



Modeling of water stress and fertilization technique in phosphate uptake by corn plants

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Abstract : Phosphorus is a limited resource in arid region, and its efficient use is a main task for sustainable agriculture. The main objective of this work is to determine the kinetics of P release from El- Nubaria sandy soil represents new reclaimed areas in Egypt, treated with prepared compost and chemical fertilizers applied individually or mixture and cultivated with corn under two irrigation regimes, i.e. 80 and 60% of calculated irrigation requirements. Four kinetic models i.e. modified Freundlich equation (MFE), Elovich, parabolic diffusion and first-order models represent both empirical and theoretical models to evaluate P desorption reactions. According to higher correlation coefficient of determination (R^2) and the low standard error (SE), Elovich and MFE models were the best fitted models. Purely organic fertilizer applied gave the lowest rate value compared to chemical one, but the constant represents the capacity factor of P released from the used soil was higher in mixture treatments than the chemical one. Application of 80% of IR and mixture between organic and chemical fertilizers could be the best management in having suitable rate of release, and optimum reserving fertilizer with minimizing of using chemical fertilizers.

Keywords: Phosphorus, desorption, Kinetic models, water scarcity, organic, mineral, fertilizers.

Introduction

Drought is a climatic phenomenon that can occur periodically in arid and semiarid zones, but occurs with greater frequency in tropical and sub-tropical regions, causing physiological damage to plants in ecosystems and agroecosystems. Due to climate changes, more frequent and prolonged drought events are expected in different parts of the world, leading to weaker crop yields and, in more severe cases, food shortages. Besides water deficiency itself, which places grave constraints on plant development and production, problems with mineral nutrition can occur as a secondary effect. In higher plants, most of mineral nutrient transport from the soil solution to the roots is dependent on the moisture in the soil.

Phosphorus (P) is an essential element that plays an important role in carbohydrate metabolism and energy transfer systems in all plants. Maintaining adequate soil phosphorus (P) status remains an agricultural priority and is a particular issue with organically managed systems¹. Phosphate (P) is the second major essential nutrient for plant growth. It plays an essential role for enzyme activation, protein synthesis and photosynthesis, its importance in agriculture is well recognized². Although the distribution of P forms differs from soil to soil as a function of the dominant soil minerals present, total soil P reserves are generally large. Soil P is typically divided into four forms: soil solution P, exchangeable P, non-exchangeable P, and P in soil minerals.

In Egypt, there are numerous policies face a crisis of chemical fertilizers 1) short-term policies (policy management of the crisis) include market regulation and rationalization of use, 2) long-term policies (policies

to bridge the gap) including the establishment of new plants for fertilizers and the advancement of based factories. These multi-ministerial decisions emphasize how the depth of the crisis chemical fertilizers³.

Drought stress induces morphological, physiological and biochemical changes, including changes to photosynthesis, plant height, dry matter production, leaf area and grain yield⁴. However, the effects of drought on P desorption or bioavailability was little handled. ⁵ indicated that mass flow is the main driving force for the movement of Ca^{2+} and Mg^{2+} . In contrast to mass flow, diffusion is an important factor for P and PO_4^{3-} . By using the rhizobox system, ⁶ developed a new rhizobox system to study the nutrient movement in the rhizosphere, they found the depletion of P in the rhizosphere suggests that P movement is governed by diffusion.

Kinetics of chemical reactions in soil and aquatic environments is a topic that is of extreme importance. There are dynamic equilibrium and kinetic reactions between the different forms of soil P that affect the level of soil solution P at any particular time, and thus, the amount of readily available P for plants. Levels of soil solution P are determined by the equilibrium and kinetic reactions between the other forms of soil P⁷.

An array of kinetic methods has been used to measure the rates of soil chemical process. Anion exchange resin (AER) for studying the kinetics of soil chemical process was established by⁸. It is well known that in batch technique the suspension is agitated using reciprocating shaker for several time intervals, and then the suspension is usually centrifuged to separate a clear supernatant solution for subsequent analysis. The use of centrifugation to separate the liquid from solid phase has several disadvantages in having inaccurate results of ion concentrations⁹. Centrifugation would create electrokinetic effects close to soil constituent's surfaces that would alter the ion distribution¹⁰.

Electrical Stirred Flow Unit (ESFU) was manufactured in NRC by ¹¹ to try to elevate the most common problems found in such techniques. The estimation of P available to crops as well as most of the P fertilizer recommendations are based on soil analyses and do not consider P release from non- exchangeable fractions ¹². The common methods of estimation of P available to crops as well as most of the P fertilizer recommendations are based on soil analyses which mean a waste of time and a lot of efforts¹². Although there are a lot of articles related with P release, there is a scarcity interested with the effect of water regime on Phosphate bioavailability from the kinetic perspective.

The objectives of this work are: (1) Evaluate the modified set up ESFU on the kinetics of phosphate desorption from sandy soil fertilized with compost, chemical fertilizers and mixture of both (2) the trust of used models in describing P desorption from the treated sandy soil under water stress conditions. Information of kinetic study of P desorption under different stress conditions and dominant P species after different P treatments would help us explore whether certain P fertilizers types result in superior (i.e., maintaining high P availability) under stress conditions, short- and long-term performance in soil and understand reasons or possible mechanisms that explain their superior performance.

Materials and Methods

Experimental location

El-Nubaria site represents new reclaimed area in North Western of Egypt and adjacent to a lot of farms cultivated with different crops. The cultivated area of National Research Centre Farm previously cultivated with different crops before our experimental started and used drip irrigation system as a main type of irrigation. This soil is characterized by pH value equal to 8.11, EC 1.32 dS/m, the soluble cations values were 0.48, 0.12, 0.69 and 0.06 meq/100g soil for Ca^{2+} , Mg^{2+} , K^{+} and Na^{+} , respectively, 0.22, 0.77 and 0.36 meq/100g soil for HCO_3^{-} , Cl^{-} and SO_4^{2-} , respectively. The texture of this soil was sandy loam. Available nutrient determined were 7.9 and 186.6 ppm for P and K, meanwhile OM and total CaCO_3 values were 0.47 and 24.9%. All chemical characterizations of used soil were done as described by¹³.

Experimental technique

To study the relationship between type of applied fertilizers and the kinetic rate of P desorption from the soil, three techniques of fertilization were applied to corn cultivar Single cross 129 white (*Zea mays* L.) was obtained from Ministry of Agriculture, Giza, Egypt, these techniques are represented by:

T1: 100% compost (10 ton/fed.; fed.= 4200m²)

T2: 75% compost + 25% chemical fertilization

T3: 50% compost + 50% chemical fertilization

T4:100% recommended chemical fertilization for corn applied based of the recommendation rate of the crop (120 kg N/fed. as ammonium sulfate + 30 kg P₂O₅/fed. as super phosphate + 24 kg K₂O/fed. as ammonium sulfate)

C: Control, for this soil, the release of P based on the native P fertilizer applied in previous crops grown in the same used soil.

Organic material, phosphorous and potassium fertilizers were added before sowing. Nitrogen fertilizer was added in three equal portions before cultivation, after two weeks from cultivation and after three weeks from second addition, respectively. All amendments were manually spread. It is worth to mention that the experiment continued for two seasons.

Agricultural practices were followed the recommendations of Ministry of Agriculture in Egypt. Enrichment compost with effective microorganisms (EM: *Bacillus subtilis* F.50, F.30, *B. Theremogensid* F.64, *Trichoderma reesei* F.418 and *Sacchromyces cerevisiae* F N.10) were used and prepared as described by ¹⁴. EM was brought from the Biotechnology Unit, Microbial Chemistry Dept. N.R.C. Some physical and chemical properties of the compost in two seasons are shown in Table (1). Portions of dried corn plant materials were ground, wet-digested and analyzed for P as described by ¹⁵.

Table (1): Some physical and chemical properties of the compost in two seasons.

S	Total nutrients%			OM%	C/N ratio	EC dS/m 1:5	pH 1:2.5	WHC
	N	P	K					
1 st	1.2	0.79	2.04	25.2	11.9	5.63	7.47	110
2 nd	1.1	0.82	2.20	37.7	17.8	5.5	7.44	160

S= season

Kinetic Models

The linear forms of several kinetic models i.e. first-order, parabolic diffusion, Elovich and power function (modified Freundlich) as shown in Table (2) were statistically compared in their ability to fit the P desorption from compost-fertilized treated soil samples using nonlinear regression procedure. The higher correlation coefficient of determination R² and the lower standard error SE are the best-fitted equation(s) described the kinetics of P desorption in different treatments.

Irrigation Requirement (IR)

Since the irrigation requirement IR calculated for corn (*Zea mays* L.) is an important factor in P bioavailability in soil system, we evaluated two irrigation moisture regimes represent 80% and 60% of total water requirement on P desorbed from the used soil and subsequently the P bioavailability by corn. The data of IR was calculated by average 8 years of meteorological parameters using CROPWAT computer model ¹⁶ (according to the climatic data recorded at El-Bustan Weather Station in North of Delta, based on calculation of Penman Monteith equation and the Kc values presented in the program and also illustrated in ¹⁷.

Table (2) kinetic models applying to describe phosphate adsorption in the studied soil

Model	Equation	References
Elovich	$Q = \ln \alpha + \beta \ln t$	[18]
First-order	$\text{Log } q = \text{log } q_0 - k_1 t$	[18]
Power Function	$q = k_d t^{b^1}$	[19]
Parabolic Diffusion	$q = b + R t^{1/2}$	[20]

q = the amount of Phosphate adsorbed in time t

k_d = desorption rate coefficient in $\text{mg kg}^{-1}\text{soil min}^{-1}$

b^1 = intensity constant in $\text{mg P kg}^{-1}\text{soil}$

α = a constant related to the initial rate of P adsorbed in $\text{mg P kg}^{-1}\text{min}^{-1}$

β = a constant in $\text{mg kg}^{-1}\text{soil}$

b = intensity constant in $\text{mg P kg}^{-1}\text{soil}$

R = the apparent diffusion rate coefficient in $\text{mg P kg}^{-1}\text{soil min}^{-1}$

q_0 = the maximum amount of P adsorbed $\text{mg P kg}^{-1}\text{soil}$

k_1 = the rate constant of the reaction in sec^{-1}

t = time (min).

Statistical analyses:

Experimental treatments were replicated three times in 2-Way Randomized Block design (2-WRB) with irrigation treatments in main plots and fertilizers treatments distributed randomize within main plots. All data obtained from this study were statistically analyzed using SAS software ²¹, analysis of variance (ANOVA) and least significant difference (LSD) were applied to make comparisons among treatment means according to ²².

Results and discussion

Kinetic of phosphate desorbed from the studied soil as affected by fertilization treatments

Although data not shown, the authors didn't find any significance between the application of 100 and 80% of IR on P uptake by corn, consequently, the discussion will be only focused on 80 and 60% of IR. Figure (1) represents the kinetics of phosphate release from the treated soils and irrigated with 80% of IR after 14 days of reaction time. Because of the S shape observed in entire reaction time for P desorption in different treatments, data was divided into two stages, the first stage from 1-60 min represents the rapid stage of P released and the second one 120-1880 min represents the rest of reaction time.

Dividing the entire reaction time into two stages, led to have almost straight lines in both short reaction time (A) and long one (B) for all treatments tested which represents that more than one mechanism controlled the release of P from the treated soils. In addition, it should be mention that all treatment kept their order in P release in both stages. It is generally believed that there is no single equation that described equally well the kinetic data of all soils ²³.

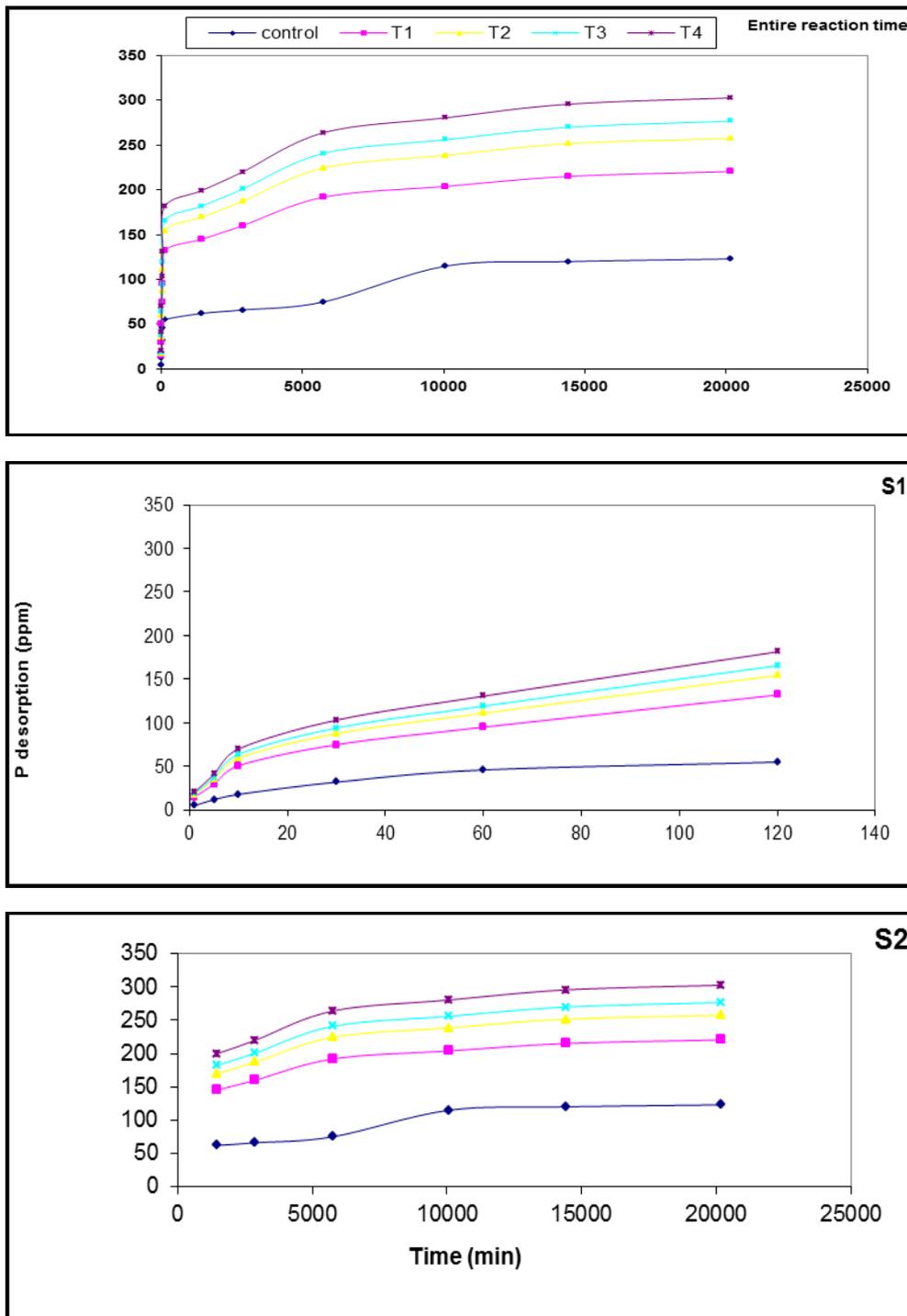


Figure 1: Kinetic of phosphate desorbed from the treated soils in both entire reaction time and 1st and 2nd stages (S1&S2)

Phosphorus release from compost individually gave the lowest values compared with other treatments tested except control, by mixing prepared compost with the chemical fertilizers; P released from the soil was significantly increased. This may be refer to that compost need more time to be decomposed, complete degradation and balanced with soil Numerically, the P desorbed from the soil was 221ppm in case of compost; gradually increase up to 257 and 277 ppm in T2 (75% compost + 25% chemical fertilization) and T3 (50% compost + 50% chemical fertilization), respectively. The highest value was observed in chemically fertilized soil 303 ppm this may be due to chemical fertilizer is ready to release P more than compost under this experiment conditions. However, it should be mention that the risky conditions of heavily application of chemical fertilizers still present and could be takes place.

Decreasing the irrigation requirement to 60% directly decreased the rate of P desorption in all treatments including control. For example, decreasing the IR led to decrease the maximum release of P in T4 (100% chemical fertilization) to about 255 ppm which almost represents 15% less than the high IR applied. Also, in the organic treated soil T4, the decreasing order observed was less than the chemical treated one by about 10% less (200 ppm), worth to mention that the other treatments were decreased with varied percentages.

Kinetic parameters of P desorption from the fertilized used soil as affected by irrigation cycle and fertilization treatments

Prior the narrative in kinetic work, it should be mention that selection of the best fitted model (s) was based on the higher coefficient of determination and the lower standard error the best fitted model (s). Accordingly, although the all models well described the kinetic data we found that MFE was the best in describing the rate of P desorption (R^2 ranged between 0.98** -0.99**) since it gave the lower SE, followed by Elovich (0.96** -0.99**) and for less extent 1st order and parabolic diffusion models (R^2 ranged between 0.89** -0.92**).

Through the entire reaction time, the succession of more than one model in describing the rate of P desorption in different treatments applied meaning that different mechanisms controlled P release from the treated sandy soil or in other words different forces retained P in treated soil and subsequently, the bioavailability of P in such systems.

The power function (modified Freundlich) equation in the linear form is: $\ln C_t = \ln k_d + b^{\setminus} \ln t$. The integrated form is $q_t = k_d t^{b^{\setminus}}$

where q_t the amount of P release at time t, k_d and b^{\setminus} are constants. Taking the derivation of integrated form: $dq / dt = k_d b^{\setminus} t^{b^{\setminus}-1}$.

Where k_d is directly proportional to the rate of P release and was considered as the apparent desorption rate coefficient. The effect of b^{\setminus} , the capacity factor, on phosphate release is more complex since there are different soil parameters and treatments such as organic amendments controlled P reaction in soil system. The reaction rate is proportional to k_d only at $t = 1$ in which case:

$dq / dt = k_d b^{\setminus}$.

The b^{\setminus} value is convenient to use as an estimate of the initial release rate when comparisons are made between power function equations. It is, however, designated as the reversibly adsorbed phosphate.

The kinetic parameters which describe P release from soil irrigated with 80 and 60% of IR are presented in Tables 3 and 4. The rate constants namely; k_d of modified Freundlich, R of the parabolic diffusion, k_1 of the first-order and β of Elovich equations, all were considerably increased in the 100% chemical fertilization applied (T4) than in both purely organic fertilization (T1) and the mixture of chemical and organic types (T2 and T3). The average values of MFE as an example in chemical fertilized soils were 0.26 decreased to 0.22 in organic fertilized soil and take in between values for the mixture of both organic and inorganic fertilizers. In contrast, data showed that the capacity factor b of MFE took a reverse trend reached to 1.55 for organic fertilizer and decreased to 1.41 in chemically fertilized soil.

Table (3) Kinetic parameters of selected equation describe phosphate desorption from compost-fertilized soil under application of 80% of IR.

Treat.	Modified Frundlich		Parabolic diffusion		Elovich equation		1 st order equation	
	k_d	b^{\setminus}	R	b	β	α	k_1	q_0
C	0.19	0.96	0.77	24.76	4.76	11.43	-0.65	4.3
T1	0.22	1.55	1.30	92.34	7.00	28.97	-0.63	3.43
T2	0.23	1.51	1.52	84.25	8.25	26.46	-0.58	3.40
T3	0.24	1.48	1.63	78.58	8.80	24.65	-0.53	3.35
T4	0.26	1.41	1.79	67.13	9.69	21.08	-0.50	3.23

Table (4) Kinetic parameters of selected equation describe phosphate desorption from compost-fertilized soil under application of 60% of IR.

Treat.	MFE		Parabolic diffusion equation		Elovich equation		1 st order equation	
	k_d	b^1	R	b	β	α	k_1	q_0
C	0.17	0.93	0.73	21.56	-3.43	10.40	-0.86	1.43
T1	0.21	1.52	1.19	88.25	6.37	26.36	-0.82	3.12
T2	0.22	1.48	1.44	80.16	7.51	24.08	-0.71	2.92
T3	0.23	1.42	1.52	74.38	8.01	22.43	-0.63	2.85
T4	0.24	1.35	1.69	63.23	8.82	19.18	-0.50	2.79

Decreasing the IR to 60% applied to corn decreased the k_d values for both chemical and organic fertilized soil to be 0.24 and 0.21 in chemical and organic fertilized soils respectively. Also, it was noted that although the capacity factor gave a reverse trend, the obtained values was less than the 80% IR.

The β value (the slop of the kinetic data) plotted according to Elovich equation (ln of time against P concentration) was shown by ²⁴ to be inversely proportional to the soil supplying power of ion to plant. ²⁵ showed that the decrease in $1/\beta$ and or increase in α enhance the reaction rate. ²⁶ reported that β constant is an important parameter to define desorption rate dI/dt throughout the whole dissolution period of added ion. Moreover, a low β value is associated with higher dissolution rate and a greater buffering of ion- dissolution rate with the increase in ion concentration, compared with high β .

The β value in Elovich equation shown to be inversely related to the phosphate supplying power of the soil was 8.25 and 8.8 in T2 and T3, respectively represented the preferring of applying 50:50 chemical to organic fertilizers instead of increasing organic fertilizer over the chemical one. These results clearly demonstrate the higher potential of P release in the soils treated with chemical ones. The constants that describe the capacity of P in used models i.e. b^1 in modified Freundlich, b in parabolic diffusion, q_0 in the first-order models, all were higher in the fertilized soil compared to control. Therefore plant P uptake from the treated soils was considerably higher than from the untreated one. In all cases, however, the kinetic parameters decreased by decreasing of IR applied.

Diffusion model and the mechanism were also succeeded in describing the rate of P desorbed from the treated soil. According to data presented in tables 3 and 4, decreasing the IR from 80% to 60 %, led to decrease the rate of P from 1.79 to 1.69 in T4 (chemically fertilized soil), in other words, the diffusion mechanism of P to plant used was influenced by the IR and assumed to be influenced the concentration of P in plant. The capacity factor represented by b decreased from 1.41 to 1.35. As it well known that phosphorus is one of macronutrients of plant, an essential part of the enzyme responsible for aiding crops to fix light energy, an integral part of nucleic acids. Its essential function is storage and transfer energy. Although there are large amount of phosphorus in the soil, It have to adding phosphorus fertilizers seasonally because it react with soil quickly and turn to unavailable form to plant absorption. Also, P is transported within the soil and is absorbed by plant roots in the soil water. Therefore a water deficiency results in less P absorption.

Correlation analysis between phosphate desorption from the fertilized soils and the phosphorus uptake by corn

The P uptake by corn grown in treated soils of the new reclaimed area was correlated with the constants of the four tested kinetic models (table 5). The correlation coefficient was highly significant with the kinetic parameters representing the rate of P release in the order: The modified Freundlich rate coefficient (k_d) ($r = 0.98^{**}$) > the rate constant (β) in the Elovich equation ($r = 0.97^{***}$) > the rate of P release coefficient (R) in the parabolic diffusion ($r = 0.96^{**}$) > the initial rate of P -release (q_0) in 1st order equation ($r = 0.85^{**}$). The β coefficient in Elovich which was found to be inversely correlated with the P supplying power of the soil 23, and

inversely related to the rate of P release from soil 27 was inversely correlated with the plant P uptake ($r = 0.97^{**}$). It should be recalled that both Elovich and modified Freundlich equations offered the best fit to the P release data from the tested adequate fit to the description data, its rate of diffusion coefficient (R) gave the high correlation coefficient with the cumulative P uptake and with the uptake of P. Similarly the first-order equation offered a lower fit to the P release data but the rate constant k_1 of the equation was highly correlated with plant P uptake.

Table (5) Correlation coefficient (r) for the relationship between phosphorus uptake by corn plants grown in treated soil and kinetic parameters of selected equations.

Seasons	MFE		Diffusion		Elovich		1 st order	
	k_d	$b \setminus$	R	b	B	α	k_1	q_0
1 st season	0.98 ^{**}	0.89 ^{**}	0.96 ^{**}	0.94 ^{**}	0.97 ^{**}	0.96 ^{**}	-0.85 ^{**}	0.97 ^{**}
2 nd season	0.72 ^{ns}	0.91 ^{**}	0.81 [*]	0.86 ^{**}	0.77 ^{ns}	0.83 [*]	-0.92 ^{**}	0.78 ^{ns}

ns= not significant ($p < 0.01$)

The correlation coefficients in the same table show that P bioavailability may be less dependent on the capacity than the rate parameters due to lower correlation coefficients and the less significant correlation between the plant P uptake and the intensity parameters in the tested equations. The $b \setminus$ value in modified Freundlich equation denotes the P capacity and was not significantly correlated with plant P uptake. The b value, which is the concentration of P at the time of ESFU work in the diffusion equation, showed significant correlation with plant P uptake but the correlation coefficient ($r = 0.63^{***}$) was considerably less than with the rate of P release ($r = 0.95^{***}$). The q_0 value in the first-order kinetic equation which represent the P intensity was less significantly correlated with P-uptake ($r = 0.57^{**}$) than the rate kinetic R ($r = 0.83^{***}$).

The high and significant correlation between P uptake and the kinetic parameters of the best fitted models, namely k_d , R, β , and k_1 however, gave higher correlation's with the plant P uptake indicating that these parameters, specially the diffusion rate coefficient (R) can better estimate P -bioavailability than the other methods in describing P uptake by plant. With an exception observed in the 1st order, Phosphate uptake by corn in the 2nd season highly significant r values were observed with the capacity factor more than the rate parameters of tested models. For example, in the MFE, the r value of $b \setminus$ was 0.91^{**} meanwhile the k_d was 0.72^{ns}, this result may represents the variation of P mechanism with repeating of crop cultivated in the same soil. Worth to mention that same trend was observed in diffusion and Elovich model.

α parameters of Elovich equation that may stand for the conditions of initial rate of P release had no significant relation with plant P uptake. As with the 1st season, both the b value in the diffusion equation and the q_0 in the first-order equation, which represent P capacity, showed high significant correlation with plant P uptake ($r = 0.94^{**}$ and 0.97^{**}).

Almost all kinetic parameters describing the rate of P release in different treatments of the studied soil were highly correlated with plant P uptake and may be used as indices for P bioavailability if the rate of release proved to be a determining step for P -uptake by plant. In the 2nd season, however, only the 1st order rate coefficient (k_1) was highly correlated with plant P -uptake. This parameter assumed superiority over other capacity parameters possible indices for P bioavailability in the 1st season. These results agree with those of 23, 25, 26 and 28. Their results on phosphate showed that both constants were related to the P supplying power of soil and or the rate of P release from soil had significant relationship between β and P bioavailability to sorghum did not establish that P dissolution is a rate determining step to P-uptake since similar relationship existed between β and equilibrium ion. On the other hand, 27 argued that the potential rate of P release from the soil as a whole was at least 250 times as great as the rate of P-uptake by crop. 29 reported that about 12% of irrigation water can be saved if farmers added medium consumptive use of irrigation water (medium=390 and 414mm) to potato plants compared to wet (wet=436 and 476mm) and dry (dry=350 and 367mm) treatments. Decreasing IR to 60%, led to decrease the rate parameters and the ability of the tested crop to absorb P. This may be due to 1) the less efficiency of P solubility in soil treated with 60% compared with 80%IR, 2) this

amount of water (60%IR) not suitable to exporting the released P to root zone, 3) decreasing soil chemical and biological properties under water stress condition.

Results indicate that the rate of P release from the soil consistently influenced by irrigation regime applied to soil system and type of fertilizer used. In addition, the capacity parameters with intensity parameters of kinetic models could be also used as indices for P bioavailability and selection of best fertilization management. Results also indicated that kinetic method used to represent the rate of P release was offered a simple and accurate method in plant nutrition. The important of this study may emphasized that the 80% of IR was the best irrigation treatment in having optimum conditions of P desorption for growing plants since it makes stimulation of plants to increased P uptake.

Conclusion

The rate constants values of the mixture treatments, however, gave intermediate values between chemical and organic fertilizers. Concerning the water regime applied, data showed that 80% of IR gave the best water management in having both high P desorption from used soil and significant P uptake by corn plant compared to control. The rate constants for selected models indicated that all types of applied fertilizers gave highly significant increase in rate of P release compared to the control (untreated soil). Purely organic fertilizer applied gave the lowest rate value compared to chemical one, but the constant represents the capacity factor of P released from the used soil was higher in mixture treatments than the chemical one, means that the reserve of organic fertilizers applied to the soil could be continued to the next crop.

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