

#### 4. RESULTS AND DISCUSSION

The main objective of this study represents a trial to elucidate the role played by some reactions involved in the P retention phenomenon that takes place on addition of soluble P compounds to the soil.

The study included eight soil samples from different locations in the A.R.E. and F.R.G.

The data obtained are presented and discussed under three main parts namely; retention and release of added P by soils, adsorption reactions of P by soils and diffusion of  $^{32}\text{P}$  in soils.

##### 4.1. Retention and release of added P by soils :

##### 4.1.1. Retention of added P by soils :

The capability of soil to retain the added P was determined using labelled  $\text{KH}_2^{32}\text{P}_{04}$  where the role of the concentration of added P, temperature and the time of reaction were taken into consideration.

The detailed data obtained for P retention are shown in the appendix (table 3). These data are summarized on a basis of average over all values in tables (4 - 7) and illustrated in Figs. (3 - 5).

Table. (4) Phosphate retention by soils incubated with P solution  $\mu\text{g. P/g. soil}$

Added P g. P/g. soil		Soil location												Wolfsheim										
		El-Hobareis			Abou El-Matamir			El-Tehrreer			Moshtohr							Meat-Ianana			El-Deer			Grünigen
	T20	T37	T20	T37	T20	T37	T20	T37	T20	T37	T20	T37	T20	T37	T20	T37	T20	T37	T20	T37	T20	T37	T20	T37
10	9.79	9.88	8.75	9.07	8.71	9.07	9.2	9.49	7.39	7.70	8.98	9.21	9.54	9.56	9.87	9.84								
M	9.84		8.91		8.89		9.35		7.55			9.1		9.55		9.86								
30	29.1	29.35	23.58	25.02	22.02	23.83	26.05	27.33	17.5	19.43	24.02	25.42	27.17	27.44	29.39	29.36								
M	29.23		24.3		22.93		26.69		18.47		24.72		27.31		29.38									
60	55.22	56.68	40.7	44.5	35.68	40.68	48.4	51.26	30.04	39.81	41.04	52.52	53.24	53.92	58.34	58.34								
M	55.95		42.6		38.18		49.83		34.93		47.18		53.58		58.34									
90	77.73	80.79	54.57	60.69	46.2	54.63	68.52	73.41	37.95	44.22	55.65	63.42	75.99	77.61	86.79	86.79								
M	79.26		57.63		50.42		70.97		41.09		59.54		76.8		86.79									
120	96.64	102.76	64.6	77.0	54.96	68.04	87.04	94.0	42.96	52.96	70.04	79.04	96.48	99.59	114.52	114.6								
M	99.7		70.8		61.5		90.52		47.96		74.54		98.04		114.56									
150	114.0	124.4	75.4	90.15	61.0	78.22	103.5	113.85	52.1	62.3	80.6	92.25	115.35	119.95	141.0	142.2								
M	119.2		82.8		69.6		108.68		57.2		86.4		117.65		141.6									
180	130.14	146.52	84.66	103.62	68.7	101.64	119.34	132.42	57.9	71.77	91.86	105.85	132.48	140.22	168.3	168.72								
M	138.33		94.1		85.17		125.88		64.84		98.85		136.35		168.51									
210	143.57	169.26	90.79	116.62	72.87	115.35	132.93	150.78	62.3	79.17	98.49	115.92	147.21	157.15	193.69	198.59								
M	156.4		103.7		94.1		141.86		70.74		107.2		152.18		196.14									
620	282.1	486.5	193.0	261.64	128.05	256.47	273.43	332.99	112.1	173.6	187.65	235.8	284.17	343.89	474.3	494.97								
M	384.3		227.32		192.26		313.21		142.85		211.73		314.03		484.64									
1240	430.8	987.5	266.8	465.41	183.8	460.45	444.9	624.96	175.49	241.8	269.2	387.7	430.28	543.95	743.59	809.3								
M	709.5		336.0		322.1		534.93		208.61		328.45		487.12		776.45									
1860	555.1	1449.6	383.7	695.64	236.84	615.66	541.1	799.8	261.95	360.22	317.35	482.36	520.8	740.28	933.24	1051.52								
M	1002.3		539.7		426.25		670.45		311.09		399.86		630.54		991.38									
Average	253		147.1		126.2		194.8		91.39		131.6		191.24		277.97									

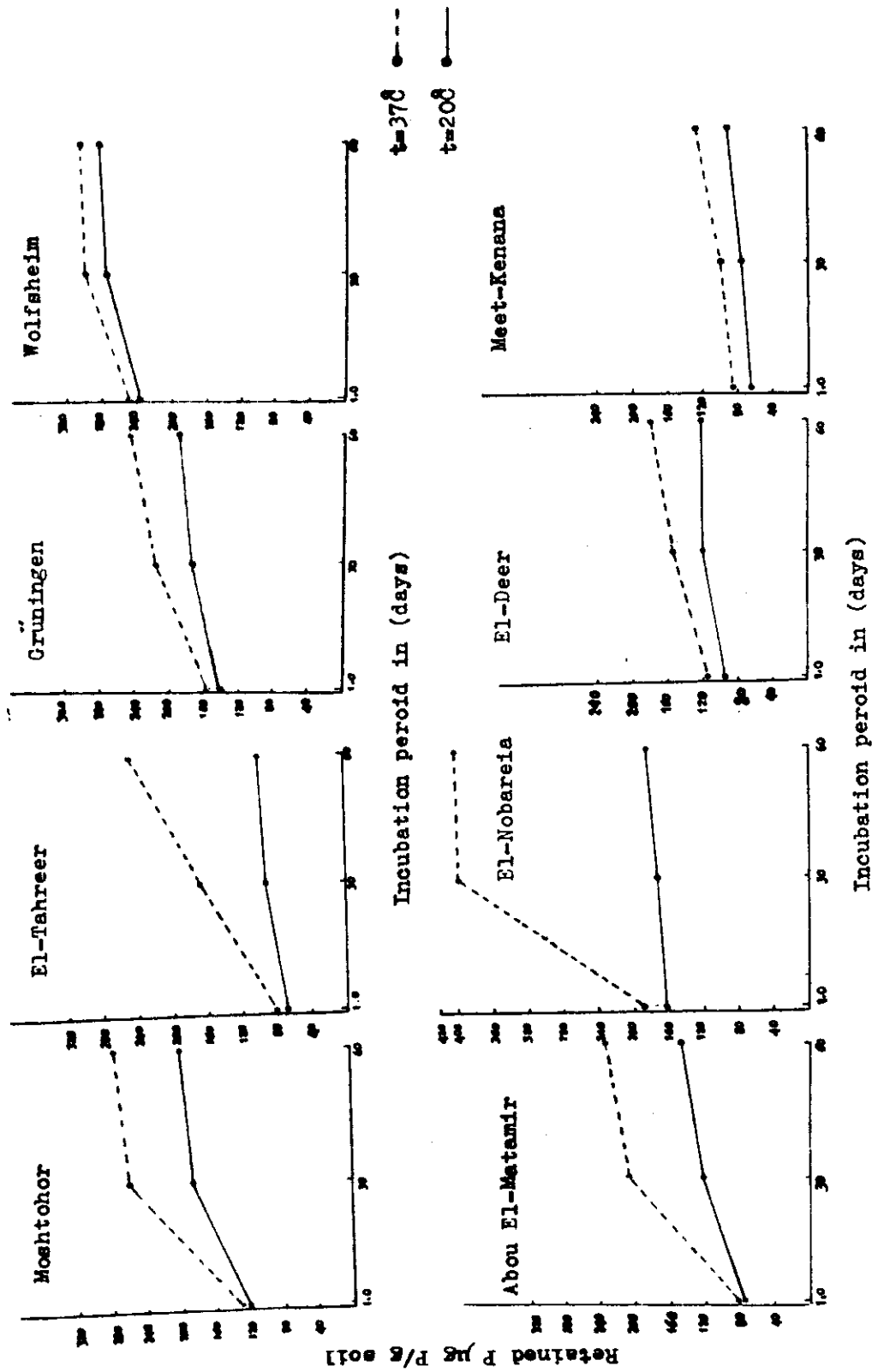
M = mean value of two temperatures.

Table (5) Effect of time of reaction and temperature on P retention by soils  $\mu\text{g. P/g. soil}$

		Soil Location															
Time of reaction		El-Mobarein		Abou El-Matanir		El-Tahreer		Moshchor		Meet-kamara		El-Deer		Grünigen		Wolfsheim	
		t 20	t 37	t 20	t 37	t 20	t 37	t 20	t 37	t 20	t 37	t 20	t 37	t 20	t 37	t 20	t 37
One day		164.75	189.58	76.85	84.23	68.65	81.67	121.22	129.84	66.18	86.03	95.31	114.87	143.33	159.06	279.82	261.51
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30 days		174.64	400	124.23	209.61	92.41	168.15	185.84	259.01	76.430	100.70	121.87	154.45	178.96	220.67	278.43	302.8
-----																	
60 days		185.78	403.55	149.73	237.80	98.53	247.65	198.69	273.95	91.28	127.72	122.54	180.54	194.07	251.36	286.57	308.67
-----																	
Average		174.92	331.08	116.94	177.21	86.53	165.82	168.58	220.93	77.96	104.82	133.24	149.95	172.12	210.36	268.27	287.66

Table (6): The retained p by soils in relation to the rate of added P and time of reaction

Added p µgp /g soil	Time of reaction									
	10	30	60	90	120	150	180	210	620	1240 1860
one day	8.71	23.11	42.23	55.9	68.84	80.93	93.48	103.93	207.4	327.17 413.14
-----										
30 days	9.35	26.61	50.88	70.02	88.39	105.59	121.8	137.22	305.10	504.45 676.56
-----										
60 days	9.32	26.59	49.61	70.01	89.36	107.16	126.75	142.22	338.88	568.20 774.63



Fig( 3 ) Retention of P by soils in relation to temperature and time of reaction (contact period)

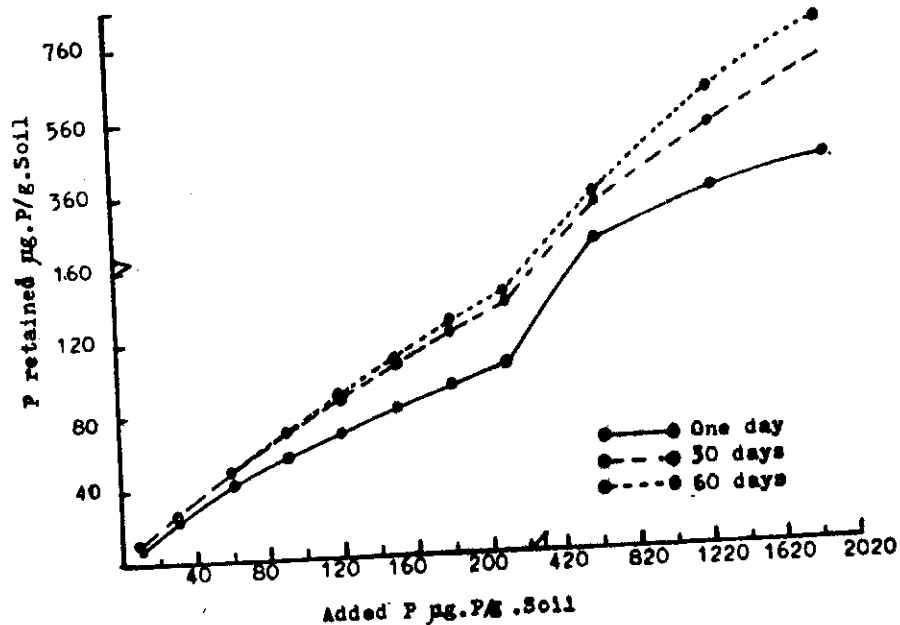


Fig. (4) P retained by soils in relation to the rate of added P and time of reaction

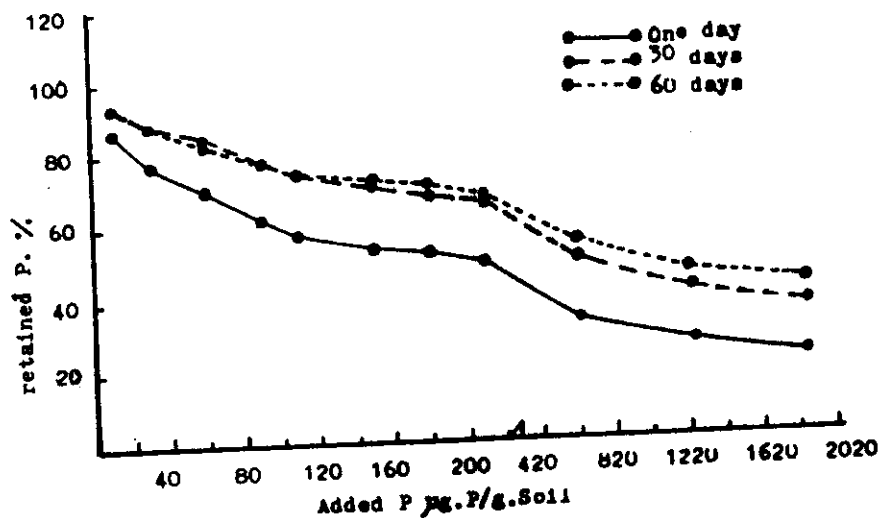


Fig. (5) Percentage of the P retained by soils in relation to rate of added P and time of reaction

4.1.1.1. Retention of P by soils in relation to the concentration of added P :

The results show clearly that the rate and extent of P retention by soils is very much governed by the concentration of soil solution P which in turn, is related to the level of P added to the soil system.

The values of P retained by all soils consistently and gradually increased with increasing concentrations of added P. This trend was true with all periods of contact with P solution and at both temperatures of incubation. The average values of retained P increased from 9.84, 8.91, 8.89, 9.35, 7.55, 9.1, 9.55 and 9.86 to 1002.3, 539.7, 426.25, 670.45, 311.09, 399.86, 630.54 and 991.38  $\mu\text{g. P/g. soil}$  with increasing the rate of added P from 10 to 1860  $\mu\text{g. P/g. soil}$  for the eight tested soils, respectively.

It is obvious that the highest capacities to retain P were obtained with Gröningen, Moshtohor, El-Nobareia and Wolfsheim soils, while the lowest capacities were observed with Meet-Kenana, El-Tahreer, El-Deer and Abou El-Matamir soils.

Noteworthy to observe that soil of the highest P retention are characterized with slightly acidic reaction (Wolfsheim), high clay content (Moshtohor) and relatively high  $\text{CaCO}_3$  content (El-Nobareia).

It is well known that under the slightly acidic pH conditions prevalent in Wolfsheim, the free oxides of Fe, AL and Mn, beside the abundant clay minerals could be effective in the P retention phenomenon. About the highly calcareous soil, of El-Nobareia, it seems quite reasonable to attribute such high-P fixing capacity to the high  $\text{CaCO}_3$  content of that soil. With respect to Moshtohor soil, the relatively high content of the clay fraction (67.8 %) could be the main factor behind its high capacity to retain P. The dominance of montmorillonite clay (77.0 %) in such soil may suggest that P is chiefly retained between the expanded layers of the crystall lattice structure through physical adsorption processes.

On the other hand, the soils of relatively low P retention are, in general, characterized with relatively low  $\text{CaCO}_3$  and clay contents.

Similar results were obtained by Ragland and Seay (1957), Barrow and Shaw (1974), Ryden and Syers (1977) and Calvert et al., (1960) who indicated that clays, cations such as AL, Fe, Ca and Mg are involved in P retention by soils.

Concerning the relative retention of P by soils, i.e. the retained P expressed as percentage of the corresponding values of added P, an expected trend is obvious, table (7) and Fig. (5). The percentage of retained P consistently decreased with the progressive increments in the rate of P added to the soil.



The values of P retention percentage at the lowest concentration of added P (10  $\mu\text{g}$ . P/g. soil) were 87.1, 93.51 and 93.21 %, while the corresponding values at the highest rate of added P (1860  $\mu\text{g}$ . P/g. soil) were 22.24, 36.37 and 41.45 % after one, 30 and 60 days of incubation, respectively. This expected trend could be attributed to the progressive occupying of the different sites responsible for P retention with increasing time of contact and rate of added P. With a saturation state being reached at a certain P concentration, beyond this concentration no more or very slight-reactions seemed to take place. The data are in agree with those reported by Hibbard (1935), Deen and Rubins (1947 a), SenGupta and Cornfield (1962), Syers et al. (1970), Sibbesen (1981) and Ibrahim and Pratt (1982).

SenGupta and Cornfield (1962) reported that between 24 and 72 h, the percentage of phosphate fixed decreased as the concentration of P increased from 100 to 1000  $\mu\text{g}$   $\text{P}_2\text{O}_5$ . They attributed such trend to the saturation of soil sites with phosphate ions at high concentration of P added and thus decreasing the percentage of added phosphate retained at these levels. Syers et al. (1970) referred that P adsorbed expressed as a percentage of total added P, was closely and inversely related to the rate of added P.

#### 4.1.1.2. Retention of P by soils in relation to temperature:

The data obtained for P retained are shown in table (3) for each soil and summarized on a basis of the average in table (5) and Fig. (3).

Values of P retained at all P concentrations and the different periods of incubation increased from 86.53 and 268.27  $\mu\text{g. P/g. soil}$  at  $20^{\circ}\text{C}$  to 104.82 and 331.08  $\mu\text{g. P/g. soil}$  in at  $37^{\circ}\text{C}$ .

It is obvious that the increased capacities to retain P due to the effect of temperature were observed with the soil Abou El-Matamir, El-Tahreer and El-Nobareia (calcareous soils), while the lowest capacities were observed with the soils of Wolfsheim, Gruningen, Meet-Kenana, El-Deer and Moshtohor soils. This may be due to the effect of high temperature on the solubility of  $\text{CaCO}_3$  and hence increasing the capacities of the former group of soils to retain P.

It seems from the above mentioned results, that all studied soils showed a similar pattern with respect to the effect of temperature. This trend was also reported by Low and Black (1950), Muljadi et al. (1966), Gardner and Jones (1973) and Barrow and Shaw (1975 b) who concluded that when the temperature was changed

during incubation, the rate of P reaction with soils changed to a value appropriate to the new temperature. While high temperatures accelerated the changes which followed the initial adsorption and thus favoured a low solution concentration, the effect of temperature on the equilibrium between adsorbed and solution phosphate was found to be in the opposite direction.

Another explanation was offered by Sharpley and Ahuja (1982) who suggested that temperature affects the rate of P sorption by changing the stability of amorphous Fe, AL complexes and Ca precipitates.

Concerning the effect of the combined factors on P retention by soils, the obtained data for the combined effect of P concentrations and temperatures are shown in table (4).

Data, in general, show that increasing the temperature of incubation from 20°C to 37°C increased the magnitude of P retention by soils particularly at the higher rates of applied P.

Incubating the soils with P solutions of 10 ppm at 20°C yielded average values of P retention ranging between 7.39 (Meet Kenana) and 9.87 µg. P/g. soil (Wolfsheim), but at 37°C, the values ranged between 9.07 (Abou El-Matamir) and 9.88 µg. P/g. soil (El-Nobareia). Increasing the P concentration to 1860 µg. P/g. soil is true increased these figures to 236.84 (Abou El-Matamir)

and 931.24  $\mu\text{g. P/g. soil}$  (Walfsheim) at  $20^{\circ}\text{C}$  and to 360.22 (Meet-Kenana) and 1449.6  $\mu\text{g. P/g. soil}$  (El-Nobareia) at  $37^{\circ}\text{C}$  respectively.

#### 4.1.1.3. Retention of P by soils in relation to time of reaction:

Data of tables (5, 6) and Figs. (3, 4) indicate that, as the time of reaction increases, so does the amount of P retained by soils at both degrees of temperature ( $20^{\circ}\text{C}$  and  $37^{\circ}\text{C}$ ).

The data obtained in table (5) and Fig. (4) generally, show that increasing the time of incubating the soils in contact with P solutions from one to 30 and 60 days, increased the magnitude of P retention by soils, particularly at the high rates of applied P. Moreover, this stimulating effect was more obvious with the 60 days incubation period as compared to the 30 days when both intervals were compared with the one day period.

Data in table (5) show that increasing the time of reaction from one to 30 or 60 days affected the rate of P retention in the following pattern :

At one day the values of retained P varied between 75.16  $\mu\text{g. P/g. soil}$  (El-Tahreer soil) and 250.67  $\mu\text{g. P/g. soil}$  (Wolfsheim soil). These values raised to 88.57  $\mu\text{g. P/g. soil}$  (Meet-Kenana) and 290.6  $\mu\text{g. P/g. soil}$  (Wolfsheim) at 30 days, but at 60 days, again the values were slightly increased to range from 109.5 and 297.6  $\mu\text{g. P/g. soil}$  for the same previously soils.

These data agrees with those obtained by Fox and Kamprath (1970), Ragan and Fox (1972), Ibrahim and Pratt (1982) and Kothandarman and Krishnamoorthy (1978) who stated that the fraction of P sorbed increased as the time of reaction increased and that the concentration of P remaining in solution decreased. They declared that P in solutions react with soil, clays or oxides, beside being adsorbed on the surface of the soil particles, and consequently its concentration in solution decreases. The decrease in concentration continues for a long time.

Concerning the effect of time of reaction on the percentage of P retention, table (7) and Fig. (5) show an increase in this percentage with increasing the time of contact, i.e. the percentage of P retention, increased from 87.10 and 22.24 (one day incubation) to 93.21 and 41.45 (60 days incubation) with increasing the rates of P application from 10 to 1860  $\mu\text{g. P/g. soil}$ , respectively.

These results, in generally, may indicate that the tested soils showed no definite retentions power which seems to be a function of the concentration in the soil solution at equilibrium and the time of reaction. Moreover, three or four regions of consistent and steady increase could be observed, Fig. (4) which may suggest the presence of more than one mechanism responsible for P retention by these soils.

#### 4.1.2. Release of soil P :

To elucidate the pattern of P release in the investigated soils, the P-treated samples were subjected twice to saving P by means of distilled water followed by extraction with sodium bi-carbonate (0.5 M solution of pH 8.5.).

The values obtained for P recovered from the P treated soils by water and  $\text{NaHCO}_3$  are shown in table (8) and depicted in Figs. (6 - 9).

##### 4.1.2.1. Soil P recovery by distilled water :

The results in table (8) and Figs. (6 and 7) show that the values of water-soluble P, recovered were closely correlated with the amount of added P. The values of correlation coefficient being 0.975, 0.989, 0.948 and 0.959 for El-Deer, Moshtohor, Gruningen and Wolfshein soils, respectively.

The obtained data indicate that with increasing the rate of P additions, the fractions of soil P recovered by water were consistently increased. However, when these fractions were expressed in terms of percentage of added P, a decreasing trend was obvious.

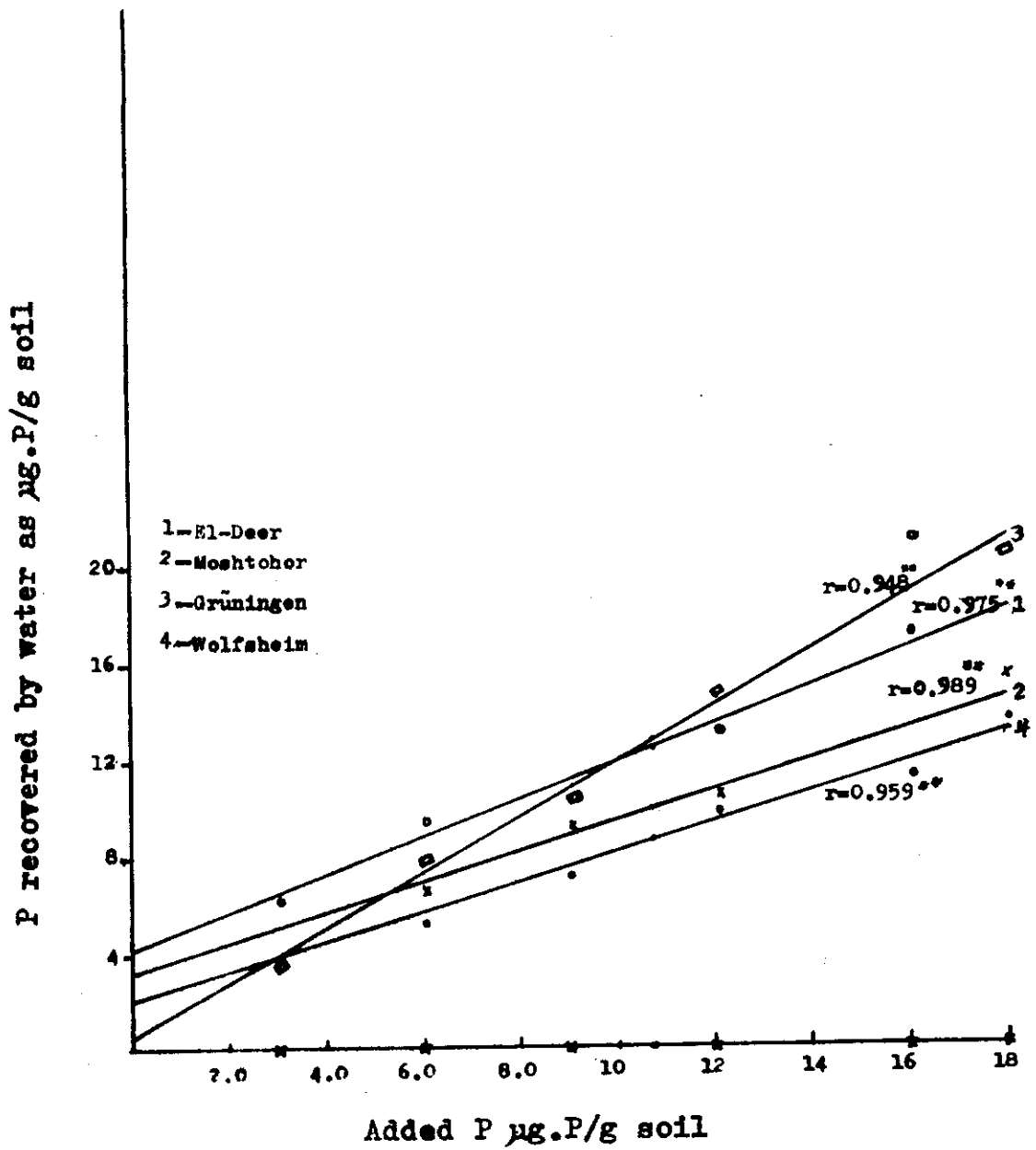
Comparing the values of P recovery expressed as percentage of the added P show that : The percentage of water P recovered

Table (8): Recovery of P from P-treated soils with water and  $\text{NaHCO}_3$  of pH 8.5  
Soil location

Added P µg.P/g soil	Extractant	El-Deer			Moshtohor			Grünigen			Wolfsheim		
		R.P.	R.P.%	R.P.	R.P.	R.P.%	R.P.	R.P.	R.P.%	R.P.	R.P.	R.P.%	R.P.%
30	Water	5.19	17.30	5.46	18.20	4.48	14.90	3.64	12.10	12.10			
	$\text{NaHCO}_3$	9.87	32.90	19.71	65.70	18.35	61.20	19.18	63.90				
60	Water	8.75	14.60	6.7	11.20	7.74	12.90	4.94	8.23				
	$\text{NaHCO}_3$	12.98	21.60	22.36	37.30	25.93	43.21	28.68	47.80				
90	Water	12.69	14.10	9.32	10.36	10.40	11.56	9.92	11.02				
	$\text{NaHCO}_3$	16.02	17.80	23.32	25.90	31.06	34.50	42.03	46.70				
120	Water	15.35	12.79	10.76	8.97	14.30	11.92	9.17	7.64				
	$\text{NaHCO}_3$	17.11	14.26	23.24	19.37	31.72	26.43	26.51	22.09				
150	Water	16.41	10.26	12.73	7.96	16.72	10.45	10.97	6.86				
	$\text{NaHCO}_3$	22.54	14.09	23.34	14.59	37.73	23.58	28.63	17.89				
180	Water	16.99	9.44	15.59	8.86	23.70	13.17	13.87	7.71.				
	$\text{NaHCO}_3$	20.49	11.38	27.29	15.16	43.57	24.21	38.30	21.28				
Average	Water	12.56	13.04	10.09	10.93	12.89	12.48	8.75	8.93				
	$\text{NaHCO}_3$	16.50	18.67	23.21	29.67	31.39	35.52	30.56	36.61				

R.P. = Values of P recovered from P-treated soil as µg.P/g.soil

R.P.% = Recovered P expressed as percentage from added P.



Fig(7) P recovered in relation to added P  $\mu\text{g.P/g}$  soil



decreased from 17.3, 18.2, 14.9 and 12.1 to 9.44, 8.86, 13.17 and 7.71 with increasing the rate of added P from 30 to 180  $\mu\text{g. P/g.}$  soil for El-Deer, Moshtohor, Grüningen and Wolfsheim soils, respectively.

It is clear that while the values of P fraction of soil, recovered from the soils incubated in  $\text{KH}_2\text{PO}_4$  solution having a concentration of 30  $\mu\text{g. P/g.}$  soil did not exceed 5.46  $\mu\text{g. P/g}$  soil, being 5.19, 5.46, 4.48 and 3.64 for the soils of El Deer, Moshtohor, Grüningen and Wolfsheim, respectively. Increasing the rate of P application up to 180  $\mu\text{g. P/g.}$  soil, progressively raised the level of soil P recovered in water to 16.99, 15.59 23.7 and 13.87 for these four soils, respectively.

#### 4.1.2.2. Soil P recovery by $\text{NaHCO}_3$ solution :

The data obtained in table (8) and illustrated in Figs. (8 and 9) show that the values of P recovered by sodium bicarbonate from the P treated soils were positively correlated with the amount of P added to these soils. This correlation was highly significant in all the soils except Wolfsheim. The values of correlation coefficient were, 0.964, 0.870, 0.979 and 0.491 for El-Deer, Moshtohor, Grüningen and Wolfsheim soils, respectively.

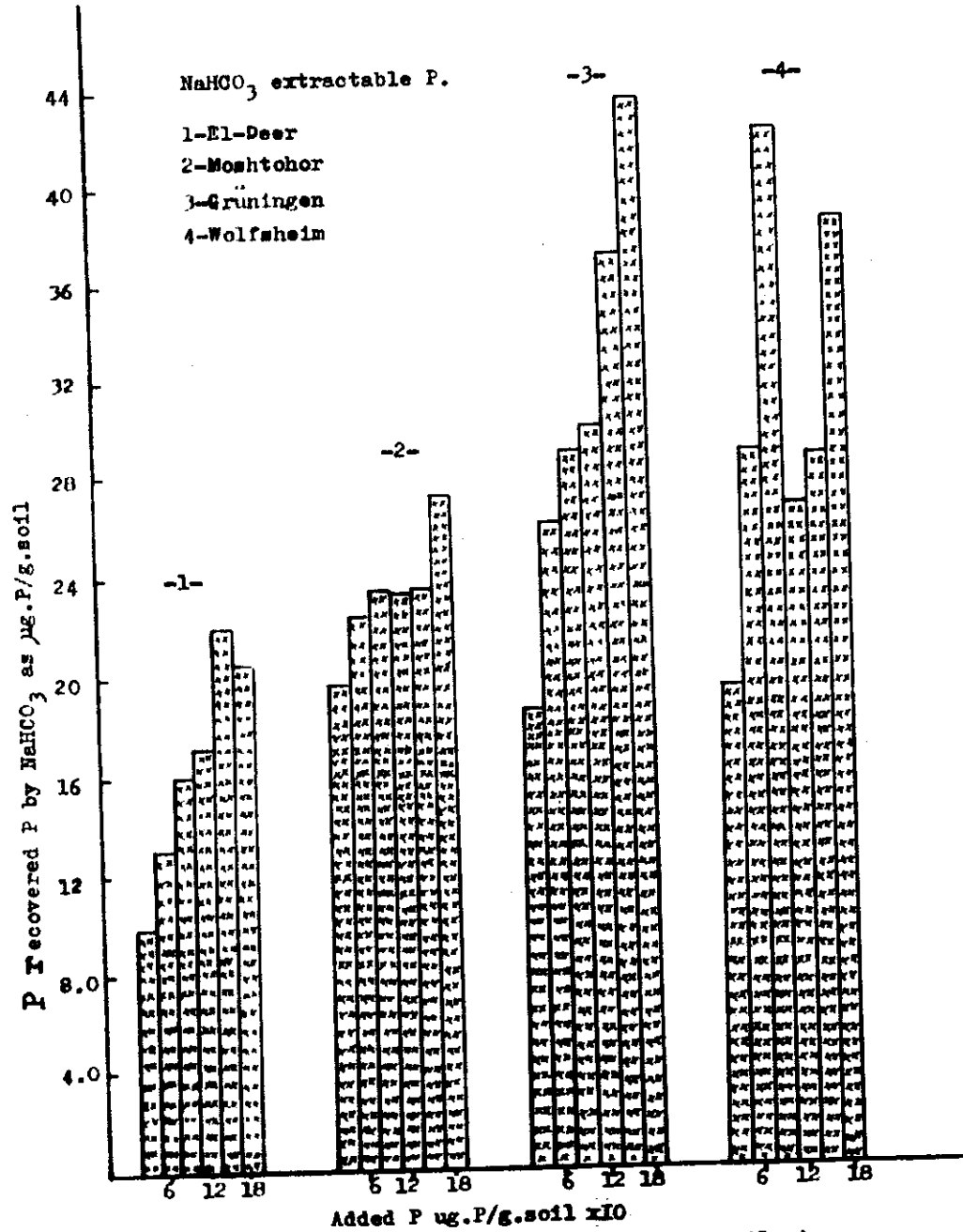


Fig (8) Values of P recovered from P-treated soils in relation to added P µg.P/g.soil

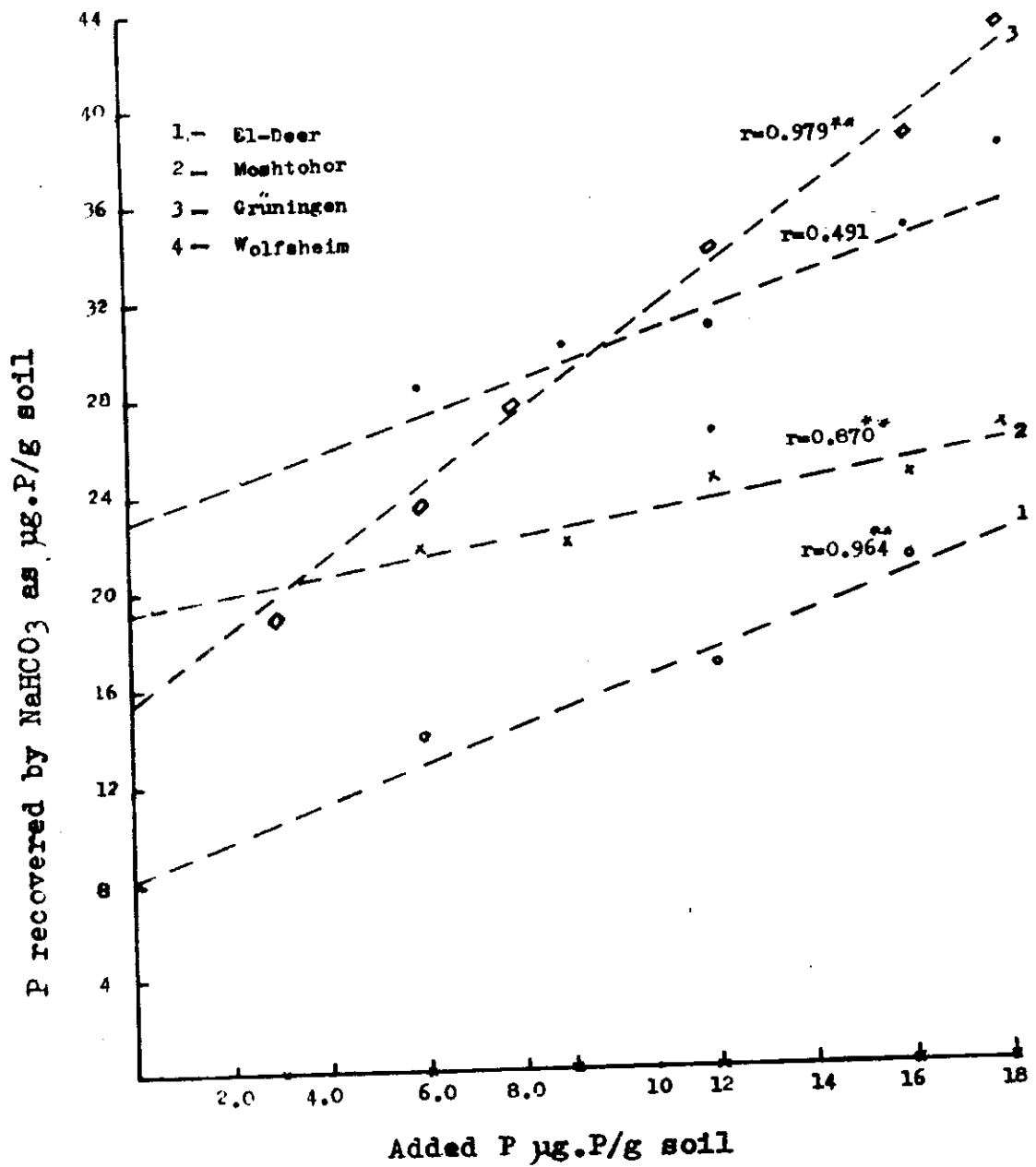


Fig.(9) P recovered in relation to added P  $\mu\text{g.P/g soil}$

Increasing the rate of added P, as, it did with distilled water, resulted in an increase in the quantities of  $\text{NaHCO}_3$  - recovered P but decreased the percentage of P recovered as related to the rate of P addition. The quantities of  $\text{NaHCO}_3$  recovered P increased from 9.87, 19.71, 23.21 and 19.18 to 20.49, 27.29, 43.57 and 38.3  $\mu\text{g}$ . P/g. soil for the soils of El-Deer, Mostohor, Grüningen and Wolfsheim by increasing the rate of added P from 30 to 180  $\mu\text{g}$  P/g. soil.

Expressing the fraction of added P recovered as percentage, show that increasing the rate of applied P from 30 to 180  $\mu\text{g}$ . P/g. soil decreased these percentages from, 32.9, 65.7, 61.2 and 63.9 % to 11.38, 15.16, 24.21 and 21.28 % for the studied soils, respectively.

These results may lead to a general conclusion, that  $\text{NaHCO}_3$  solution is of higher capability than distilled water as an extractant for P from P-treated soils.

Similar results were recorded by Olufemi and Akinola (1981), Fuller and McGeorge (1950), who found that the amount of P extracted with water increased by increasing the rate of added P from 0 to 250 pounds of  $\text{P}_2\text{O}_5$  per acre, and concluded that only a small portion was securely fixed against extraction with water.

Hibbard (1935) showed that the gradual decrease of water soluble  $\text{PO}_4$  may be partly because of the formation of a loose complex rather than a definite compound and partly because imperfect contact of the added  $\text{PO}_4$  with the soil particles.

While Olsen et al. (1954) pointed out that the increase in available P as determined by  $\text{NaHCO}_3$  extracting over that by water, is probably due to the increased solubility of Ca - phosphates as a result of lowering  $\text{Ca}^{++}$  activity in solution. They also reported that extraction with  $\text{NaHCO}_3$  removes about 1/2 of the P on the surface of soil particles that readily exchanges with  $^{32}\text{P}$  in the soil solution beside minimizing secondary precipitation and adsorption reaction.

#### 4.2. Adsorption of P by soils :

Phosphorus adsorption by soils takes place as a result of physical and chemical attracting forces. Both types of adsorption can be satisfactorily described by Langmuir adsorption isotherm or Freundlich equation. Because the adsorption reactions require only short time periods, it was meant in this study to select the values of P retained by the soils under consideration after incubating them with P solutions for 24 hours.

The data were, at first, treated according to the classical form of Langmuir adsorption isotherm developed by Olsen and Watanabe (1957), then after according to the modified forms of Muljadi et al. (1966) and Gunary (1970).

The fitness of the data to Freundlich equation was also investigated.

The values and parameters required for these investigations namely,  $P_i$ ,  $c$ ,  $c/x/m$ ,  $\log c \times 10^2$  and  $\log x/m$ , are tabulated in the appendix (table 9).

For sake of simplicity, the results are discussed separately with respect to Langmuir and related forms of adsorption isotherms and Freundlich equation as well. Plotting the data of P adsorption according to Langmuir equation and the other derived forms of Muljadi et al. (1966) and Gunary (1970) is indicated in tables (10 - 13) and Figs. (10 - 13).

#### 4.2.1. Adsorption of P as represented by Langmuir:

The linear form of the Langmuir equation reads :

$$c/x/m = \frac{1}{kP_{\max}} + \frac{c}{P_{\max}}$$

where  $c$  = equilibrium P concentration,  $\mu\text{g. P/ml}$

$x/m$  = P adsorbed,  $\mu\text{g. P/g. soil}$

$P_{\max}$  = P adsorption maximum  $\mu\text{g. P/g. soil}$

$k$  = affinity constant related to the bonding energy  $(\mu\text{g. P/ml})^{-1}$ .

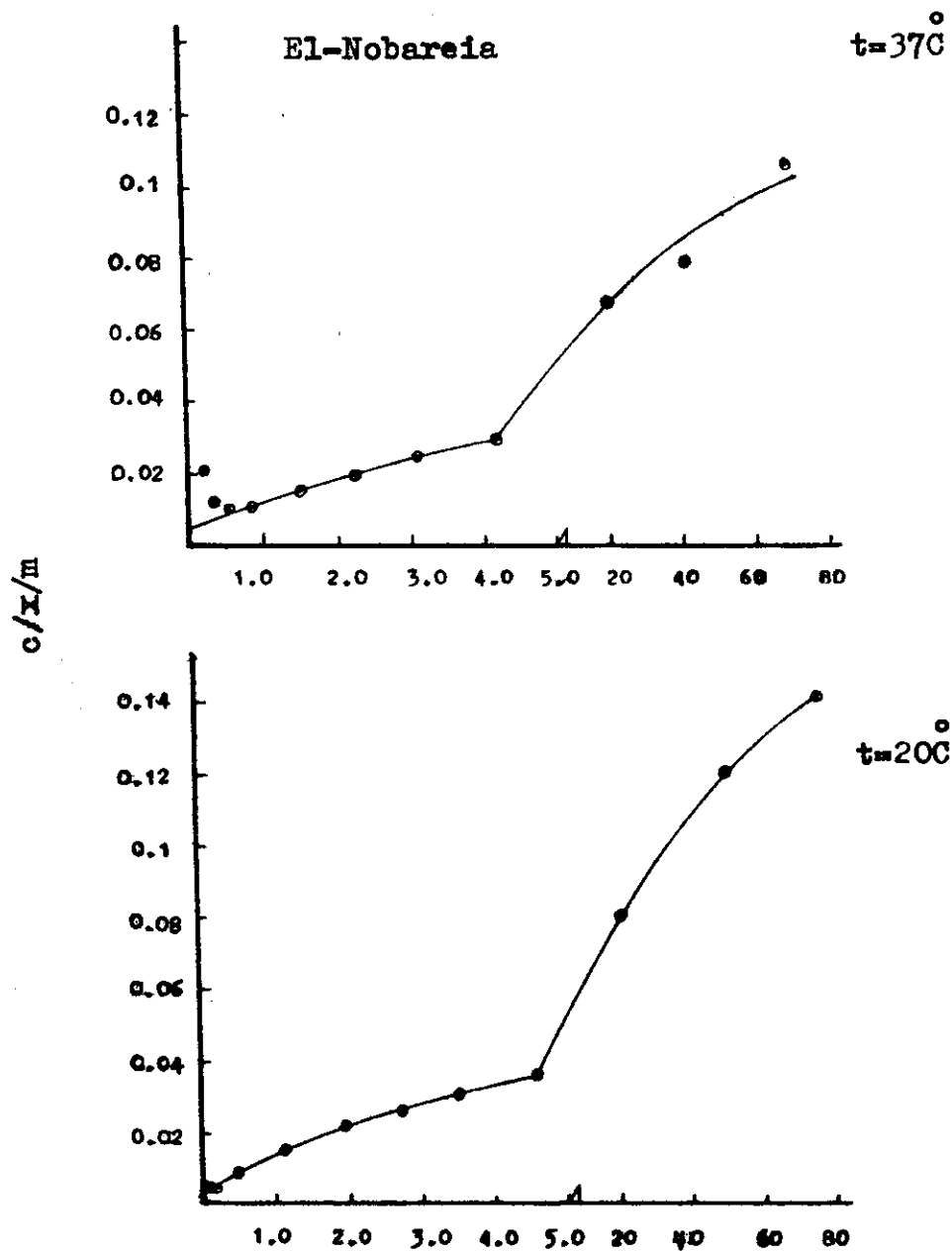
The data generally showed close fitness to Langmuir adsorption isotherm. The values of correlation coefficient expressing this relationship were always highly significant.

Table (10) Data obtained from plotting Langmuir isotherm

Soil location	Temperature					t= 37 °C				
	k	P <sub>max</sub>	r	Regression equation		k	P <sub>max</sub>	r	Regression equation	
El-Nobareia	0.1017	555.6	0.959	y= 0.0177 + 0.0018 C		0.0765	714.29	0.954	y=0.0163+0.0014 C	C
Abou El-Matemir	0.1086	204.1	0.991	y= 0.0451 + 0.0049 C		0.0983	242.72	0.986	y=0.0417+0.00412 C	C
El-Tahreer	0.0634	217.4	0.951	y= 0.0725 + 0.0046 C		0.0832	243.9	0.971	y=0.0493+0.0041 C	C
Moshtohor	0.0548	434.8	0.972	y= 0.042 + 0.0023 C		0.0570	476.2	0.952	y=0.0351+0.0021 C	C
Meest-Kenana	0.030	277.8	0.936	y= 0.1195 + 0.0036 C		0.0262	400.0	0.935	y=0.0952+0.0025 C	C
El-Deef	0.0646	312.5	0.982	y= 0.0495 + 0.0032 C		0.0736	370.3	0.977	y=0.0357+0.0027 C	C
Grünigen	0.0735	500.0	0.961	y= 0.0272 + 0.002 C		0.0829	555.6	0.981	y=0.0217+0.0018 C	C
Walfabein	0.1542	833.3	0.990	y= 0.0078 + 0.0012 C		0.1692	909.1	0.983	y=0.0055+0.0011 C	C
Mean	0.0814	416.9				0.0536	489.0			

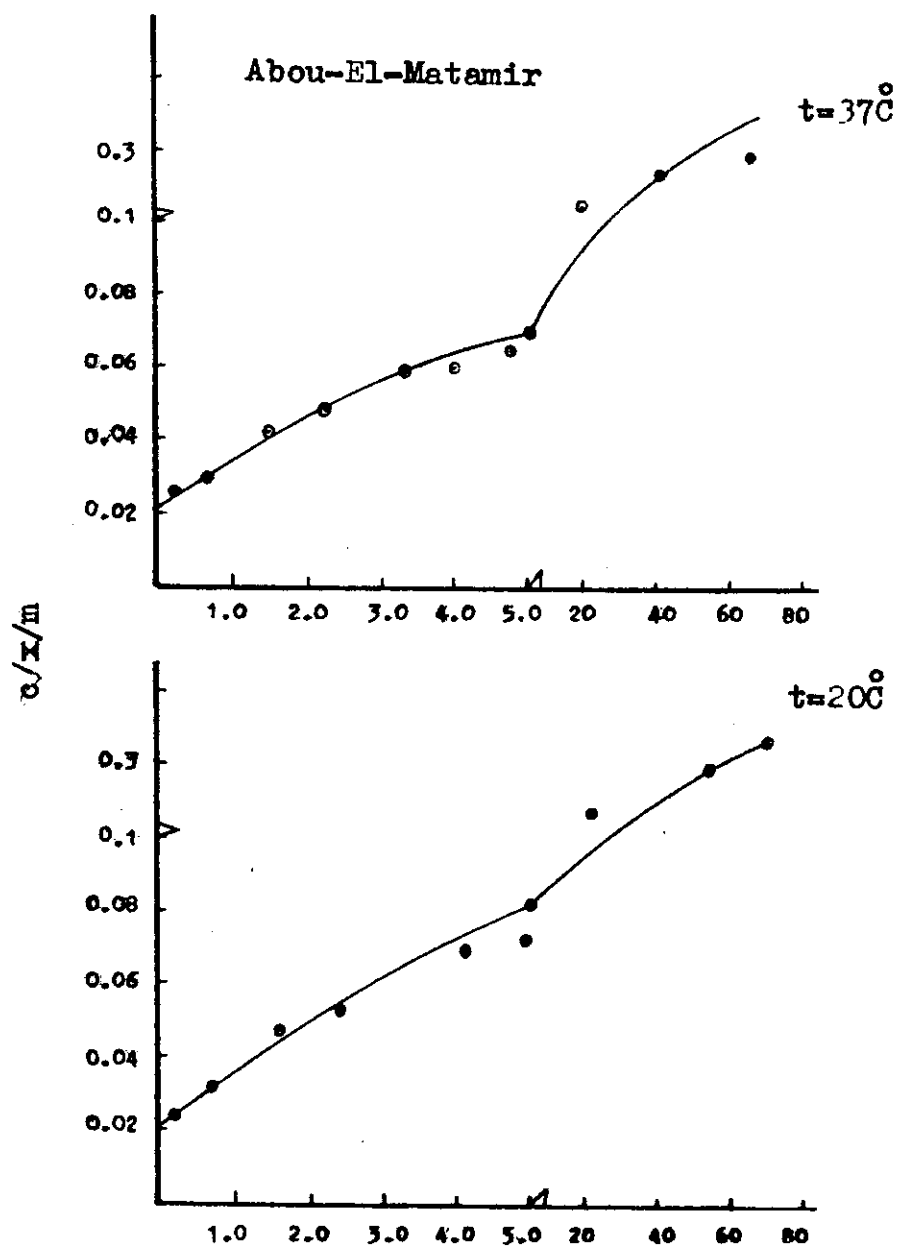
k 'Affinity constant related to the bonding energy" (µg.P/ml)<sup>-1</sup>

P<sub>max</sub> 'P adsorption maximum" µg.P/g.soil

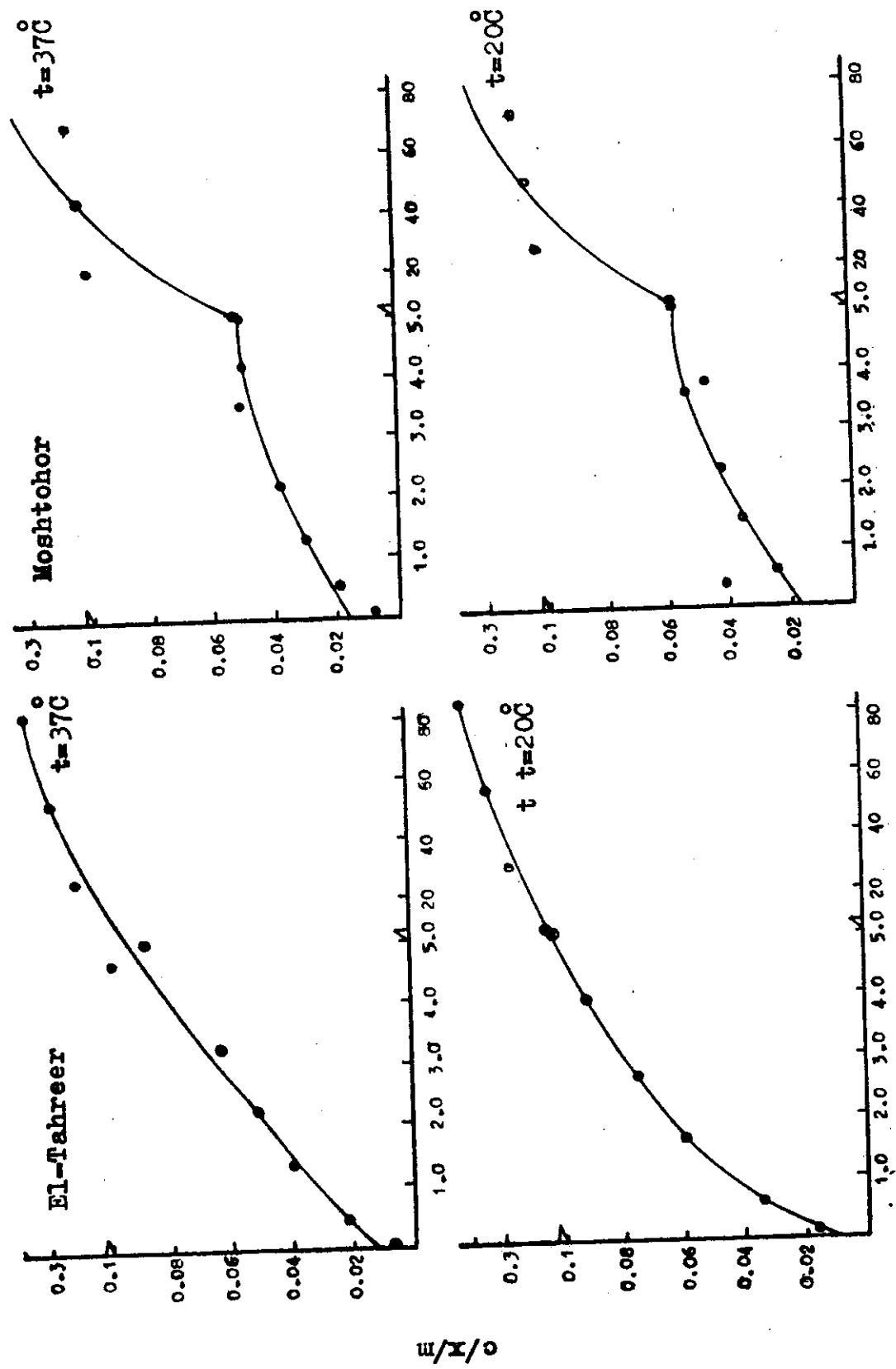


Equilibrium P concentration (c)  $\mu\text{g.P/ml}$ .  
 Fig(10) Plotting equilibrium P concentration (c)  
 against  $c/x/m$ .





Equilibrium P concentration (c)  $\mu\text{g.P/ml}$ .  
Fig(10)Cont.



Equilibrium P concentration( $c$ ) $\mu\text{g.P/ml}$ .

Fig(10)Cont.

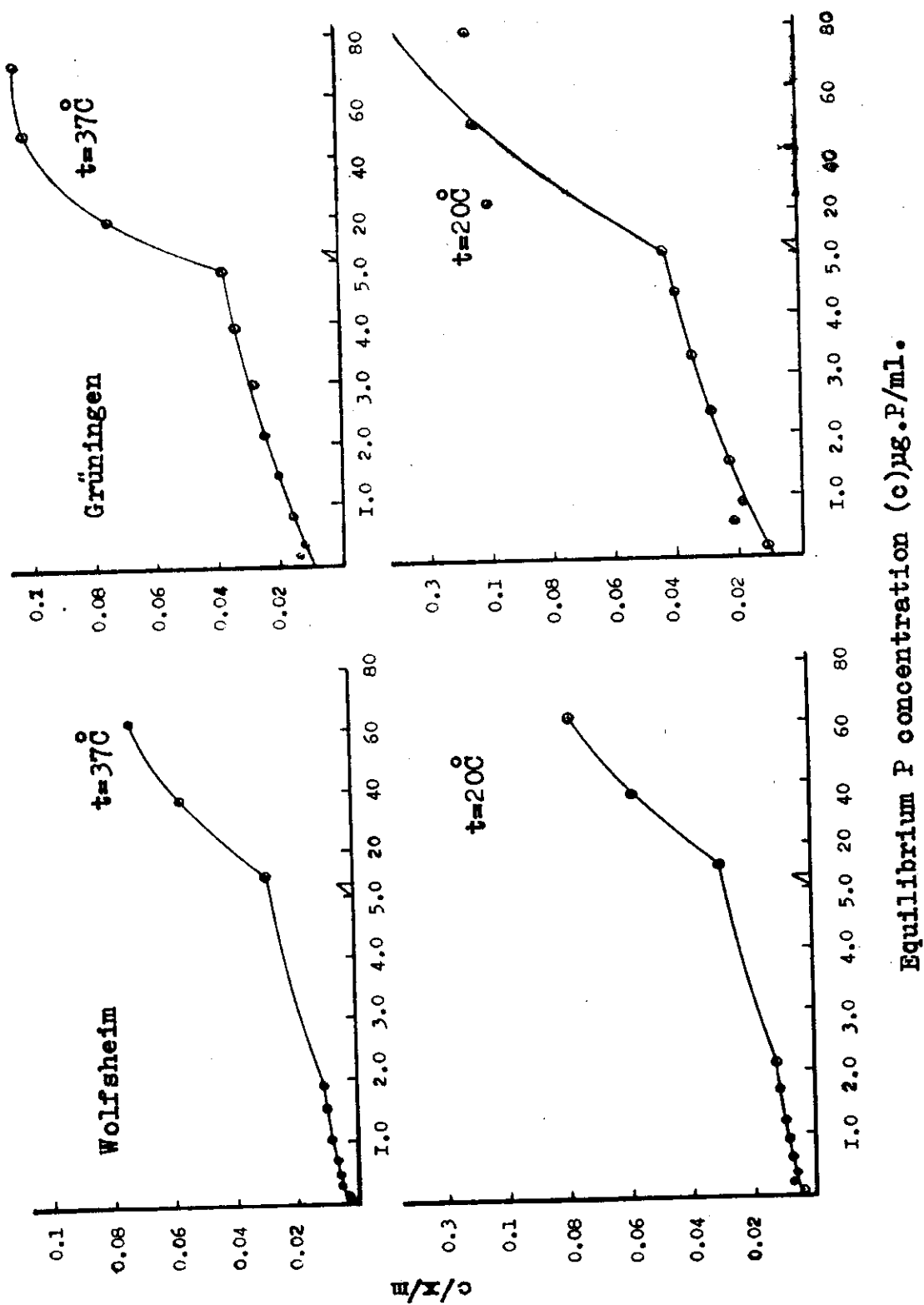


Fig.(10)Cont.

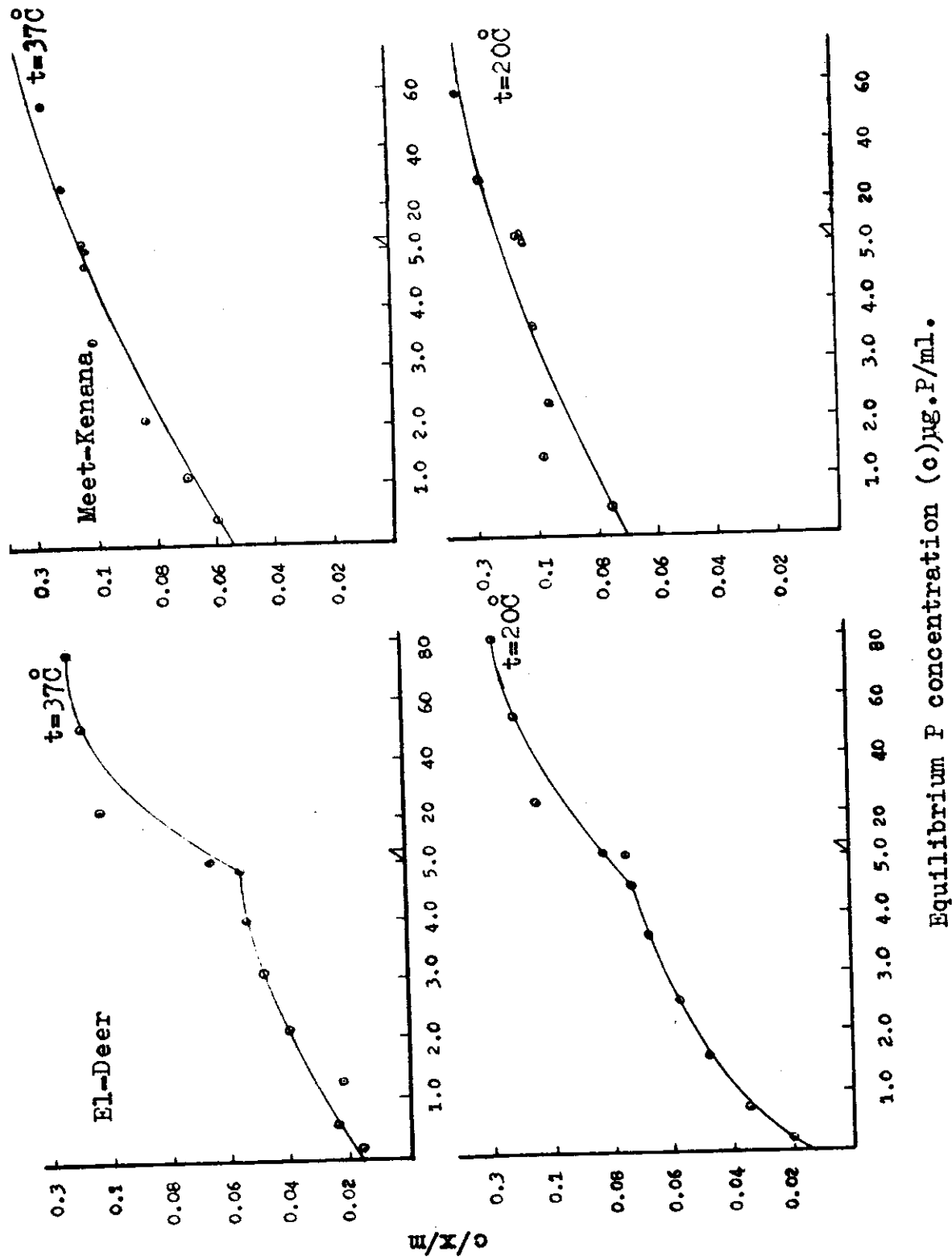


Fig.(10)Cont

In more details, treating the data according to the adsorption isotherm of Langmuir in the linear form showed the following relations :

This used form of Langmuir isotherm was able to represent with significant fitness the data of P retention with all the soils and at 20 as well as at the 37°C. The values of correlation coefficient ranged between 0.936 and 0.991 at 20°C and 0.935 and 0.986 at 37°C. It is obvious that changing the temperature from 20 to 37°C did not affect the fitness of the data to Langmuir adsorption isotherm.

Plotting the  $c/x/m$  values versus  $c$ , Fig. (10) show at least two regions of P adsorption suggesting a possible existence of more than one site or mode of P adsorption through the tested range of P concentrations. Fig. (10) also showed a slight convex to the "x" axis, particularly with the high P concentration. The curvilinear relationship between  $c/x/m$  and  $c$  was observed by Adamson (1960), Larsen (1967), Clark (1970) and Bache and Williams (1971) who attributed such trend to migration of the sorbed phosphate into subsurface layers, or to variations in heat of adsorption caused by surface heterogeneity and increasing interactions

between adsorbate molecules on the surface and in the solution with increasing surface coverage, Adamson (1967).

Data in Table (10) shows the values of the two constants of Langmuir equation namely, the "K" constant that relates to the bonding energy or the affinity by which the adsorbate is attached to the adsorbent, and the  $P_{\max}$  which express the maximum P adsorption by soil system. The data reveal that the values of "K" ranged from 0.0297 to 0.154 and from 0.0258 to 0.175 ( $\mu\text{g. P/ml}$ )<sup>-1</sup> at 20 and 37°C, respectively.

It is obvious that the values of "K" were relatively low in the light-textured alkaline soils as compared with those of heavy texture or with the slightly acidic soil of Wolfsheim which may reflect the relatively high bonding energy of P in such soils. This energy could be arise from the abundance of  $\text{CaCO}_3$ , clay and free or active oxides of Fe and AL. etc. These results are in close agreement with those obtained by Calvert et al. (1960) and Ryden and Syers (1977).

The values of P adsorption maximum ( $P_{\max}$ ) at 20°C varied between 204.1 to 833.30  $\mu\text{g. P/g. soil}$  with an average of 416.9  $\mu\text{g. P/g. soil}$ . Increasing the temperature of reaction to 37°C,

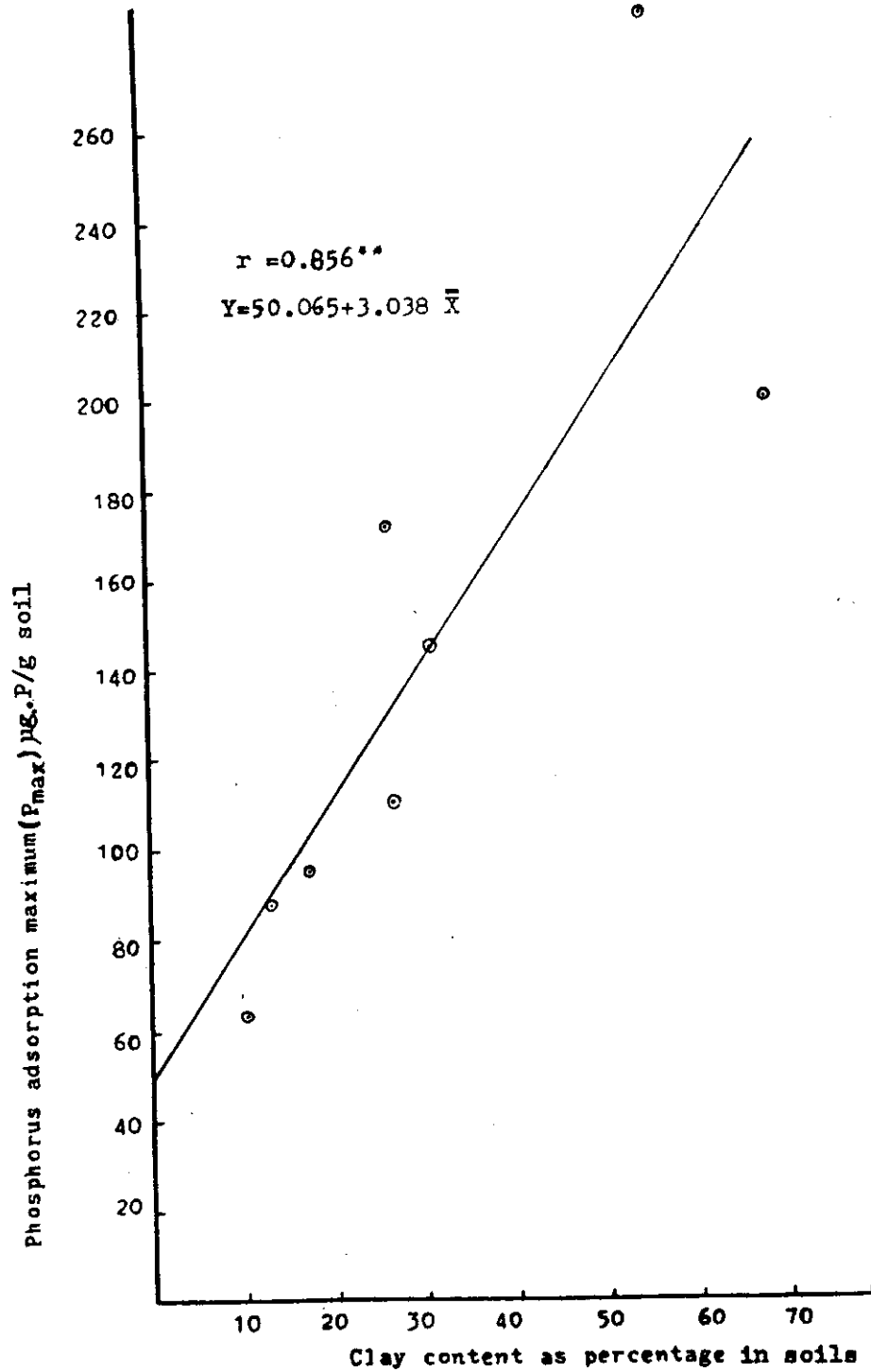
generally, increased the values of " $P_{\max}$ ", being in the range from 242.72 to 909.1  $\mu\text{g. P/g. soil}$  with an average of 489.0  $\mu\text{g. P/g. soil}$ . These values are in accordance with those obtained by Olsen and Watanabe (1957), Gunary (1970), El-Rashidi (1972) and Kuo and Lotse (1972) who stated that phosphate adsorption increased with increasing the temperature.

The constant ( $P_{\max}$ ) was found to be closely and positively correlated with the clay abundance in soils (Fig.11). The correlation coefficient was 0.856 . Such trend was obvious only at the low temperature, ( $20^{\circ}\text{C}$ ). This relation is very well established by many investigators, Olsen and Watanabe (1957), Rennie and McKercher (1959), Weir and Soper (1962), El-Rashidi (1972), Sadik and Abd El Aal (1978) and Abd El Aal et al. (1981) who reported that the maximum P adsorption values were significantly related to the clay content of the soils.

It is noteworthy to mention that the values of both "K" and  $P_{\max}$  constants, depend chiefly on the P concentration in the medium at which the adsorption process takes place as well as the amount initially bonded to the adsorbent.

#### 4.2.2. Adsorption of P by soils as represented by the modified forms of Langmuir adsorption isotherm :

The Langmuir adsorption equation is applicable to soil



Fig(11) The relationship between ( $P_{max}$ ) of Langmuir isotherm and clay percentage in soils



systems provided that particular P concentrations are used. With higher P concentrations, deviation from the equation and thus a curvilinear relation is obvious, Larsen (1967), Bache and Williams (1971).

To eliminate such curvature, many trials were done. These trials, in general, are concentrated in two main directions. The first is the use of Langmuir - derived equations containing more than one constant, each related to a discrete surface of adsorption, Muljadi et al. (1966), Holford and Mattingly (1975a-1975b), Rajan and Perrott (1975) and Garrison (1982). The second is introducing another term into the Langmuir equation ( $c/x/m = A + Bc + D \sqrt{c}$ ) as proposed by Junary (1970). Both directions, represented by Muljadi two-layer equation and Junary equation in the form recommended by Abd El-Aal (1985) were used to test whether they fulfil better fitness with the data obtained in this study.

#### 4.2.2.1. Adsorption of P by soils as represented by Muljadi equation:

Representing the available data on P adsorption by the equation of the two-layer adsorption (Muljadi et al. 1966) instead of the form of Langmuir equation derived by Olsen and Watanabe (1957) for monolayer adsorption, Tables (11, 12) and Fig. (12), reveal the following results :

Table (11): Maximum P adsorption ( $P_{max}$ ), P affinity constant (K) obtained from angmuir isotherm for the two sites of adsorption.  $t = 37^{\circ}\text{C}$

Soil location	Maximum P adsorption $\mu\text{g. P/g soil}$		Affinity constant		Maximum p adsorption $\mu\text{g. P/g soil}$		Affinity constant	
	$P_{max 1}$	$P_{max 2}$	$K_1$	$K_2$	$P_{max 1}$	$P_{max 2}$	$K_1$	$K_2$
El-Nobareia	144.9	909.1	1054	1.19	0.0182	243.9	1333.3	1577.2 0.363 0.0143
Abou El-Matmir	95.2	238.1	333.3	0.395	0.0513	120.5	324.7	445.2 0.311 0.0325
El-Tahreer	63.7	359.71	423.41	0.604	0.0147	78.7	353.4	432.1 0.706 0.0219
Moshtohor	200.	769.23	969.23	0.1563	0.0133	131.6	833.3	964.9 0.4471 0.0143
Meet-Kanana	87.72	684.93	772.65	0.1462	0.0057	101.01	769.2	870.21 0.1623 0.00765
El-Deer	109.9	400	509.9	0.314	0.02765	120.5	526.32	646.72 0.4611 0.02238
Grünigen	172.41	934.6	1107.01	0.395	0.0123	185.19	751.9	937.09 0.432 0.0258
Wolfsheim	285.7	1030.9	1316.6	0.7292	0.0519	263.2	1176.47	1439.67 1.15 0.0425
Average	144.94	665.82	810.76	0.4912	0.0244	155.58	758.57	914.15 0.504 0.0227

The subscripts (1) and (2) denote reaction sites of both lower and higher P concentration respectively.

Table (12) Fraction of adsorption maximum (a) for the studied soils  $t = 20^{\circ}\text{C}$

Soil location															
El-Nobareia				Abou El Matamir				El-Tahreer				Moshtohor			
a*	1-a	(1-a)c	a*	1-a	(1-a)c	a*	1-a	(1-a)c	a*	1-a	(1-a)c	a*	1-a	(1-a)c	a*
0.0093	0.991	0.05	0.025	0.975	0.195	0.019	0.981	0.128	0.009	0.991	0.367				
0.027	0.973	0.146	0.064	0.936	0.636	0.043	0.957	0.584	0.023	0.977	0.557				
0.052	0.948	0.446	0.102	0.898	1.446	0.065	0.935	1.55	0.041	0.959	1.35				
0.070	0.930	1.04	0.135	0.865	2.08	0.085	0.915	2.48	0.055	0.945	2.15				
0.085	0.915	1.78	0.148	0.852	2.63	0.101	0.899	3.53	0.068	0.932	3.49				
0.099	0.901	2.45	0.186	0.814	3.36	0.110	0.890	4.98	0.080	0.920	3.28				
0.112	0.888	2.13	0.203	0.797	3.93	0.124	0.876	5.96	0.093	0.907	4.77				
0.123	0.877	4.03	0.21	0.790	4.57	0.131	0.869	7.04	0.104	0.896	5.33				
0.242	0.758	15.49	0.372	0.628	13.91	0.255	0.745	21.69	0.198	0.802	20.11				
0.392	0.608	30.04	0.540	0.460	24.92	0.381	0.619	34.23	0.310	0.690	32.80				
0.505	0.495	37.21	0.553	0.447	31.28	0.470	0.53	44.68	0.395	0.605	45.91				
$\frac{x}{m} = \text{amount of adsorbed P.}$												$P_{\text{max}} = \text{maximum P. adsorption}$			

t -20°C

Table (12) cont.

Soil location												
Meet-Kenana				El-Deer				Grünlingen				Wolfsheim
a	l-a	(1-a)c	a	l-a	(1-a)c	a	l-a	(1-a)c	a	l-a	(1-a)c	a
0.0078	0.992	0.456	0.0163	0.984	0.1672	0.0081	0.992	0.099	0.0074	0.993	0.04	
0.075	0.983	1.317	0.039	0.961	0.673	0.0227	0.977	0.547	0.0219	0.978	0.186	
0.0303	0.970	2.192	0.065	0.935	1.477	0.0425	0.958	0.852	0.0434	0.957	0.306	
0.0373	0.963	3.446	0.086	0.914	2.312	0.0585	0.942	1.45	0.0604	0.936	0.562	
0.0452	0.955	4.831	0.105	0.895	3.258	0.0732	0.927	2.206	0.0837	0.916	0.806	
0.0555	0.945	5.950	0.120	0.88	3.978	0.0860	0.914	2.016	0.1017	0.898	1.087	
0.0578	0.942	7.114	0.144	0.856	4.72	0.0979	0.902	3.924	0.1211	0.879	1.494	
0.0658	0.934	7.80	0.156	0.844	5.579	0.1083	0.892	4.717	0.1373	0.863	1.881	
0.1238	0.876	24.05	0.309	0.691	16.695	0.1843	0.816	18.712	0.3235	0.677	8.531	
0.2032	0.797	45.18	0.986	0.514	27.64	0.3260	0.674	33.532	0.4935	0.507	18.963	
0.2982	0.702	60.0	0.529	0.471	37.369	0.4167	0.583	46.65	0.6061	0.394	24.398	

Table(12) cont.

t = 37°C

Soil location												
El-Nobareia				Abou El Matamir				El-Tahreer				Moshtchor
a	l-a	(l-a)c	a	l-a	(l-a)c	a	l-a	(l-a)c	a	l-a	(l-a)c	(l-a)c
0.0063	0.994	0.209	0.020	0.980	0.225	0.02	0.98	0.059	0.009	0.991	0.079	-
0.018	0.982	0.333	0.051	0.949	0.645	0.049	0.951	0.437	0.025	0.975	0.488	-
0.035	0.965	0.521	0.081	0.919	1.379	0.078	0.922	1.245	0.044	0.956	1.23	-
0.049	0.951	0.808	0.106	0.894	2.0	0.101	0.899	2.02	0.058	0.942	2.05	-
0.060	0.940	1.42	0.128	0.872	2.9	0.110	0.89	2.93	0.07	0.93	3.28	-
0.071	0.929	2.10	0.150	0.850	3.42	0.122	0.878	4.13	0.085	0.915	3.86	-
0.081	0.919	2.87	0.167	0.833	3.99	0.153	0.847	4.91	0.099	0.901	4.52	-
0.089	0.911	3.77	0.177	0.823	4.56	0.173	0.827	5.95	0.109	0.891	4.95	-
0.175	0.825	15.54	0.305	0.695	13.71	0.306	0.694	18.74	0.206	0.794	17.54	-
0.324	0.676	27.48	0.385	0.615	25.28	0.439	0.561	30.18	0.341	0.659	29.70	-
0.414	0.586	40.57	0.514	0.486	32.46	0.530	0.47	39.20	0.434	0.566	40.15	-

t = 37°C

Table (12) Cont.

Soil location												
Meest-Kenana				El-Deer				Grünigen				Wolfoheim
a	l-a	(l-a)c	a	l-a	(l-a)c	a	l-a	(l-a)c	a	l-a	(l-a)c	(l-a)c
0.008	0.992	0.407	0.0138	0.986	0.1381	0.0098	0.990	0.129	0.0068	0.993	0.025	
0.0187	0.981	1.109	0.0353	0.965	0.531	0.0278	0.972	0.340	0.0202	0.980	0.088	
0.030	0.970	2.07	0.0916	0.908	1.172	0.0522	0.948	0.758	0.0399	0.960	0.278	
0.0384	0.962	3.356	0.0832	0.917	1.98	0.0731	0.927	1.363	0.0591	0.941	0.433	
0.0454	0.9546	4.573	0.1004	0.90	2.82	0.0925	0.908	1.978	0.0772	0.923	0.646	
0.0558	0.944	5.297	0.1160	0.884	3.58	0.1085	0.892	2.675	0.0952	0.905	0.932	
0.0612	0.939	6.356	0.1364	0.864	4.23	0.1243	0.876	3.459	0.1119	0.888	1.359	
0.0690	0.931	7.383	0.1442	0.856	5.272	0.1385	0.862	4.230	0.1355	0.865	1.643	
0.1560	0.844	22.70	0.2837	0.716	16.912	0.2812	0.719	14.16	0.2997	0.70	8.628	
0.2479	0.752	41.52	0.4313	0.569	29.37	0.4234	0.577	28.467	0.4677	0.532	19.887	
0.3569	0.643	54.41	0.5176	0.482	37.23	0.5359	0.464	33.373	0.6085	0.392	24.508	

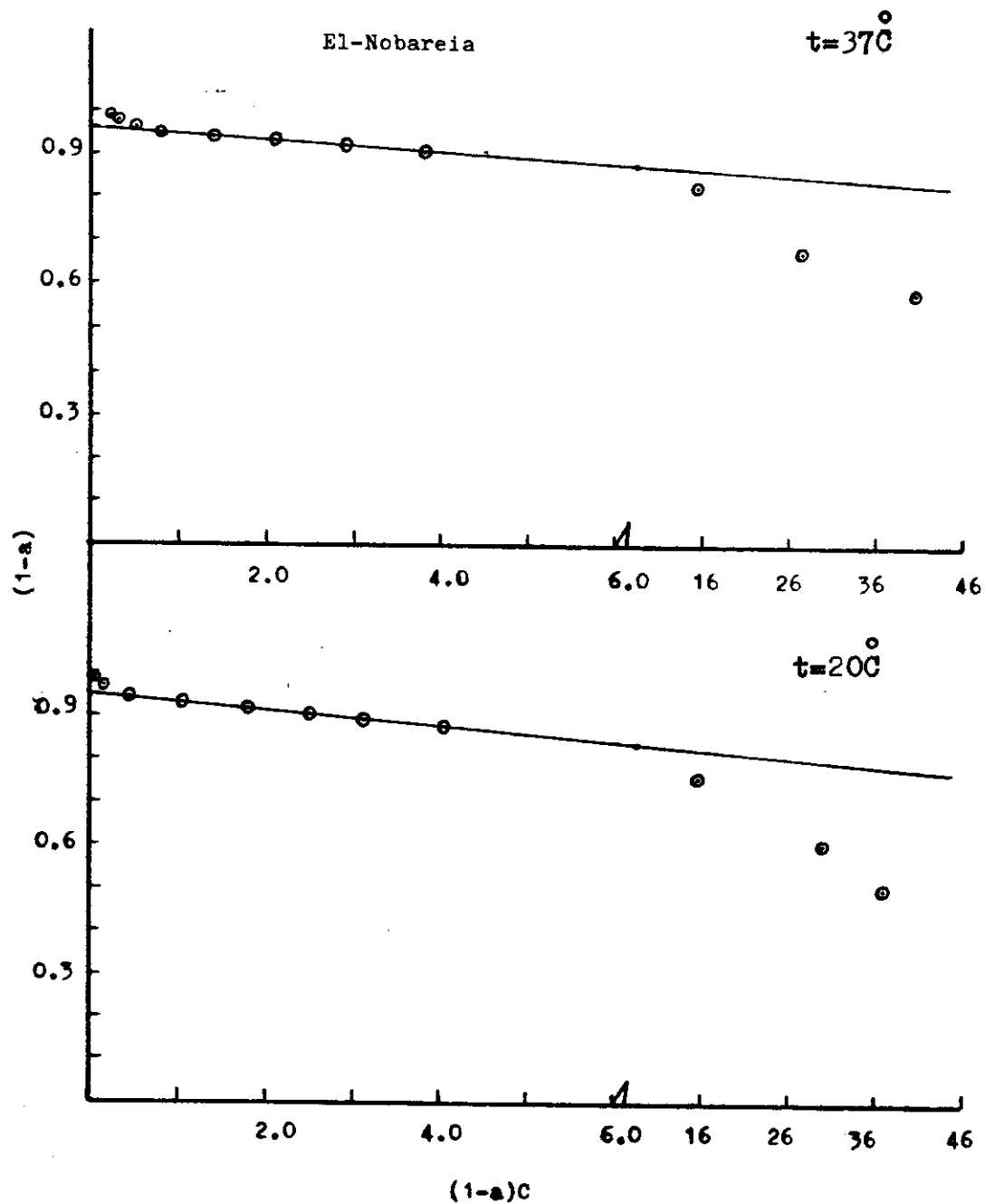
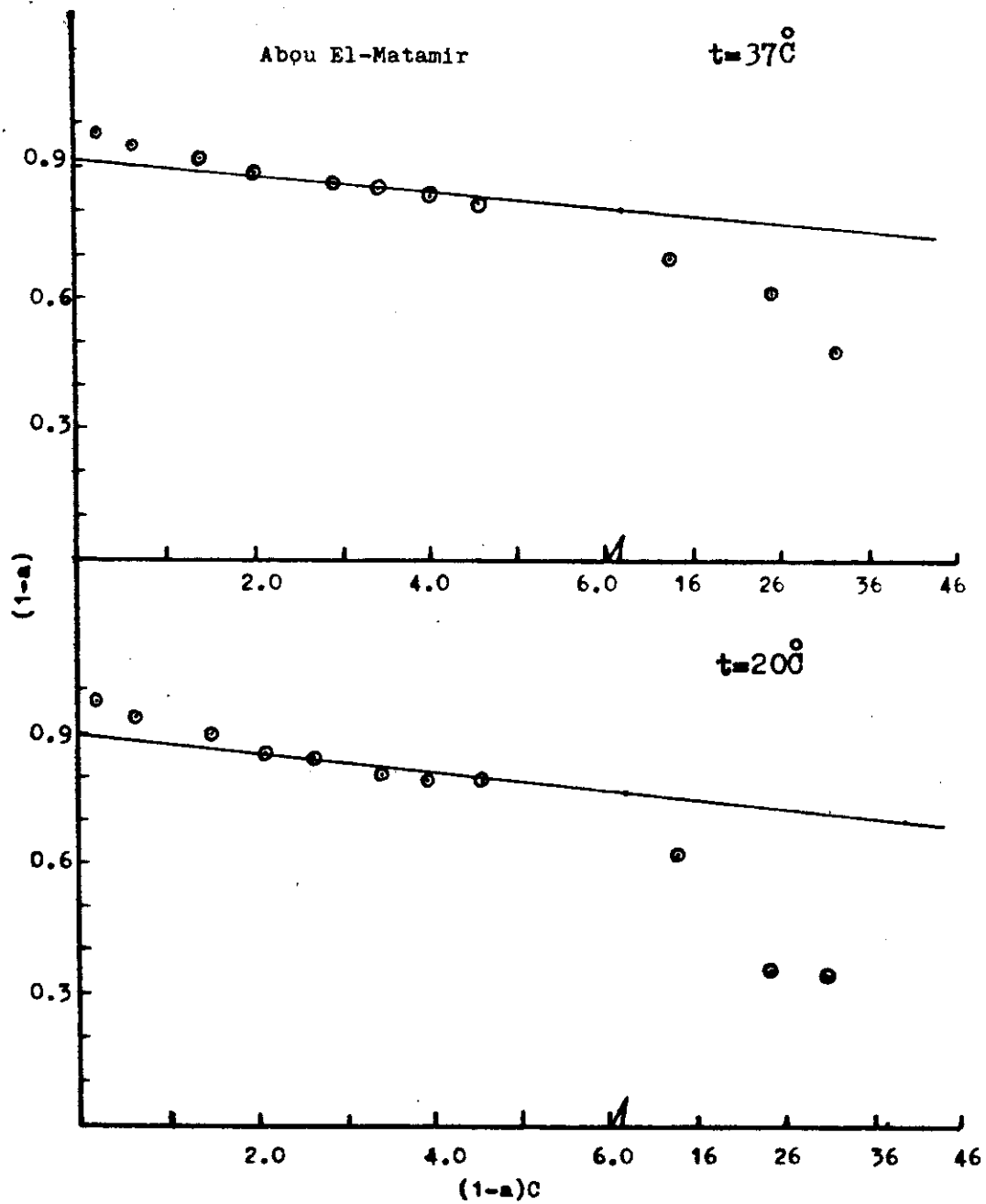
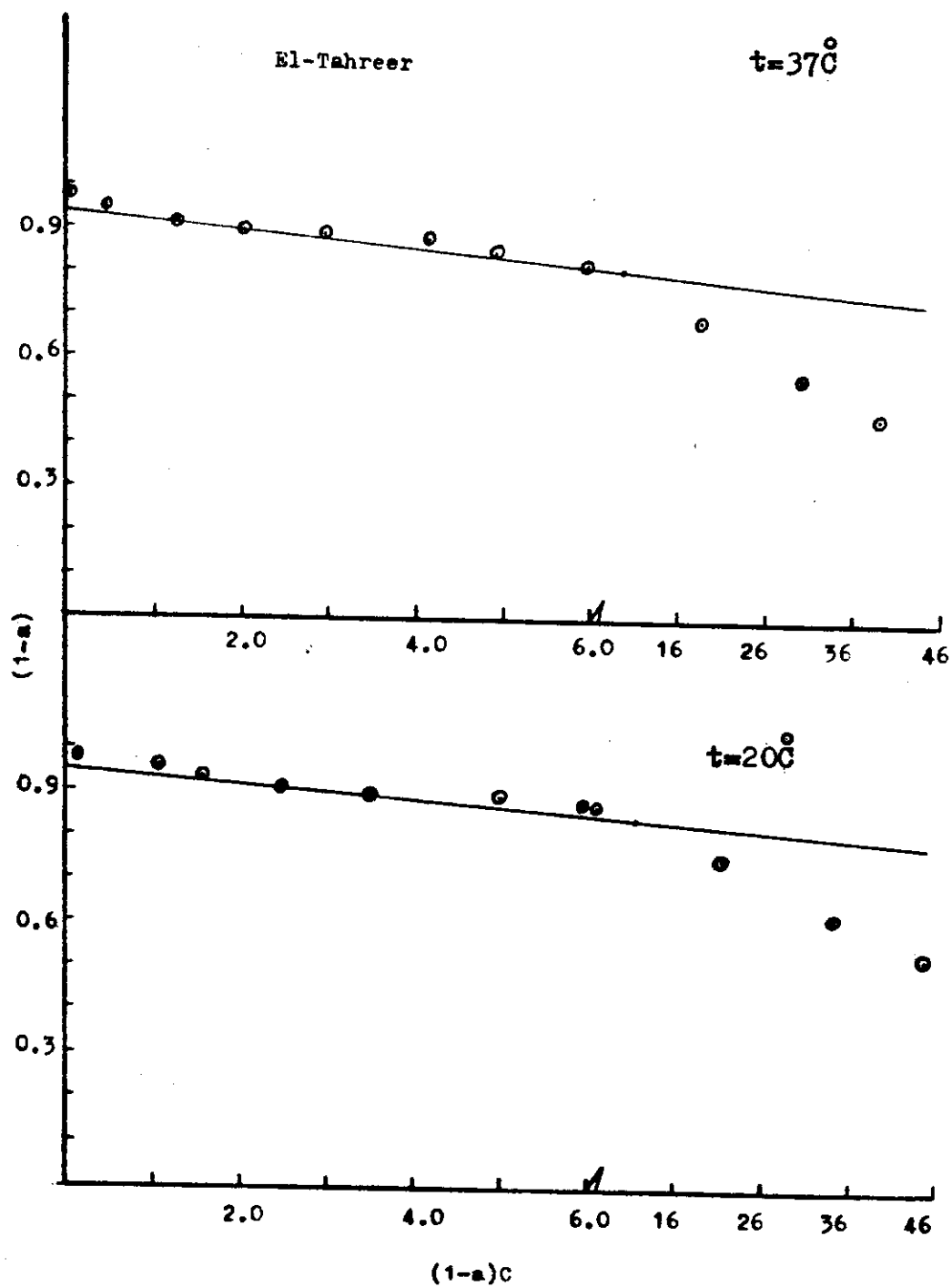


Fig.(12) The relationship between proportion  $(1-a)$  of adsorption sites unoccupied by phosphate and phosphate concentration



Fig(12) Cont.





Fig(12) Cont.

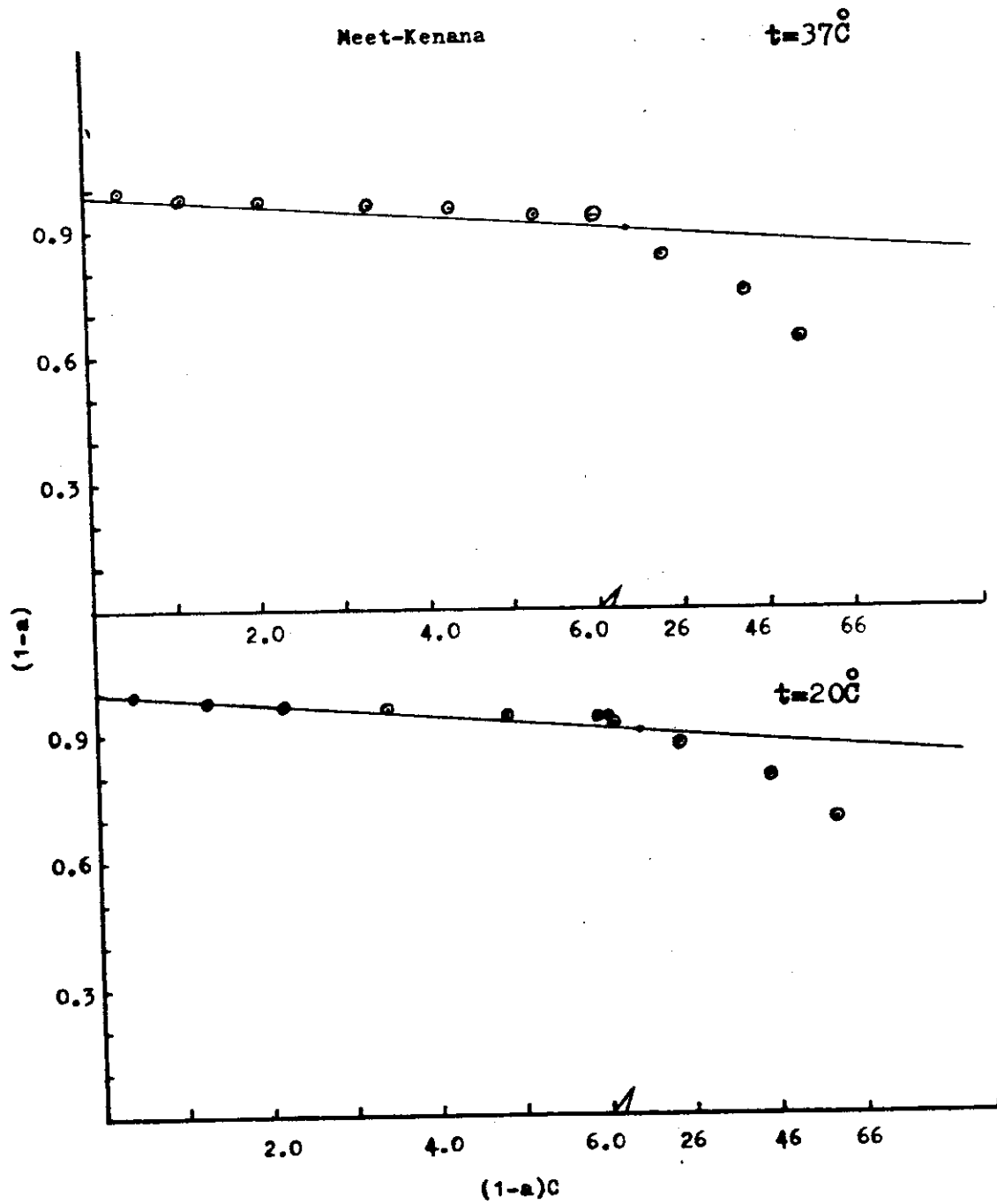


Fig.(12) Cont.

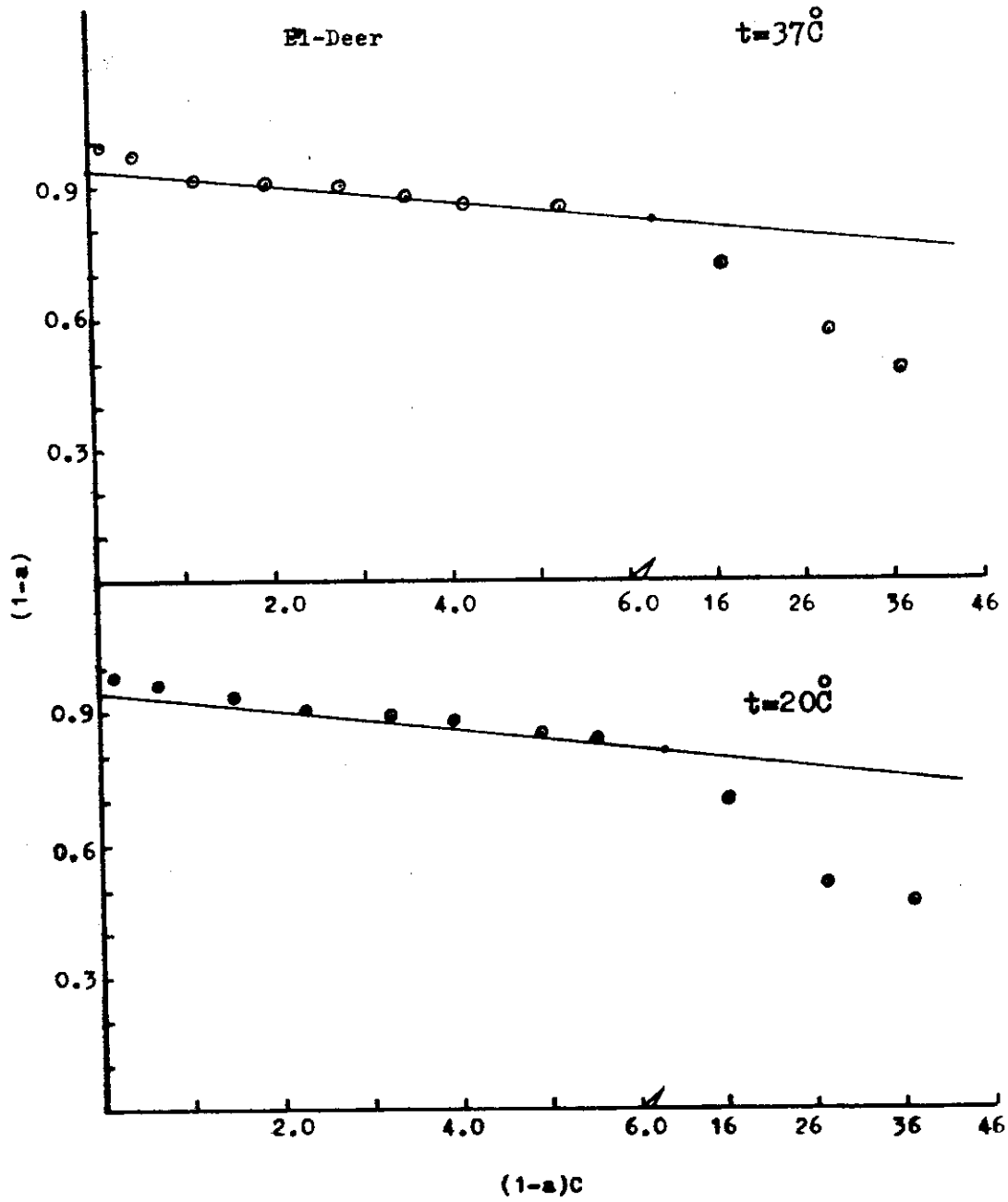


Fig.(12) Cont.

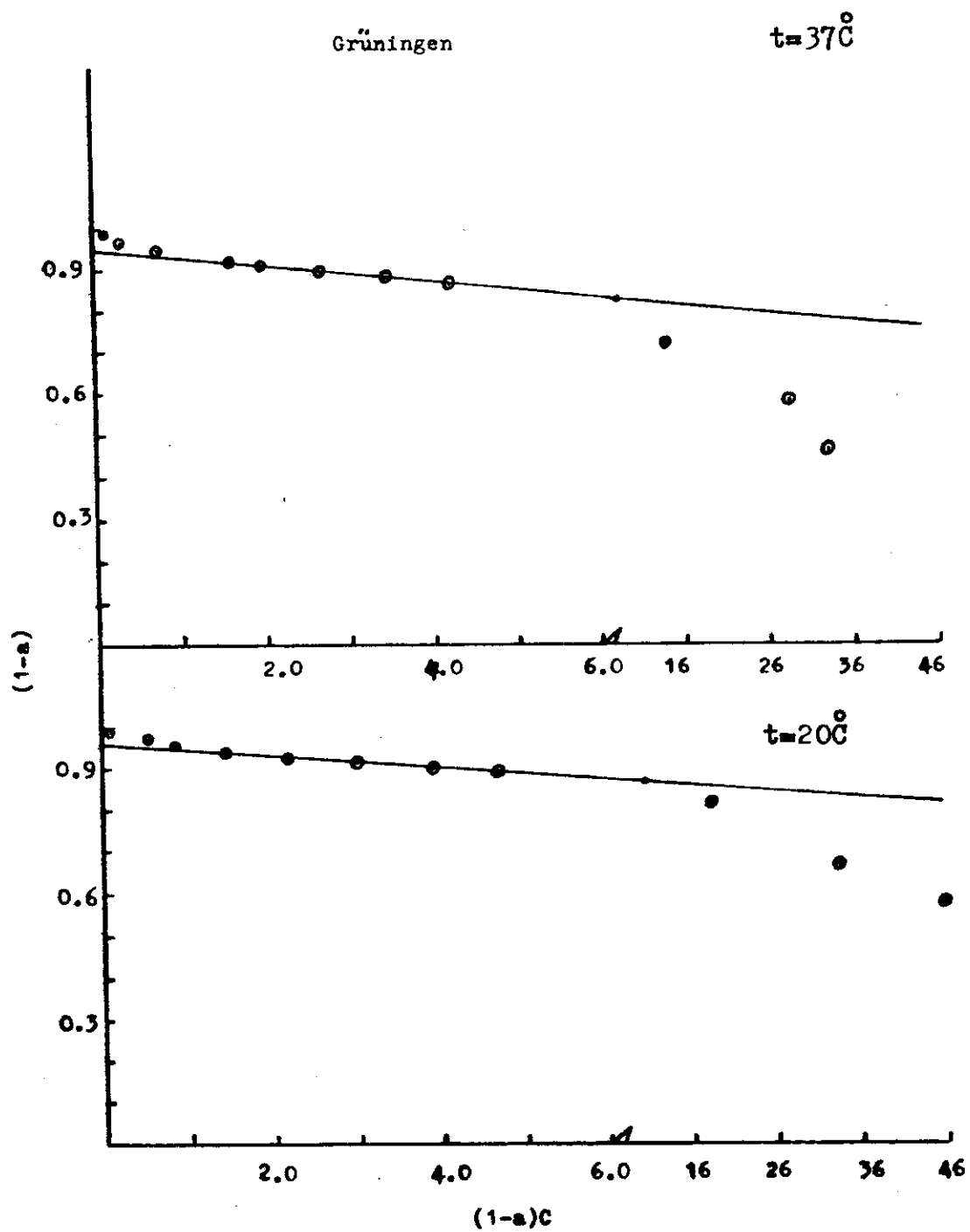


Fig.(12) Cont.

Wolfsheim

$t=370^{\circ}$

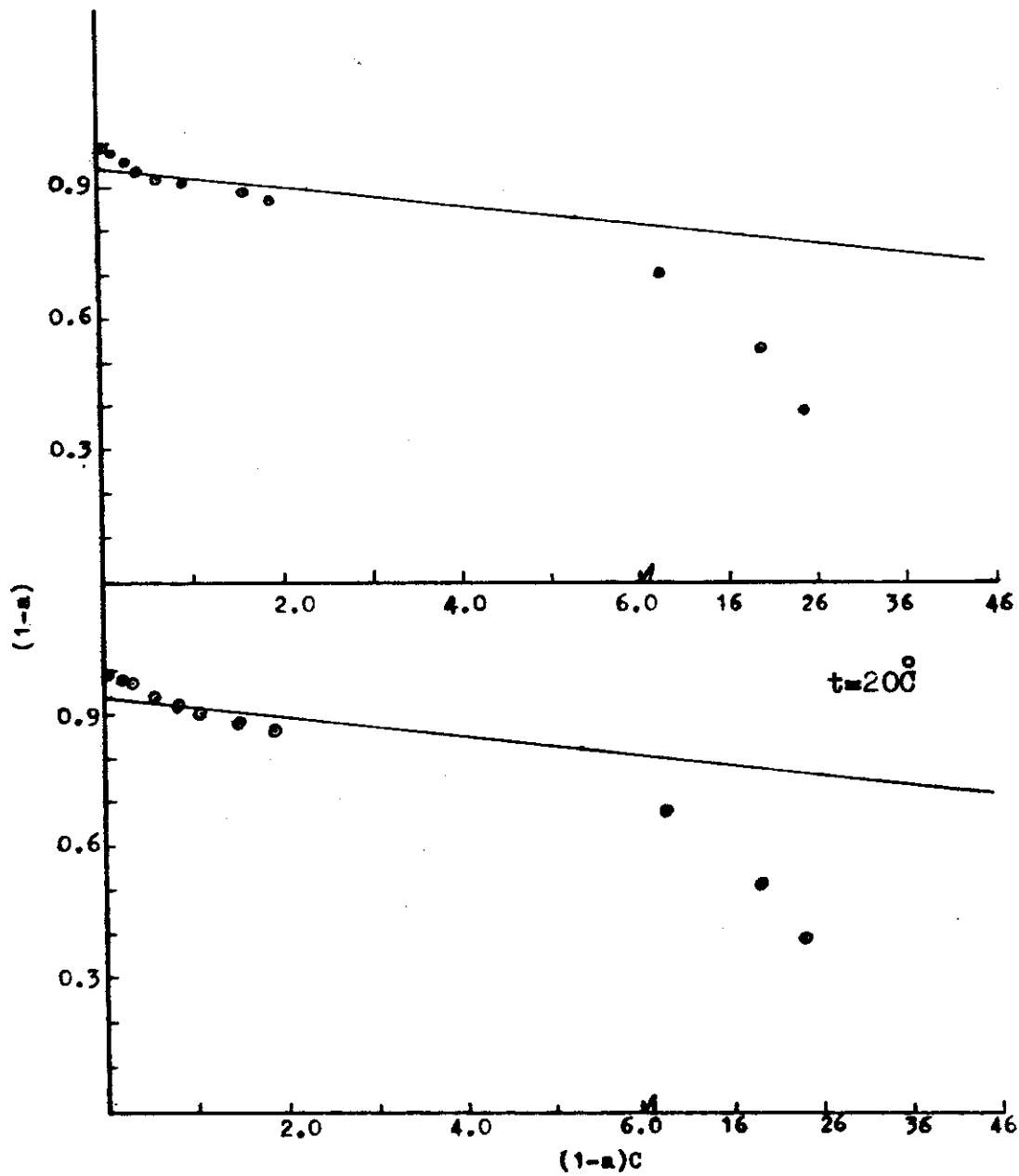


Fig.(12) Cont.

Data in table (12) and Fig. (12) show good lines for all eight soils at  $(1-a) > 0.628$ . At  $(1-a) < 0.876$  the line is no longer linear because all the sites in region 1) are not occupied. The same relationship between fraction  $(1-a)$  and  $(1-a)_c$  has been found by Muljadi et al. (1966) and Yousef (1976).

Representing the data with Muljadi et al. (1966), slightly increased the value of the correlation coefficient in many cases but it failed to behave so with some cases.

Values of the "K", the affinity constant, were higher for the first site than the second one, ranging between 0.491 to 0.024 and between 0.504 to 0.023 at 20 and 37°C, respectively.

This finding is in agreement with that reported by Muljadi et al. (1966), Youssef (1976) and Hingston et al. (1972) who stated that adsorption of phosphate increases the negative charge on the surface of the soil and hence reduces the affinity of the surface to adsorb P.

Values of maximum P retention ( $P_{max}$ ) for the first site of reaction were lower than those of the second one. These values amounted from 11.35 % to 28.56 % at 20°C and from 11.61 to 27.07 % of the maximum amount of P adsorption at 37°C, showing no significant variations.

Concerning the effect of temperature on the maximum P adsorption. The values of  $P_{\max 1}$ ,  $P_{\max 2}$  and  $P_{\max}$  averaged over all the eight soils, 144.94, 665.82 and 810.76 at 20°C and increased to 155.58, 758.57 and 914.15 µg. P/g. soil respectively as the reaction temperature increased to 37°C.

It seems from the above mentioned results that the values of  $P_{\max}$  increased as the temperature increased and these values for the second reaction site, were clearly higher than those obtained for the first one.

Similar findings were also obtained by Muljadi et al. (1966), Ballaux and Peaslee (1975) and Youssef (1976).

#### 4.2.2.2. Adsorption of P by soils as represented by Junary equation:

Treating the data of P adsorption by soils, according to the modified form of Langmuir equation proposed by Gunary (1970) showed the following results, table (13) :

Inspite of the very well fitness of the data to Langmuir adsorption isotherm, the modified form of this equation proposed by Gunary ( $c/x/m = A + Bc + D \sqrt{c}$ ) succeeded to improve the fitness of the data in all cases.

Table (13) Data obtained according to Gurney equation (1970)

Soil location	Parameters				Regression equation	
	B	A	D	r	S	
El-Nobareia	0.00432	0.0041	0.0031	0.996	231.48	$I/y = 0.00432 + 0.0041/c + 0.0031/\sqrt{c}$
	0.01084	0.03249	-0.03380	0.968	92.25	$I/y = 0.01084 + 0.03249/c - 0.0338/\sqrt{c}$
Abou El-	0.00295	0.01362	0.02097	0.999	338.98	$I/y = 0.00295 + 0.01362/c + 0.02097/\sqrt{c}$
Matamir	0.00364	0.01905	0.01269	0.999	274.73	$I/y = 0.00364 + 0.01905/c + 0.01269/\sqrt{c}$
El-Tahreer	0.00164	0.000359	0.04299	0.999	609.76	$I/y = 0.00164 + 0.000359/c + 0.04299/\sqrt{c}$
	0.00135	-0.00149	0.03414	0.999	740.7	$I/y = 0.00135 - 0.00149/c + 0.03414/\sqrt{c}$
Moshtohor	0.0087	0.04825	-0.02217	0.970	114.9	$I/y = 0.0087 + 0.0483/c - 0.02217/\sqrt{c}$
	0.00141	0.00105	0.02793	0.999	709.22	$I/y = 0.00141 + 0.00105/c + 0.02793/\sqrt{c}$
Meat Kenana	0.000693	0.05084	0.03722	0.999	144.3	$I/y = 0.00069 + 0.05084/c + 0.03722/\sqrt{c}$
	0.000337	0.03606	0.03153	0.999	2967.4	$I/y = 0.000337 + 0.03606/c + 0.03153/\sqrt{c}$
El-Deer	-0.00103	0.00660	0.03406	0.999	-	$I/y = -0.00103 + 0.0066/c + 0.03406/\sqrt{c}$
	0.00152	0.00915	0.01691	0.997	657.9	$I/y = 0.00152 + 0.00915/c + 0.01691/\sqrt{c}$
Grüningen	-0.00870	-0.000026	0.03669	0.989	-	$I/y = -0.0087 - 0.000026/c + 0.03669/\sqrt{c}$
	0.00376	0.0136	-0.000053	0.998	265.96	$I/y = 0.00376 + 0.0136/c - 0.000053/\sqrt{c}$
Wolfheim	-0.000393	0.00275	0.00692	0.998	-	$I/y = -0.000393 + 0.00275/c + 0.00692/\sqrt{c}$
	0.00102	0.00181	0.00449	0.999	980.39	$I/y = 0.00102 + 0.0018/c + 0.00449/\sqrt{c}$

. Low temperature = 20 °C

.. High temperature = 37 °C

S = Maximum P adsorption  $P_{max} = \frac{I^*}{S}$



Similar improvement in P adsorption relations was also obtained by Abd El-Aal (1985), with respect to kaolinite and montmorillonite clays.

The effect of temperature on the degree of fitness of Gunary equation was also not influenced obvious, as in the former results of Langmuir equation proposed by Olsen and Watanabe (1957).

The P adsorption maximum values obtained with Gunary equation were clearly higher than those obtained with the original form of the Langmuir equation, particularly with the soils of Abou El-Matamir, El-Tahreer and Meet Kenana at both temperatures (20 and 37°C). With the soils of Moshtohor, El-Deer and Wolfsheim however, the increase in the values of  $P_{max}$  was noticed only at the high temperature (37°C).

Similar increased in the values of P. maximum were also reported by Abd El-Aal (1985), with the application of Gunary modification.

These results may suggest that P retention by soils could be either a monolayer adsorption and thus obeys the Langmuir equation much better, or more than one layer adsorption that could be efficiently represented by the modified forms of Langmuir equation.

#### 4.2.3. Adsorption of P by soils as represented by Freundlich equation:

The data of P adsorption was also treated according to Freundlich equation, by plotting the logarithms of equilibrium P concentration ( $\log c$ ) against the logarithm of adsorbed P ( $\log x$ ), table (9) and Fig. (13).

The data showed, in general, a close agreement with Freundlich equation giving high significant values of correlation coefficient ranging between 0.982 to 0.999 and 0.962 to 0.999 at 20 and 37°C, respectively. These values of correlation coefficient were slightly higher in comparison with those obtained with Langmuir isotherm.

Similar results were also reported by Russell and Dow (1954), Gunary (1970), Bache and Williams (1971), Barrow and Show (1975) and Abd El-Aal (1985).

The better fitness of the data to Freundlich equation may be because of the gradual decrease in affinity of P to be adsorbed, Hayward and Trapnell (1964). Agreement to this purely empirical equation implies that the energy of P adsorption decreases exponentially with increasing saturation of the surface of solid materials, as reported by Bache and Williams (1971). However, using this equation does not enable neither to calculate the adsorption P maximum " $P_{\max}$ ", nor the energy by which P is bonded to the solid surface "K".

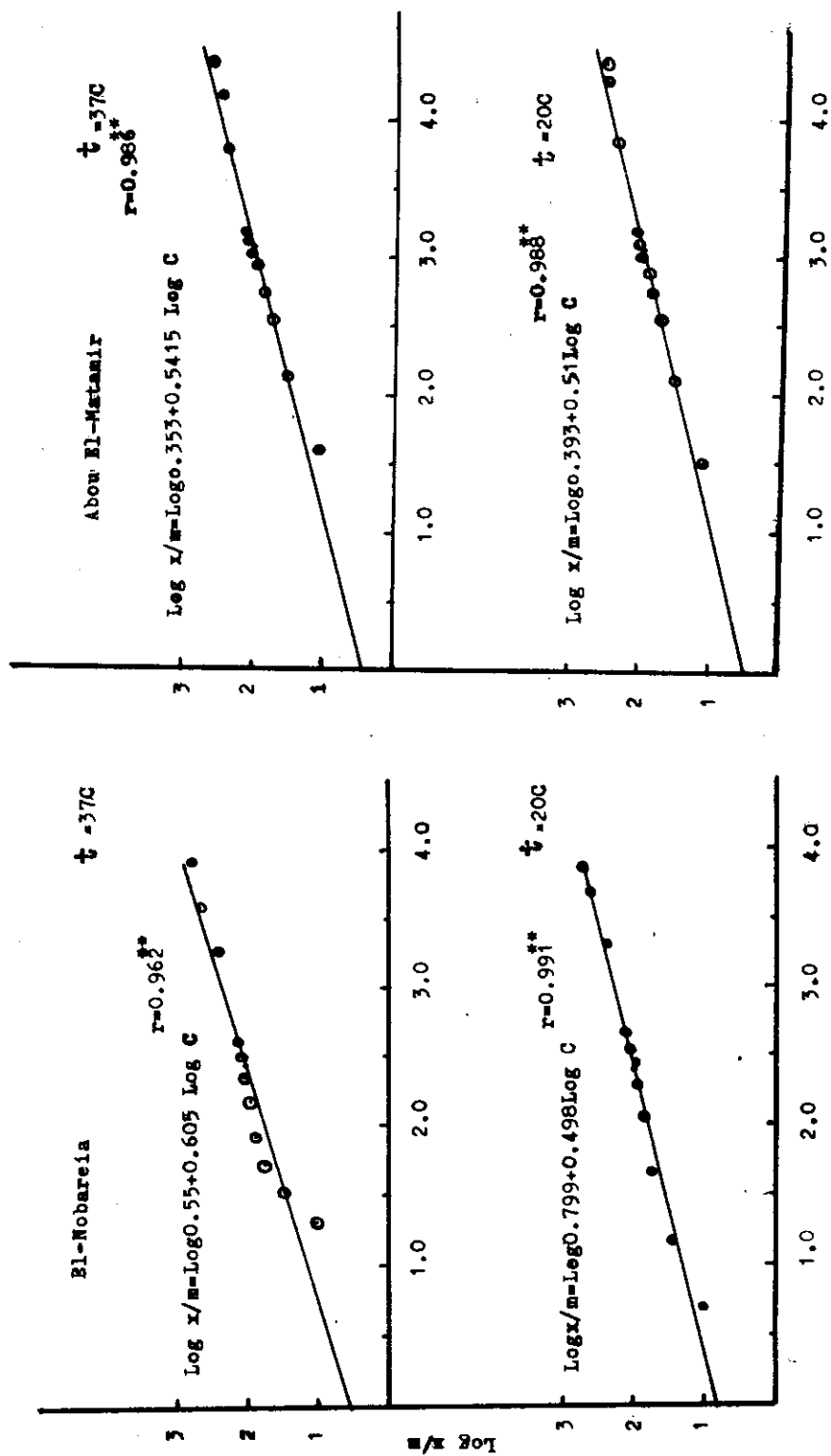


Fig.(13) Phosphorus adsorption by soils according to Freundlich equation.

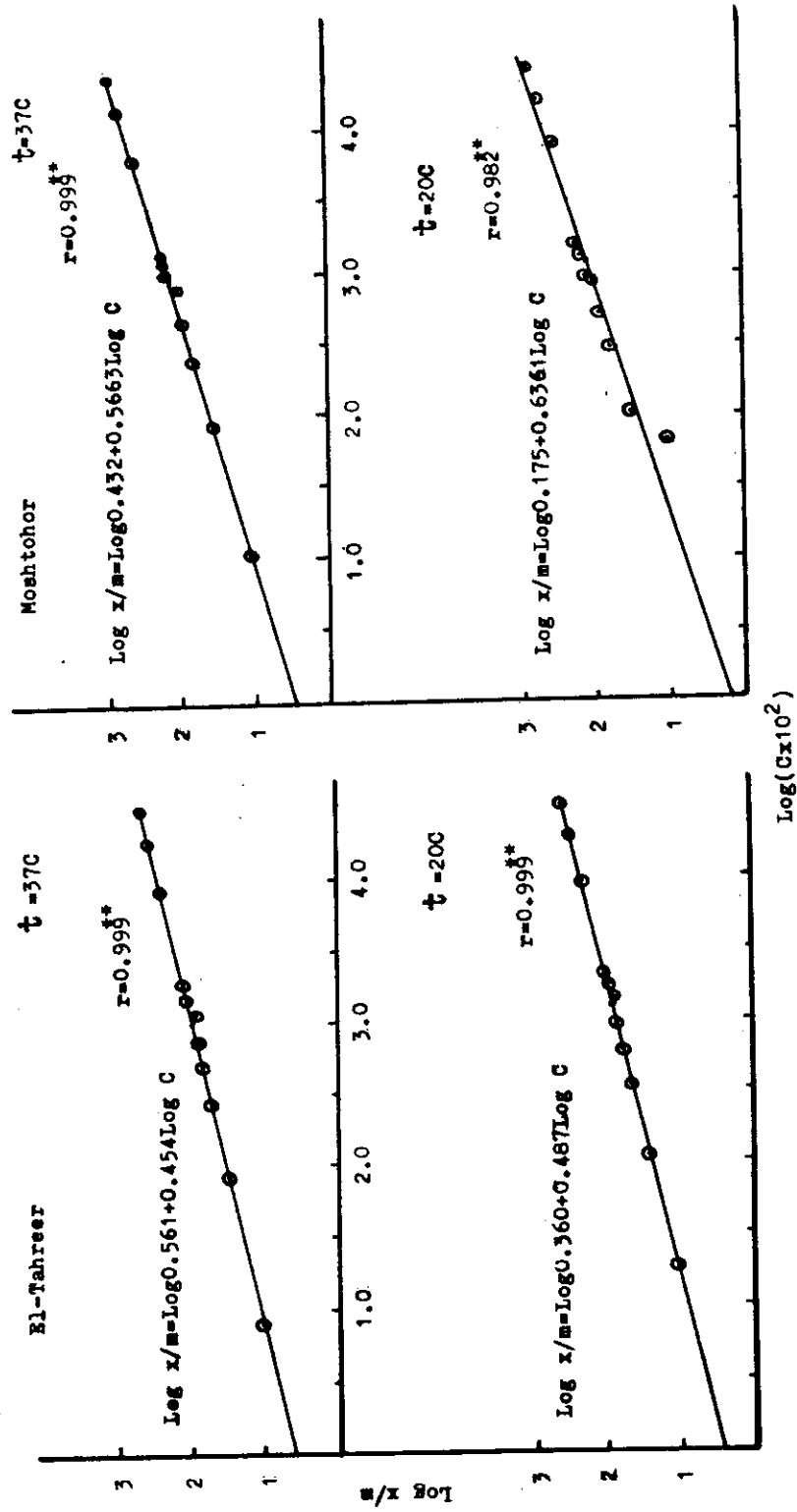


Fig.(13)Cont.

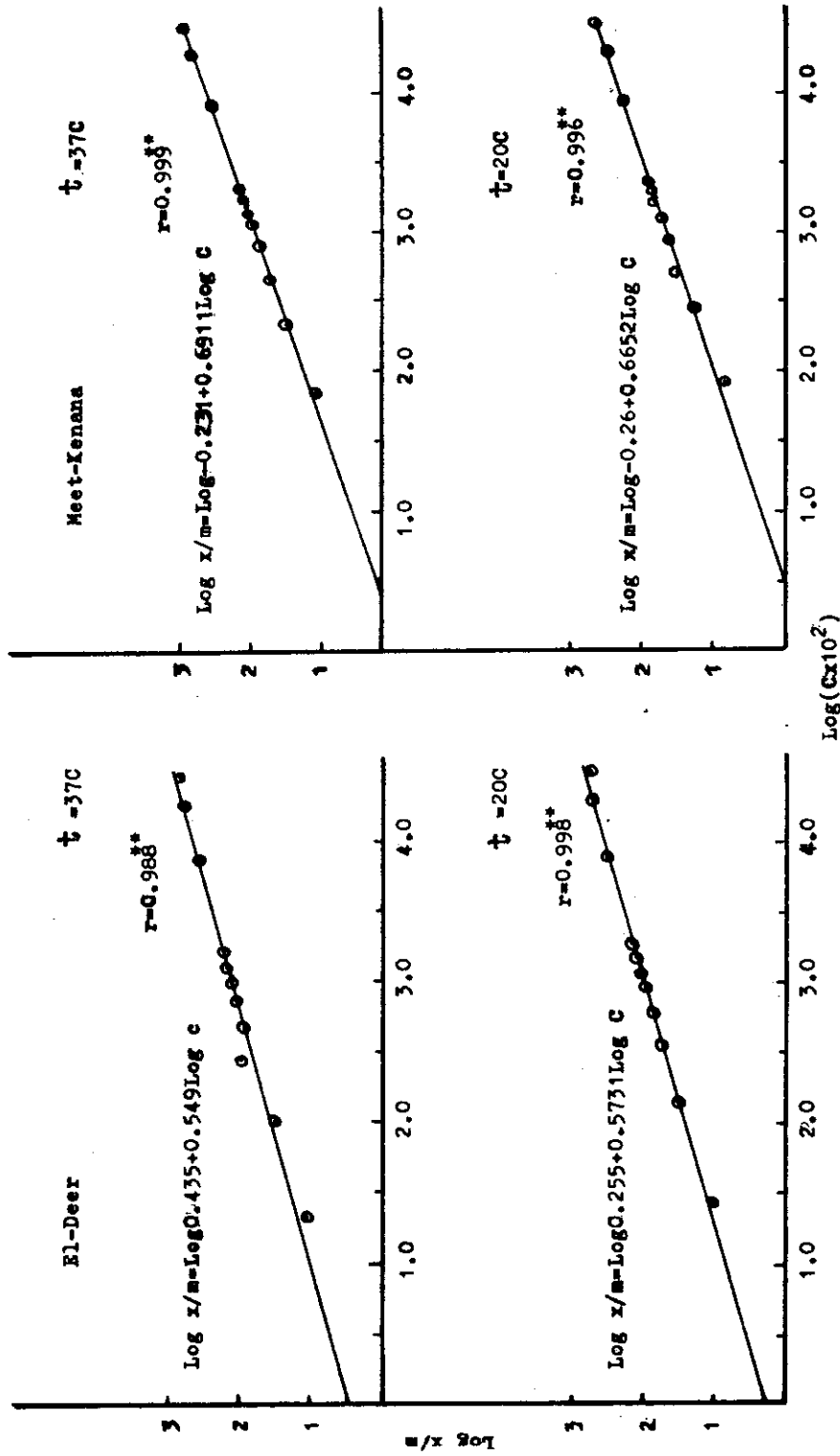


Fig. (13) Cont.

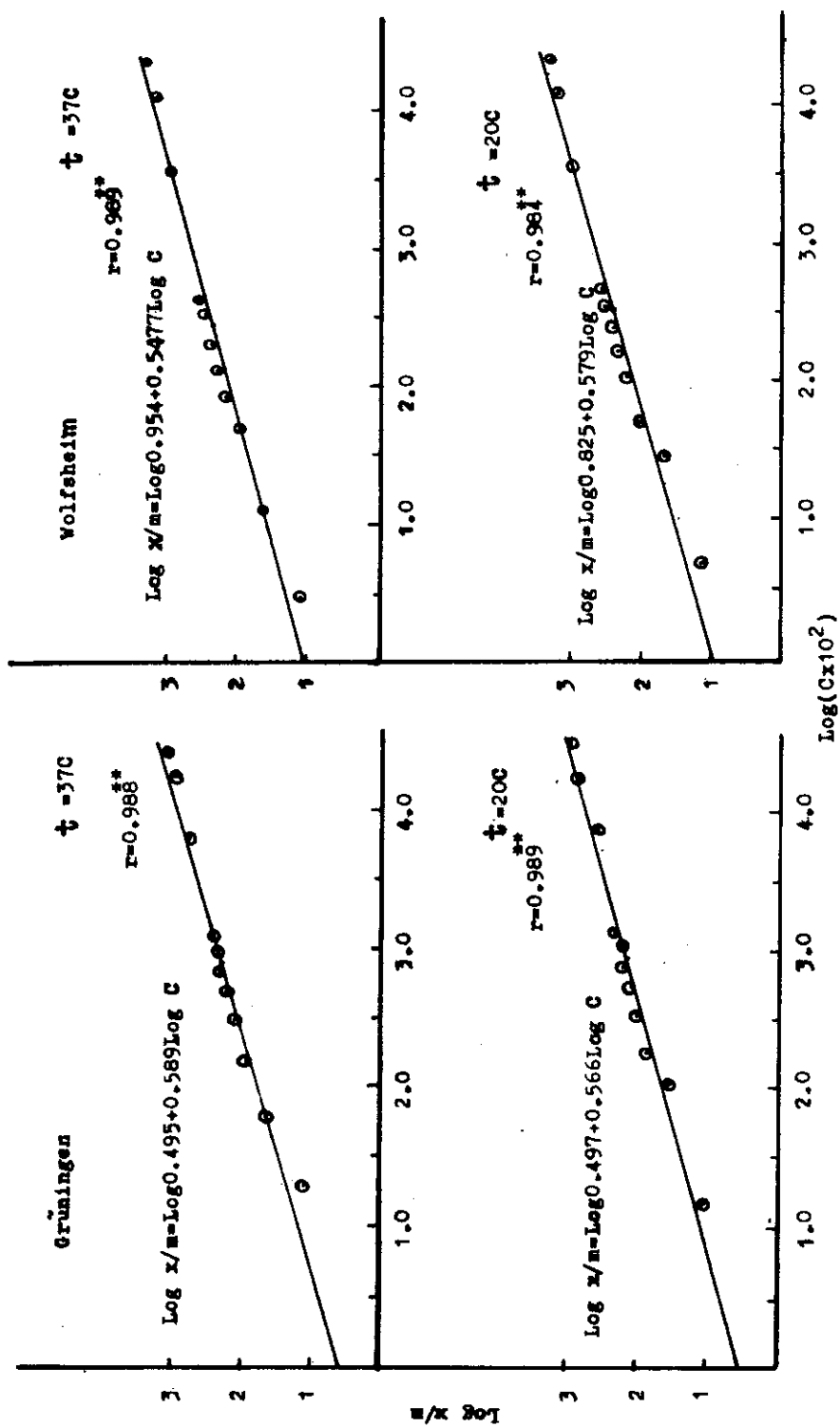


Fig.(13)Cont.

#### 4.3. Diffusion of $^{32}\text{P}$ in soil systems :

Phosphate ions are fixed by several mechanisms in the soil and thus they hardly move towards plant roots through the processes of P diffusion resulting from a concentration gradient, water movement created due to moisture gradient and via the movement by different types of soil organisms. However, diffusion is, generally considered the most important of these processes, Barber (1962).

In an attempt to evaluate the role of P diffusion in soil, the self diffusion coefficient of P was determined in five soil samples differing widely in their general properties. The self diffusion coefficient was determined as a function of soil moisture content, rate of applied P and the clay content of these soils.

##### 4.3.1. Diffusion of $^{32}\text{P}$ as a function of soil moisture content " $\theta$ "

Values of self diffusion coefficient " $D$ " measured at 0.4, 0.6, and 0.8 of the water holding capacity " $\theta$ " and the regression equations derived for " $D$ " and " $\theta$ " are presented in tables (14, 15) and Figs. (14 - 17).

The results show that the values of self diffusion coefficient " $D$ " determined according to the transient state at 0.4, 0.6 and 0.8  $\theta$ , varied between  $2.57 \times 10^{-8}$  and  $22.98 \times 10^{-8} \text{ cm}^2/\text{sec}$ . These values are comparable to those obtained by Olsen and Watanabe (1963), Olsen et al. (1965) and Mahtab et al. (1971).





Table (15): Results of linear regression analysis

Soil location	(1)		(2)	
	Correlation coefficient	Linear regression Equation	Correlation coefficient	Linear regression equation
El-Mobareia	r=0.962**	D= -8.65 +31.25 $\theta$	r= 0.965**	D= 6.11 + 30C
Abou - El Matamir	r=0.995**	D= -3.27+19.98 $\theta$	r=0.935**	D= 6.65 + 15.65 C
Moshtohor	r=0.989**	D= -11.075 +39.33 $\theta$	r=0.982**	D= 9.74 + 20.98C
Meet-kenana	r=0.999**	D= -4.46 +19.95 $\theta$	r=0.933**	D= 4.71 + 21.09C
El- Deer	r=0.988**	D= -8.71 +31.63 $\theta$	r= 0.977**	D= 9.06 + 9.13 C

(1) D= Plotted in linear form as a function of soil moisture content  $\theta$

(2) D= Plotted in linear form as a function of added phosphorus (c)

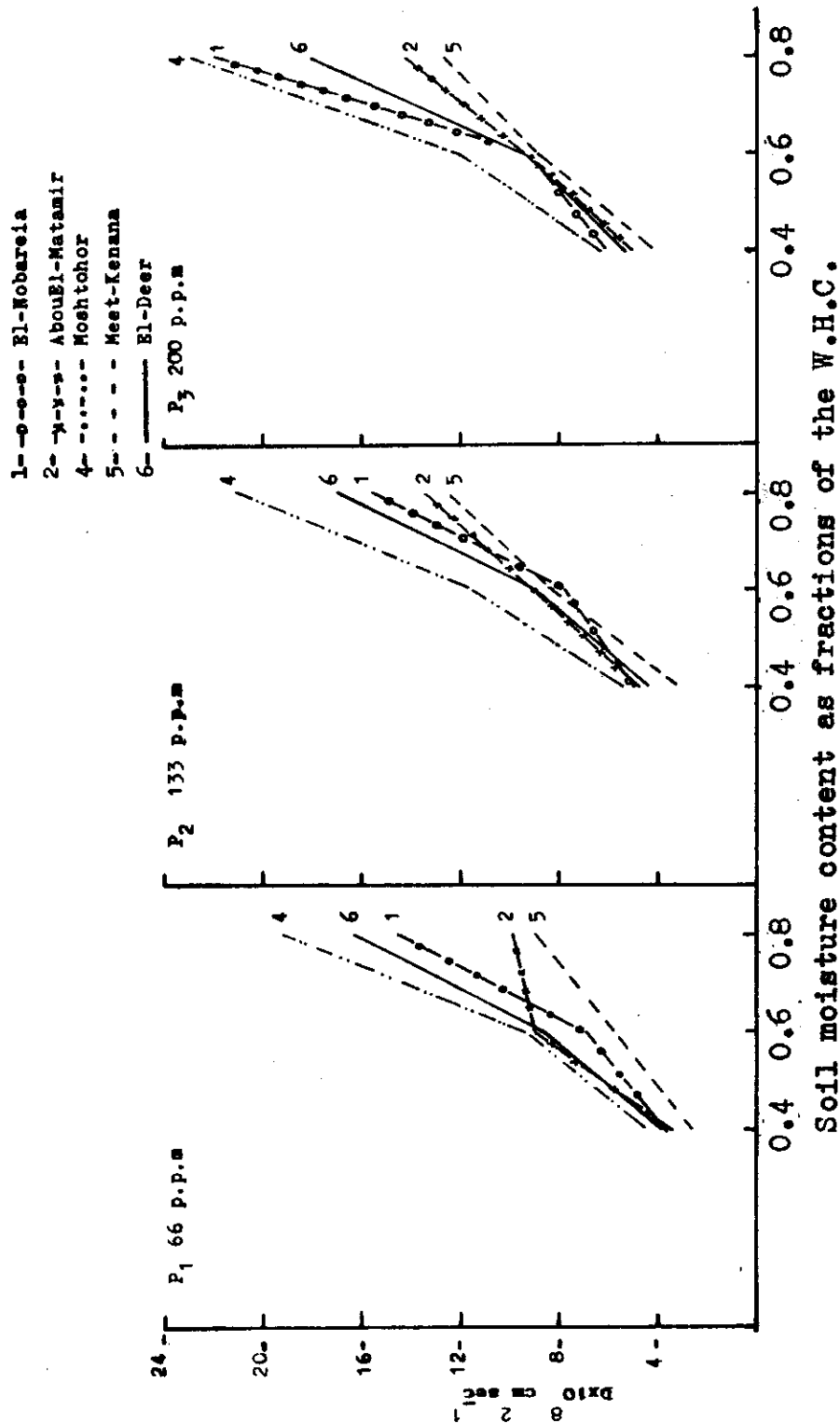


Fig. (14) Self-diffusion coefficient of P in relation to soil moisture content( $\theta$ )

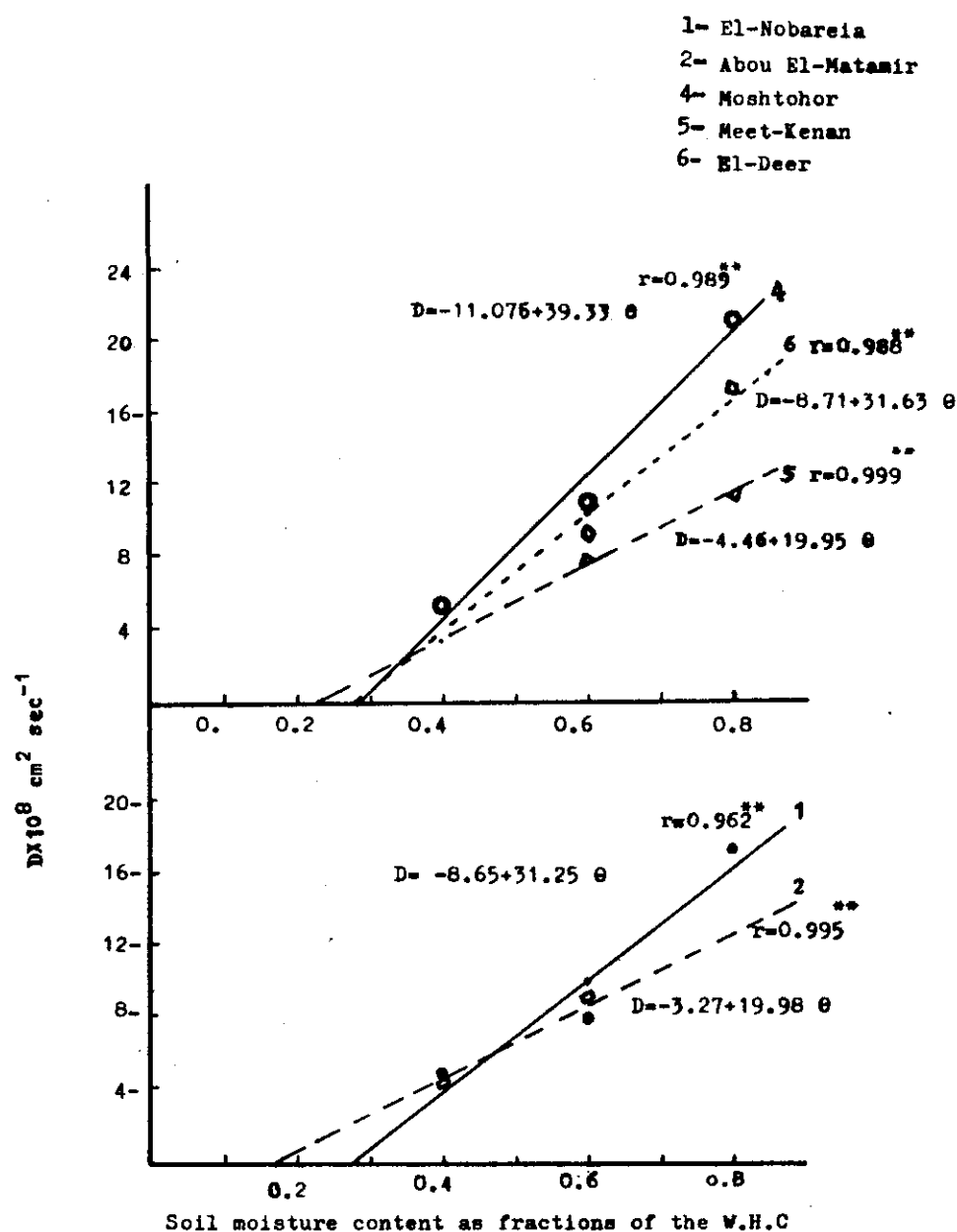


Fig.(15) Self-diffusion coefficient of P as a function of soil moisture content ( $\theta$ )

It is easy to detect for instance that the high "D" values were corresponding to high moisture content and also to relatively high content of clay fraction. Regarding the influence of soil moisture, the most important findings can be presented as follows:

Increasing the soil moisture content sharply, and in many cases abruptly, increased the values of "D". This trend was obvious with all the soil samples and under the different levels of applied P. The average overall values of "D" yielded with the three levels of soil moisture " $\theta$ ", respectively were ;

4.90, 8.00 and  $17.40 \times 10^{-8} \text{ cm}^2/\text{sec}$  for El-Nobareia soil;  
4.50, 9.17 and  $12.50 \times 10^{-8} \text{ cm}^2/\text{sec}$  for Abou El-Matamir soil,  
5.40, 11.03 and  $21.13 \times 10^{-8} \text{ cm}^2/\text{sec}$  for Moshtohor soil,  
3.40, 7.74 and  $11.38 \times 10^{-8} \text{ cm}^2/\text{sec}$  for Meet Kenana soil and  
4.56, 9.06 and  $17.2 \times 10^{-8} \text{ cm}^2/\text{sec}$  for El-Deer soil.

The corresponding increases in the "D" values due to increasing the soil moisture content " $\theta$ " from 0.4 to 0.6 and 0.8, respectively were :

67.3 % and 261.5 % in El-Nobareia, 109.5 % and 178.5 % in Abou El-Matamir, 105.8 % and 296.4 % in Moshtohor, 128.3 % and 238.4 % in Meet-Kenana, 101.2 % and 281.0 % in El-Deer soil.

The data show clearly that the increase in the water content of the clay textured soils has more effect on diffusion coefficient

than in the lighter-textured soils. This may be because the clay soil generally holds so much more water that raise these "D" values. Moreover, the clay soils oftenly contains water enough to maintain a considerable rate of P diffusion.

Similar trend was also reported by many investigators, where the "D" values of P in soils increased from  $0.4 \times 10^{-7}$  to  $15.5 \times 10^{-7} \text{ cm}^2/\text{sec}$  and from  $10.25 \times 10^{-10}$  to  $27.76 \times 10^{-10} \text{ cm}^2/\text{sec}$ , respectively with increasing the volumetric moisture content from 0.22 to 0.55 (Olsen et al., 1965) and from 35 to 100 % of the available moisture (Mahtab et al., 1971). Olsen et al. (1965) indicated that " $\theta$ " affects ( $D_p$ ) in both physical and chemical ways. They reported that as  $\theta$  decreases in a given soil, the cross-sectional area available for diffusion becomes smaller, the path length increases, and the viscosity and negative adsorption become more important as the water films decrease in thickness.

For the water contents below that held at 15 bars, the "D" value is almost 0 but increases rapidly as the water in excess of that held at 15 bar increases (Harrell, 1980).

#### 4.3.2. P diffusion as a function of the rate of P application :

Phosphorus self-diffusion coefficient measured as a function of added P in five different soils and the linear regression equations of "D" and P concentrations are shown in table (14) and Fig. (16).

Results show that the diffusion coefficient "D" represents a linear function of added P for all samples. The correlation coefficients are all above 0.93 suggesting a very close relationship.

The "D" values obtained under the different rates of applied P "c" averaged over all soil moisture contents ( $\theta$ ) increases with increasing the rate of applied P. In this regard, increasing the rate of applied P from 66 to 200 p.p.m., increased the "D" values of P in soils from 8.37 to  $12.46 \times 10^{-8} \text{ cm}^2/\text{sec}$ , from 7.44 to 9.58, from 10.98 to 13.85, from 5.77 to 8.67 and from 9.67 to  $10.92 \times 10^{-8} \text{ cm}^2/\text{sec}$  for El-Nobareia, Abou El-Matamir, Moshtohor, Meet Kenana and El-Deer soils, respectively.

Accordingly, it may be concluded that the relationship between the rate of applied P and the values of self-diffusion coefficient could be illustrated in a linear form and represented by the equations  $D = a + b_c$ , table (14) and Fig. (16). These findings are in agreement with those reported by Lewis and Quirk (1962 - 1967), Phillips et al. (1968), Mahtab et al. (1971), Harrel and Saeed (1977).

#### 4.3.3. P diffusion as a function of soil clay content :

Fig. (17) shows a linear relationship between self-diffusion coefficient and soil content of clay, represented by the regression equation :

$D = 7.28 + 8.17 \text{ clay fraction}$ . This relation exhibited high significance with corresponding "r" values of 0.949.

It is obvious that the clay content % of these soils was 13.16 %, 17.43 %, 27.03 %, 31.15 % and 67.8 % for Meet-Kenana, Abou El-Matamir, El-Deer, El-Nobareia and Moshtohor soil; respectively. The values of "D" increased in a trend parallel to that of the clay fraction content of these soils namely; 7.51, 8.73, 10.27, 10.11 and  $12.53 \times 10^{-8} \text{ cm}^2/\text{sec}$ , respectively.

This results are also in agreement with many other studies, Olsen and Watanabe (1963), Olsen et al. (1965) and Mahtab et al. (1971).

Olsen et al. (1965) attributed the increase in "D" values with increasing clay content to a tortuosity factor, which also increased with increasing clay content. Another effect of clay is its effect on the moisture content of the soil which in turn, increase the cross sectional area available for diffusion and also increases the volumetric moisture content, hence causing higher rates of diffusion P coefficient values.

The purpose of this investigation is to study some reactions involved in the release and retention of phosphorus in soils and hence may affect the P supply to growing plants.

The study included eight surface soil samples six of them were collected from various locations of A.R.E. and the other two samples were obtained from F.R.G. The soils of Egypt were represented by the locations of El-Nobareia, Abou El-Matamir, El-Tahreer, Moshtohor, Meet-Kenana and El-Deer soils, representing both calcareous and alluvial soils whereas those of F.R.G. were collected from Gröningen and Wolfsheim which are of slightly acid reaction.

The soil samples were identified through mechanical, physical, chemical and mineralogical analysis.

The work included two main experiments using labelled  $^{32}\text{P}$ . The first experiment deals with the retention and release of P and adsorption reactions responsible for P retention in soils. The effect of a wide range of P concentrations (10 - 1860  $\mu\text{g}$ . P/g. soil), temperature (20 and 37°C) and time of reaction (one, 30 and 60 days) on the amount of P retained were taken into consideration.



To elucidate the pattern of P release in soil, four soil samples previously incubated for 30 days in solution having P concentration of 30, 60, 90, 120, 150 or 180  $\mu\text{g}$ . P/g. soil at  $20^{\circ}\text{C}$  were subjected twice to saving P by means of distilled water followed by extraction with  $\text{NaHCO}_3$  of pH 8.5.

Concerning the adsorption of P by soils, the data obtained for P retention after 24 hours was treated according to Langmuir isotherm, thenafter according to the modified forms of Muljadi et al. (1966) and Gunary (1970) and also the Freundlich equation.

The second experiment deals with  $^{32}\text{P}$  diffusion in the soils of El Nobareia, Abou El-Matamir, Moshtohor, Meet Kenana and El-Deer. Values of self-diffusion coefficient "D" were measured according to the transient state method under different levels of soil moisture content (40, 60 and 80 % of the W.H.C.), as a function of P concentrations ranging from 66 to 200 p.p.m.P and also as a function of clay fraction content. The linear regressions equations of "D" and both the P concentrations and soil moisture fraction "θ" were calculated.

The main results obtained can be summarized as follows :

- 1 - Values of P retained, in general, increased steadily with increasing the concentration of added P , temperature and also with the time of reaction.

The average values of retained P increased from 7.55 and 9.86  $\mu\text{g. P/g. soil}$  to 311.09 and 1002.3  $\mu\text{g. P/g. soil}$  with increasing the rate of added P from 10 to 1860  $\mu\text{g. P/g. soil}$ .

The highest capacities to retain P were obtained with Wolfsheim followed by El-Nobareia and Moshtohor soils, while the lowest capacities were observed with the soil of Meet-Kenana and El-Tahreer. The soils of high P retention are characterized with slightly acidic reaction (Wolfsheim), high clay content (Moshtohor) and relatively high  $\text{CaCO}_3$  content (El-Nobareia). According to these results, it can be concluded that the acidic pH conditions prevailed in Wolfsheim that leads to relatively higher concentrations of free oxides, such as Fe, AL and Mn beside the abundances of clay minerals and the soil content of calcium carbonate could be main factors seriously affecting the soil capacity to retain P.

2 - The values of retained P expressed as percentage of the corresponding values of added P consistently decreased with the progressive increments in the rate of added P to the soil. When P was applied at a rate of 10  $\mu\text{g. P/g. soil}$ , these values were 87.1, 93.51 and 93.21 % but decreased to 22.24, 36.37 and 41.45 % with the rate of 1860  $\mu\text{g. P/g. soil}$  after one, 30 and 60 days of incubation, respectively. This trend was attributed to the progressive occupying of the different sites responsible for P retention with increasing the time of contact and rate of added P.

3 - Results, in general, show that increasing the temperature of incubation from 20°C to 37°C increased the P retention by soils particularly at the higher rates of applied P. Incubating the soils at 20°C with P solutions of 10 p.p.m. P concentration yielded average values of P retention ranging from 7.39 (Meet-Kenana) to 9.87 µg. P/g. soil (Wolfsheim) and from 9.07 (Abou El-Matamir) to 9.88 µg. P/g. soil (El-Nobareia) at 37°C. Increasing the P concentration to 1860 µg. P/g. soil raised these figures to 236.84 (Abou El-Matamir) and 931.24 µg. P/g. soil (Wolfsheim) at 20°C and to 360.22 (Meet-Kenana) and 1449.6 µg. P/g. soil (El-Nobareia) at 37°C.

The calcareous soils of Abou El-Matamir, El-Tahreer and El-Nobareia showed increasing capacities to retain P with increasing temperature from 20°C to 37°C, that may be due to increasing the solubility of  $\text{CaCO}_3$  and hence P retention capacity of the soil.

4 - Increasing the time of contact increased the percentage of retained P from 87.10 and 22.24% after one day incubation to 93.21 and 41.45 % at 60 days with increasing the rates of P application from 10 to 1860 µg. P/g. soil.

These results, in general may indicate that the tested soils showed no definite powers of P retention which seems to be a function of the equilibrium P concentration in the soil solution and the time of reaction. Moreover, three or four regions of consistent

and steady increase in P retention could be observed, which may suggest the presence of more than one mechanism responsible for P retention by soils.

5 - The water soluble P fractions, released or recovered from P-treated soils were closely correlated with the amount of added P with values of correlation coefficient being 0.975, 0.989, 0.948 and 0.959 for El-Deer, Moshtohor, Gruningen and Wolfsheim soils, respectively.

Increasing the rate of P application of these soils from 30 to 180  $\mu\text{g}$ . P/g. soil progressively raised the level of soil P recovered in water from 5.19, 5.46, 4.48 and 3.64 to 16.99, 15.59, 23.7 and 13.87  $\mu\text{g}$ . P/g. soil for the tested oil samples, respectively. However, when these fractions were expressed in terms of percentage of added P, a decreasing trend was obvious. The percentage of water P recovered decreased from 17.3, 18.2, 14.9 and 12.1 to 9.44, 8.86, 13.17 and 7.71 with increasing the rate of added P from 30 to 180  $\mu\text{g}$ . P/g. soil for the above mentioned soils, respectively.

6 - The values of P recovered by  $\text{NaHCO}_3$  from the P-treated soils were positively correlated with the amount of P added to these soils except with Wolfsheim soil where this relation was not significant. The values of correlation coefficient were 0.964, 0.870, 0.979 and 0.461 for the tested soils, respectively. The quantities of  $\text{NaHCO}_3$  recovered P ranged from 9.87 and 23.21  $\mu\text{g}$ . P/g. soil to 20.49 and 43.57  $\mu\text{g}$ . P/g. soil with increasing the rate of added P from 30 to 180  $\mu\text{g}$ . P/g. soil. Expressing the fraction of added P recovered as percentage of added P, yielded an opposite trend as this percentage decreased from 32.9, 65.7, 61.2 and 63.9% to 11.83, 15.16, 24.21 and 21.28% for the tested soils, respectively.

7 - The results of all soils showed close fitness to Langmuir adsorption isotherm at both temperatures (20 and 37°C). The values of correlation coefficient ranged between 0.936 and 0.991 at 20°C and 0.935 and 0.986 at 37°C.

Plotting the  $c/x/m$  values versus " $c$ " suggested a possible existence of more than one site or mode of P adsorption through the tested range of P concentrations. This relation showed a slight convex to the x axis particularly with the high P concentration.

The values of " $K$ " constant that relates to the bonding energy or the affinity by which the adsorbate is attached to the adsorbent ranged from 0.0297 to 0.154 and from 0.0258 to 0.175 at 20 and 37°C, respectively. These values were relatively low in the light-textured alkaline soils as compared with those of heavy texture or with the slightly acidic soil of Wolfsheim which may reflect the relatively high bonding energy of P in such soils. This energy could be arise from the abundance of  $\text{CaCO}_3$ , clay and free or active oxides of Fe, AL and Mn.

The values of the maximum P adsorption constnat ( $P_{\text{max}}$ ) varied from 204.1 and 833.30 with an average of 416.9  $\mu\text{g. P/ml}$  at 20°C. Increasing the temperature of reaction to 37°C clearly , increased these values, from 242.72 to 909.1 with an average of 489.0  $\mu\text{g. P/g. soil}$ .

These values were positively correlated with the clay abundance in soils, with a correlation coefficient of 0.856. Such trend was obvious only at the low temperature (20°C).

It is noteworthy to mention that the values of both "K" and " $P_{\max}$ " constants, depend chiefly on the P concentration in the medium at which the adsorption process takes place as well as the P amount initially bonded to the adsorbent.

8 - Plotting the data according to the Langmuir equation containing two surfaces sites derived by Muljadi et al. (1966) yielded, better fitness, high "K" values for the first site of adsorption and lower values for the second site but decreased the " $P_{\max}$ " at the first site and increased at the second one. The values of  $P_{\max}$  increased as the temperature increased from 20°C to 37°C and these values for the second reaction site, were clearly higher than those obtained for the first one.

The values of  $P_{\max 1}$ ,  $P_{\max 2}$  and  $P_{\max}$  average over all the eight soils increased from 144.94, 665.82 and 810.76 at 20°C to 155.58, 758.57 and 914.15 µg. P/g. soil, respectively at 37°C.

It seems that such forms of equation include "low concentration reaction" being responsible for relatively small " $P_{\max}$ " having much higher affinity for the active site than the larger quantities

of " $P_{\max}$ " taken up by the second reaction "high concentration reaction" and having low affinity for the second site.

9 - The second trial to eliminate the curvature of Langmuir was by introducing a square-root term into the Langmuir equation,  $c/x/m = A + Bc + D \sqrt{c}$  as proposed by Gunary (1970). Application of this form slightly improved the fitness of the data in all cases and tended to increase the values of  $P_{\max}$  in some cases at both temperatures,  $20^{\circ}\text{C}$  and  $37^{\circ}\text{C}$ . The results also showed highest significant and positive correlations when the data was tested by the Freundlich isotherm,  $x = ac^b$ . The values of correlation coefficient ranged between 0.982 to 0.999 and 0.962 to 0.999 at  $20^{\circ}\text{C}$  and  $37^{\circ}\text{C}$ , respectively.

10 - The values of self-diffusion coefficient "D" determined varied between  $2.57 \times 10^{-8}$  and  $22.98 \times 10^{-8} \text{ cm}^2/\text{sec}$  under the conditions of this experiment. The low values of "D" were corresponding to relatively low moisture content and light texture.

11 - Increasing the soil moisture content sharply, and in many cases abruptly, increased the "D" values. This trend was obvious with all the soil samples and under the different levels of soil moisture and applied P as well.

The corresponding increases in the "D" values due to increasing the soil moisture content " $\theta$ " from 0.4 to 0.6 and 0.8, respectively

were 67.3 % and 261.5 % for El-Nobareia, 109.5 % and 178.5 % for Abou El-Matamir, 105.8 % and 296.4 % for Moshtohor, 128.3 % and 238.4 % for Meet-Kenana and 101.2 % and 281 % for El-Deer soil.

The data show clearly that the reduction in water content of the clay textured soils has less effect on diffusion coefficient than in the lighter textured soils. This may be because the clay soil generally holds so much more water that raise the "D" values, moreover, the clay soils oftenly contains water enough to maintain a considerable rate of P diffusion..

12 - The results showed a very close relationship between the "D" values and the added P, showing values of correlation coefficient more than 0.93.

The "D" values obtained under the different rates of applied P average over all the moisture content " $\theta$ " increased with increasing the rate of applied P from 66 to 200 p.p.m. Accordingly, it was concluded that the relationship between the rate of applied P and the values of "D" could be illustrated in a linear form represented by the equation,  $D = a + bc$  where a and b are constants.

A linear relationship between self-diffusion coefficient "D" and soil content of clay was also obtained and represented by the regression equation  $D = 7.28 + 8.17 \text{ clay fraction}$  which exhibited a high significancy with a corresponding "r" value of 0.949.



The values of "D" over all three rates of added P and three levels of moisture content ( $\theta$ ) averaged  $7.51 \times 10^{-8} \text{ cm}^2/\text{sec}$  in Meet Kenana (13.16 % clay),  $8.73 \times 10^{-8} \text{ cm}^2/\text{sec}$  in Abou El-Matamir (17.43 % clay),  $10.27 \times 10^{-8} \text{ cm}^2/\text{sec}$  in El-Deer (27.03 % clay),  $10.11 \times 10^{-8} \text{ cm}^2/\text{sec}$  in El-Nobareia (31.15 % clay), the "D" values increased to  $12.53 \times 10^{-8} \text{ cm}^2/\text{sec}$  in Moshtohor soil (67.8 % clay).

The study reported here may suggest that the extra water of the clay soil increase the cross sectional area available for diffusion and also increases the volumetric moisture content, hence causing higher rates of diffusion P coefficient values.