightarrow Ca^{2+} + HCO_3^-$$

She added that the carbonate buffer capacity of many calcareous soils is so large for natural acid inputs to have any effect on soil pH. From the principal of solubility products, carbonates must be completely dissolved out of the soil before the soil pH can drop.

Regarding the effect of incubation period on pH value of the investigated calcareous soil, it could be detected from Table (13) and Fig. (9) that the soil pH determined at the time zero (one hour after saturation) slightly decreased to its lowest value at the third cycle beyond which it tended to a gradual increase but it still remained below the initial value. This behaviour occurred in absence of the applied compost as well as upon its

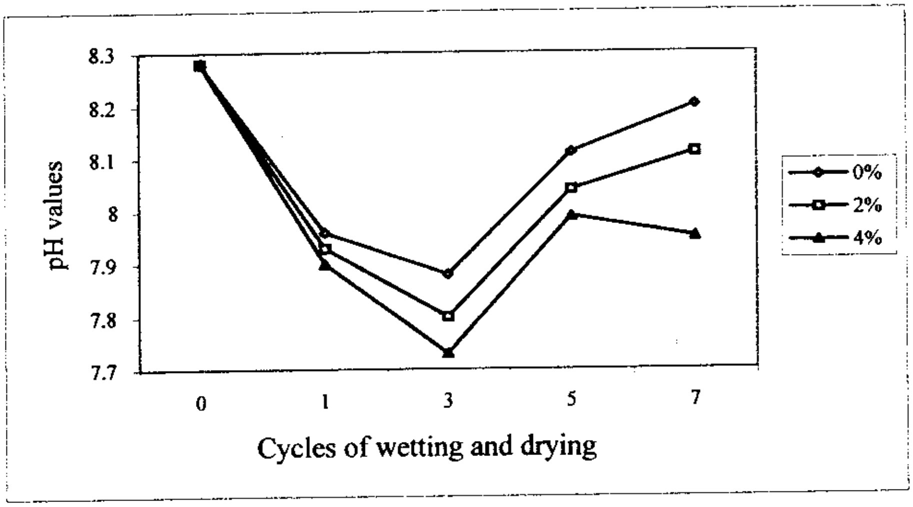

Fig. (9): Effect of alternate cycles of wetting and drying and bagasse compost application on pH values of Borg El-Arab soil

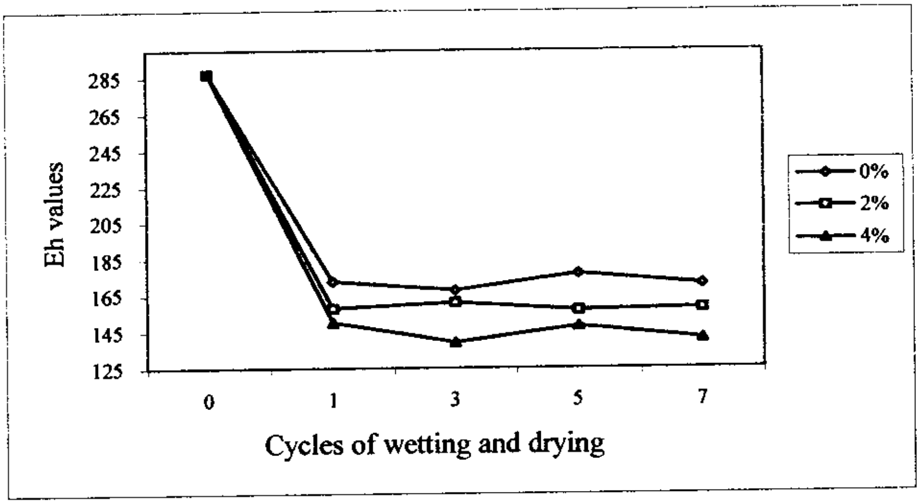

Fig. (10): Effect of alternate cycles of wetting and drying and bagasse compost application on Eh values of Borg El-Arab soil presence, yet the changes seemed more remarked in the latter case especially at the higher rate of the applied compost.

4.3.1.2. Effect on the redox potential Eh and the redox parameter *(pH+pe)*:

Application of bagasse compost caused the reduction in Eh value and consequently the pe value resulted due to the cycles of alternate wetting and drying to be more obvious, particularly at the higher rate of the applied compost. Such a result agrees to some extent, with that of **Hassan (1995). Tian-ren (1985)** indicated that the organic matter is the principal source of electrons. Release of electrons during organic matter decomposition lowers the Eh or *pe* and consequently the redox parameter *(pH+pe)*.

The reduction in the initial values of the redox potential Eh or *pe* and redox parameter *(pH+pe)* were obvious within the investigated cycles. Values of Eh, *pe* and *(pH+pe)* achieved the minimum at the third cycle, thereafter tended to increase slightly. Decomposition of the organic matter, as mentioned before, supplied the soil solution with electrons resulted in decrease in Eh (or *pe*) of the soil. This process probably attained its highest rate at the third cycles, therefore, the remained amount of organic matter was not sufficient for providing electrons enough to reduce soil Eh or *pe*.

4.3.2. Effect on availability of Fe and Mn and their relation to the redox parameter:

4.3.2.1. Effect on Fe availability:

Data presented in Table (14) and illustrated graphically in Fig. (11) show the changes occurred in values of DTPA-

Table (14): Effect of application of different rates of bagasse compost on DTPA-extractable Fe from Borg El-Arab soil under alternate cycles of wetting and drying.

Rate of applied bagasse compost % [R]	DTPA-extractable Fe (mg kg^{-1})					
	Time zero	Cycles of wetting and drying [C]				Mean
		1st	3rd	5th	7th	
0	4.00	6.00	4.00	3.34	2.00	3.87
2	4.00	10.00	8.00	6.00	6.00	6.80
4	4.00	14.00	10.00	8.08	8.00	8.82
Mean	4.00	10.00	7.33	5.81	5.33	6.50
LSD (0.05):	[R] = 0.15		[C] = 0.19		[R×C] = 0.33	

extractable Fe as a result of applying bagasse compost to Borg El-Arab under the investigated cycles of alternate wetting and drying.

It is noticeable that application of the compost to the calcareous soil resulted in increase in its content of DTPA-extractable Fe. Increasing rate of the applied compost was associated with increase in DTPA-extractable Fe. Mean value of the DTPA-extractable Fe in absence of the applied compost was about 3.9 mg kg^{-1} increased upon application of the compost at a rate of 2 % to about 6.8 mg kg^{-1}. Rising rate of the applied compost to 4 % was associated with a further increase in DTPA-extractable Fe to a mean value of about 8.8 mg kg^{-1}. These results agree with those of **Takkar et al. (1969)** who found that higher amounts of extractable Fe were significantly and positively correlated with soil content of the organic carbon. **Loeppert and Hallmark (1985)** went almost to similar results.

This increase in DTPA-extractable Fe may be due to decrease occurred in the soil redox parameter *(pH+pe)* that associated the application of the compost. Besides, the Fe released due to decomposition of organic matter might be considered as an additional source for increasing soil content of DTPA-extractable Fe.

DTPA-extractable Fe achieved its highest value at the first cycle thereafter it tended to decrease gradually to attain a minimum value at the seventh cycle. It could be said that, generally, the higher the soil redox parameter, the lower the value of DTPA-extractable Fe and vice versa, however, the highest value of DTPA-extractable Fe did not correspond the lowest overall redox parameter. This might be attributed to contribution of some other factors in controlling Fe availability. One of these factors is thought to be the soil high content of $CaCO_3$. **Bear (1964)** declared that soluble Fe^{2+} undergoes a sequence of reactions with $CaCO_3$ in the calcareous soils resulting in ferric oxide Fe_2O_3 in which Fe is unavailable for plant. Also, $Ca(OH)_2$ which is a byproduct of the abovementioned reactions contributes to increase soil pH. Thus, it might be concluded that availability of DTPA-extractable Fe beyond the first cycle is final product of many factors among which the redox parameter, soil pH and soil content of $CaCO_3$. However, reduction in Fe availability due to chemical precipitation through reaction with $CaCO_3$ seems not to be the solely mechanism by which availability of Fe is reduced. Forming insoluble metal organic complexes may be another factor contribute to reduction of Fe availability.

4.3.2.2. Effect on Mn availability:

It is obvious from data presented in Table (15) and illustrated graphically in Fig. (12) that application of bagasse compost to the calcareous soil increased significantly its content of DTPA-extractable Mn. Mean value of DTPA-extractable Mn increased from 16.91 mg kg^{-1} in absence of the applied compost to 20.45 and 21.95 mg kg^{-1} upon application of the compost at rates of 2 and 4 %, respectively. It seems that the increment in DTPA-extractable Mn due to application of the compost at a rate of 2 % as compared to the control is relatively higher than that resulted due to application of the compost at a rate of 4 % as compared to that of 2 % i.e. the increase in DTPA-extractable

Table (15): Effect of application of different rates of bagasse compost on DTPA-extractable Mn from Borg El-Arab soil under alternate cycles of wetting and drying.

Rate of applied bagasse compost % [R]	DTPA-extractable Mn (mg kg^{-1})					
	Time zero	Cycles of wetting and drying [C]				Mean
		1st	3rd	5th	7th	
0	7.00	21.75	21.00	18.50	16.25	16.90
2	7.00	34.00	21.75	20.50	19.00	20.45
4	7.00	38.50	22.75	19.75	21.75	21.95
Mean	7.00	31.42	21.83	19.58	19.00	19.77
<u>LSD (0.05):</u>	[R] = 0.41		[C] = 0.53		[R×C] = 0.91	

Mn due to rising rate of the applied compost was a descending one. The effects of organic matter might be attributed to its role as an electron source for redox reactions and to its function as a microbial substrate **(Reisenour, 1988).**

Results similar to those obtained herein were shown by **Asghar and Kanehiro (1980)** who concluded that application of organic matter increased the extractable amount of Mn. They added that this can occur by direct reduction of Mn due to organic reducing agents effect. Also, **Abd El-Latif and Abd El-Fattah (1985)** showed that addition of organic materials to the calcareous soil markedly increased the available Fe and Mn.

Likewise, **Kamh (1991)** found that in calcareous soils, application of organic matter to soil at a rate of 1 % increased the available Mn by about seven times as much as the control.

Available Mn content was affected by period of incubation and cycles of alternate wetting and drying in a way similar, to a great extent, to that of available Fe. The highest mean value of DTPA-extractable Mn was recorded at the first cycle beyond which Mn availability tended to decrease gradually. Reduction in pH value as well as the redox parameter *(pH+pe)* may account for the increase in Mn availability but they are not quite enough to externalize why the availability of Mn at the first cycle was highest although neither the pH value nor the overall redox parameter was lowest.

The decrease in value of the DTPA-extractable Mn after the first cycle, on the other hand, is probably due corresponding to gradual increase in pH and *(pH+pe)* value. Moreover, the chemisorption of Mn on $CaCO_3$ surface may be responsible for

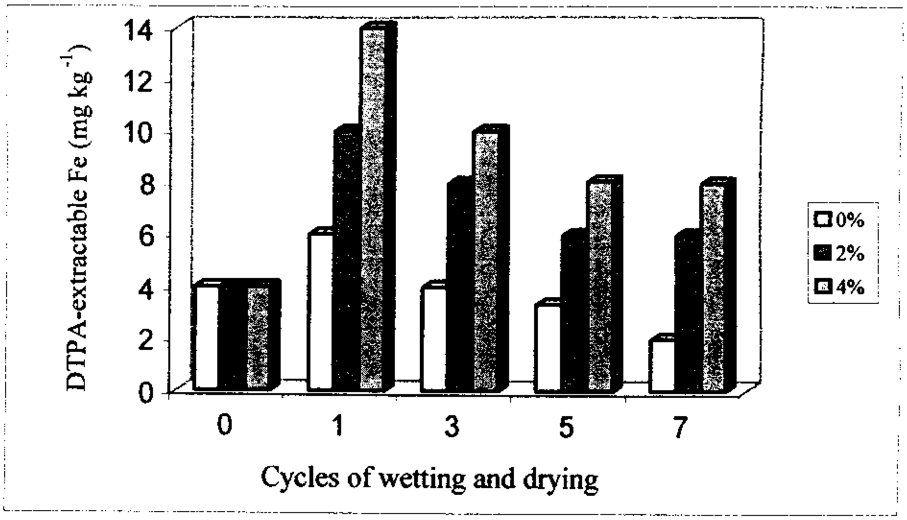

Fig. (11): Effect of application of bagasse compost on DTPA-extractable Fe from Borg El-Arab soil under alternate cycles of wetting and drying.

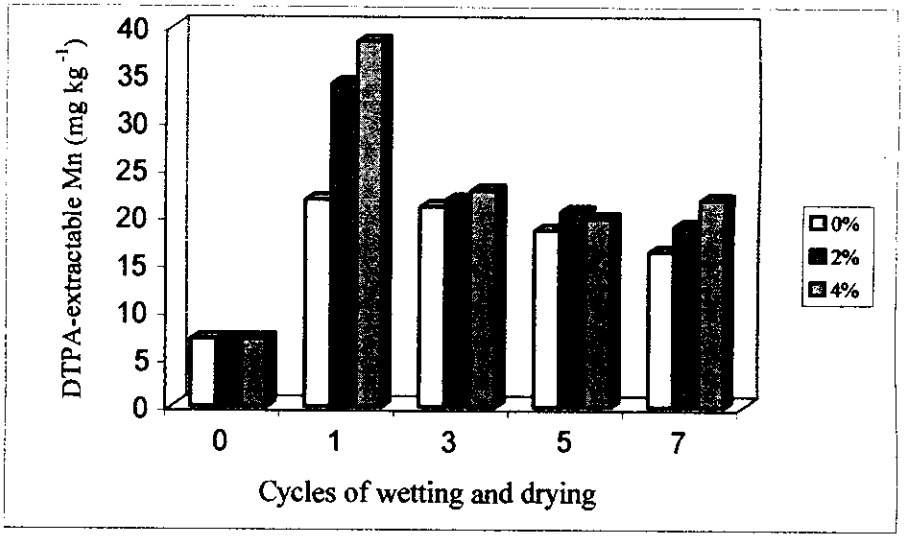

Fig. (12): Effect of application of bagasse compost on DTPA-extractable Mn from Borg El-Arab soil under alternate cycles of wetting and drying.

most loss of Mn^{2+} from solution. Also, formation of $MnCO_3$ species nucleated on $CaCO_3$ surfaces, with separate-phase of $MnCO_3$ being formed may be considered another reason for decreasing Mn availability.

4.4. Effect of application of elemental sulfur on Borg El-Arab soil under alternate cycles of wetting and drying:

4.4.1. Effect on pH, Eh and the redox parameter *(pH+pe)*:

Data presented in Table (16) and illustrated graphically in Fig. (13 and 14) reveal the changes in soil pH, redox potential Eh and the redox potential *(pH+pe)* occurred in the calcareous soil of Borg El-Arab due to treating this soil with elemental sulfur at three different rates 0, 0.2 and 0.4 % under cycles of alternate wetting and drying.

4.4.1.1. Effect on pH:

In absence of applied elemental sulfur, once the soil was exposed to alternate cycles of wetting and drying pH values were decreased and achieved the minimum at the third cycle, beyond which the soil tried to regain its initial pH value, thus soil pH rose but remained slightly below the initial level. The accumulation of CO_2 during wetting reestablished reducing conditions resulted in reduction in soil pH whereas during the drying cycles CO_2 diffused more rapidly to atmosphere causing pH to rise. This finding stands in well agreement with that of **Sajwan and Lindsay (1986)** who declared that pH of the calcareous soil decreases due to the effect of increased partial pressure of CO_2 on $CaCO_3$ solubility. They pointed out that the exact pH is largely controlled by the resulting partial pressure of CO_2.

Application of elemental sulfur to Borg El-Arab soil was associated with further decreases in values of soil pH. It was

Table (16): Effect of application of different rates of elemental sulfur on pH, Eh, *pe* and the redox parameter *(pH+pe)* of Borg El-Arab soil under alternate cycles of wetting and drying.

Rate of applied elemental sulfur % [R]	Soil parameter	Cycles of wetting and drying [C]					Mean
		Time zero	1st	3rd	5th	7th	
0	pH	8.28	7.96	7.88	8.11	8.20	8.09
	Eh (mV)	287	173	168	177	171	195.2
	Pe	4.85	2.92	2.84	2.99	2.89	3.30
	pH+pe	13.13	10.88	10.72	11.00	11.09	11.36
0.2	PH	8.28	7.93	7.68	7.93	8.09	7.98
	Eh (mV)	287	162	153	158	157	183.4
	pe	4.85	2.74	2.59	2.67	2.65	3.10
	pH+pe	13.13	10.67	10.27	10.60	10.74	11.08
0.4	pH	8.28	7.74	7.62	7.87	7.99	7.90
	Eh (mV)	287	157	148	153	153	179.6
	pe	4.85	2.65	2.5	2.59	2.59	3.04
	pH+pe	13.13	10.39	10.12	10.46	10.49	10.92
		Means of the applied elemental sulfur					
	pH	8.28	7.88	7.73	7.97	8.09	7.99
	Eh	287.0	164.0	156.3	162.7	160.3	186.1
	pe	4.85	2.77	2.64	2.75	2.71	3.14
	pH+pe	13.13	10.65	10.37	10.69	10.77	11.12
<u>LSD (0.05):</u>			[R]		[C]	[R×C]	
	pH		0.09		0.12	NS	
	Eh (mV)		2.59		3.34	5.79	
	pH+pe		0.08		0.10	0.18	

NS = not significant

noticed that the applied sulfur caused the reduction in soil pH occurred due to alternate wetting and drying cycles to be more obvious particularly when rate of the applied sulfur was raised to 0.4 %.

Tiedje et al. (1984) revealed that processes in wetted soils can be listed according to their approximate sequence of occurrence as follows: elimination of oxygen (anoxia), denitrification, Mn^{4+} reduction, Fe^{3+} reduction and SO_4^{2-} reduction. Accordingly reduction of sulfur requires as mentioned before very strong reduction conditions which can be found only under flooding conditions. On the other hand, alternate wetting and drying cycles permit oxidation of sulfur to occur particularly during the drying cycles where oxygen diffuses to soil and carbon dioxide diffuses out of it. Oxidation of elemental sulfur, then can occur chemically as well as biologically as mentioned before giving out protons and electrons hence the soil pH is reduced.

Taking into account effect of time of incubation under alternate cycles of wetting and drying, data in Table (16) and Fig. (13) illustrate that soil pH decreased from a mean value of 8.28 at the time zero (in practice one hour after incubation) to 7.87 at the first cycle (corresponding to a reduction of 0.31 pH unit) and achieved its lowest mean value 7.7 at the third cycle wherein oxidation of the applied sulfur is expected to attain the maximum. It is of interest to indicate that elemental sulfur at its higher rate of application began to be oxidized early giving H_2SO_4 that enormoused reduction of soil pH at the first cycle and resulted in the lowest soil pH at the third one.

The aforementioned discussion illustrates that oxidation of elemental sulfur begins once O_2 (g) diffuse from atmosphere to soil and reaches its maximum level around the third cycle. Yet, the increase in pH values beyond the third cycle might be a final product of alternate reduction conditions and oxidation ones besides the effect of the hydrolysis of the exchangeable cations present on soil complex and hydrolysis of $CaCO_3$ itself on rising soil pH.

The slightly reducing effect of applied elemental sulfur on soil pH is confirmed by the results of **Modaihsh et al. (1989)** who found that sulfur application at the rate of 5 g S° kg^{-1} (0.5 %) slightly decreased the soil pH of a loamy sandy calcareous soil containing 42.4 % $CaCO_3$ from 8.5 to 8.36. On the other hand ,**Hassanein (1991)** found that added sulfur (S°)did not affect soil pH in a highly calcareous soil.

The slight decrease in soil pH of Borg El-Arab soil is probably due to its high content of $CaCO_3$ (41 %) which might have a high buffering capacity.

4.4.1.2. Effect on the soil redox potential (Eh) and the redox parameter *(pH+pe)*:

Patterns of changes in Eh values of the calcareous soil of Borg El-Arab during the studied cycles of alternate wetting and drying were similar, to a large extent, to those of pH. This means that the Eh value markedly decreased from its initial value (287 mV) to values ranging from 168 to 177 mV within the studied successive cycles of alternate wetting and drying in absence of applied sulfur.

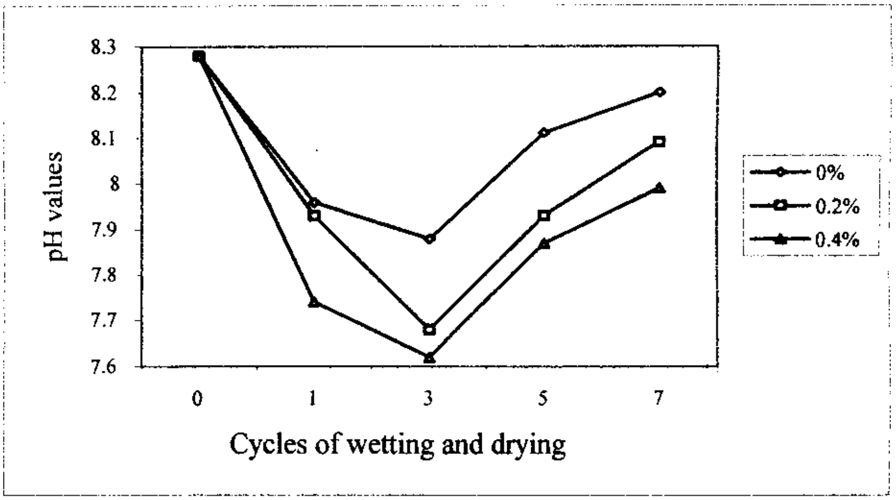

Fig. (13): Effect of sulfur application on pH values of Borg El-Arab soil under alternate cycles of wetting and drying.

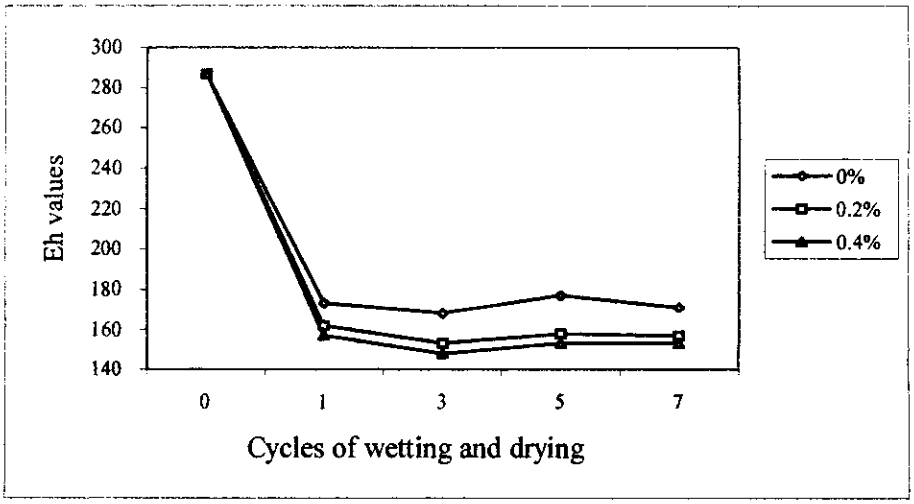

Fig. (14): Effect of sulfur application on Eh values of Borg El-Arab soil under alternate cycles of wetting and drying.

Upon application of elemental sulfur at a rate of 0.2 %, the initial Eh value was further reduced to ones ranging from 153 to 162 mV during the same studied cycles. The corresponding values of Eh attained upon application of the elemental sulfur at its highest rate (0.4 %) were relatively lower than those achieved upon application of the elemental sulfur at a rate of 0.2 %. Decomposition of organic matter may be considered as an additional source of electrons thus increased activity of aqueous electrons and as a result the Eh (or pe) decreased. The reduction in the Eh values was associated always with corresponding reduction in pe since the latter value is obtained by dividing the former by a constant value 59.2. Consequently, values of the redox parameter *(pH+pe)* underwent changes similar to those of pH, Eh and *pe* ones, i.e. application of elemental sulfur was associated with reduction in the overall redox parameter and the maximum reduction occurred due to application of the highest rate of applied elemental sulfur 0.4%.

Table (16) shows that the overall redox parameter was reduced to a lowest value during the third cycle of alternate wetting and drying regardless of the rate of applied sulfur. The rise occurred in the value of this parameter after the third cycle is probably attributed to the partial hydrolysis of the cations adsorbed on the soil complex as well as the hydrolysis of $CaCO_3$ itself and consequent increase in pH which is a component of the overall redox parameter. Moreover, no further release of electrons could occur after the third cycle because it is supposed that almost all the applied sulfur would be oxidized within period of this cycle and thus no further decrease in Eh (or pe) value could occur.

4.4.2. Effect on availability of Fe and Mn and their relation to the redox parameters:

4.4.2.1. Effect on Fe availability:

Data presented in Table (17) and Fig. (15) show values of DTPA-extractable Fe due to application of elemental sulfur to the calcareous soil of Borg El-Arab under alternate cycles of wetting and drying. It could be seen that application of elemental sulfur at a rate of 0.2 % increased the DTPA-extractable Fe from a mean value of 3.87 mg kg^{-1} to a mean value of 4.48 mg kg^{-1}. Increasing rate of the applied elemental S°was associated with a further increase in mean values of DTPA-extractable Fe to 6 mg kg^{-1}. Similar findings were reported by **Hassan and Olson (1966), Procopiou et al. (1976), Cates et al. (1982) and Khalefa (2002)**.

The increase in values of DTPA-extractable Fe may be attributed to the reduction occurred in pH, Eh, *pe* and the redox parameter *(pH+pe)* caused due to the applied sulfur. Moreover, it could be shown that the higher the rate of the applied elemental sulfur, the higher the reduction occurred in all the abovementioned parameters and consequently the attained value of DTPA-extractable Fe.

Regarding effect of period of incubation of soil on values of DTPA-extractable Fe, data in Table (17) reveal that mean value of DTPA-extractable Fe increased from an initial mean value of 4 mg kg^{-1} at the time zero to a maximum mean value of 8.99 mg kg^{-1} within the first cycle of alternate wetting and

Table (17): Effect of application of different rates of elemental sulfur on DTPA-extractable Fe from Borg El-Arab soil under alternate cycles of wetting and drying.

Rate of applied elemental sulfur % [R]	DTPA-extractable Fe (mg kg^{-1})					
	Time zero	Cycles of wetting and drying [C]				Mean
		1st	3rd	5th	7th	
0	4.00	6.00	4.00	3.34	2.00	3.87
0.2	4.00	7.60	4.33	3.47	3.00	4.48
0.4	4.00	13.36	5.67	3.66	3.34	6.01
Mean	4.00	8.99	4.67	3.49	2.78	4.79
LSD (0.05):	[R] = 0.23		[C] = 0.29		[R×C] = 0.51	

drying. Such an increase is probably due to a corresponding reduction in mean value of the overall redox parameter from 13.13 to 10.65 i.e. due to reduction in *(pH+pe)* parameter by about 2.48 unit. Thus, it could be said that the increase in DTPA-extractable Fe is about 2.012 mg Fe kg^{-1} soil per each unit decrease in the redox parameter *(pH+pe)*. However, the relation between DTPA-extractable Fe and the corresponding *(pH+pe)* values seemed not to be so simple because some other factors in the calcareous soil may slant it and contribute to Fe availability. Therefore, the increase in DTPA-extractable Fe between the first and third cycle was supposed to be 0.28 mg Fe kg^{-1} soil to correspond a reduction in *(pH+pe)* equals 0.14 according the above mentioned DTPA-extractable Fe – *(pH+pe)* relation. Instead, the the mean value of DTPA-extractable Fe decreased to 3.51 mg kg^{-1}. One of the factors that affects DTPA-extractable Fe other than the redox parameter might be the soil content of $CaCO_3$. **Bear (1964)** summarized the pathways through which available Fe^{2+} is converted into mono-available form in the calcareous soil in the following reactions:

$$Fe^{2+} + CaCO_3 \longrightarrow FeCO_3 + Ca^{2+}$$

$$4\,FeCO_3 + O_2 + Ca(HCO_3)_2 \longrightarrow 2\,Fe_2(CO_3)_3 + Ca(OH)_2$$

$$Fe_2(CO_3)_3 + 3\,H_2O \longrightarrow Fe_2O_3 + 3\,H_2CO_3$$

These equations illustrate the role of $CaCO_3$ in precipitating Fe and also rising soil pH from a mean value of 7.7 in the third cycle to 7.97 in the fifth one then to 8.09 in the seventh cycle corresponding to increases in mean value of *(pH+pe)* from 10.37 to 10.69 then 10.77. However, it was thought that adsorption of Fe on soil might be another mechanism by which available Fe is converted to unavailable form. To examine such a hypothesis, it was supposed that DTPA-extractable Fe which was highest at the first cycle is the initial concentration of available Fe in soil i.e. 8.99 mg Fe kg^{-1}. Thus the amounts of DTPA-extractable Fe decreased to 4.67, 3.51 and 2.11 for the third, fifth and seventh cycle, respectively. Meanwhile, 4.32, 5.48 and 6.88 mg Fe kg^{-1} soil were adsorbed by the above mentioned cycles, respectively. Thus, plotting values of concentration of DTPA-extractable Fe in equilibrium solution (C) as independent variables against c/x/m ones as the dependent variables (x/m) fitted Langmuir adsorption isotherm at a high level of significance ($r = 0.996^{**}$). The regression equation obtained was $c/x/m = -0.52 + 0.34\ C$. This finding might indicate to the adsorption mechanism as a reliable factor for interpreting decrease in DTPA-extractable Fe beyond the first cycle of alternate wetting and drying.

4.4.2.2. Effect on Mn availability:

Data presented in Table (18) reveal that application of elemental sulfur to the calcareous soil resulted in increase in its content of DTPA-extractable Mn. Values of DTPA-extractable Mn increased significantly from a mean value of 16.90 mg Mn kg^{-1} in absence of the applied sulfur to a mean value of 22.1 mg Mn kg^{-1} upon application of elemental sulfur at a rate of 0.2 %. The corresponding mean value attained upon rising rate of the applied elemental sulfur to 0.4 % was 26.12 mg Mn kg^{-1}. **Hassan and Olson (1966), Rayan et al. (1974), Procopiou et al. (1976)** and **Cates et al. (1982)** went almost to similar results.

Table (18): Effect of application of different rates of elemental sulfur on DTPA-extractable Mn from Borg El-Arab soil under alternate cycles of wetting and drying.

Rate of applied elemental sulfur % [R]	DTPA-extractable Mn (mg kg^{-1})					
	Time zero	Cycles of wetting and drying [C]				Mean
		1st	3rd	5th	7th	
0	7.00	21.75	21.00	18.50	16.25	16.90
0.2	7.00	40.10	25.38	20.50	17.50	22.10
0.4	7.00	49.80	28.38	22.50	22.90	26.12
Mean	7.00	37.20	24.92	20.50	18.89	21.71
LSD (0.05):	[R] = 0.54		[C] = 0.70		[R×C] = 1.20	

The increase in DTPA-extractable Mn obtained herein seems to be dependent on reduction of soil pH, Eh, *pe* and the redox parameter *(pH+pe)* together with some other factors.

The DTPA-extractable Mn, generally, increased as the pH, Eh and *(pH+pe)* parameter decreased. However, DTPA-extractable Mn achieved its highest values at the first cycle rather than the third one at which values of pH, Eh and *(pH+pe)* were minimums. Mean value of DTPA-extractable Mn increased from 7.0 mg Mn kg^{-1} (which is the initial value) to 37.2 mg Mn kg^{-1} at the first cycle (i.e. an increment of about 30.2 mg Mn kg^{-1}). Such an increase may be due to reduction in *pH+pe* from an initial mean value of about 13.13 to 10.65 (i.e. a decrement of about 2.48). Hence, it could be concluded that the DTPA-extractable Mn was increased from its initial mean value (at the time zero) by a rate of 30.2/2.48 = 12.19 mg Mn kg^{-1} per each unit decrease in *(pH+pe)* value to its highest content at the first cycle. Although the overall redox parameter *(pH+pe)* continued to decrease until the third cycle yet such a reduction in its value was not associated with a corresponding increase in DTPA-extractable Mn indicating that some other factors might contributed to Mn availability under these conditions. However, beyond the third cycle the reduction in Mn availability seemed associating to the increase in *(pH+pe)* parameter.

Such results coincided with those of **McBride (1979)** who interpreted depending on:

1- Chemisorption of Mn on $CaCO_3$ surfaces which may be responsible for most loss of Mn from the soluble form.

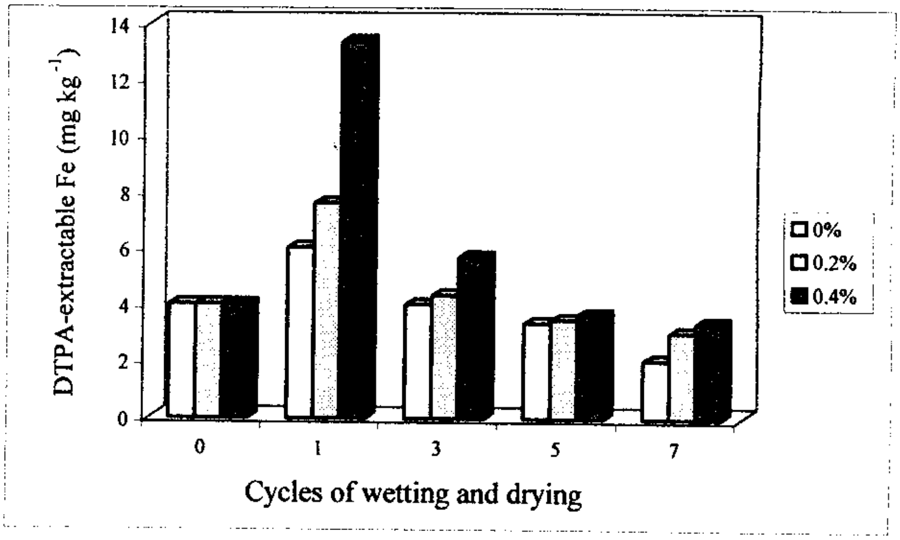

Fig. (15): Effect of application of sulfur on DTPA-extractable Fe from Borg El-Arab soil under alternate cycles of wetting and drying.

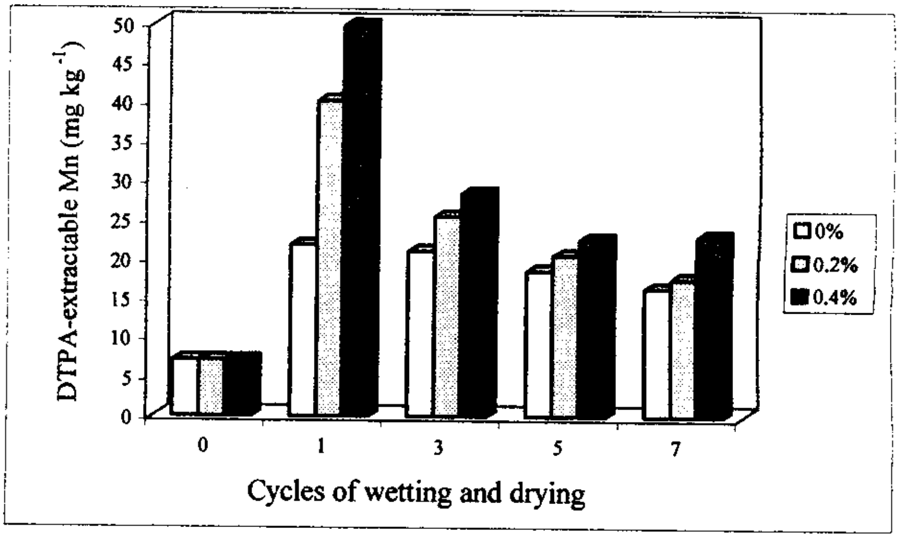

Fig. (16): Effect of application of sulfur on DTPA-extractable Mn from Borg El-Arab soil under alternate cycles of wetting and drying.

2- Formation of $MnCO_3$ species nucleated on $CaCO_3$ surfaces, with separate-phase of $MnCO_3$ not being formed **(McBride, 1979).**

Boischot and Durroux (1950) claimed that fixation of Mn by $CaCO_3$ was an adsorption phenomenon, incomplete at pH 8.5 and progressive with increased alkalinity. They added that the fixed amount of Mn was positively related to the time of contact and with the content of $CaCO_3$.

As it was done in case of DTPA-extractable Fe, it was proved that adsorption of Mn obeyed Langmiur isotherm and could be represented by the regression equation

$$c/x/m = -2.19 + 0.17\,C \qquad (r = 0.997^{**})$$

Where c: is the concentration of Mn in the equilibrium solution,

x/m: the amount of adsorbed Mn in µg kg^{-1} soil.

4.5. Redistribution of Fe and Mn among the different solid-phase fractions in Moshtohor and Borg El-Arab soils under alternate cycles of wetting and drying:

4.5.1. Redistribution of Fe:

The redistributions of Fe among the different fractions of the incubated soils of Moshtohor and Borg El-Arab under alternate cycles of wetting and drying are shown in Table (19) and illustrated graphically in Figs. (17, 18 and 19).

As mentioned before these soils underwent a reduction and their contents of organic matter in particular underwent decomposition resulting in decrease in Eh or *(pH+pe)* and increase in partial pressure of carbon dioxide (pCO_2). The reduction process resulted in reduction of valence of Fe from the higher valence (III) to the lower one (II), and in general, decreased the easily reducible oxides (ERO) and, to some extent, the reducible oxides particularly within the first cycle. Organic matter decomposition led to the release of Fe, in general, thus decreased the organic matter fraction and accordingly increased the carbonate (CARB) fraction due to the increase of CO_2 pressure. It could be concluded from the abovementioned observations, that with the decrease of Eh and *pH+pe* of the soils due to the alternate cycles of wetting and drying Fe was redistributed, generally, from the stable, non-available forms into the labile potential available and readily forms. This conclusion stands in well agreement with the results of **Han and Banin (2000)** who reported that, in the native arid-zone soil, Fe was mainly in the RES and RO fractions. Wetting results in reduction

Table (19): Distributions of Fe among the different solid-phase fractions of Moshtohor and Borg El-Arab soils under alternate cycles of wetting and drying.

Soil	Cycles of wetting and drying	Fe in the different soil fractions (mg kg^{-1})							Fe in the different soil fractions as percentage of the total (%)						
		EXC	CARB	ERO	OM	RO	RES	TOT	EXC	CARB	ERO	OM	RO	RES	TOT
The Nile alluvial non-calcareous soil of Moshtohor	Time zero	1.9	130.7	189.2	79.5	1590.2	44108.5	46100	0.004	0.284	0.410	0.172	3.449	95.680	100
	First cycle	2.3	139.6	186.5	73.8	1589.6	44108.2	46100	0.005	0.303	0.405	0.160	3.448	95.679	100
	Third cycle	2.1	145.8	189.9	71.5	1585.0	44105.7	46100	0.005	0.316	0.412	0.155	3.438	95.674	100
	Fifth cycle	2.2	140.2	185.5	70.2	1601.1	44100.8	46100	0.005	0.304	0.402	0.152	3.473	95.663	100
	Seventh cycle	2.1	138.6	186.1	70.9	1598.9	44103.4	46100	0.005	0.301	0.404	0.154	3.468	95.669	100
The calcareous soil of Borg El-Arab	Time zero	1.2	100.5	101.9	19.6	1199.5	11177.3	12600	0.010	0.798	0.809	0.156	9.520	88.709	100
	First cycle	2.5	109.1	100.6	18.8	1196.2	11172.8	12600	0.020	0.866	0.798	0.149	9.494	88.673	100
	Third cycle	2.3	108.2	100.4	15.3	1199.6	11174.2	12600	0.018	0.859	0.797	0.121	9.521	88.684	100
	Fifth cycle	2.1	109.8	100.6	15.0	1201.2	11171.3	12600	0.017	0.871	0.798	0.119	9.533	88.661	100
	Seventh cycle	2.0	111.2	101.1	14.1	1201.8	11169.8	12600	0.016	0.883	0.802	0.112	9.538	88.649	100

Note: **EXC**, soluble plus exchangeable fraction; **CARB**, bound to carbonate fraction; **ERO**, easily reducible fraction; **OM**, bound to organic matter fraction; **RO**, bound to reducible oxides; **RES**, bound to the residual fraction and **TOT**, total fraction.

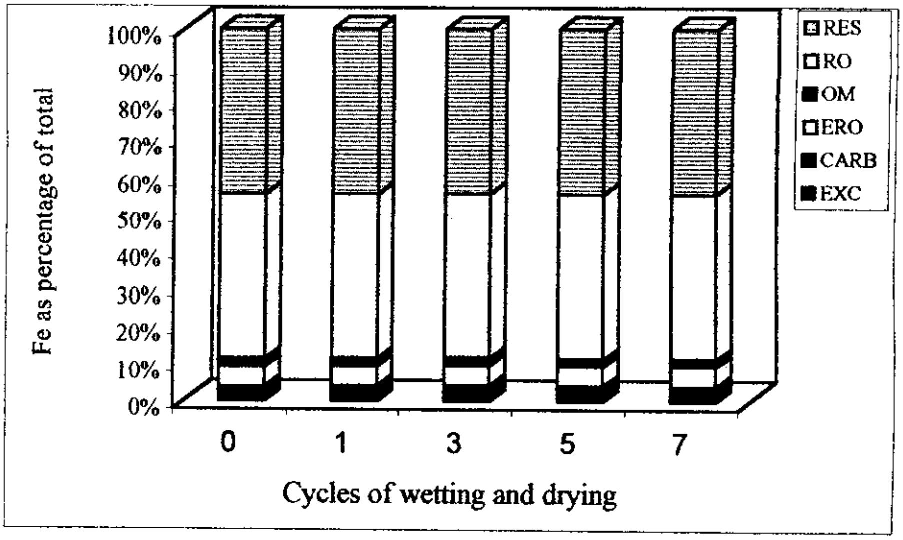

Fig. (17): Redistribution of Fe among its solid phase components in soil of Moshtohor under alternate cycles of wetting and drying.

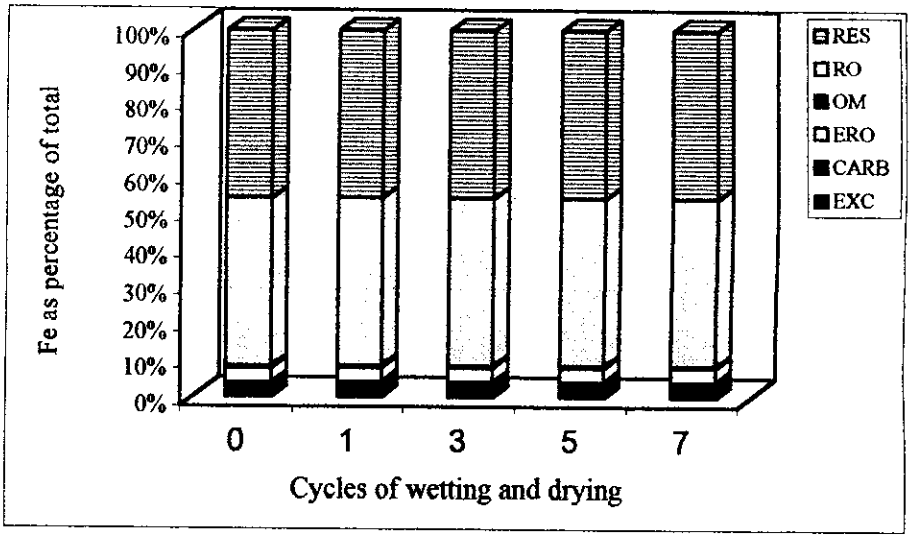

Fig. (18): Redistribution of Fe among its solid phase components in soil of Borg El-Arab under alternate cycles of wetting and drying.

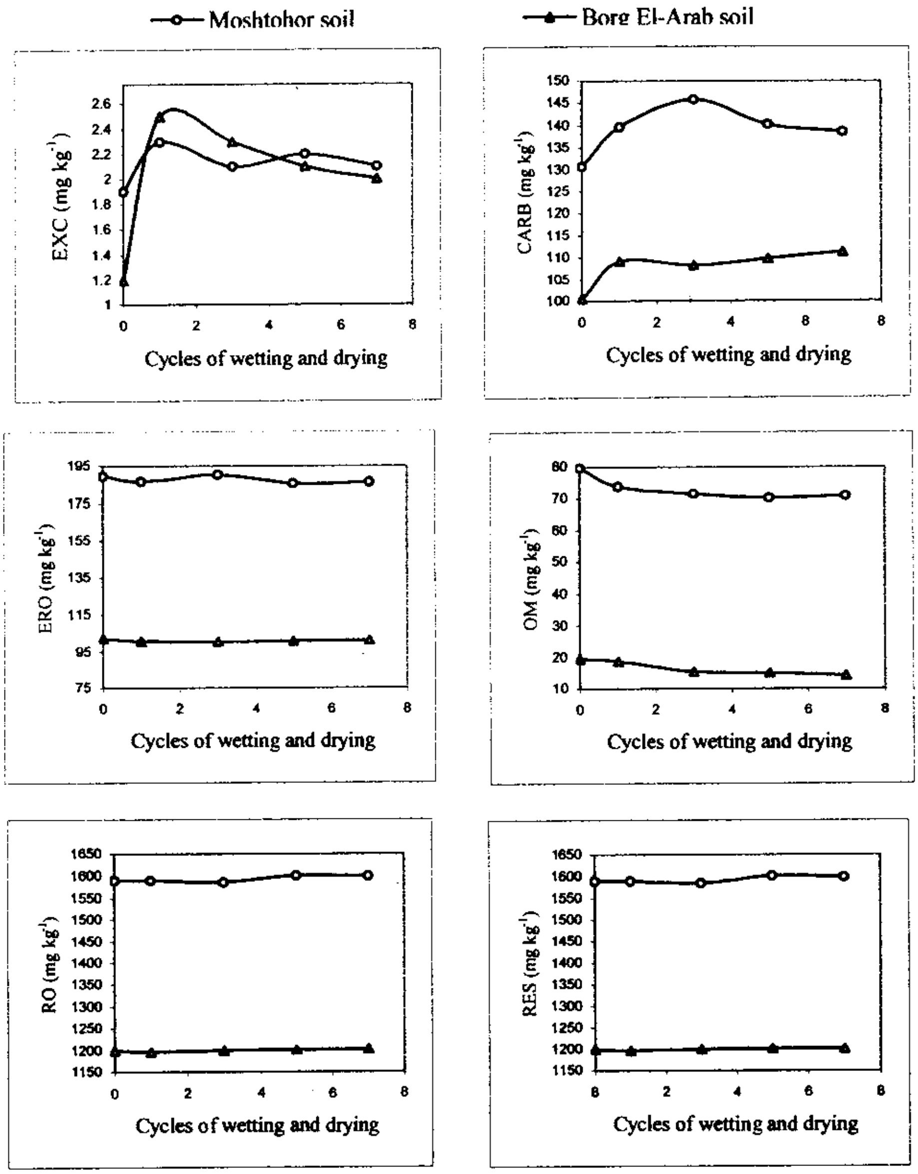

Fig. (19): The major pathways of redistribution of Fe in soils of Moshtohor and Borg El-Arab alternate cycles of wetting and drying.

of Fe (III) in the RO fraction into Fe (II) or mixed Fe^{2+}/ Fe^{3+} in the ERO, CARB (siderite, $FeCO_3$) and EXC fractions.

Fe redistribution among the different fractions of Borg El-Arab soil differed from the corresponding one of Moshtohor soil due to the variations in their mineralogical, physical and chemical composition.

As a final conclusion for this part of study it can be said that the analysis of pathways of redistribution of Fe among its solid-phase fractions could be very helpful to predict the changes in availability of these nutritive elements under alternate cycles of wetting and drying simulating to a great extent, what occurs in the soils due to successive irrigations.

4.5.2. Redistribution of Mn:

Regarding the redistribution of Mn among the different soil fractions of the Nile alluvial non-calcareous soil of Moshtohor, it could be noticed that from Table (20) and Figs. (20,21 and 22) at the time zero, Mn was predominately in the residual fraction (RES) followed by the reducible fraction (RO) then the easily reducible, the carbonate and the organic matter fractions (Table, 20). In comparison we note that Mn in Borg El-Arab was found primarily in residual fraction followed by the easily reducible, the reducible, carbonate and the organic matter (OM) fractions. Very small amount of Mn was found in EXC fraction in both soils.

The percentages of the RES and EXC fractions in Moshtohor soil were higher than those of Bog El-Arab soil. This was partly related to differences in the abundance of various soil components that compete with each other for the element **(Han**

Table (20): Distributions of Mn among the different solid-phase fractions of Moshtohor and Borg El-Arab soils under alternate cycles of wetting and drying.

Soil	Cycles of wetting and drying	Mn in the different soil fractions (mg kg^{-1})							Mn in the different soil fractions as percentage of the total (%)						
		EXC	CARB	ERO	OM	RO	RES	TOT	EXC	CARB	ERO	OM	RO	RES	TOT
The Nile alluvial non-calcareous soil of Moshtohor	Time zero	7.0	23.9	41.3	23.2	63.2	1116.4	1275	0.549	1.875	3.239	1.820	4.957	87.561	100
	First cycle	41.9	35.8	18.5	25.2	59.1	1094.5	1275	3.286	2.808	1.451	1.976	4.635	85.843	100
	Third cycle	43.2	40.2	18.6	24.1	58.2	1090.7	1275	3.388	3.153	1.459	1.890	4.565	85.545	100
	Fifth cycle	44.8	43.2	15.9	22.2	58.1	1090.8	1275	3.514	3.388	1.247	1.741	4.557	85.553	100
	Seventh cycle	43.0	44.2	15.6	21.9	58.2	1092.1	1275	3.373	3.467	1.224	1.718	4.565	85.655	100
The calcareous soil of Borg El-Arab	Time zero	1.1	35.4	48.5	21.2	41.0	231.8	379	0.290	9.340	12.797	5.594	10.818	61.161	100
	First cycle	13.5	50.3	35.3	17.4	32.2	230.3	379	3.562	13.272	9.314	4.591	8.496	60.765	100
	Third cycle	12.5	63.8	33.8	17.4	30.6	220.9	379	3.298	16.834	8.918	4.591	8.074	58.285	100
	Fifth cycle	11.2	68.7	32.0	17.1	29.3	220.7	379	2.955	18.127	8.443	4.512	7.731	58.232	100
	Seventh cycle	10.8	71.3	30.8	16.9	29.8	219.4	379	2.850	18.813	8.127	4.459	7.863	57.889	100

Note: **EXC**, soluble plus exchangeable fraction; **CARB**, bound to carbonate fraction; **ERO**, easily reducible fraction; **OM**, bound to organic matter fraction; **RO**, bound to reducible oxides; **RES**, bound to the residual fraction and **TOT**, total fraction.

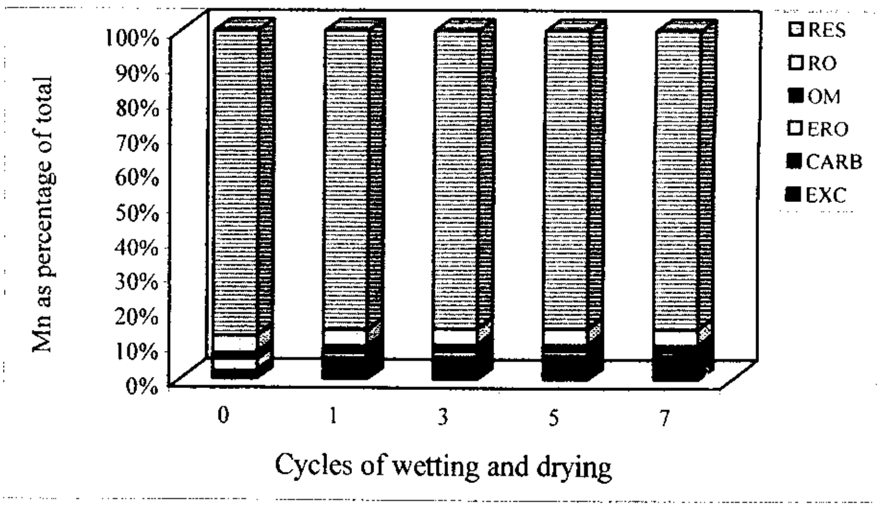

Fig. (20): Redistribution of Mn among its solid phase components in soil of Moshtohor under alternate cycles of wetting and drying.

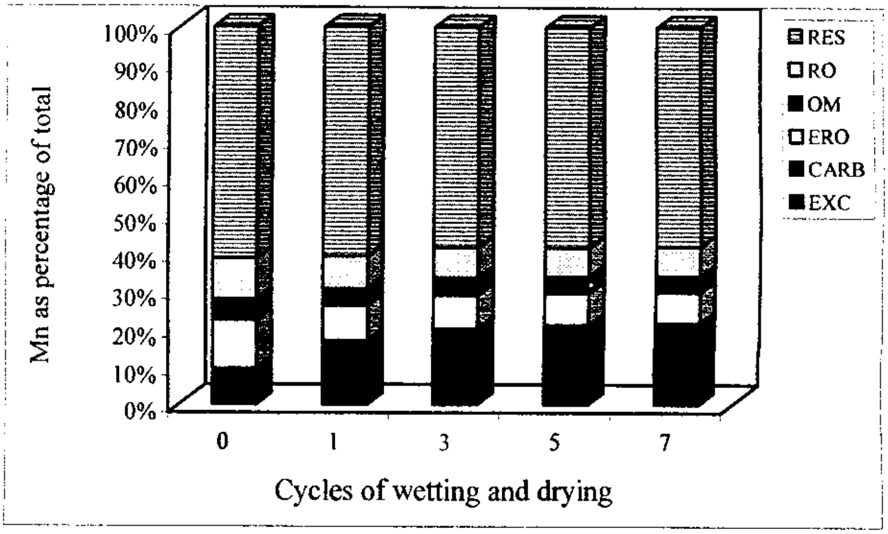

Fig. (21): Redistribution of Mn among its solid phase components in soil of Borg El-Arab under alternate cycles of wetting and drying.

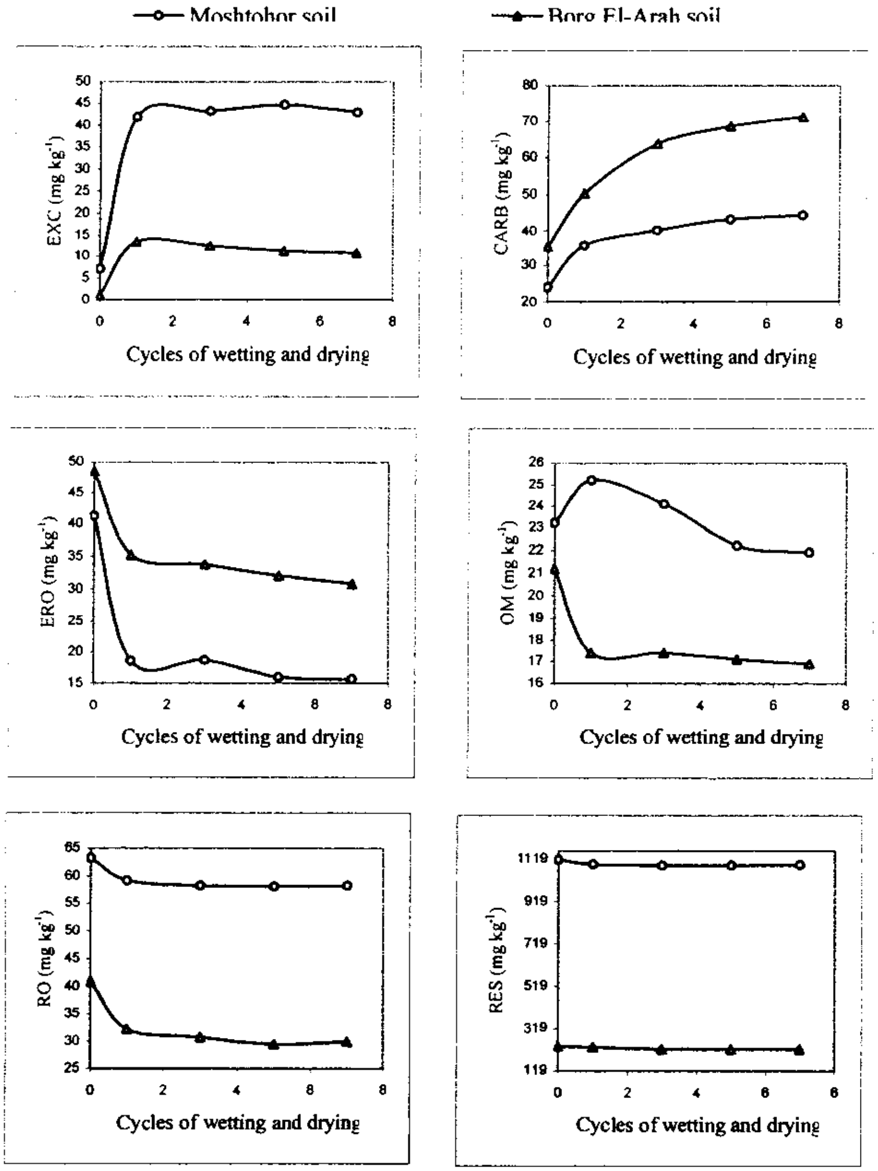

Fig. (22): The major pathways of redistribution of Mn in soils of Moshtohor and Borg El-Arab alternate cycles of wetting and drying.

and Banin, 1996). Paradoxically, however, carbonate fraction in the calcareous soil contained relatively more Mn than in the non-calcareous one probably due to the higher carbonate content of the former than the later.

Data in Table (20) reveal a rapid initial stage of transformation of Mn from the ERO fraction to the EXC and carbonate fractions in both soils. Beyond the third cycle there were more stable and slow changes among fractions. The slow redistributions involved the OM and reducible oxides from which some Mn was transported to the more mobile fractions.

The initial redistributions of Mn among soil fractions during incubation were concomitant with changes in pH and Eh. Initially, after one hour of incubation, the values of the redox parameter *(pe+pH)* were 12.25 and 13.13 in Moshtohor and Borg El-Arab soils, respectively. In both soils, *pH+pe* decreased to values of about 10.67 and 10.88 at end of the first cycle and almost remained stable thereafter.

Most of the changes resulted from pe changes where Eh decreased from 257 and 287 mV after one hour of incubation to 158 and 173 mV at end of the first cycle in Moshtohor and Borg El-Arab soils, respectively and changed very little thereafter. During the same period, pH of the Moshtohor soil decreased from 8.18 to about 8.00 and the corresponding decrease in soil pH of the calcareous soil was from 8.28 to about 7.96. With the decrease of pH and *pH+pe* of soils as a result of incubation under alternate cycles of wetting and drying, Mn was chemically reduced and redistribution among soil fractions. As a result conclusion, these results suggested that upon wetting, anaerobic activity predominates and consequently reducible form of Mn released from minerals such as pyrolusite (β-MnO_2; Mn^{4+}) and possibly, magnetite (□-MnOOH; Mn^{3+}) originally present in the ERO fraction and redistribution to the Mn^{2+} ion present in the EXC fraction or to the rodochrosite ($MnCO_3$, Mn^{2+}) present in the CARB fraction.

The studied soils differed obviously in their detailed redistribution pathways. In Moshtohor soil, Mn was redistribution from the ERO fraction mainly into the EXC fraction. In Borg El-Arab soil, Mn was redistribution from the ERO fraction mainly into the CARB fraction and only a relatively smaller part of it moved into the EXC fraction and then was slowly redistribution to the CARB fraction.