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An overview of the adsorption, desorption and release kinetics of phosphorus in soils

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Abstract
Phosphorus (P) fertilizers are added to agricultural soils to improve the soil P fertility, but the release rate of P can greatly influence on P fertility of soils. In high weathered soils there are more difficulties for management of phosphorus (P) fertilization due to their high adsorption rates. The P release kinetics process in highly weathered soils mainly governed by the rapid sites on adsorption and slow sites on desorption, resulting in high levels of hysteresis. Organic acids are most effective in the release of inorganic P (Pi). P release was found higher in sandy loam texture as compared to loam texture soils due to low positive charge points and adsorption capacity. Other soil properties such as organic matter (OM) contents and cation exchange capacity (CEC) also found highly correlated in respect to P release. The main objectives of this study to understand the effects of kind of soils and land-use type on the release kinetics of P under different management practices as well as to investigate the relationship between physical and chemical properties of soils and kinetics parameters from soils. Observed that release kinetics were rapid initially later on it slower rate. To explain this kinetics of P release used different models i.e. parabolic diffusion and power equation model were found to be satisfactory for P release.

Keywords: Adsorption, desorption, cation exchange capacity, hysteresis, release kinetics

Introduction

Phosphorus (P) is a most important essential nutrient element for plants and constitutes the most limiting nutrient for crop production. The application of phosphatic fertilizer has improved soil productivity and fertility but it also having negative effects *i.e.* soil acidification, metal toxicity and less P-use efficiencies (Yao *et al,.* 2017; Wang *et al.,* 2017) [44, 39]. Every year large quantities of phosphate fertilizers are applied in soil but most of the P added is not used due to strong sorption/fixing processes (Tilman, 1999; Quesada *et al.,* 2011) [36, 28]. Long-term application and higher rate of P in to the soils can lead to P accumulation more than that required for optimum plant growth. Residual P can also an important pool to supply P to plants. The majority of total soil phosphorus present in primary minerals, precipitated, adsorbed, or in organically complexed forms, and only approximately 6% (1.5%–11%) is readily available to plants (Menezes-Blackburn *et al.,* 2018) [26].

Thus, continuous P application is required to sustain yields of crops, which causes P accumulation in surface soil, as P application as fertilizer exceeds P removal by crops, increasing the risk of P losses to ground and surface waters and contributing to eutrophication (Liang *et al.,* 2016; Almas *et al.,* 2017) [4]. The replenishment of a P-depleted soil solution is affected predominantly by the release of residual P from clay minerals, organic matter (OM), and Fe and Al hydroxides (sesquioxides).Other factors which influences the P availability in the soil, however the sorption and desorption to constituents of variable surface charge minerals is considered the most important factor (Weng *et al.,* 2011) [41]. In tropical soils where high weathering occurs, high amount of Fe and Al oxides and 1:1 clay minerals type are present (Quesada *et al.,* 2011) [28].

According to Gerard (2016) [17], despite advances in research still many uncertainties about the P sorption capacity of the soil, especially in the process of reversibility. In a number of cases, sorbed P by the solid phases cannot be desorbed and adsorption isotherms do not coincide with desorption, indicated element kinetics is influenced by the hysteresis phenomenon, which shows that the process is partially irreversible (Sander *et al.,* 2005) [30]. According Bohn *et al.* (1985) [9], hysteresis formation occurs through bidentate and binucleated bonds, which are more irreversible linkages than monodentate.

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These mechanisms are mainly affected by residence time and P loading rate, strong and stable bonds (Abdala *et al.,* 2015) [1]. Phosphorus kinetic is studied mainly by experiments type batch and leaching column. Accumulation of phosphorous in irrigated agriculture having attention, because of potential water eutrophication.

Phosphorous-fertilizer recommendation fails due to differences in P status and release among different soils and land use. The distribution of various species of P in soils among different land uses and soil properties are different. It has been suggested that most effective in releasing Pi from calcareous soils by oxalic acid and in acidic soils by citric acid due to the stronger chelating ability of oxalic acid with Ca in calcareous soils but citric acid with Fe/Al in acidic soils respectively (Bais *et al.,* 2006) [8]. In contrast, Wang *et al.* (2018) studied that citric acid resulted from increased mobilization of the moderately labile NaOH-Pi (Fe/Al-P) and HCl-Pi (Ca-P) fractions than oxalic acid. Gang *et al.,* (2012) [16] showed that the pattern of P mobilization was highly soil-type dependent and controlled by intrinsic P status, such as amounts and distribution of P fractions in the soil.

However, being a relatively new technique, there are few studies evaluating the kinetics of P in the soil, especially in highly weathered soils in which there is a constant search for ways to reduce the effects of P sorption. The importance of maintaining an adequate amount of phosporus (P) in soils to maximize crop production (Withers *et al.,* 2001) [42]. Therefore, understanding about soil inorganic P (Pi) dynamics is necessary to improving the P management in agricultural systems and to increasing farm productivity.

Results and Discussion

Yang *et al.,* (2019) [43] studied in the amended soil, both the extractable P and efficiency of added P showed a significant decrease between 1 and 24 h ($P < 0.05$), and the smallest changes found between 1440 and 2160 h ($P > 0.05$). The efficiency of added P was 42.3%–60.5% and, on average, 57.7% of the applied P becomes non extractable after 2160 h in black soil. Various kinetic equations for release of P are essential to establish a mathematical model to quantitatively describe the P release process. The kinetic equations such as first-order and second-order equation, Elovich equation, power function and parabolic diffusion model that can be used to illustrate the relationship between P released and time in fertilized soils. The Elovich equation and parabolic diffusion model fitted better than the other three equations. Because of low standard error value, the Elovich equation was considered as the most appropriate equation.

Different parameters of kinetic equations to explain the release of phosphorus are

Kinetic equations	Kinetic equations result
First-order equation ($\ln Q_t = \ln Q_e - k_1 t$)	$\ln Q_t = -8E - 5t + 4.7239$
Second-order equation ($1/Q_t = 1/Q_e + k_2 t$)	$1/Q_t = 8E - 7t + 0.0089$
Elovich equation ($Q_t = 1/\beta \ln(\alpha\beta) + (1/\beta)\ln t$)	$Q_t = -4.6399 \ln t + 133.79$
Power function ($Q_t = at^b$)	$Q_t = 137.11t - 0.0433$
Parabolic diffusion model ($Q_t = Q_e + Rt^{1/2}$)	$Q_t = 117.93 - 0.49t^{1/2}$

When we calculate the products of α and β by the Elovich equation was much larger than unity, supporting the assumption of $\alpha\beta t > 1$. The parabolic diffusion equation model also fitted better. The slope (R) showed that negative value in extractability with time and represents the rate of supplementation from soil solid-phase P due to the decrease of P concentration in soil solution resulted from crop absorption. It can also used as an index of transformation rate. Both oxalic and citric acids increased the solubility of Al-P and Fe-P. The amounts of Al-P solubilized by oxalic and citric acids were found 17.69–46.48 and 13.29–37.60 mg kg^{-1}, respectively. The Fe-P-solubilized by oxalic and citric acids were found 0.24–21.11 and 2.65–16.10 mg kg^{-1}, respectively. For Fe-P-solubilized, the concentrations ≤1.5 mmol L^{-1} led to lower solubility capability of oxalic acid than citric acid, whereas citric acid had the greater solubility capacity at ≥1.5 mmol L^{-1}. The amount of Al-P-solubilized was greater significantly than other Pi fractions ($P < 0.05$), indicating that Al-P was more easily solubilized, followed by Fe-P.

Guedes *et al.,* (2016) [20] showed that adsorption of was best fitted by the Langmuir model as compared to the Freundlich model. Due to these reason Langmuir model estimated the maximum phosphorus adsorption capacity (MPAC) ranges 785 mg kg^{-1} Hortic Anthrosol to 1838 mg kg^{-1} in Xanthic Ferralsol-2, considered soils with low to medium sorption capacity (Curi *et al.,* 1988) [10]. By Langmuir model the order of P adsorption capacity were observed: Hortic Anthrosol < Xanthic Ferralsol-1 < Rhodic Ferralsol-3 < Xanthic Ferralsol-2. Many factors that can influence the fit of the Langmuir and Freundlich models i.e. heterogeneity of the adsorptive surface, concentration of the solutions and ionic strength, as well as experimental conditions also. The different kind of soils and different regional conditions may require different adjustments for the illustration of adsorption. Adsorption and desorption as a function of contact time with solution in stirred flow system. Study showed that the amount of P desorbed in all soils was smaller than the amount adsorbed and the order of q max for desorption observed: Xanthic Ferralsol-1 < Hortic Anthrosol < Xanthic Ferralsol-2 < Rhodic Ferralsol-3. The difference between amounts of adsorbed and desorbed (hysteresis) which is characterized by irreversibility of the adsorption. The release kinetics of phosphorus was described by the pseudo first-order model. It showed with two different phases with two types of adsorption site. The first phase occurs in rapid sites, observed that marked decline in adsorption and desorption rates. The next phase occurs in slow sites characterized by decrease rate, but at a lower proportion.

The role of clay on P sorption particularly seen in acidic and weathered soils having pH dependent temporary charges, where kaolinitic minerals are predomionantely found (Azeez and Van Averbeke, 2011; Guedes *et al.,* 2015) [7, 19]. In Langmuir model P adsorption mainly characterized by L-type isotherms, which shows the relationship between concentration of phosphorus in solution and the adsorbed on solid phase decreases with increasing solute concentration, generating a progressive saturation of the solid phase (Limousin *et al.,* 2007) [24].

A similar type adsorption behavior was observed by Ghilherme *et al*. (2000) [18] studied the presence of iron oxides having high affinity for phosphate in the soil. However Fink *et al*. (2016) [14, 15] observed accumulation of organic matter and reduce P retention in soils. The role of kaolinite in

phosphorus adsorption was reported by Wei *et al.* (2014) [40], observed that this mineral can present a sixth of phosphorus binding capacity compared to goethite capacity.

However, Perez *et al.* (2014) [27] and Weng *et al.* (2011) [41] studied that iron oxides are most important components that responsible for P adsorption. Thus, the organic matter management is very important to reduce phosphates adsorption in soils, where strong presence of iron oxides (Almeida *et al.*, 2003) [5]. The maximum adsorption showed by Feox were 6.5 times higher than FeDCB and Fe2O3, were 4 and 5 times higher, respectively, due to greater number of adsorption sites that these oxides can generate (Langmuir, 1997) [22]. Therefore, factors such as the higher amounts of Feox, FeDCB and Fe2O3 and acidic conditions in the soil are main source of positive charges, significantly increasing the P adsorption capacity.

Hysteresis correlated with clay associated with crystalline and poorly crystalline oxides, which controlling the phosphorus hysteresis in these soils. Because of kaolinite can associate with Fe oxides, resulting increasing the soil adsorptive potential and drastically reducing the desorption (Wei *et al.*, 2014) [40]. In Goethite, the adsorption occur through modentate and bidentate bonds in inner sphere complex (Abdala *et al.*, 2015) [1], but in case of poor crystalline oxides (ferrihydrite) adsorption occur through bidentate and binucleated in inner sphere complex, with high binding energy (Arai and Sparks, 2001) [6]. The effect of hysteresis desorption mechanism of organic substances, metals and phosphorus type herbicides which is mainly controlled by the retention force which ions and molecules are subject due to colloids of the soil solid matrix such as clays, oxides and organic matter (Vega *et al.*, 2009; Fernández-Calviño *et al.*, 2015; Rampoldi *et al.*, 2014) [37, 13, 29].

In oxides difficult the desorption process, because of more energy required to eliminate the central atoms of the crystal configuration is greater than the energy required for these to be formed (Sparks, 2003). Organic matter may inhibiting adsorption process and reduce the formation of high stability complexes, due to inverse relationship between hysteresis and OM. Afif *et al.* (1995) [2] observed that organic anions compete with phosphates anions at the same adsorption sites resulting reducing P adsorption process.

Ahmadi (2018) [3] observed that higher application of phosphatic fertilizers in agricultural lands (intensive crop systems) resulting phosphorus accumulation in soils. It indicates that intensive agricultural crop system management practices may accumulate P in surface soils and low P fertilizer-use efficiency is low. Kinetics of P release was initially rapid than slower reaction. The P release is characterized by diffusion-controlled process that also observed for other ions such as k^+. The observed pattern due to the heterogeneity of the adsorption sites with different adsorption affinities. The initial rapid release mainly attributed by rapid dissolution of poorly crystalline or amorphous phosphates in the soils, which were meta stable and finally converted into crystalline forms i.e. octa-Ca-phosphate and Ca-hydroxyl-apatite. Both rapid and slow phase may be related to desorption of surface labile P and slow dissolution of the crystalline phosphate compounds in the soils.

The maximum and minimum amount of P was released in sandy loam texture and loam textured soils respectively. In all types of soils, the amount of P released was lower than the Olsen extracted P and olsen-P removed 3 times additional phosphorus than cumulative phosphorus extracted by 0.01 M CaCl2. Different kind of kinetic models were used to explain the P release from the soils indicate that release of P is a diffusion-controlled process.

Espinoza *et al.* (2013) [11] studied the kinetics of P release represents that zero order, first order and second-order models were not adapted to the release kinetics of P in the amended soil. Some models following at least two first-order kinetics (Shariatmadari *et al.*, 2006) [31] in calcareous soils. The Steffens 1994 [35], reported Elovich simple model in Alfisols with organic fertilizers and McDowell and Sharpley 2003 [5] showed power equation have been reported as best describing P release. The Elovich simple model and power models showed larger initial desorption rate and lower desorption constant augmented release (Fekri *et al.*, 2011) [12] as amendment dose increased (McDowell and Sharpley 2003) [5]. But parabolic diffusion model was not behaved in the same manner. The initial rapid desorption phase involves labile P, bounded P at reactive surfaces in the aqueous phase, soluble P from recent amendment, physically adsorbed orthophosphate, and complexed by organic matter. These rapid reactions of P initially correspond to dissolution of poorly crystalline or amorphous phosphates. Less mobile P fractions are directly proportional to the number of sites occupied by phosphate. After that slow reactions of P release mainly originated from diffusion from interior sites inside soil solid phases, aggregates or slow dissolution of amorphous or crystalline solid phases of P. The rate of gradual reduction in P release over time period may result from decreasing surface charge and decreasingly interacting adsorbed phosphorus ions (Fekri *et al.*, 2011; Siddique and Robinson 2004; Sims and Pierzynski 2005) [12, 32, 33].

Conclusion
Phosphorus kinetics in highly weathered soils adsorbed mostly through rapid adsorption sites where water-soluble phosphate was converted into non extractable form within a very short time period due to strong affinity with the soil solid matrix. Desorption occurs through slow desorption sites. Factors such as low Fe oxides and good organic indicating optimization of P fertilization, reducing the effects of adsorption, as well as increasing reversibility of P adsorbed to soil. Better crop-management practices increasing soil P results more potential to release of P. Both oxalic and citric acids can be potentially increasing the solubility amount of Al-P, Fe-P, and Ca-P. Most appropriate model is parabolic diffusion and power equation modeling for cumulative P release. The parameters of kinetics from models were found highly correlated with clay conent, pH, CaCl2-P, CaCO3 and CEC. The time-dependent release of P was described by an Elovich equation.

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