

Flow and Distribution of Phosphorus in Soils from a Geochemical and Agronomic Approach



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Abbreviations

ACPwithoutP	Absorption of the crop in the plot without P
ACPwithP	Absorption of the crop in the plot with P
CPA	Amount of P added to the plot
DAP	Diammonium phosphate
MAP	Monoammonium phosphate
P	Phosphorus
Pi	Inorganic phosphorus
Po	Organic phosphorus
PR	Phosphate rock
Pt	Total phosphorus
RP	Recovery of P
TSP	Triple superphosphate

1 Introduction

Crop productivity is determined by potentially defining factors (e.g., solar radiation, temperature, CO₂ concentration, plant characteristics) that usually limit it in ecosystems (e.g., water, soil fertility) and/or the factors that reduce it (e.g., diseases, pests, weeds), which is manifested in the growth rate of a crop (van Ittersum et al., 2003), where soil fertility plays a determinant role in the different agroecosystems (Henao & Baanante, 1999; Drechsel et al., 2001; Mueller et al., 2012). From this point the importance is taken to consideration, the definition of an adequate level of fertility contemplates calculating a concentration or range of this that does not produce deficiencies in the growth of crops, but at the same time that does not imply a risk of contamination of the water or air of the ecosystems (Pinochet, 1995; Johnston & Dawson, 2005).

The world population is increasing geometrically, which is estimated to reach nine billion inhabitants in the year 2050 (FAO, 2009). This implies an increase in the demand for food, fibers, biofuels (FAO, 2009; Roberts, 2009; Godfray et al., 2010) and, consequently, the need to develop strategies to increase crop productivity will become evident, where the management of soil fertility, especially N, P, and K, will be the key to obtain high crop yields, with the least risk of contamination of water or air in ecosystems (van der Wiel et al., 2019), having in perspective the level of soil fertility is the consequence of a state of equilibrium originating from the balance between the addition, removal and transformations of nutrients in the soil system (Hartemink, 2006; Phong et al., 2011; Zhan et al., 2015; Dayton et al., 2020).

Under natural conditions, nutrient addition occurs through solid and liquid atmospheric deposition, biological fixation of gaseous nutrients, and the entry of nutrients from sediments and effluents. Removal involves leaching from the soil, gaseous losses (denitrification and others), surface or subsurface runoff (nutrient

dissolved in water), and erosion (loss of soil plus nutrient). The transformation represents the income from the weathering of the minerals (transfer of reservoirs). As is the case of the release of cations from the primary minerals and the mineralization of organic matter (release of N, P and S), which constitute the native income from the soil and other forms of transformation are given by the chemical and physical reactions that determine the retention of minerals in colloids through adsorption, the formation of precipitated products and the transmission of mineral sources from inorganic to organic forms by the microbial action, such as the immobilization of N.

Depending on agronomic practices and the physical-chemical relationship of nutrients with soil colloids, the relationship between the processes of addition and removal of nutrients suggests that agricultural systems can accumulate (input of nutrients > export of nutrients in crops) or de-accumulate nutrients (export of nutrients in crops > nutrient inputs). A predominance of de-accumulation can lead to a progressive reduction in soil fertility and a predominance of accumulation can result in over-fertility of the soil and even increase the potential risk of contamination (Pinochet, 1995; Johnston & Dawson, 2005), especially of water bodies by eutrophication processes of aquatic ecosystems (Bennett et al., 2001; Sharpley, 2016).

In this context, soil fertility is a matter of concern for the agricultural policies of all countries, especially when referring to phosphorous fertility, since the availability of P in many of the agricultural systems constitutes a strong limitation of the production of crops (Sharpley & Tunney, 2000; Tóth et al., 2014). The physical-chemical relationship between phosphate ions and colloids in the soil, and the field evidence shows the accumulation capacity of P in soils and the potential to maintain or build their fertility (Whalen & Chang, 2001; McLaughlin et al., 2011; Zhang et al., 2019). However, the unbalanced P balances that are registered in many localities of the world, which can manifest themselves in low fertility or in a potential risk of contamination, have created the urgency to develop strategies aimed at increasing the efficient use of P (Buerkert et al., 2001; Simpson et al., 2011; MacDonald et al., 2011; Van Dijk et al., 2016), such as adjusting the fertility level according to the supply required to satisfy the demand of the crop, replenishing what is taken out of the system, selecting the correct source and place of addition, and identifying cultivars based on their strategies for the use of P (Sharpley et al., 2005; Norton, 2014; Shi et al., 2015). Faced with these challenges, it is essential to review the existing scientific information regarding the dynamics of P in soils.

2 Residual Effect of P on Soils

At the beginning of the twentieth century, interest grew in the effect of the nutrients that were applied to the soil via fertilizers. Thus, the effect of fertilization has been evaluated by quantifying the relative yield of the crops during the years following the initial application of the fertilizer, which have been compared with the yields obtained in unfertilized plots (Syers et al., 2008). At that time, it was considered

that P was lost or irreversibly fixed in the soil and therefore with little or no capacity to increase soil fertility. This conclusion was reached because researchers at the time possibly tried to measure the residual effect of one or more small doses of P, in soils with a low level of available P and high retention capacity. However, some studies have shown that the P retained in the soil can be recovered if the concentration of available P is reduced (Barrow, 1983a), a situation that was later corroborated through the analysis of a series of field experiments that showed that it is possible to recover over 80% of the P added to the soil by removing it in the harvest of successive crops (Syers et al., 2008).

Concern about precipitation implied that it was not considered that much of P could be subject to adsorption reactions on soil colloids (Syers et al., 2008). According to the works with an agronomic approach that have described the adsorption of ions on characteristic surfaces of dominant colloids in soils (Posner & Barrow, 1982) today it is recognized that the P retained in the soil can be released, reflecting in a high accumulated recovery originating from successive crops. Subsequently, this process was simulated in a reaction model between P and soil (Barrow, 1983b), which was based on three assumptions: (1) adsorption reactions occur between phosphate ions and a reaction surface; (2) the properties of the reaction surface are normally distributed and; (3) the initial adsorption induces a diffusion gradient toward the interior of the reaction surface. The model adequately described adsorption/desorption when exposing the soil to different concentrations of P, pH, temperature and contact time between P and the soil.

The crops, during their vegetative and productive cycle, do not use all the P added to the soil for the season, leaving a fraction of absorbable P for the subsequent crop. Thus, the P available for crop production in seasons after the addition of P has been called the residual effect of P (Howard, 2006; Syers et al., 2008; Li et al., 2011). Therefore, it can be inferred that the amount of residual P present in the soil is basically determined by two processes: (1) the absorption of the crop and subsequent export of P at harvest and (2) the reactions that determine its retention in the soil, which according to Javid and Rowell (2002) can be classified as fast and slow reactions. The fast reactions would be being dependent on the colloids and their proportion in the soil, and the slow ones would respond to the laws that govern the diffusion of ions.

The evaluation of the residual effect of P in short-term experiments led to the conclusion that P is used inefficiently in agriculture, with recovery percentages of added P that remains between 10 and 20%. Currently, the recognition of the accumulation of P in the soil and its reversibility has reoriented the analyses done by the researchers. Thus, Johnston and Syers (2008) argue that the traditional method by difference to calculate efficiency is not suitable for P (Eq. 1) since it was initially developed for nitrogen (N). The N contained in fertilizers rarely remains in the soil as inorganic, nitrate that was not absorbed by the crop or immobilized by soil organisms, is potentially lost through leaching or denitrification (Riley et al., 2001; Zhang et al., 2015). However, on rare occasions a very small amount of added P is lost from the soil, but mostly tends to accumulate as a reserve (Zhang et al., 2019). When the efficiency of P is measured by the balance method (Eq. 2), the P

removed by successive crops, during a suitable period of time, can exceed 80% of the P added to the soil via fertilizer (Ibrikci et al., 2005; Sá et al., 2017).

$$RP = \frac{ACP \text{ with P} - ACP \text{ without P}}{APAP} \quad (1)$$

$$RP = \frac{\sum ACP \text{ with } P_t - \sum ACP \text{ without } P_t}{APAP} \quad (2)$$

In Eq. (1): ACPwithP = absorption of the crop in the plot with P, ACPwithoutP = absorption of the crop in the plot without P, APAP = amount of P added to the plot. Equation (2) considers the recovery of P by successive sowings during a time (t) of recovery of P from successive crops. In both Eqs. (1) and (2), RP refers to the recovery of P by the crop.

The reactions that occur over time when a phosphate fertilizer comes into contact with the soil largely determine the residual effect of P. Results have suggested that low solubility phosphate products originate when the soil solution reaches high concentrations of P, a favored condition at the beginning of each fertilization event (Lindsay et al., 1962; Ghosh et al., 1996). By adding P to the soil, the fertilizer granule is hydrated and subsequently the diffusion of phosphate ions begins, delimiting a zone of high P concentration in the closest part to the fertilizer and another zone of low concentration in the distal limit of influence of the same limit and, according to McLaughlin et al. (2011), in the zone of higher P concentration the precipitation reactions would be dominant and in the zone of low concentration the adsorption reactions would dominate (Fig. 1).

The initial reactions that are triggered when P is added to the soil depend largely on its particular properties of the fertilizer, where the reactivity of the soil determines the fate of P (Fig. 2). The current sources of P used in agricultural systems are manufactured basically from phosphate rock (PR), whose P content generally fluctuates between 9 and 17% of P. By treating PR with sulfuric acid, simple superphosphate can be produced (7–10% P) or with phosphoric acid to produce triple superphosphate (17–24% P). From phosphoric acid triple superphosphate (TSP: 0-46-0), diammonium phosphate (DAP: 18-46-0), or monoammonium (MAP: 15-52-0) is produced, depending on whether it is combined with RF or with ammonia. These sources of P seem to end up all forming dicalcium phosphate in soil, regardless of their manufacturing process, and the main difference lies in the pH and the concentration of P in the perimeter of influence of the fertilizer granule. The latter was evidenced in an acid oxisol (pH ~ 4) and a calcareous inceptisol (pH ~ 8), collected in Rondonopolis—Brazil and Idaho—USA, respectively. In the first soil, the pH increases by adding MAP or DAP, while in the second soil, the pH is reduced. In the first soil the total P added was distributed in the first 28 mm of diameter, while in the second soil the total P added was distributed in the first 50 mm of diameter (Pierzynski et al., 2014).

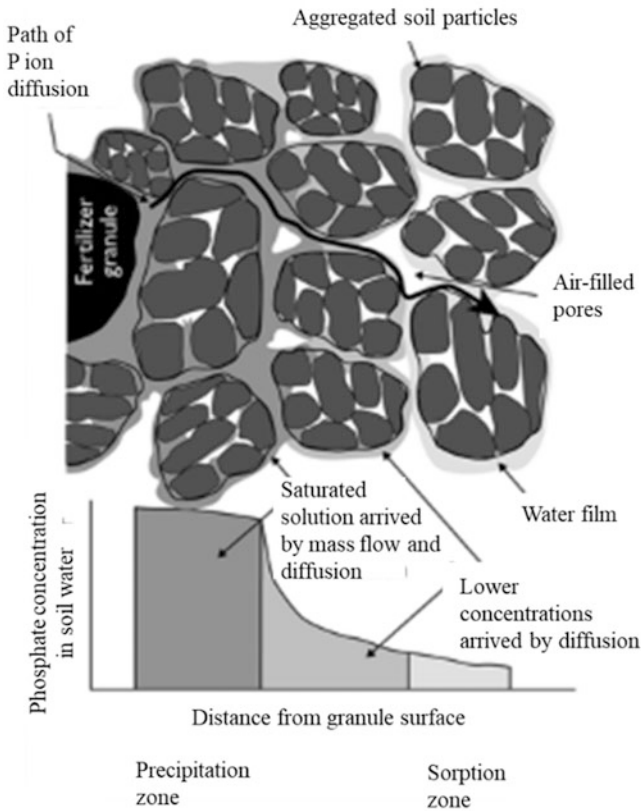


Fig. 1 Representative diagram of the movement of P by diffusion from a soluble fertilizer granule through the pores of a well-aggregated soil (McLaughlin et al., 2011)

The development of soil analysis methods opens the opportunity to measure the residual effect of nutrients considering their availability to potentially be absorbed by crops, under specific site conditions (soil, climate) and management (crop rotation, crop management of residues, fertilization techniques). In the case of P, the analysis methods do not strictly determine the concentration of available P, but provide an index of the amount of P that can be absorbed by the culture (significant correlation between the availability index and the absorption of the culture) (Kumar et al., 1991; Tiessen & Moir, 1993). These methods have been developed considering specific characteristics of the soils, which considerably limits their generalization (Kumar et al., 1991; Watson & Mullen, 2007; Jordan-Meille et al., 2012; Ziadi et al., 2013).

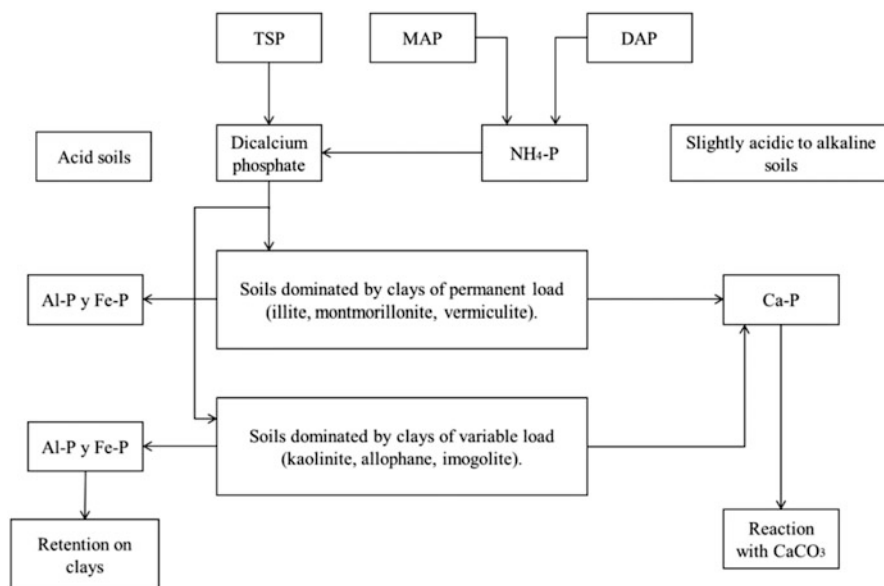


Fig. 2 Dynamics of phosphorous fertilizer in the soil. (Adapted from Fixen, 1992)

3 Phosphorus Shapes in Soil

The amount of P contained in soils exceeds widely the amount absorbed by crops, regardless of the degree of soil evolution, or of its pedogenesis (Yang & Post, 2011), which is contained in organic (Po) and inorganic (Pi) reservoirs (Johnston & Syers, 2008). However, from an agronomic perspective, the availability of P in the soil is limiting for crop production in many regions of the world (Lynch, 2011), which predicts an increase in the demand for phosphate fertilizers and the constant development of strategies that allow increasing the efficient use and recycling of P (Sharpley et al., 2005; Norton, 2014).

It has been found that the level of total P (Pt) in oxisols and ultisols can be quite low, not exceeding 18 mg P kg^{-1} , while in soils derived from volcanic ash it can be much higher with $3300 \text{ mg P kg}^{-1}$ (Fassbender, 1993). Po represents between 20 and 75% of Pt (Brady & Weil, 1999), consisting essentially of polyphosphates (ATP, nucleic acids), phosphonates (phosphonic acid), diester phosphate (phospholipids), monoester phosphate (carbohydrate phosphates, inositol phosphate) (Fuentes et al., 2006). In a meta-analysis by Yang and Post (2011), it became clear that the proportion of each P form is related to parent material and time. The so-called labile Pi constitutes a small fraction of Pt, in all soil orders, through all stages of development, even in oxisols this form did not represent more than 5% of Pt. Secondary Pi, defined as Pi adsorbed on the surface of secondary minerals of Al and Fe, represents a small fraction that increases with the degree of weathering, but in no case it exceeded 20%. The apatite content decreases with weathering, thus, entisols exhibit

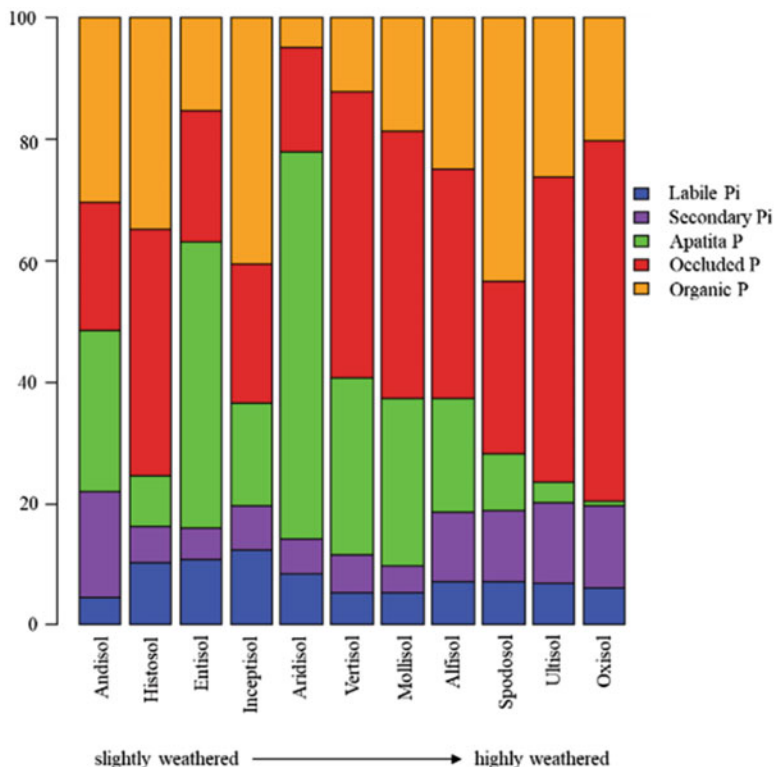


Fig. 3 Forms of P expressed as a percentage of total soil P (Yang & Post, 2011)

apatite content greater than 40% and oxisols do not exceed 3%. Aridisols, with an intermediate stage of development, exhibit apatite content greater than 60% attributable to dry climate conditions where these soils predominate (Fig. 3).

The reduced fertility of P that soils generally exhibit in various regions of the world (Lynch, 2011), basically responds to the naturally low content of P in the soil in reference to other elements, low or no solubility of most of the compounds of P, and progressive adsorption of the soluble P added via fertilizer, and even formation of poorly soluble secondary minerals. In addition, soil fertility problems are exacerbated by P outputs from the system annually: 5–50 kg P ha⁻¹ are removed by plants in the harvested biomass, 0.1–10 kg P ha⁻¹ by wind erosion of mineral and organic particles, 0.01–3 kg P ha⁻¹ is lost by surface runoff, and due to the low solubility of P, losses by leaching are not very quantifiable (Brady & Weil, 1999).

3.1 Soil Inorganic Phosphorus

Soil Pi represents an important fraction of Pt, which under alkaline conditions is forming compounds linked to Ca, under acidic conditions compounds linked to Al,

Fe, and Mn, and under intermediate conditions phosphate ions tend to replace hydroxyl groups located in the edges of the clays (Brady & Weil, 1999; Penn & Camberato, 2019). The soil solution also constitutes a small reservoir of Pi, since it can reach an average concentration of 0.2 mg P L^{-1} (Bolland et al., 2003), a situation that would represent 60 g P ha^{-1} at 20 cm depth, with an apparent density of 0.7 g cm^{-3} , and with 21% humidity.

Plants take up P from the soil solution. However, the amount of P in solution (60 g P ha^{-1}) is far from satisfying the demand for crops such as wheat or peas, which can achieve yields of 10,000 in southern Chile (Sandaña et al., 2009; Valle et al., 2009) and 7000 kg ha^{-1} (Valle et al., 2009), respectively. If we consider a wheat yield of $10,000 \text{ kg ha}^{-1}$ and an average P concentration in the vegetable dry matter of 2 mg g^{-1} (Schachtman et al., 1998; Sharma et al., 2013) it can be argued that wheat crop is able to remove 20 kg P at harvest, which means that the crop totally exhausts the solution (60 g P ha^{-1}) from the soil more than 300 times. It has been suggested that precipitation/dissolution, adsorption/desorption, and immobilization/mineralization reactions control recovering P concentration in the soil solution (Frossard et al., 2000; Penn & Camberato, 2019).

P sorption isotherms are derived from describing the amount of P adsorbed per unit mass of soil as a function of the concentration of P in solution. From the analysis of P sorption isotherms it has been possible to establish the maximum retention capacity of the soil and the existence of a balance between P adsorption and desorption (Anghinoni et al., 1996; Jiao et al., 2008; Wang et al., 2013), determining that a certain level of P in solution is linked to a specific amount of P adsorbed in the soil. That is, if the concentration of P in solution is increased (addition of fertilizers), the amount of P adsorbed in the soil increases and, if the concentration of P in solution is depleted (export of P in the harvest of crops) it decreases the amount of P adsorbed in the soil. This approach has reasonably explained how small amounts of P in solution can cover the demand for P by crops.

Adsorption can occur at the surface and intraparticle level, in the first case the P in solution is retained on the surface of the soil colloids and in the second case the initially retained P diffuses into the microaggregates, as a consequence of a gradient of unbalanced concentration (Barrow, 1983a, b; Bolland et al., 2003). Desorption refers to the passage of P adsorbed to solution, mainly caused by a depletion of P in solution (Bolland et al., 2003). The adsorbed P can be trapped between the clay minerals of the soil and the precipitated oxides of Al and Fe, this condition is called occluded P (McLaren & Cameron, 1996). In Fig. 4 the adsorption and occlusion of Pi is shown.

In the soil, the phosphate ion is subject to reactions that produce low solubility compounds depending on the pH, and therefore the P contained in these compounds is less susceptible to being absorbed by plants (Bohn, 1993; Busman et al., 2002; Hopkins & Ellsworth, 2005). Generally, the reactions by which the phosphate ions are removed from the soil solution give rise to: Al, Fe, and Mn phosphates, compounds that are formed when P reacts with metal ions in solution (Fig. 5a); reversible external sphere adsorption that favors anion exchange, where the phosphate ion in solution is subject to exchange with OH^- and SO_4^{2-} ions (Fig. 5b);

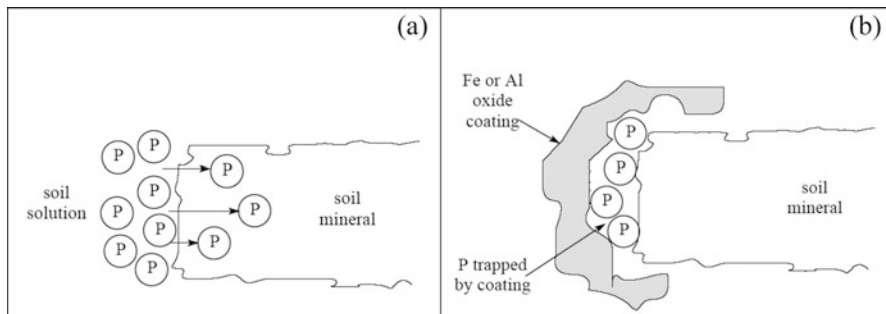


Fig. 4 Surface and intraparticle adsorption (a) and occlusion (b) of P in the mineral fraction of the soil. (Adapted from McLaren & Cameron, 1996)

retention of the external sphere on the surface of hydrated oxides where the availability of P tends to be much lower, since the reaction can be repeated, binding the phosphate ion to two adjacent hydrated oxides (Fig. 5c).

In alkaline soils, the availability of P is linked to the solubility of the compounds that tend to form when the phosphate ion interacts with divalent bases (Ca, Mg). In alkaline soils, the phosphate ion reacts rapidly with Ca, giving rise to the formation of a systematic sequence of compounds that decrease in solubility (Naeem et al., 2013). The highly soluble monocalcium phosphate $[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ reacts with the calcium carbonate present in the soil (CaCO_3). Monocalcium phosphate plus water and calcium carbonate originate dicalcium phosphate dihydrate, subsequently under the same domain conditions of calcium carbonate, tricalcium phosphate originates. In each transition there is release of carbon dioxide and the insolubility decreases in each transition with respect to monocalcium phosphate (Table 1).

3.2 Soil Organic Phosphorus

The soil Po has a high agronomic and ecological significance since it can represent more than 50% of Pt (Haygarth et al., 2018), which is corroborated by observing a significant contribution of Po to the P availability that is estimated through routine laboratory methods (Cade-Menun et al., 2018). Soil Po has been difficult to study due to the fragility of the molecules that contain it, a situation that limits its extraction with acids or bases. Chromatographic partitioning is a technique that has made it possible to objectively study the Po of the soil. However, much of the scientific knowledge of Po is due to nuclear magnetic resonance (NMR) as it is a better known technique than chromatographic partition.

Four organic molecules that contain P in their structure are recognized in the soil: polyphosphates (ATP), phosphonates (phosphonic acid), phosphate monoester (inositol phosphate) and phosphate diester (phospholipid) (Cade-Menun, 2005; Cheesman et al., 2014). The nature of P associated with humic materials in the

Table 1 Minerals formed by precipitation of P in calcareous soils (Adapted from Brady & Weil, 1999)

Mineral	Formula	Transition (weeks)	Insolubility ^a
Monocalcic phosphate	Ca(H ₂ PO ₄) ₂ ·2H ₂ O		
Dicalcic dehydrate phosphate	CaHPO ₄ ·2H ₂ O	2–3	60
Dicalcic phosphate	CaHPO ₄		
Octocalcic phosphate	Ca ₄ H(PO ₄) ₃ ·2.5H ₂ O		
Tricalcic phosphate	Ca ₃ (PO ₄) ₂	8–10	900
Apatite hydroxide	Ca ₅ (PO ₄) ₃ OH	52–104	
Fluorapatite	Ca ₅ (PO ₄) ₃ F		

^aReferential insolubility with respect to the solubility of monocalcium phosphate

soil is little known, a situation that does not diminish their importance as a source of P for plants. These organic molecules can be grouped into two organic fractions of the soil, a fraction that actively participates in plant nutrition and another fraction that appears to be relatively stable and therefore not available to plants. The amount of Po is more influenced by climate, biological activity, relief, vegetation and time and to a lesser degree by the parent material of the soil.

The most abundant organic compound in the soil that contains P is inositol phosphate representing more than 50% of the total Po (McLaren et al., 2015). The abundance of inositol phosphate in the soil is possibly due to its relative stability under acidic and alkaline conditions, and active interaction with humic acids present in the soil. Nucleic acids and phospholipids probably do not exceed 2% of total Po in most soils; these reach the soil in relatively high amounts as remains (residues) or secondary metabolites of microorganisms, plants and animals. However, the low amount present suggests that they undergo rapid mineralization unlike inositol phosphate, which suggests that these phosphate compounds appear to be more important for plant nutrition than suggested by the small amounts in the soil.

It has been observed that the concentration of P in solution and in leachates is high when there are biological depositions of animals in soils, where P is forming part of organic compounds (Azevedo et al., 2018). Po forms are more mobile than Pi in soils, possibly due to their low reaction with minerals present in the soil. In the deep horizons of soils that receive biological depositions from animals, it is common to see that Po exceeds 50% of P in solution. This explains the greater availability of P in the deep horizons of the soils when they are fertilized by Po sources, compared to when they have been fertilized with Pi sources (Rigo et al., 2019).

The forms of Po are subject to pass to Pi by mineralization and through the immobilization process the forms of Pi pass to Po. The amount of Pi added to the soil via fertilizers that is immobilized is unknown but is estimated to be important. There is evidence that some of the forms of Po product of immobilization are too stable to be used by plants. It is possible to reduce the immobilization rate by modifying the pH of the soil, going from acid to slightly acidic, but the accumulation of di and tricalcium phosphate increases. Thus, it has been observed that calcium amendment applications can reduce the need for phosphorous fertilizers in some cases by increasing the mineralization/immobilization ratio.

4 Fractionation of P Contained in Soils

As a result of the development of techniques to analyze the contained P in soils, the sequential extraction of P has been possible. This way of analyzing P has been shown to reasonably support the hypothesis of P reservoirs in equilibrium (Johnston & Syers, 2008; Syers et al., 2008). This hypothesis assumes that P is retained by soil components with different degrees of energy (depending on the type of bond that forms between P and soil colloids) and consequently they would determine several P reservoirs with different availability grade. One of the first methods of sequential extraction was proposed by Chang and Jackson (1957), which quickly stopped being used due to its low representation in agronomic terms. Subsequently, other procedures have been proposed with the same objective (Table 2). Thus, in order to have a practical explanation, conceptual diagrams of soil P reservoirs categorized according to biological availability have been suggested.

The method of Hedley et al. (1982) has shown to be reasonably reproducible and sufficiently sensitive to changes in conditions in agroecosystems (Tiessen & Moir, 1993; Cross & Schlesinger, 1995). The strength of this method is that it allows the extraction of inorganic and organic forms of P with labile to nonlabile characteristics. Several modifications of this sequential extraction method have been proposed, among the best known are that of Condrón and Goh (1989) and that of Tiessen and Moir (1993). In the first case, the microbial P was excluded, the 0.1 M NaOH extraction plus ultrasound was replaced by extraction with 0.5 M NaOH, and the

Table 2 Sequential extraction methods for P

Method	Extraction	Designation
Chang and Jackson (1957)	1. 1.0 M NH ₄ Cl 2. 0.5 M NH ₄ F 3. 0.1 M NaOH 4. 0.25 M H ₂ SO ₄ 5. Citrate-ditionite 6. 0.1 M NaOH	P labile P-Al P-Fe P-Ca P-Fe reduced P-Al and P-Fe occluded
Bowman and Cole (1978)	1. 0.5 M NaHCO ₃ 2. 1.0 M H ₂ SO ₄ 3. 0.5 M NaOH	P labile P moderately labile P resistant
Hedley et al. (1982)	1. Resin 2. 0.5 M NaHCO ₃ 3. Fumigation, 0.5 M NaHCO ₃ 4. 0.1 M NaOH 5. 0.1 M NaOH + ultrasound 6. 0.1 M HCl 7. H ₂ SO ₄ and H ₂ O ₂	P very labile P labile P microbial P-Al and P-Fe P intra added P-Ca P residual
Ivanoff et al. (1998)	1. 0.5 M NaHCO ₃ 2. Fumigation, 0.5 M NaHCO ₃ 3. 1.0 M HCl 4. 0.5 M NaOH 5. Ignition, 1.0 M H ₂ SO ₄	P labile P microbial P moderately labile P no labile P residual

Table 3 Geochemical and ecological significance of the P fractions resulting from the sequential extraction of Hedley et al. (1982) modified by Tiessen and Moir (1993)

Fraction of P	Geochemical	
	Significance	Ecological
Resin-Pi	Absorbed in the surface of crystalline compounds. Not occluded.	Immediately available para las plantas, directly interchangeable con la solution of soil. Quick rotation.
NaHCO ₃ -Pi	Absorbed in the surface of crystalline compounds and in soil colloids. Not occluded.	Easily available for plants. Quick rotation.
NaHCO ₃ -Po	Weakly adsorbed to humic and fulvic acids. Not occluded.	Easily mineralizable. Quick rotation.
NaOH-Pi	Chemically adsorbed to amorphous and crystalline Al and Fe compounds. Not occluded.	Low availability for plants. Slow rotation.
NaOH-Po	Strongly associated with humic and fulvic acids. Not occluded.	Low availability for plants. Slow rotation.
HCl-Pi	Associated with calcium compounds.	Low availability for plants.
[HCl]-Pi	Minerals rich in phosphorus with low solubility such as apatite. Occluded.	Low availability protected phosphorus for plants. Very slow rotation.
[HCl]-Po	Associated with organic matter not extractable in alkali. Occluded.	Low availability protected phosphorus for plants. Very slow rotation.
[H ₂ SO ₄]-P	Highly resistant inorganic and organic forms. Occluded.	Low availability protected phosphorus for plants. Very slow rotation

[] refers to a highly concentrated acid

0.5 M NaOH extraction was introduced after the 1 M HCl extraction. In the second case, the main modification was that the 0.5 M NaOH extraction was replaced by extraction with concentrated HCl.

After the works of Hedley et al. (1982), Tiessen and Moir (1993), Tiessen et al. (1984), Cross and Schlesinger (1995), it is possible to give a geochemical and ecological meaning to the P extracted sequentially (Table 3) according to the extraction scheme presented in Fig. 6. On this basis, conceptual models of the soil P system have been proposed (Fig. 7).

5 Considerations for Studies of Phosphorous Fertility of Soils

The behavior of P from different fertilizer sources is subject to reactions that determine its accumulation in specific reservoirs, depending on the characteristics of the soils, which have originated under particular conditions of topography, vegetation, and temperature and humidity regimes. In such circumstances, it is necessary to evaluate the residual effect of the fertilizer P, identify the destinations (reservoir fractions) of the added P and their relationship with its availability. Unlike

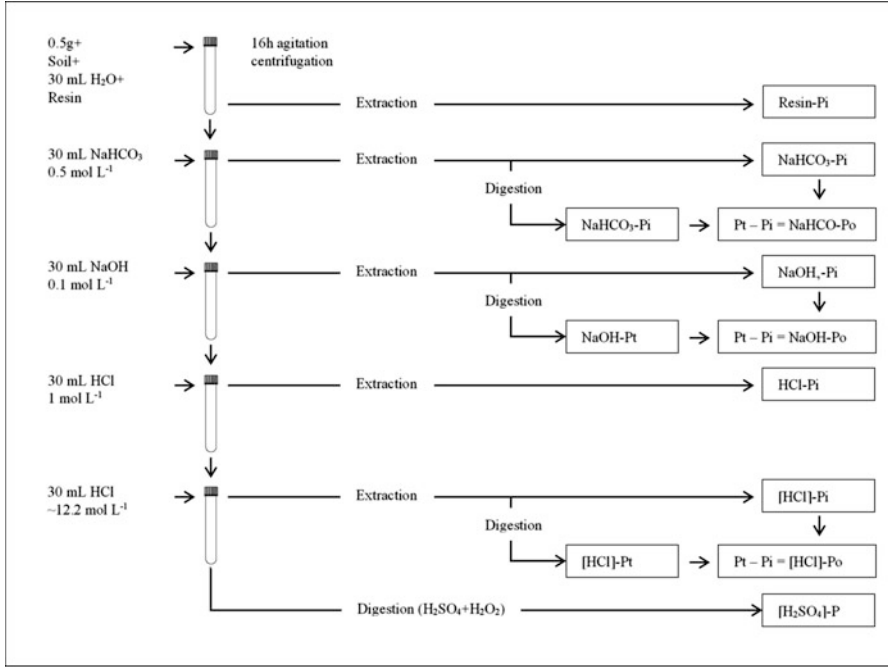


Fig. 6 Sequential extraction of P with the method of Hedley et al. (1982) and modified by Tiessen and Moir (1993). [] refers to a highly concentrated acid

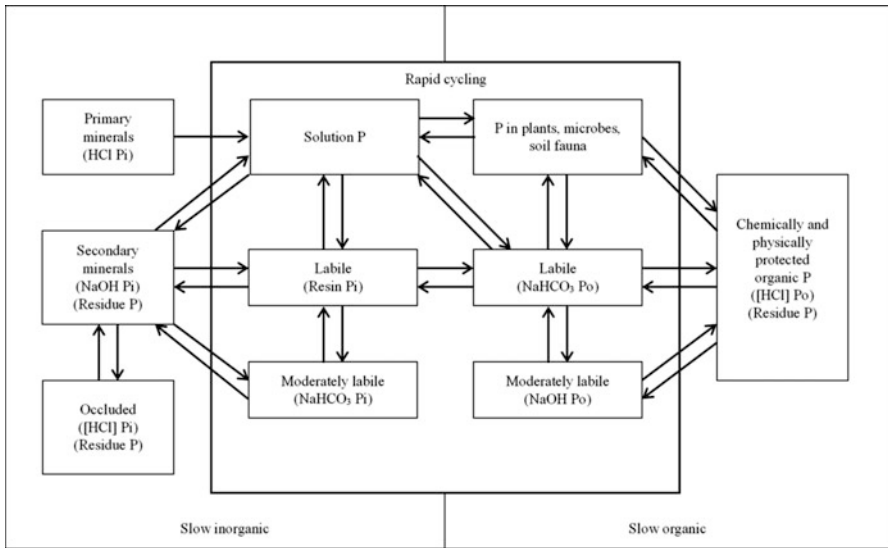


Fig. 7 Conceptual flow diagram between soil P fractions and their respective associated extractants. (Adapted from Tiessen et al., 1984; Tiessen & Moir, 1993). [] refers to a highly concentrated acid

other elements, P does not cycle between the biosphere (soil, plants, animals and the atmosphere), as is the case of nitrogen, so that very often soils exhibit low levels of phosphorous fertility and a high demand for P in most agroecosystems. This threatens the future depletion of P from the reservoirs (Cordell et al., 2009; Schröder et al., 2011). In addition, in agroecosystems, P can be lost through runoff and pass into lakes, rivers, and even oceans, causing contamination of aquatic ecosystems. In this context, the International Soil Information and Reference Center (ISRIC), in one of its latest reports presented by Batjes (2011), declares the need to initiate research programs aimed at improving the understanding of P behavior regarding its availability and dynamics in soils.

The laboratory methods developed to estimate the P available for the absorption by crops during growing season have made it possible to reasonably predict the yield of the crops or the productive response to a certain dose of P fertilizer (Ziadi et al., 2013). Therefore, these methods for estimating the available P should show the biological importance of each of the P fractions, when correlated by the available P with the different fractions that make up the P of soils. It would be expected that the estimated availability with the different methods (Olsen, Bray-P1, Mehlich-3) is a function of several of the fractions that make up the soil P and even that each method is associated with specific fractions. This information contributes to have a higher and efficient P utilization. Data related to the dynamics of P contributes to achieving a level of phosphorous fertility that allows reaching the maximum yields of crops and pastures, and not increasing (pollution), it beyond what is necessary or reducing it (degradation) once, it has reached.

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