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Kinetics of Phosphorous Release in Soils with Different Parent Materials as Influenced by Time and Soil Properties in South Eastern Nigeria

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ABSTRACT

This study was conducted to assess Phosphorous (P) release in soils derived from three parent materials, Shale, Sandstone and Basalt and to find the best fitting models to describe P release to 0.01m $CaCl_2$ extraction in a duration of 1 – 72 hours at different concentration of P added, (0, 20 40 and 80 $mgl^{-1}p$). Two 20g of soil were suspended in 20ml of 0.01m $CaCl_2$ and equilibrated at 25^0C. The suspensions were shaken for 1 hour and left for the equilibrating time before the suspense was centrifuged for 10 minutes and P in the extract was determined. The physical and chemical properties were also measured. The result showed that, the texture of the soils varied from loamy sand (sandstone) to sandy loam in shale and basalt. Electrical conductivity, organic matter, total nitrogen, available phosphorous and Ca, Mg, K were moderate. The results also revealed that sandstone soil with high sand content had higher release of P than the Shale and Basaltic Soil with high clay content. The trend was sandstone > shale > basalt. Parabolic diffusion equation successfully described the P release in the soils with the highest R^2 values of 0.983.

Keywords: Phosphorous, Kinetic release, Parent material, Soil properties, Zero order, First order, Parabolic diffusion equations

1.0 Introduction

Phosphorous (P) is the second most critical nutrient element influencing crop productivity, Umoh and Osodeke (2016) reported that P fertilization in soils encourages its mineralization and uptake by plant, hastening plant maturity and improved good quality seeds of Mung bean. The P use efficiency by plant in soils of Eastern Nigeria ranges as low 10 to 20%; due to high affinity levels of P in the soils; the remaining available nutrient can also be lost to leaching if not used by plant due to heavy seasonal rainfall leading to P deficiency in soils (Umoh *et al.*, 2014, Umoh *et al.*, 2015; Umoh *et al.*, 2018 and Umoh *et al.*, 2019). The rate of P released and the availability in soils can significantly be influenced by factors such as soil texture, pH, exchangeable Fe, Al, type and the amount of clay and soil organic matter level

(Ahmadi 2018; Umoh *et al.,* 2017). Bioavailability of P to plants usually occurs through mineralization of organic matter. Islas – Espinoza *et al.*, (2014) reported that undecomposed organic residue added to soil, lowered P released and increased P absorption which may reduce leaching or runoff of P . Umoh *et al.*, 2018; Umoh *et al.*, 2021) observed that Shale and Basaltic soils with higher clay content had high nutrient availability. Schneider *et al*.,(2016)observed that high concentration of Ca and Mg competes with K for adsorption sites and displaced K to be released in soils. Kinetic equations are used to provide an index of P released in soils. Plant nutrient availability is facilitated by the element's rate of release into soils. According to Umoh *et al.* (2017), fertilization causes an increased in P concentration in the soil solution, which causes an equilibrium to shift and cause P fixation. In a study on K release in soils, Umoh *et al.* (2022) found that, a significant amount of K was converted into fixed form and the K released varied depending on the parent material. They also noticed a sharp release of K during the initial contact due to the dissolution effect.

Many equations have been developed to quantify soil P release in soils (Fekri *et al*., 2011; Hossseinpur and Pashamokhtari, 2008). Islas-Espinoza (2014) employed simplified Elovich equations, first order, parabolic diffusion and power functions. Since there is little information available on the kinetic release of P in these soils, the purpose of this study was to compare the P release in soils using various equations.

2.0 Materials and Method

2.1 Location of study area

The soils used in the study were derived from Ikom (Basalt), Amaeke (Sandstone) and Itu (Shale) located in Southeastern Nigeria (Table 2.1). The rainfall is bimodal and characterized by heavy annual rainfall of about 2500 – 3000mm, high temperature with a mean of $28C^0$, relative humidity is high between 75% and 90% and solar radiation ranges from 6-15 hours per day.

Table 2.1: Distribution of soil parent materials by sample location

Soil types	Location	State	Soil Class USDA	Coordinates	Mineralogy
Basalt soil	Ikom	Cross River	Inceptisol	5.96^0N 8.70^0E	Smectite
Shale	Itu	Akwa Ibom	Oxisols	5.20^0N 7.98^0E	Smectite
Sandstone	Amaeke	Abia	Ultisol	5.35^0N 7.40^0E	Kaolinite

2.2 Field Sampling and Sample Preparation

The surface bulk soil samples were collected from three locations of the study area based on their parent materials, from 0 – 20cm depth with a soil auger. These samples were air dried, crushed and sieved to pass through a 2mm mesh then used for physicochemical analysis and potassium release study.

2.3 Physicochemical Analysis

The following soil parameters were determined according to Udo *et al.*, (2009). Particle size distribution was analysed by the Bouyoucos hydrometer method using sodium hexametaphosphate as a dispersing agent. The soil pH was measured in a soil to water ratio of 1:2.5 using a glass electrode pH meter. Electrical conductivity was determined in the extract from 1:2.5 soils: water suspension using a conductivity bridge. Soil organic carbon was determined by the wet oxidation method and the values were multiplied with factors of 1.72 to obtained organic matter. Total nitrogen was determined by the micro Kjeldahl method. Available P in the soil was determined by the Murphy and Rilay method after extraction by Bray $P-^{1}$extractant. The exchangeable cation in the soil was extracted using in NH_4OAC K and Na in the extracts were measured using flame photometry while Mg and Ca were determined by atomic absorption spectrophotometry. Effective cation exchangeable capacity (ECEC) was obtained by the summation of the exchangeable cation and exchangeable acidity. Base saturation (%) was calculated by the sum of exchange cation x 100/ECEC.

2.4 Potassium Kinetic Release Study

Twenty (20) grams of < 2mm sieved soils were weighed into separate 50ml centrifuge tubes containing 10ml of 0.05m $CaCl_2$ and stock P solution of $1000Pml^{-1(}H_2P0_{4)}$prepared were added at varying concentrations of 0, 50, 100, 150 and 200mg/litres of 0, 20, 40, 80 mgl^{-1} and allowed to equilibrate by shaking daily for 30 minutes at different time intervals of 1, 24, 48, 60 and 72 hours at the end of the equilibrium periods, the supernants were decanted and filtered using Whatman filter paper no. 42 and P was determined by colorimetry method described by Udo *et al.,* (2009). The P released with time was fitted to the equations in table 2.2.

2.5 Experimental Design

The soil sample from the three (3) parent material was treated with four different rates of P solution using (H_2P0_4) as follows: 0, 20, 40, $80mgl^{-1}$. This was extracted for varying periods of 1, 24, 48, 60, and 72 hours. It consisted 60 samples replicated 3 times making a total of 180 samples generated. The study was a factorial experiment fitted into a randomized complete block design (RCBD). Treatment included 3 parent materials, 4 rates of K, 5 periods all replicated three (3) times.

2.6 Statistical Analysis

The linear forms of the kinetic equations (Table 2.2) were fitted to the experimental data. The least square regression analysis was used to ascertain the equation that best described K release in these soils. The goodness of fit was determined by the coefficient of determination (R^2).

Table 2.2: Kinetic equations used in the study

Kinetic Equation	Expression Form
Zero order	$P_o – P_t = a – K_ot$
First order	$In\ P_1 = In\ P_o – K_It$
Parabolic diffusion	$P_t/P_o = c + r\ t^{0.5}$

P_o, P_I, P_t = Amount of P mgkg-1 releases at equilibrium while a, k, c are the intercept, indices of K release rate at time f(h). **Source:** Hosseinpur and Pashamokhatari (2008)

3.0 Results and Discussion

3.1 Physical and Chemical Properties of the Studies Soil

The results of the soil properties are presented in Table 3.1. Sandstone had the highest sand content (78.5%) while shale soil had the lowest (67.0%). Sandstone had the lowest silt content (8.10%) while shale and basalt were similar. A similar trend was also observed in clay content, sandstone being the lowest and shale the highest (22.7%). The texture of the soils varies from sandy loam to loamy sand; the pH ranged from 5.00 to 5.60 showing a moderate acidic condition, electrical conductivity was low, organic matter, total nitrogen; available phosphorous, exchangeable cations were moderate, according to the rating of Udo *et al.*, (2009). This result is in conformity with the work of Onweremadu *et al.,* (2009) who observed similar result for soils in southeastern Nigeria.

3.2 Phosphorous Release in Soils

The rate of P released from soils is a dynamic process and it is important in the evaluation of soil P availability to plant. The figure 3.1 (a - e) shows the interactive effect of parent materials and P levels on the amount of P released with time. The amount of P released in the three soils at different time interval varies. Shale soil had the highest released after 1 to 24 hours (figure 3.1 a & b), followed by sandstone and basaltic soils, but after 48 hours to 72 hours, a sharp release was observed in sandstone soils while the released concentration of P in basalt and shale was slow. This finding could be attributed to the properties of the soils, the higher sand content of the soil are more prone to high nutrient released and similar finding were by Umoh *et al.,*(2019) while shale and basalt has high content of clay. Hosseinpur *et al.,* (2008) reported that, clay soil can expand upon hydration and the ions trapped will then slowly diffuse to exchange sites. The observed pattern of initial rapid release followed by slower release, is owed to the two phases of P release which could be due to the heterogeneity of the adsorption sites with different adsorption affinities (Umoh *et al.,*2014). The initial fast release has been mainly attributed to rapid dissolution of phosphate in soils. Ahmadi (2018) stated that the initial rapid release can be attributed to the labile P while the latter stage may be converted to fixation.

The amount of P released increased with increasing times of extraction and also increased with increasing concentration of P added in the soil, except in sandstone which a decline was observed at 40mgkg^{-1} of additions within the 48 hours to 72hours (Figure. 3.1 c, d, e). Similar finding was observed by Umoh *et al.,* (2019) where the amount of nutrient release increase with the increasing amount added to the soils. Also the higher content of Ca in the soils (Table 2.1) can displace P release. Schneider *et al.,* (2016) affirmed that Ca and Mg compete with K for adsorption sites and displaced the nutrient element released in soils. The figure 3.2 (a, b, c) also shows the amount of P released with time from the three parent materials. Sandstone soil had the highest released while basalt had the lowest. The trends were as follows: sandstone > shale > basalt. The higher release in sandstone is an indication that P can be lost to leaching if not used up by plants (Umoh *et al.,* (2019) and Sunday *et al.,*(2020)) and the slower release in basalt and shale is an indicative of high nutrient reserve probably due to high clay content of the soils as shown in Table 2.1.

3.4 Phosphorous Release in Soils by Kinetic Equations

The cumulative amount of P released with time in soil obtained is presented in Tables 3.2-3.4. The P released in soils based on the different equations varied. The concentration released ranged from 2.038 to 5.192 mg kg^{-1} within the parent materials in zero order reaction Table 3.3. The trend were: Sandstone (5.192 mg kg^{-1}) > Shale (2.617 mg kg^{-1}) > Basalt

(2.038 mg kg^{-1}). The Parameter R^2 ranged from 0.482 to 0.834 with mean of 0.658. In the first order reaction of P released values ranged from 1.169 to 1.777 mg kg^{-1} (Table 3.3). The trend was sandstone (1.777 mg kg^{-1}) > shale (1.279 mg kg^{-1}) > Basalt (1.169 mg kg^{-1}). The parameter R^2 ranged from 0.522 to 0.967 with mean of 0.733. In parabolic diffusion for P released, values ranged from 11.87 to 1.846 mg kg^{-1} (Table 3.4). The trends were: sandstone (-4.355) > basalt (1.846 mg kg^{-1}) > shale (-11.87 mg kg^{-1}). The parameter of R^2 ranged from 0.955 to 0.999 with mean of 0.983. This results indicated that, the amount of P released in zero order, first order and parabolic diffusion models increased with increasing amount of P added, 0mg kg^{-1} had the lowest and 80 mg kg^{-1} had the highest, when comparing the best fitted equations, parabolic diffusion equations successfully described the P release in the soils with the highest R^2 values of 0.983 than other equations.

Table 3.1: Physicochemical properties of the experimental soils

		Shale	**Basalt**	**Sandstone**
Sand	%	67.00	68.20	78.50
Silt	%	10.27	10.80	8.10
Clay	%	22.73	21.00	13.40
Texture		SL	SL	LS
pH		5.40	5.60	5.00
EC ds/m^3		0.20	0.10	0.10
O.M %		3.40	4.40	3.80
T.N %		0.20	0.20	0.20
Av. P mgkg^{-1}		5.70	7.30	8.30
Ex Ca	Cmolkg^{-1}	4.70	5.80	5.00
Mg	Cmolkg^{-1}	3.00	3.40	2.40
Na	Cmolkg^{-1}	0.08	0.05	0.07
K	Cmolkg^{-1}	0.30	2.20	0.20
EA	Cmolkg^{-1}	1.76	1.34	1.62
ECEC	Cmolkg^{-1}	8.08	11.45	7.67
B.Sat. %		82.0	89.5%	82.6%

EC = Electrical Conductivity, OM = Organic Matter, TN = Total Nitrogen, AV.P =Available Phosphorous, Sl = Sandy loam, Ls = Loamy sand, Exca = Exchangeable cation, Mg = Magnesium. Na – Sodium, EA – Exchangeable acidity

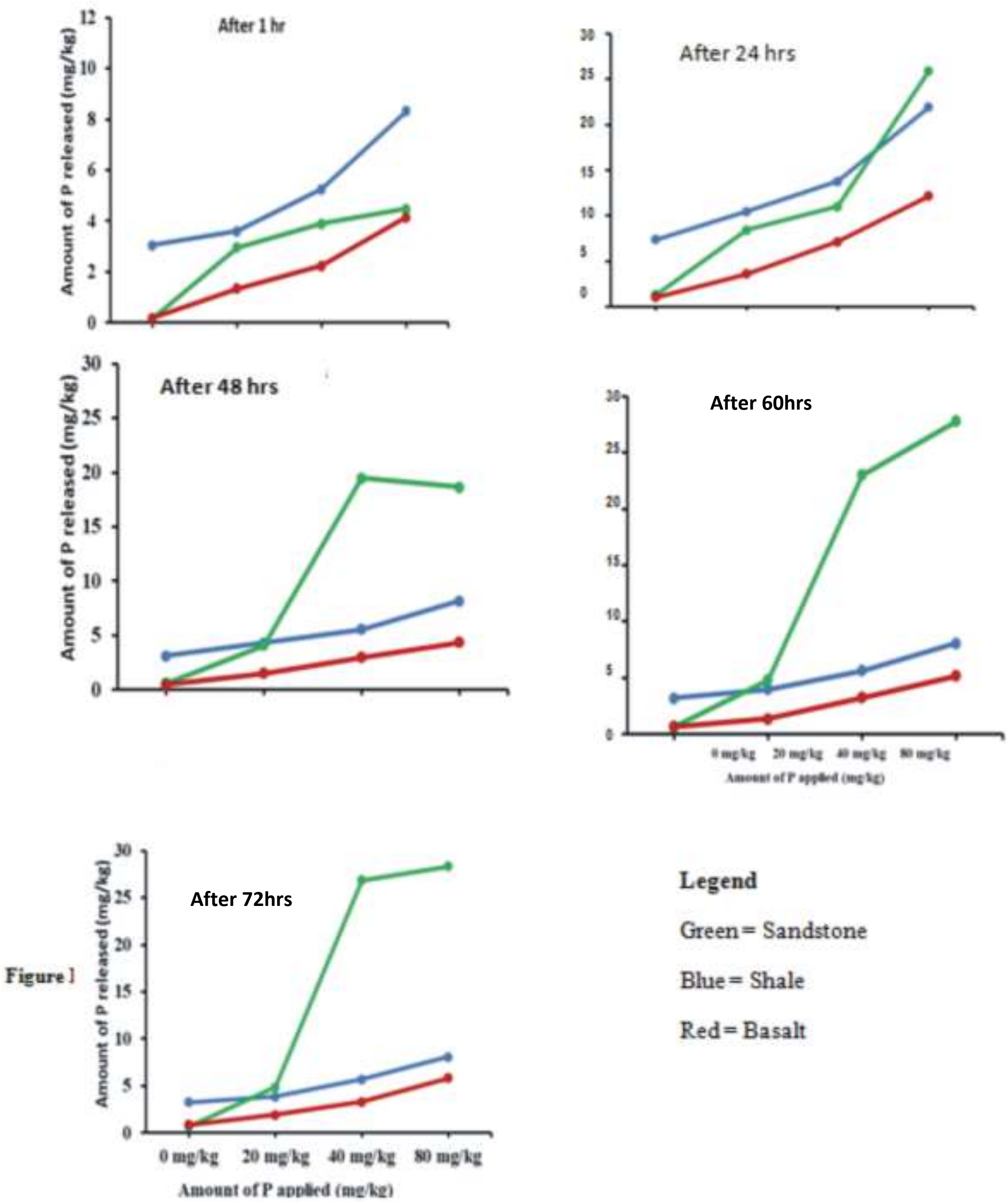

Figure 3.1: Amount of P released with time from the three parent materials; numbered in a clockwise direction.

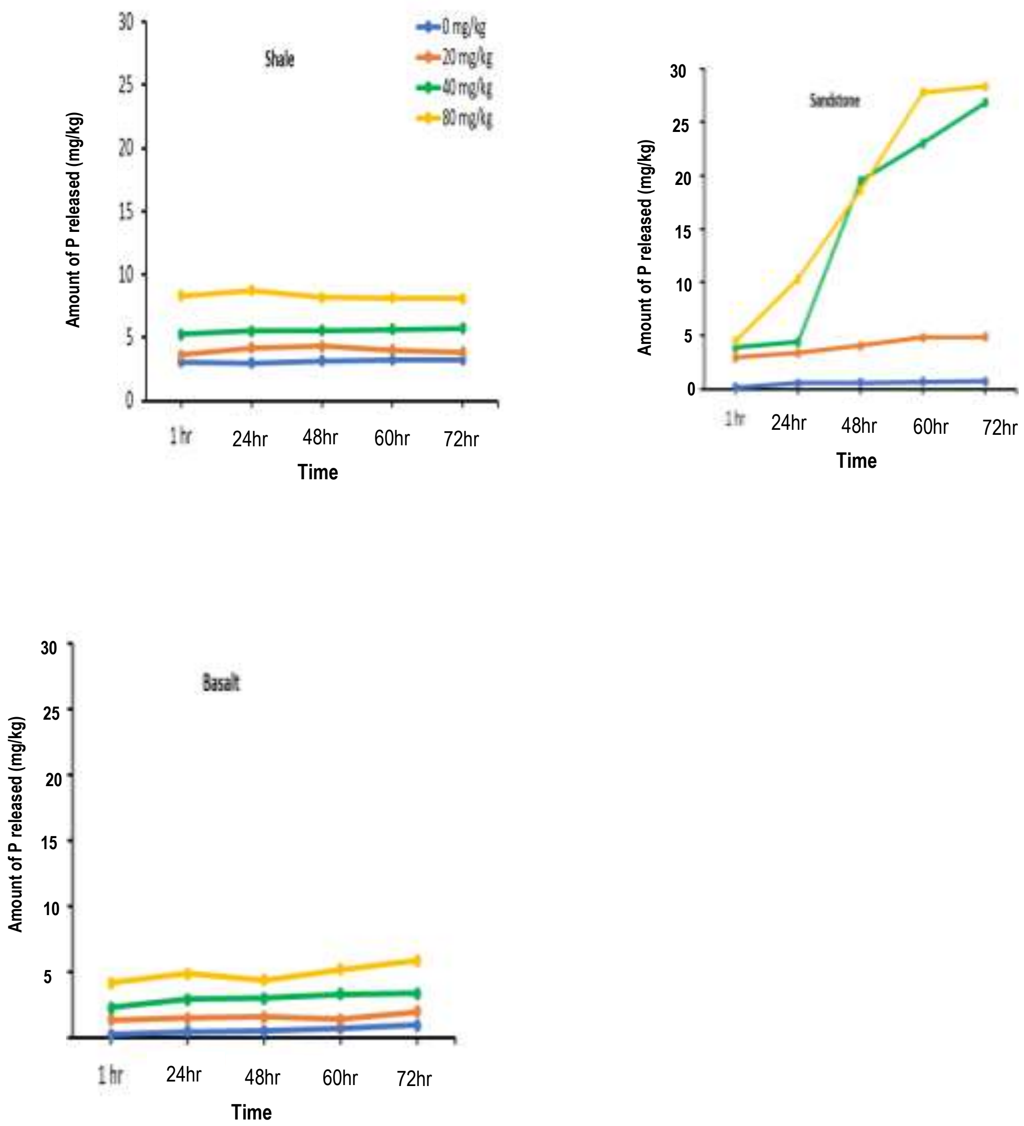

Figure 3.2: Amount of P released with time from the three parent materials

Table 3.2: Slope (a), intercept (P_o) and coefficient of determination (R^2) for zero order reaction of P release from soils of three parent materials

	Quantity of P applied (mg/kg)				
	0	20	40	80	Mean
Sandstone					
P_o	3.0555	3.8178	5.3566	8.5395	5.192
A	-0.548	-0.6775	-0.9574	-1.5747	0.939
R^2	0.7949	0.8836	0.8241	0.8322	0.834
Shale					
P_o	0.24	2.9704	2.8033	4.4548	2.617
A	-0.0165	-0.4443	0.6485	0.4141	0.381
R^2	0.2804	0.808	0.3612	0.4787	0.482
Basalt					
P_o	0.1995	1.3502	2.3665	4.2344	2.038
A	-0.0047	-0.2284	0.378	-0.7113	0.181
R^2	0.1614	0.7919	0.8825	0.8082	0.659

R^2 = 0.658

Table 3.3: Slope (K), intercept (P_o) and coefficient of determination R^2 for first order reaction of P release from soils of three parent materials

	Quantity of P applied (mg/kg)				
	0	20	40	80	Mean
Shale					
P_1	1.2929	1.5738	1.8698	2.37	1.777
K	-0.3698	-0.3822	-0.372	-0.404	0.382
R^2	0.9324	0.989	0.9489	0.9565	0.957
Sandstone					
P_1	-1.4224	1.1815	1.0126	1.4997	1.279
K	-0.0869	-0.2553	0.1597	0.0763	-1.0531
R^2	0.3257	0.9105	0.338	0.5152	0.522
Basalt					
P_1	-1.6164	0.4278	1.0105	1.5717	1.169
K	-0.0243	-0.3213	-0.2995	-0.3172	0.241
R^2	0.1561	0.8686	0.9652	0.8925	0.721

R^2 = 0.733

Table 3.4: Slope (c), intercept (P_t) and coefficient of determination (R^2) for parabolic diffusion for P release from soils of three parent materials

	Quantity of P applied (mg/kg)				
	0	20	40	80	Mean
Sandstone					
P_t	-2.1813	-3.2794	-4.6662	-7.2939	-4.355
C	3.1116	4.0887	5.5221	8.3578	5.270
R^2	0.9998	0.9996	0.9999	0.9998	0.999
Shale					
P_t	0.0402	-3.5726	-20.867	-23.012	-11.87
C	1.0118	3.972	14.863	16.615	9.115
R^2	0.9735	0.992	0.9197	0.9329	0.955
Basalt					
P_t	-0.4776	-0.616	-2.2975	-3.9922	1.846
C	1.3222	1.5339	2.9705	4.7234	2.638
R^2	0.9855	0.9981	0.9974	0.9987	0.995

$R^2 = 0.983$

4.0 Conclusion and Recommendation

The results of this work showed variations in soil texture, and its range from sandy loam in shale and basalt to loamy sand in sandstone. The pH was moderately acidic across soil types. The soil organic matter, total nitrogen, available phosphorous and exchangeable cations were moderate. The amount of P released in the soil type varied; with sandstone being the highest. The amount of P released increased with increasing time of extraction, 72 hours recorded the highest. From the three equations used, parabolic diffusion model successfully described the P released in the soils compared with the zero order and the first order.

The parabolic diffusion is recommended to be used in describing the P release kinetics in the soils.

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