

REVIEW

Iron oxides and organic matter on soil phosphorus availability

Óxidos de ferro e matéria orgânica na disponibilidade de fósforo no solo

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ABSTRACT

Continuous crop expansion has led to a growing demand for phosphate fertilizers. A sound knowledge of the dynamics of phosphorus, and its interaction with iron oxides and organic matter, can be useful to develop effective strategies for sustainable management, especially in a scenario of increasing shortage of mineral phosphate resources. In this paper, we review the relationship of phosphate to iron oxides and organic matter, and its effect on phosphorus availability. Crops typically obtain phosphate from weathered minerals and dissolved fertilizers. However, the amount of phosphorus present in the soil solution depends on the extent to which it is adsorbed or desorbed by iron oxides, which may be influenced by interactions with organic matter. Therefore, systems for fertilizer recommendation based on methodologies considering interactions between soil components such as oxides and organic matter, and the phosphorus sorption capacity resulting from such interactions (e.g. residual P analysis), may be more reliable to ensure efficient, rational use of phosphate.

Index terms: Goethite; hematite; phosphorus adsorption; phosphorus desorption; organic carbon.

RESUMO

A contínua expansão da produção agrícola tem levado a uma crescente demanda de fertilizantes fosfatados. O conhecimento da dinâmica do fósforo no solo e suas interações com óxidos de ferro e matéria orgânica podem ser úteis no desenvolvimento de estratégias eficientes para o manejo sustentável, especialmente em um cenário de crescente escassez de fontes de minerais fosfatados. Nesta revisão bibliográfica foi abordado a relação do fósforo com óxidos de ferro e matéria orgânica, e seu efeito na disponibilidade de fósforo. As culturas, normalmente, obtêm fósforo de minerais intemperizados ou fertilizantes dissolvidos. No entanto, a quantidade de fósforo presente na solução do solo depende das reações de adsorção e dessorção por óxidos de ferro, as quais podem ser influenciadas por interações com a matéria orgânica. Portanto, os sistemas de recomendação de fertilizantes com base em metodologias que consideram as interações entre componentes do solo, tais como óxidos e matéria orgânica, e a capacidade de adsorção de fósforo, resultantes de tais interações (por exemplo, análise de P remanescente), pode ser mais confiável para garantir o uso eficiente e racional de fertilizantes fosfatados.

Termos para indexação: Goethita; hematita; adsorção de fósforo; dessorção de fósforo; carbono orgânico.

INTRODUCTION

The world population is expected to rise from 7.2 billion at present to 9.1 billion by 2050; also, food demand is estimated to double over this period. The increasing food demand for food and shortage of fertilizer worldwide (Cordell et al., 2009; Grantham, 2012) has raised the need for efficient use of nutrients in order to meet the demands for increased agricultural production while ensuring environmental sustainability (Tenkorang; Lowenberg-DeBoer, 2008; Worstall, 2013). Brazil is expected to play a central role in this scenario (Tollefson, 2010), where traditional food production practices will have to be transformed into sustainable, healthy, economically efficient agriculture (Sachs et al., 2010).

Productivity can be boosted through appropriate crop nutrition, which involves a number of chemical, physical and biological processes occurring in soil that are influenced by mineralogy, organic composition, fertilization and soil management. The dynamics and kinetics of these processes are affected by interactions between clay fraction and organic components of soil, which influence nutrient availability to plants (Barber, 1995; Sposito, 2008). Phosphorus (P) is especially influential on agricultural production in countries such as Brazil (Novais; Smith, 1999), where soils—largely highly weathered Oxisols and Ultisols—are typically poor in this element. These two types of soil account for approximately 170 million hectares in 72 countries and

50% of all terrestrial agriculture in the world. In Brazil, they occupy 58% of the territory (IBSRAM, 1985), and are rich in iron and aluminium oxides, as well as in 1:1 phyllosilicates such as kaolinite; also, they contain substantial amounts of 2:1 minerals (Kämpf; Curi, 2003; Schaefer et al., 2008).

PHOSPHORUS

Phosphorus is one of essential elements and also one of the most important macronutrients for plant life. In fact, P plays a crucial role in phosphorylation and in the production of adenosine triphosphate by photosynthesis. It is the eleventh most abundant element in the terrestrial crust, with average content of 1050 mg kg^{-1} (Heirinch, 1980), and is found in more than 370 minerals (Huminicki; Hawthorne, 2002). However, only minerals in the apatite group contain enough P to justify its mineralization, whether as hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$], fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] or chlorapatite [$(\text{Ca}_5(\text{PO}_4)_3\text{Cl})$] (Hughes; Rakovan, 2002).

Morocco and Western Sahara in Africa, and China—mainly—in Asia, have 66% of all phosphate rocks in the world (Fixen, 2009). However, there are estimates that P mineral reserves will decay over this century if phosphate

demand and production continue to grow at the current rate (Vaccari, 2009). According to Cordell et al. (2009), extraction of phosphatic rocks might peak in 2030 and then decline in parallel to an increase in price.

Global use of P increased markedly from 1961 to 2007 (Metson; Bennett; Elser, 2012); however, the imminent P crisis has refocused international attention in recent years, especially, after the 2008 rise in the price of phosphate rocks by about 800% (Gilbert, 2009). This scenario has raised increasing awareness of the P shortage and, together with also increasing worries about the environmental impact of P pollution, has boosted research to improve the use of this element by reducing losses in the agro-ecosystem (Dawson; Hilton, 2011; Fernandez-Mena; Nesme; Pellerin, 2016).

PHOSPHORUS IN SOIL

Phosphorus in soil parent materials is primarily in mineral form (Figure 1) and especially as apatite (calcium phosphate) (Tiessen et al., 1984). The action of different factors (e.g., parent material, climate, slope, organisms, time) and processes (translocation, transformation, addition,

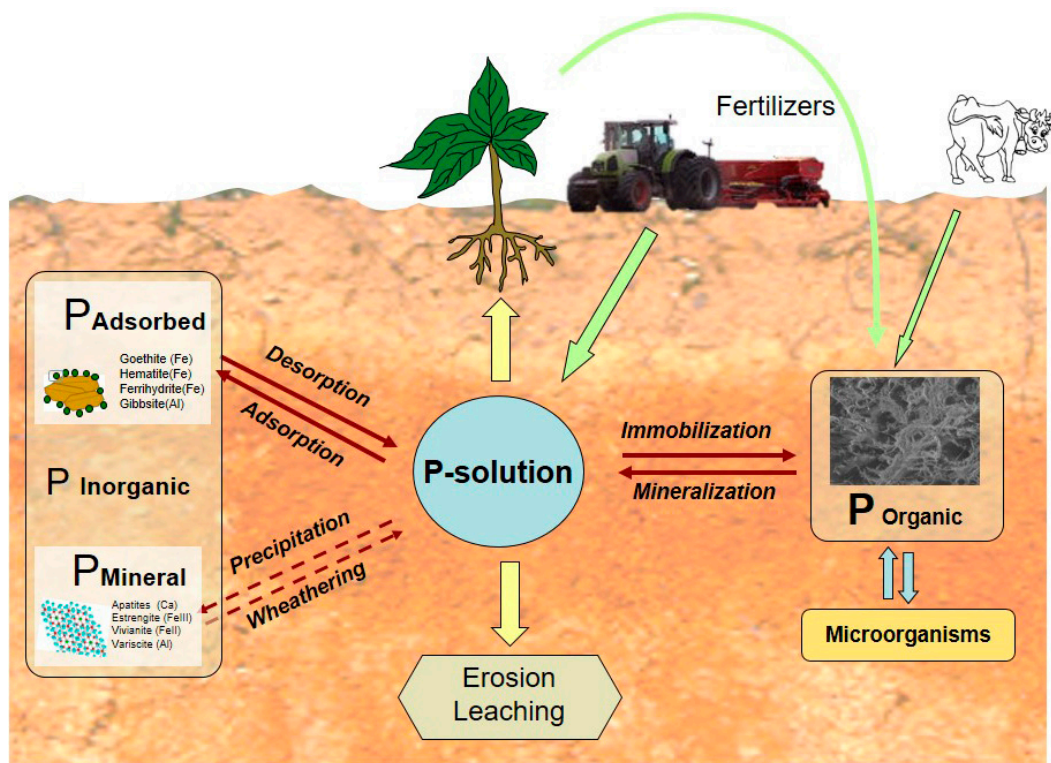


Figure 1: Phosphorus cycle in the environment.

removal) involved in soil formation drives the primary mineral to a thermodynamic equilibrium with stable pedogenic forms. In these transformations, P from primary minerals is released into the soil solution, from which plants can absorb it. Concomitantly, elements such as Ca, Mg, K and Na, silicates and carbonates, are leached. Transformation of Fe and Al into oxides, hydroxides or oxyhydroxides creates new functional groups for P adsorption.

Soil weathering causes dissolved phosphate from primary minerals to (a) precipitate with some cations and lead, for example, to the neo-formation of calcium phosphate in alkaline soils (Beck and Sánchez, 1994); (b) be adsorbed by functional groups of iron or aluminium oxides to form thermodynamically stable complexes (Bortoluzzi et al., 2015; Fink et al., 2016b) or (c) form biologically active organic compounds that remain as organic P in soil (Conte et al., 2002; Martinazzo et al., 2007; Dodd; Sharpley, 2015). Transformations between inorganic and organic forms of P are governed by factors affecting its mineralization and immobilization (e.g., microbial activity, moisture, physico-chemical and mineralogical soil properties) (Santos et al., 2008; Shen et al., 2011; Tiecher et al., 2012).

The dissolution of minerals or phosphate fertilizers, and the mineralization of organic components in soils, produce different anionic species (Lindsay et al., 1989) that are protonated to a variable extent depending mainly on pH (Hinsinger, 2001). Inorganic P species derived from orthophosphoric acid (H_3PO_4) such as H_2PO_4^- and HPO_4^{2-} are preferentially absorbed by plants. To what extent P remains in the soil solution depends on the degree to which it is adsorbed, desorbed and mineralized (Hinsinger, 2001; Fink et al., 2016b). Most tropical and subtropical soils in Brazil are low in available P because of strong phosphate adsorption on soil minerals (Almeida et al., 2003; Johnson; Loeppert, 2006; Bortoluzzi et al., 2015).

IRON OXIDES IN SOILS

Brazilian soils —particularly well-drained soils (Schaefer et al., 2008)— typically contain iron oxides in amounts ranging from a few grams to about 800 g kg^{-1} (Kämpf; Curi, 2003). Goethite and hematite are the most common pedogenic iron oxides, accompanied by maghemite and ferrihydrite in small amounts (Kämpf; Schwertmann, 1982; Schaefer et al., 2008; Carvalho Filho et al., 2015). The presence and abundance of these iron oxides depend on the conditions of soil evolution (Bortoluzzi et al., 2015). Thus, Oxisols, which are found near the Equator Line, contain aluminium oxides

(gibbsite) mainly. On the other hand, the oxides hematite, goethite, maghemite and magnetite prevail in tropical and subtropical Oxisols (Alleoni; Camargo, 1995). Ferrihydrite and lepidocrocite are found in poorly drained soils and exhibit greater, and faster phosphate adsorption (Wang et al., 2013) as a result of their nanometric size and poorly crystalline structure leading to a high specific surface area (SSA). The presence of goethite is favoured by the high organic matter contents and acid pH of the soils (Cornell; Schwertmann, 1996), which usually exhibit a higher affinity for this mineral than for hematite (Guzmán et al., 1994).

Structurally, hematite ($\alpha\text{-Fe}_2\text{O}_3$) consists of O layers superimposed on the z-axis, with Fe^{3+} occupying 66% of all octahedra formed and each octahedron sharing a face with another in the upper layer (Bigham et al., 2002). The (SSA) of synthetic hematite ranges from 2 to $115 \text{ m}^2 \text{ g}^{-1}$ (Cornell; Schwertmann, 1996; Barrón et al., 1988); whereas that of natural hematite does not exceed $47 \text{ m}^2 \text{ g}^{-1}$ (Torrent et al., 1994).

Goethite ($\alpha\text{-FeOOH}$) is the most abundant iron oxide. Its structure comprises a double network of $\text{FeO}_3(\text{OH})_3$ octahedra on the z-axis. The octahedron spaces juxtaposed to the network are empty as a result of Fe^{3+} occupying only one-half of all spaces; also, each double network is bonded to another by hydrogen bonding and by sharing the apical oxygen (Bigham et al., 2002). SSA for goethite ranges from 21 to $70 \text{ m}^2 \text{ g}^{-1}$ (Cornell; Schwertmann; 1996; Torrent et al., 1990).

Ferrihydrite is an iron oxyhydroxide precursor of hematite formation (Bigham et al., 2002) with a varying formula as a result of its also varying degree of hydration and of continuous reorganization of atoms in its structure. Michel et al. (2010) synthesized an ordered ferrihydrite with an increased crystalline structure [$\text{Fe}_{8.2}\text{O}_{8.5}(\text{OH})_{7.4} + 3\text{H}_2\text{O}$] and ferrimagnetic behaviour, but failed to directly observe this phase in soils. Because of its low atomic order, identifying this iron oxide requires using X-ray diffractometry with synchrotron radiation and supplementary techniques such as selective chemical extraction with ammonium oxalate and Vis-IR or Mössbauer spectroscopy. This mineral is present in soil and sediments predominantly in form of nanometric particles and hence with a high SSA [up to $400 \text{ m}^2 \text{ g}^{-1}$ according to Schwertmann; Taylor (1989)].

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is typically formed by oxidation ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$) of magnetite. This mineral is isomorphic to hematite and isostructural to magnetite; also, it possesses a cubic structure consisting of iron tetrahedra and octahedra in addition to empty spaces formed by effect of changes in Fe valence (Bigham et al., 2002;

Schwertmann; Taylor, 1989). A stoichiometric imbalance of spins makes maghemite magnetic. This mineral is present in amounts up to 297 g kg⁻¹ in soils (Souza et al., 2010; Costa et al., 1999); also, it can exhibit a high SSA depending on the particular formation conditions (Camargo et al., 2015).

PHOSPHORUS ADSORPTION ON IRON OXIDES

The high affinity of iron oxides for phosphate has for decades boosted research into the adsorption, desorption and diffusion dynamics of P, and its availability, in soils (Table 1). Some studies have revealed that the actual importance of P adsorption by other clay minerals has been underestimated. Thus, P is adsorbed less markedly by functional groups at the edges of 1:1 and 2:1 minerals, and this affects the amount and energy of P adsorption—and hence P availability to plants (Devau et al., 2009). Recently, Gérard (2016) revisited experimental studies on the topic conducted over the past 70 years and concluded that the P adsorption capacity of clay minerals may be similar to or even higher than that of iron and aluminium oxides depending on the SSA of the particular soil components.

Phosphorus adsorption and desorption depend on concentration, crystallinity, SSA, and the configuration

and concentration of hydroxyl groups on the surface of iron oxides. These factors in turn are affected by the formation route, parent material, degree of weathering, soil solution composition, drainage conditions and pH (Barrón; Torrent, 1996; Inda; Kämpf, 2005; Schaefer et al., 2008). Well-drained soils weathered to a variable degree have been found to differ in maximum phosphorus adsorption capacity (P_{max}) depending on the particular type of iron or aluminium oxide and on its properties (Curi; Franzmeier, 1984; Torrent et al., 1994; Barrón; Torrent, 1996; Almeida et al., 2003; Cessa et al., 2009; Lair et al., 2009; Broggi et al., 2010; Fink et al., 2014).

Adsorption of phosphate in the soil solution by functional groups in iron oxides results in the formation of surface complexes with no intercalated water molecules that are specifically adsorbed (Figure 2). These surface complexes are called “inner sphere complexes” to indicate that they are strongly bonded to highly structured mineral surfaces via covalent binding (Essington, 2003; Sparks, 2003; Sposito, 2008). Phosphorus is preferentially adsorbed by hydroxyl surface groups in iron oxides, which are protonated below pH 7–9 (zero-charge point; Table 2) (Essington, 2003; Sparks, 2003; Sposito, 2008). Hydroxylation occurs when Fe ions on mineral surfaces are exposed to water and complete

Table 1: Selected studies on phosphorus adsorption in soils.

Authors, year	Subject of the study
Lewis and Quirk, 1967	Phosphorus diffusion and uptake by plants grown in different soils
Barrow, 1974	The relationship between P addition and adsorption in soils
Bhat et al., 1973	The relationship between P desorption in soil and diffusion to plant roots
Barrón et al., 1988	Phosphorus adsorption in various soils containing aluminous hematite
Torrent et al., 1990	Phosphorus adsorption and desorption onto goethite of variable morphology
Torrent et al., 1992	Stages of P adsorption onto natural goethite
Mesquita and Torrent, 1993	Phosphorus adsorption in soils of diverse mineralogy from the Brazilian Cerrado
Afif et al., 1995	The influence of organic matter and specific surface area on P adsorption in Brazilian soils
Fontes and Weed, 1996	The effect of mineralogy and specific surface area on P adsorption in Brazilian soils
Kreller et al., 2003	Competitive adsorption of phosphate and organic matter on iron oxides
Liptzin and Silver, 2009	The reducing effect of iron oxides on P availability in soils under high carbon additions
Pinto et al., 2013	Phosphorus adsorption and desorption as indicators of soil fertility
Bortoluzzi et al., 2015	The role of hematite and goethite in P adsorption in subtropical soils
Fink et al., 2014; 2016a; 2016b	Phosphorus adsorption, desorption, diffusion and absorption in soils rich in goethite, hematite or kaolinite.

its coordination with hydroxyl groups (Stumm, 1992). Hydroxyl groups may be coordinated by one (type A, $\equiv\text{Fe}-\text{OH}^{-0.5}$), two (type B, $\equiv\text{Fe}_2-\text{OH}^0$) or three Fe atoms (type C, $\equiv\text{Fe}_3-\text{OH}^{+0.5}$), corresponding to hydroxyls of simple, double or triple coordination (Figure 2), respectively (Russel et al., 1974; Essington, 2003; Sparks, 2003; Sposito, 2008). Type A hydroxyls are the most easily protonated (Fontes et al., 2001) as a result of the charge balance in Fe—O bonds, where the electron cloud of oxygen is more electronegative than in doubly or triply coordinated hydroxyls. Protonation of these functional groups confers Lewis acid properties, with the metal cation reacting with empty electronic orbitals. These sites are very reactive because a positively charged water molecule ($\equiv\text{Fe}-\text{OH}_2^{+0.5}$) is very unstable and easily exchanged with an organic or inorganic anion in solution. Protonation weakens the Fe—OH bond by displacing the electron cloud of oxygen to the hydrogen side (Fontes et al., 2001). As a result, hydroxyl protonation triggers two different processes in P adsorption, namely: (a) protonated surfaces generate a positive electric field that attracts phosphate ions; and (b) phosphate replaces protonated hydroxyl groups. The phosphate may be absorbed in monodentate or bidentate form depending on the number of OH groups in the phosphate that are bonded to Fe atoms, or in binuclear form when two OH phosphate groups are adsorbed by two Fe atoms (Figure 2).

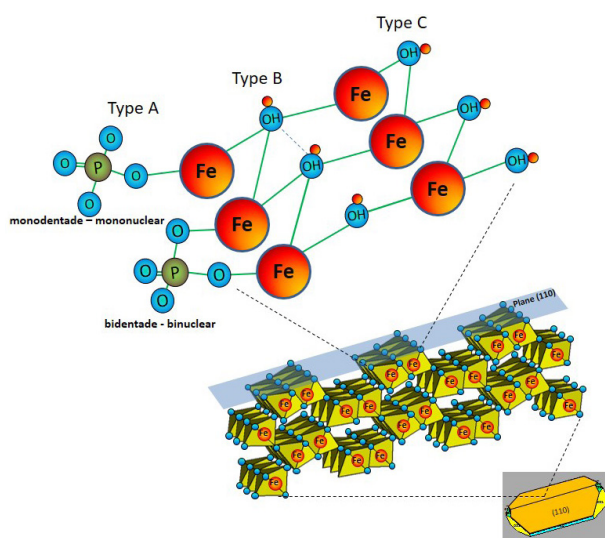


Figure 2: Phosphorus adsorption in monodentate/mononuclear and bidentate/binuclear forms onto goethite surfaces.

Table 2: Zero-charge point (ZCP) for major organic and inorganic soil components. Adapted from Essington (2003), Sparks (2003) and Sposito (2008).

Component	ZCP
Organic matter	3.0–9.0
Hematite [$\alpha\text{-Fe}_2\text{O}_3$]	6.7–8.5
Goethite [$\alpha\text{-FeOOH}$]	7.8–9.0
Magnetite [Fe_3O_4]	7.0
Gibbsite [$\text{Al}(\text{OH})_3$]	9.0
Quartz [$\alpha\text{-SiO}_2$]	2.0–3.0
Kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$]	4.6–4.7
Montmorillonite	2.5

Thermodynamically, all adsorbed phosphate may be desorbed (Barrow, 1983a, 1983b); however, the desorption kinetics depends on the interplay of various factors such as the types of clay minerals where the phosphate is adsorbed (Chintala et al., 2014). According to Parfitt (1989), the binding energy increases in the sequence monodentate > bidentate > binuclear complexes and the probability of phosphate desorption increases in the reverse sequence.

Barrón and Torrent (1996) estimated the concentration of monocoordinated hydroxyl groups in various goethite and hematite faces, which adsorb P via binuclear complexes. Adsorbed phosphate can increase the proportion of binuclear complexes through so-called “phosphorus aging” (Santos et al., 2008; de Campos et al., 2016). This accounts for the reported fact that phosphate diffuses with time, through defects on the mineral surface, thereby significantly increasing P_{max} and decreasing desorption (Barrow, 1985; Torrent et al., 1992; Barrow, 1987). Willian and Reith (1971) found 8–20% of all P added to soil to remain available one year after application, and the proportion to decrease to 2.7% after 6 years.

Barrón et al. (1988) and Torrent et al. (1994) found P_{max} for hematite to range from 0.8 to 4.1 $\mu\text{mol P m}^{-2}$ in natural samples and from 0.2 to 3.3 $\mu\text{mol P m}^{-2}$ in synthetic samples, depending on the size, morphology, and degree of Al substitution in its crystal structure. In goethite, P_{max} ranges from 1.62 to 3.13 $\mu\text{mol P m}^{-2}$ (Torrent et al., 1994); in ferrihydrite, it is close to 7 $\mu\text{mol P m}^{-2}$ (Guzman et al., 1994). Although the average phosphate adsorption per surface area unit is similar for goethite and hematite, the goethite typically adsorbs more P as a result of its higher SSA (Torrent et al., 1994). This is consistent with the results of Parfitt (1989) and Wang (2013), who found P adsorption to decrease in the mineral sequence ferrihydrite > goethite > hematite. Ferrihydrite can considerably alter P_{max} in soil, even at

low concentrations in well-weathered soils (Johnson and Loeppert, 2006; Ranno et al., 2007; Fink et al., 2014). Fink et al. (2016a) examined the effect of SSA on P adsorption in two Oxisols with similar contents in iron oxides and found P_{\max} to be twice greater in the soil where goethite prevailed over hematite.

INTERACTION OF ORGANIC MATTER WITH IRON OXIDES AND PHOSPHORUS

Organic matter is an important influential factor for chemical, physical and biological soil properties. Negatively charged functional groups in organic substances (e.g., carboxyl, phenol) can interact with positively charged minerals such as iron oxides and alter phosphorus adsorption as a result (Schwertmann; Kodama; Fischer, 1986; Liu et al., 1999). In fact, adsorption of organic functional groups onto iron oxides can (a) promote anion adsorption via cation bridges (Al^{3+} and Fe^{3+}); (b) increase SSA by inhibiting mineral crystal growth; (c) alter surface charges; (d) boost competition with other anions for adsorption sites; and (e) cause adsorbed anions to be desorbed (Hinsinger et al., 2011; Borggaard et al., 2005; Guppy et al., 2005; Hinsinger, 2001). These phenomena are illustrated in Figure 3.

As can be seen, condition I in the figure increases P adsorption (Yaghi; Hartikainen, 2013); however, if it decreases the P concentration in the soil solution, then the bond is reversible. In condition II, the presence of organics acids inhibiting crystal growth increases SSA in iron oxides and hence P adsorption (Barrón et al., 1988). However, Mikutta et al. (2006) found citrate (an organic anion) to block goethite pores and prevent phosphate diffusion into mineral defects as a result.

Organic acids in soil also can compete for P adsorption sites (condition IV; Schwertmann; Kodama; Fischer, 1986; Bayon et al., 2006; Redel et al., 2007; Zamuner et al., 2008) or, if previously adsorbed, alter the surface charge of iron oxides and cause phosphates to be electrostatically repelled (condition III; Antelo et al., 2007). Phosphorus sorption is decreased in both cases.

Several studies have shown humic acids to affect the reduction of phosphorus adsorption (Sibanda; Young, 1986; Andrade et al., 2003; Antelo et al., 2007) and hence the increase in P availability (Pavinato; Merlin; Rosolem, 2008). Recently, Yan et al. (2015) studied the phosphorus adsorption capacity of humic acid complexes of ferrihydrite and goethite under variable conditions of pH and ionic strength. The authors found P adsorption to

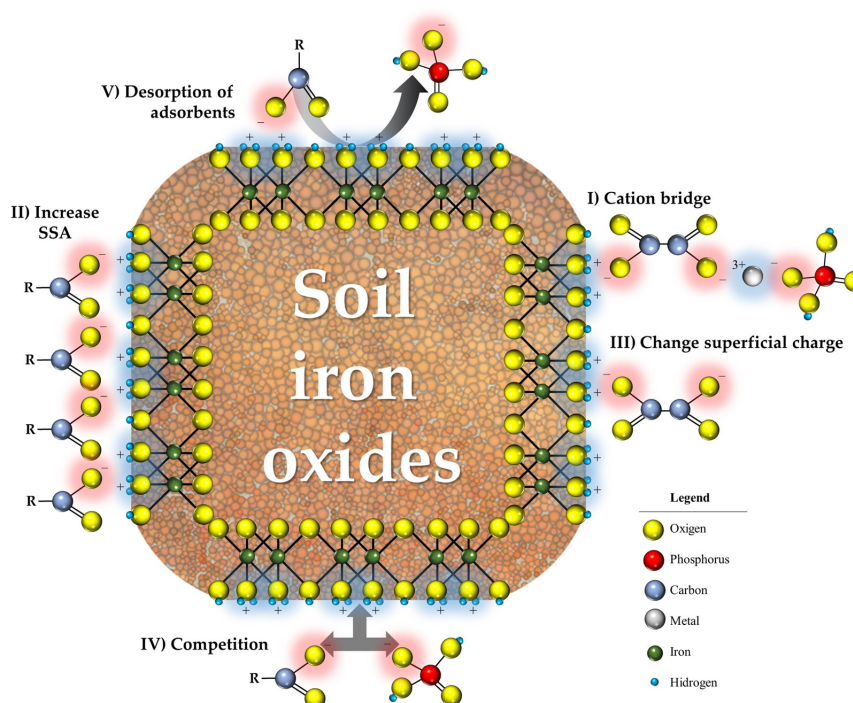


Figure 3: Effects of organic carbon on phosphorus adsorption onto iron oxides.

be substantially reduced by iron oxides in the presence of organic compounds. However, Borggaard et al. (2005) and Guan, Chang and Chen (2006) found the adsorption energy of P onto iron oxides to be much higher than that of organic acids, being that the natural concentration of organic carbon in soil had no effect on P adsorption. These results are consistent with those of Afif et al. (1995), who found the concentration of low-molecular weight organic acids in extracts from P-containing soils to increase; this suggests that the acids may delay but not prevent P adsorption. The previous results make phosphate desorption by organic matter unlikely (condition V in Figure 3), even though Souza et al. (2014) found the addition of citrate to soil to increase P desorption.

Some studies have revealed that increasing the organic matter content of soil does not decrease P_{\max} (Boschetti; Quintero; Benavidez, 1998; Valladares; Pereira; Anjos, 2003; Fink et al., 2014, 2016a); others, however, suggest that organic matter affects the binding energy of adsorbed P (Kreller et al., 2003, Rheinheimer; Anghinoni; Conte, 2003) and can therefore increase the efficiency of phosphate fertilizer—possibly as a result of phosphate adsorption with little energy (e.g., via cation bridges; Guppy et al., 2005; Figure 3).

Some recent studies have addressed the dynamics of P adsorption in the presence of C added in biochar forms (Yao et al., 2012; Lin et al., 2012; Xu et al., 2014). Biochar is a product of the pyrolysis, with oxygen limitation, of biological materials (Cernansky, 2015) whose characteristics depend on the production conditions (viz., residue composition, temperature, time, oxygen supply during burning). Biochar has proved to be an efficient sorbent for organic pollutants by effect of its high SSA and porosity (Lehmann, 2007; Glaser; Lehmann; Zech, 2009; Cornelissen et al., 2005). An increased number of phenol, hydroxyl, carboxyl and quinone groups can increase negative surface charge (Cohen-Ofri et al., 2006) and decrease P adsorption as a result. However, this assumption requires further investigation in order to confirm the favourable and adverse effects of biochar on tropical soils.

CONCLUSIONS

The growing global demand for food and fibre, and the impending shortage of phosphate mineral reserves, have made it indisputably necessary to understand the processes and mechanisms governing phosphorus availability in soil. Iron oxides and organic matter are the soil constituents most strongly affecting the reactions and rate of phosphorus adsorption and desorption, especially in highly weathered

soils. A sound knowledge of the interaction of iron oxides and organic matter with soil P is essential with a view to developing effective nutrient management strategies for agro-ecosystems allowing crop productivity to be maintained or even increased with a concomitant reduction in phosphate fertilizer use. Recent studies in highly weathered Brazilian soils have shown that organic matter and various iron oxides have a direct effect on P adsorption/desorption and availability (Bortoluzzi et al, 2015; Fink et al., 2016b, 2014). As a result, fertilizer recommendation systems based on soil buffering categories established in terms of clay content may be ineffective. Therefore, systems for fertilizer recommendation based on methodologies considering interactions between soil components such as oxides and organic matter, and the phosphorus sorption capacity resulting from such interactions (e.g., residual P), may be more reliable to ensure efficient, rational use of phosphate fertilizers.

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