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On the tropical soils; The influence of organic matter (OM) on phosphate bioavailability

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ABSTRACT

Application of organic manure (OM) and crop residues in agricultural soils can potentially influence positively or negatively the availability of soil phosphorus (P) through soil mineralization, sorption, or desorption of soil-bound P. Traditionally, the addition of OM can reduce the capacity of the soil colloids to adsorb P, thus increasing the release of P in soil solution, but also added OM can increase the adsorption site and increase the fixation or sorption of P to soil colloids, thus reducing the availability of P in soil solution and loss to the environment. The highly weathered tropical soils (HWTS) are susceptible to P insufficiency because HWTS have high P adsorption and fixation; this is mainly due to high concentration of P adsorbent. The main P adsorbents in HWTS include Al, Fe, Ca, and clay minerals, which are principally the same binding or adsorbent for OM compounds, but in excess, are toxic (Al and Fe) to crops. Thus, the presence of OM in HWTS can compromise the adsorption and availability of P in agricultural soils following phosphatic fertilizer applications. In this study, the influence of OM on P adsorption and availability was characterized to have a clear understanding of how OM influences P availability in agricultural soils, especially in highly weathered tropical soil. It is clearly outlined that the application of OM and crop residues can positively or negatively influence the availability of P in agricultural soils for plant uptake and dictate the P that is available for loss to the environment. Thus, the addition of organic matter as a strategy to increase P bioavailability for plant uptake must be treated with care because their contribution is not strait forward to be positive in many agricultural soils.

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1. Introduction

Phosphorus (P) is among the essential macronutrients required by plants and animals in large quantities and their role are nonreplaceable by other elements. P is vital for plant and animal growth, cell division, and growth. In addition, P as a nucleic acids component is vital in biological energy transfer processes. The soil availability of P depends on the interaction of P with other soil components, which can tie up P to complex forms, thus making P unavailable for plant uptake (Pejin et al., 2012). In the soil, phosphorous (P) is converted from soluble P to insoluble P through two critical processes such as adsorption and precipitation. P can adsorb to clay minerals and iron (Fe)- or Aluminium (Al)-oxides, especially in acidic soils. The precipitation of P with Al, Fe, or Ca ions to form Fe-/Al-/Ca-phosphates in acidic and alkaline soils tend to fix 70-90% of added P from phosphatic fertilizer or mineralizable materials, thus leading to reduced plant-available P. This scenario has been observed to reduce the fertilizer efficiency and necessitated the increased P fertilizers application rates in agricultural fields (Fink et al., 2016; Guppy et al., 2005; Yu et al., 2013). On the other hand, the additional amount of P added may enhance aquatic ecosystems' contamination and eutrophication. leading to increased production cost and unprofitable farming (Ohno et al., 2007: Stanimirovic et al., 2019).

Most soils in Sub-Saharan Africa are highly weathered soils with high Al and Fe oxides accompanied with high clay content, which hasten P fixation and sorption. Generally, there are different factors which influence P sorption, such as soil texture, pH, clay mineralogy, concentration of Al and Fe oxide, and soil organic matter (SOM) (Shao and Chu, 2008). However, there are many factors and adsorbents of P in agricultural soils Fe- and Al- (hydr)oxides are the main P adsorbents in tropical soils (Fink et al., 2016). Application of OM in agricultural soil can increase or decrease P sorption on soil colloids depending on the OM types, inherent P concentration, and concentration of additional P added from organic and inorganic fertilizer (Bortoluzzi et al., 2015; Chintala et al., 2014). Negatively, SOM can reduce or inhibit P adsorption to soil colloids because both are negatively changed and utilize the same binding sites in soil colloids (Antelo et al., 2010). The ionization of OM results in to release of negatively charged functional groups such as carboxylic acid, hydroxide, and phenol groups. Accordingly, the quantity and nature of soil organic matter have a very significant influence on P availability for growing plants. While many soils contain important amounts of organic phosphorus, the influence of organic matter on phosphorus availability is not clear and not well correlated (Broadbent, 1986). Thus, the application of organic manure or any other materials that can extensively increase the availability of soil organic matter can positively or negatively influence the availability of P, especially in tropical soils where few studies have been conducted. The study by Yu et al. (2013) found that application of poultry manure compost or organic fertilizer increased the available phosphorus (P) and

organic matter content in all soils; however, the quantity of P and organic matter decreased with an increase in incubation time. The organic materials added via the treatments reduced the strength of P adsorption in the soil derived from basalt. For soils derived from granite and river alluvial deposits, the strength of P adsorption declined after poultry manure compost was added but increased after the application of organic fertilizer. That means the role or influence of OM to P availability may be area and soil mineralogy dependent or specific.

Generally, the concentration of P in agricultural soils especially in the tropics which are highly weathered, P is available in deficient amount compared to optimum P requirement for better crop growth. The low amount of available P is exacerbated by either due to increased precipitation by Ca, Fe, and Al or adsorption to metal oxides and ions such as Cd, Pb, Cr, etc. To raise and sustain the fertility status of soils, large input of inorganic P fertilizer is required, which may result in the excessive buildup of soil-bound P and saturation of soil with P. Thus, added P, through fertilization, will then not be able to bind to the soil colloids anymore. Interaction of OM with P in the soil influences the amount of available P in solution, which has significant effects on plant P availability, but also P leaching and eventually eutrophication of ground and surfaces water resources (Guppy et al., 2005). Despite the great role of OM in the soil for plant growth and microbial activities, its role in the availability of applied phosphatic fertilizers has been contradictory over different research studies; some researchers reported decreased P sorption while others reported increased P sorption upon OM addition (Chintala et al., 2014; Fink et al., 2016; Gérard, 2016; Guppy et al., 2005). It is unclear to what extent SOM content is a relevant influencer of P-availability in highly weathered tropical soils, relative to other factors like pedogenic Fe and Al content and soil pH. Frequently, in the topsoil high degrees of phosphate saturation exist and it is not known to what extent mediation of SOM content on P-sorption is effectuated at different degrees of phosphate saturation. This review characterizes how soil organic matter influences the availability of P from added phosphatic fertilizer and relates to P loss to the environment.

2. Review scope methodology

To achieve preparation of this review, a literature search was conducted for peer-reviewed publications and reports on the role of organic matter on nutrient availability, sorption and desorption of P, nutrient loss and nutrient dynamics, soil fertility management in highly weathered tropical soils from a different databases such as Web of Science, PubMed and Science Direct. The search was conducted using different keywords such as "nutrient saturation and losses", "sorption and desorption", water eutrophication", "metal cations" and "impact of metal cations on availability of P", "environmental challenges". Furthermore, the search was narrowed down to a precise definition concerning the role of soil organic matter on the availability of P for plant uptake on how negatively and positively influence the P availability.

3. Phosphate cycle agricultural soils

For a better thought of the P dynamics and its availability, it is vital to comprehend the cycle of P in the soil. Generally, P in agricultural soils is highly reactive, it does not exist in its pure form, it reacts with oxygen to form phosphate (PO_4^{3-}) a chemically stable chemical form. The existence of phosphate in the soil depends on the soil pH and prevailing forms are termed jointly orthophosphate (o-P) hereafter. The o-P in the soil is present in several pools, that are constantly subject to internal cycling. Primary phosphates rocks or minerals through weathering they release P to soil solution which is readily available for plant uptakes (Fink et al., 2016). Apatite mineral $(3[Ca_3(PO_4)_2]CaX_2)$ is usually the primary source of P from the parent material where X is anions (F⁻, Cl⁻, OH^{-} or CO_{3}^{2-}). The deposits are rich in apatite (e.g., rock phosphate), which are in sediments deposited at the bottom of ancient seas; the rock phosphate reserves are on the order of 5×10^{13} kg, making a total of 12×10^{12} kg P based on the average P content of 10% (Stevenson and Cole, 1999). Besides, phosphate can be added to the soil from inorganic fertilizers such as triple superphosphate (TSP) or organic fertilizers such as farmyard manure, pig slurry, and composts. Rocks phosphates from various sources are treated with inorganic acids (e.g., sulphuric and phosphoric acid) to produce more soluble phosphate fertilizer. For example, 'Super phosphate' fertilizer is produced by mixing approximately equal quantities of 60–70% H₂SO₄ and rock phosphate.

$$\begin{array}{rl} 3[Ca_{3}(PO_{4})_{2}CaF_{2} \ + \ 7H_{2}SO_{4} \ + \ 3H_{2}O \ \leftrightarrow \ 3Ca(H_{2}PO_{4})_{2}H_{2}O \\ & + \ 7CaSO_{4} \ + \ 2H_{2}O \ + \ 2HF \end{array} \tag{1}$$

When gypsum is removed with excess H_2SO_4 concentrated 'Superphosphate', 20% P is produced.

Even though the total reserve of phosphate rock appears to be appreciable, phosphate is a limited resource when considered in world demand. Thus, P-deficiency is likely to intensify soon due to a shortage of mineable phosphate, and crop yield will be limited by P release from the insoluble form in the soil. Due to existing current forecasts as to when the shortage will develop vary considerably, depending on which the estimates are made for unknown reserves and the P content of the rock. At the present mining rate (about $7\times 10^{10}\,\text{kg}$ of rock per annum), reserves will be depleted in about 700 years. However, if the usage of P fertilizer continues to grow at current rates of 0.261 billion tons per annum (Akhtar et al., 2017), the known reserves will be depleted in a much short time (about 100 years). Therefore, recycling soil fixed P and reusing waste materials with high P content as fertilizer, i.e., sewage sludge, manure, compost, crop residues, and slurry, should be introduced (Stevenson and Cole, 1999). To form secondary P minerals, dissolved o-P can precipitate metal cations such as Ca²⁺, Fe³⁺ Al³⁺, K⁺ from primary minerals and fertilizers. In acidic soils, mainly Al-P and Fe-P-based minerals dominate (e.g., strengite), while Ca-P is predominantly in alkaline soils.

In contrast, o-P can be removed from the soil through crop uptake, soil erosion, leaching, and water runoff (Vanden Nest et al., 2016). Dissolved o-P can also be transformed by plants and microorganisms to organic P forms such as ATP and DNA (Bortoluzzi et al., 2015). The o-P transformation between organic and inorganic forms is determined by different factors which determine the organic matter mineralization, i.e., microbial activity, soil moisture content, chemical soil properties (Tiecher et al., 2012). The soil P dynamics include soils, plants, and microorganisms. In standard systems, all utilized P by plants is put back in the soil by incorporating animal and plant residues. As the primary source and reservoir of phosphorus are the rocks phosphate or other rock deposits, these gradually release o-P into the ecosystems by dissolution into soil pore water as inorganic o-P.

4. Significant phosphorus reactions in soil

4.1. Speciation of orthophosphate ions

In nature, phosphate exists in three o-P forms, depending on the soil pH, i.e., $H_2PO_3^-$, HPO_4^{2-} and PO_4^{3-} . These chemical forms usually combine up to three positive changed ions like potassium (K⁺), hydrogen (H^+) , Al^{3+} , ammonium (NH_4^+) , Fe^{3+} , and Ca^{2+} . The amounts of various o-P ions in the soil solution are determined by soil pH, availability of metal cations, i.e., Fe³⁺, Al³⁺, Ca²⁺, and other competing ligands (e.g. Citrate and oxalate) in the soil solution (Hinsinger, 2001; Sato, 2003). For example, at pH $_{(H2O)}$ 7.2, there are the same amount of $H_2PO_3^-$ and HPO_4^{2-} in soil solution (Fig. 1). At pH below 7.2, $H_2PO_4^-$ is dominant, while at pH above 7.2, HPO_4^{2-} becomes a significant species. At soil pH 5.0-8.0, the most favorable pH range for crop growth, the H⁺ is available in small concentrations; thus, the amount of o-P in $H_2PO_3^-$ and HPO_4^{2-} forms is minimal compared to total P in soil colloids. Therefore, the available P in soil solution will combine with supplementary positive ions in the soil such as Ca^{2+} , Al^{3+} and Fe^{3+} to form stable components, such as in acidic (i.e., Fe-P and Al-P) and alkaline (i.e., Ca-P) soil conditions (Barrow, 2020, 2017: Kruse et al., 2015).

The speciation of P ions in the soil solution also relies on the availability of metal cations such as Mg²⁺, Ca²⁺, Al³⁺, and Fe³⁺, which have a strong tendency to react and form complicated species, e.g., Fe³⁺ +H₂PO₄ \leftrightarrow FeH₂PO₄2⁺. Also, the availability of these meatal cations depends on soil pH. In acidic soil (pH < 6), the availability of Al³⁺ and Fe³⁺ increases while Ca²⁺ and Mg²⁺ is dominant in neutral and alkaline soils.

The presence of other competing ligands in the soil solution controls the P speciation. For example, the occurrence of organic ligands such as citrate and oxalate compete with o-P ions to form complexes with metal cations which in turn determine the P species availability (Guppy et al., 2005; Hinsinger, 2001). Therefore, phosphorus can be found in different positively or negatively charged ions or uncharged species in addition to the o-P ions in the soil solutions.

4.2. Precipitation-dissolution of phosphate minerals

The o-P ions precipitate readily with metal cations such as Al^{3+} , Fe^{3+} , Mn^{2+} , Ca^{2+} , and Mg^{2+} , to form phosphate minerals. The



Fig. 1. Description of how soil pH influences the distribution of orthophosphate species in soil solution (Sato, 2003).

phosphate mineral produced depends on soil pH because it determines the occurrence and abundance of metallic cations in the soil solution that can precipitate with o-P. Hence, in neutral to alkaline soils, o-P ions are complexed as Ca-phosphates, i.e., soluble apatite (Fink et al., 2016; Sato, 2003).

$$\begin{aligned} \mathsf{Ca}^{2+} + \mathsf{H}_2\mathsf{PO}_4^- + 2\mathsf{H}_2\mathsf{O} &\leftrightarrow \mathsf{Ca}\mathsf{HPO}_4{\cdot}2\mathsf{H}_2\mathsf{O} \text{ (brushite)} \\ + \mathsf{H}^+ \log k &= 0.63 \end{aligned} \tag{2}$$

In conflict, o-P ions react and precipitate as Fe-P and Al-P in acidic soils to form strengite, vivianite, and variscite.

$$\begin{array}{l} \text{Al}^{3+}_{(aq)} + \text{H}_2\text{PO}_4^{-}_{(aq)} + 2\text{H}_2\text{O} \leftrightarrow \text{Al}(\text{OH})_2\text{H}_2\text{PO}_{4(s)} \\ + 2\text{H}^+\log\text{K} = -2.56 \end{array} \tag{3}$$

The equilibrium of P precipitation and dissolution governs the solubility and availability of Phosphate minerals along with pH, concentration of o-P and metal cations. For example, considering the equation 4 below which applies for hydroxyapatite:

$$Ca_{5}(PO_{4})_{3}OH + 7H_{3}O^{+} \leftrightarrow 3H_{2}PO_{4}^{-} + 5Ca^{2+} + 8H_{2}O$$
(4)

Thus, the dissolution of the hydroxyapatite can be increased if protons are supplied or if o-P or Ca²⁺ ions are eliminated from the soil solution. Adsorption of o-P ions by other soil constituents may well thus encourage the dissolution of calcium-phosphate.

4.3. Adsorption-desorption of o-P ions on soil colloids

Sorption and desorption reactions in the soil equilibrate o-P in solids with that in soil solution. The o-P can adsorb to the surfaces and edges of hydrous oxides, clay minerals, and carbonates by replacing OH⁻ (De Bolle, 2013). Adsorption of o-P in the soil is usually enhanced by the presence of metal oxides of Fe or Al, collectively named sesquioxide, organic complexes of Al and Fe, edges of silicate clays, and calcite.

Added inorganic o-P can be adsorbed weakly (electrostatically) or strongly (covalent bond) onto these variables charged surfaces. As mostly o-P species in the soil solution are negatively charged, o-P will be sorbed to soil constituents that bear positive charges such as hydroxyl, carboxyl, clays groups. Metal hydroxides have a variable charge. Their ability to adsorb anions such as P ions upsurge with diminishing pH due to higher protonation at low pH (Barrow, 2017; Barrow and Debnath, 2015). Both Aluminium and iron oxides have 7 and 10 points of zero charges, which creates their surfaces net positively charged over the whole pH range, usually encountered in the soil (i.e., 3.5-9.5). Weakly crystalline Al, usually determined as NH₄-oxalate extractable Al (Al_{ox}), is effective at adsorbing P selectively in the presence of competing anions such as Cl⁻, NO³⁻ and SO₄²⁻. The Al_{ox} is also abundant and has a relatively higher point of zero charges (PZC). Therefore, the o-P adsorbed by Al can be steady in a wide pH range.

Furthermore, the o-P sorption and desorption vary in concentration, crystallinity, and surface area on the soil colloids. It is observed that there is preferentially adsorption of o-P by hydroxyl surface groups in Fe hydroxides as they are protonated below pH 7–9 (Hinsinger, 2001; Fink et al., 2016).

5. Interaction of organic matter interactions with soil mineral surfaces

The presence of SOM is regarded as being critical for soil function and soil quality (Jarvie et al., 2019). The positive influences of SOM result from several complex interactive edaphic factors. Some of the SOM's effects on soil functioning include improvements in soil structure, absorption and retention of pollutants, aggregation, cycling and storage of plant nutrients, and soil biodiversity. SOM increases soil fertility by providing cation exchange sites and acting as the reserve of plant nutrients, such as nitrogen (N), phosphorus (P), and sulphur (S), together with micronutrients. SOM is characteristically approximate to contain 50% C. The terms soil organic carbon (SOC) and SOM are often used interchangeably, with measured SOC content often serving as a proxy for SOM. The concentration of SOM in soils generally ranges from 1% to 6% of the total topsoil mass for most upland soils (Troeh and Thompson, 2005)

SOM fractions; Different techniques have been proposed to separate soil samples into different SOM fractions with distinct physical and chemical features, based on various stabilizing mechanisms and soil functions (von Lützow et al., 2007). The most used technique is physical fractionation since the physical conformation of OM, and its location in the soil matrix explains its protection of SOM against mineralization. Also, as with chemical methods, physical fractionation may create fewer artefacts.

Physical fractionation has consequently been very frequently used in soil studies to evaluate SOM accessibility. Splitting OM fractions by physical methods can separate SOM fractions that differ in turnover times, significantly incompletely decayed plant litter in the non-aggregate related light fraction from mineral connected SOM and intra-aggregate particulate organic matter (iPOM) (Whalen and Hendershot, 2007). Physical fractionation usually entails various degrees of soil dispersion size fractionation (Torn et al., 2009), followed by fractionation according to density or aggregates to separate SOM based on their size and difference in density (Sollins et al., 1996).

5.1. Free particulate organic matter (POM)

The SOM can be classified as mineral-free or mineral-associated OM (June et al., 1990). The former is composed of either free or occluded (fPOM). The fPOM is a fraction containing a partially decayed plant substance, fungal hyphae, spores, and pollen grains, with a particle size ranging between 53 and 2000 μ m and often covered with soil particles (Plante and McGill, 2002). It is a primary source of food and energy for micro-organisms and nutrients for plant growth since fPOM is usually easily decomposable. The fPOM, as does bulk SOM, increases aggregate firmness, water infiltration, and soil aeration, cation exchange capacity, and buffers soil pH binds environmental pollutants such as heavy metals and pesticides, though to a more minor degree than bulk SOM because of fPOM's relatively tiny surface area due to its larger size. The fPOM is very vulnerable to the changes in soil management, and, consequently, its variation throughout time is more indicative of the effect of management practices than total organic matter (Fabrizzi et al., 2003).

5.2. Dissolved OM

Dissolved organic matter (DOM) consists of all organic compounds present in soil solution and is the most active and mobile form of SOM. DOM is defined as SOM with a size limit of 0.45 μ m. According to Lützow et al. (2007), DOM can be obtained by using several extracts ranging from cold water to aqueous solutions of different ionic strength to simulate the soil solution. The extracts from agricultural fields and forests differ in DOC content and quality. Agricultural fields' DOC was faster degradable as indicated by high experimental OC mineralization values than DOM extracted from forest floors. They concluded that possibly this reflects a quicker turnover of DOM in agricultural soils than in forest soils (Chenu and Plante, 2006).

5.3. Mineral-bound OM

Mineral-bound OM can be defined as all OM adsorbed to minerals or entrapped in small micro aggregates (Chenu and Plante, 2006). Mineral binding of OM is a medium of OC stabilization and is the central aspect of soil functioning (Mikutta et al., 2010; Schneider et al., 2010). Generally, organic molecules that form strong chemical bonds with mineral surfaces become less prone to desorption or mineralization and become relatively resistant to microbial mineralization. OM-mineral bonds occur through hydrogen bonding, anion and cation exchange, ligand exchange, and van der Waals bonding. The relative amount of SOC associated with the mineral-bound OM fraction is highly variable and ranges from less than 1 to more than 100 g OC kg⁻¹ soil. This wide distribution can partly be due to the (1) techniques used for dispersing aggregates and (2) differences in density cut-offs (1.6–2.2 g/cm) used for isolating clav-sized fractions (Kögel-Knabner et al., 2008). Apart from these methodological issues, variations in the percentage of OC in the mineral bound OM fraction can be mainly due to variations in the amount and type of minerals. For instance, soil richer in short-range ordered Fe-oxyhydroxides and Alsilicates show more significant concentrations in mineral-bound OC fractions than those soils richer in poorly reactive clay minerals. Short-range ordered Al and Fe sesquioxide contents seem to be strongly associated with OC stabilization in many soil systems. In addition, Fe(III) and Al form strong complexes with humic substances. They are probably the essential cations for bridging the negative charge of mineral and organic surfaces in well-drained, neutral to acidic soils.

5.4. Organic matter stabilization

Stabilization of OM is a process or mechanism that leads to persistent turnover times of OM in the soil because of protecting OM from mineralization. Generally, stabilized OM is older than unstabilized OM. However, turnover times of stabilized OM are not absolute values because they depend on the area's environmental conditions and soil properties (e.g., climate, soil mineralogy) (von Lützow et al., 2007). Selective enrichment occurs when specific organic molecules resist degradation by micro-organisms. Chemical stabilization occurs when the interactions of organic substances and inorganic substances lead to a decrease in the availability of the organic substrate to microorganisms due to surface condensation. Physical stabilization occurs when accessibility of the organic substrates to micro-organisms is reduced due to occlusion within aggregates, commonly observed in clayey soil for OM, which is within the soil aggregate.

5.4.1. Organic matter stabilization by mineral surfaces and metal ions interaction

OM can attain stability when bound to mineral surfaces, where soil OM in fine silt and clay fractions are observed be older and had a mineralization rate by having a long turnover time than OM in other soil OM fractions (Chenu and Plante, 2006). Sorption of soluble OM to subsoil material was observed to reduce OM mineralization by 20–30% compared to OM in soil solution (Chenu and Plante, 2006).

Ligand exchange: Anion exchange with OH groups on mineral surfaces, carboxyl groups, or phenolic OH groups of the OM is a critical mechanism for forming strong organo-mineral complexes such as Fe–O–C bonds. It is observed that the complexation of OM on mineral surfaces due to ligand exchange is prominent at lower pH, with a peak at a pH range of 4.3–4.7, which is a pKa value that ranges most carboxylic acids and organic carboxyl (von Lützow et al., 2007). DOM with higher content of carboxylic-C

and aromatic-C form strong complexes with sesquioxide via ligand exchange in acidic soils (von Lützow et al., 2007).

Polyvalent cation bridges: metal cations such as Ca^{2+} , Fe^{3+} and Al^{3+} in the soil bind with anions such as COO^- and maintain the neutrality at the surface by neutralizing the charge both on the negatively charged soil colloids and the acidic OM functional group, acting as a bridge. The cations involved in cation bridges are determined by soil pH. In neutral to alkaline soil Ca^{2+} and Mg^{2+} are dominant while Fe^{3+} and Al^{3+} are dominant in acidic soils (von Lützow et al., 2007).

5.4.2. The sorption of organic matter in the soil

Sorption of DOM compounds such as low molecular weight organic acids (LOAs) to soils and metal oxides follows principles of inorganic anion sorption, occurs primarily via ligand exchange, and is closely linked with sesquioxide (Guppy et al., 2005). The preferred sorption sites for OM are mouths of micropores which result in very strong bonding and multiple ligand attachment, edges of minerals, rough surfaces, and micropores, and the first molecules of OM to sorb are best stabilized (Guggenberger and Kaiser, 2003; Kaiser and Guggenberger, 2003). There is preferential sorption of hydrophobic OM (OM with aromatic rings and aliphatic C chains), compared to the hydrophilic OM (OM rich in carbohydrates); sometimes competition exists between Hydrophilic and hydrophobic OM, especially in the soil with few binding sites (Kaiser et al., 1996). The sorption of DOM onto Fe^{2+} and Al^{3+} is determined by pH and other competing inorganic anions (i.e., SO²⁻, o-P).

6. Competition mechanisms for mineral binding sites between OM and phosphate

There are many potential direct and indirect mechanisms which affect the sorption of P and OM on soil surfaces. Added OM crumbles, and its products can adsorb to the binding sites of the mineral surface, resulting in reduced P sorption and hence increased P concentration in soil solution and available P for plant uptake (De Bolle, 2013; Guppy et al., 2005; Kaiser and Guggenberger, 2003). OM can increase the availability of phosphorus (P) in the soil through abiotic processes such as decomposition and mineralization of organic P in soil or ligand exchange. However, mineralbound OM can also reduce phosphate adsorption capacity, favouring the release of o-P in soil solutions (Yusran, 2010). Three abiotic mechanisms have been proposed to explain how the addition of OM can reduce P harbouring in soil. First, soluble organic molecules can be adsorbed explicitly to soil minerals through ligand exchange that competes with o-P (Guppy et al., 2005; Yusran, 2010; Fink et al., 2016). Second, soluble OM reacted with Al³⁺ or Fe³⁺ bound to the surface of the soil mineral phase to form a soluble complex, which was previously harbored or insoluble Al and Fe-phosphates. Third, the OM can be absorbed by soil particles, resulting in higher negative charges of the particles, and thus leading to increased repulsion towards the o-P anion.

Generally, SOM and o-P are negatively charged anions and bind to the same binding site on the soil surface. The addition of organic additives to the soil has been observed to increase phosphorus solubility and decrease phosphorus sorption in fixed soils (Bhatti et al., 1989; Guppy et al., 2005). Adsorption of organic functional groups to iron oxides or other metal oxides can (i) promote the adsorption of anions through cation bridges (Al³⁺ and Fe²⁺) and (ii) increase the specific surface area (SSA) to inhibit crystallization of minerals. There is. Fe²⁺ and Al³⁺, (iii)) changes in surface charge, (iv) enhanced competition with other anions for adsorption sites, (v) increased desorption of adsorbed P (Fink et al., 2016; Guppy et al., 2005).

6.1. Direct competitive mechanisms of OM on P sorption

OM directly affects P sorption in the soil through different mechanisms, such as; *Metal complexation by Fe and Al oxides:* OM reacts with metal oxides of Fe^{2+} and Al^{3+} , forms complexes with surface metals, and releases these metals into the soil solution. This resulted in a decrease in the number of sorption sites due to the removal of metal oxides in soil surfaces. In addition, the reduction of P binding sites results in reduced P sorption (Fink et al., 2016; Hunt et al., 2007). This allows more P to be released in soil solution allowing it to be available for plant uptake but also available to be lost via leaching and surface water runoffs.

Reduction of Specific Surface Area (SSA): OM in the soil act as a binding agent; it binds the tiny soil particles to a large aggregate to produce a good soil structure. Kaiser et al. (2003) reported that SSA in mineral soil had a positive relationship with the content of Fe oxyhydroxides and a negative relationship with the content of OM. Potential sorption of phosphorus consequently a decrease with reduction of the area of the mineral soil surface This effect of OM on the reduction of SSA is more excellent at larger OM loadings like in grassland where there is the constant addition of organic matter via manure applications, that is why most grassland and pastureland has been identified as an essential source of P contributor to water eutrophication because their soils get saturated faster leaving more P in soil solution (Kaiser et al., 2003). Competition for adsorption sites: Dissolved organic carbon (DOC) compounds such as humic (HA) and fulvic acids (FA), which are released upon decomposition of OM, compete with added P for binding sites since both are negatively charged (Hunt et al., 2007). According to Yu et al. (2013), in their research of the effects of OM application on o-P adsorption, decomposition products from manure such as humic acids and citrate were observed to have a greater affinity for Al oxides is important sorbent for o-P. Hence, OM addition will induce a competitive effect to binding sites between decomposition products and o-P on the soil surfaces, resulting in reduced P sorption. However, its effect is small in soil with higher content of Al and Fe. such as highly weathered tropical soils like ferralsols. Since the DOC bind in the same binding sites of the soil complexes, the added o-P finds the binding sites are already occupied, or if both are added simultaneously, the DOC is more likely to bind than o-P (Yu et al., 2013). In addition, the Sorption of OM compounds to the soil mineral surface increases the negative charge or decreases the point of zero charge (PZC), thus inhibiting P sorption due to increased repulsion for incoming negatively charged anions such as phosphate (Guppy et al., 2005). It is observed that the sorption of OM can alter the surface charge of iron oxides and cause phosphates to be electrostatically repelled (Antelo et al., 2010).

6.2. The indirect mechanism for OM and P competition

The addition of OM can indirectly influence the availability of P in highly weathered soils directly as follows: Added OM can improve physical soil properties such as water-holding capacity, soil pH, aeration, and other soil properties, which can promote plant growth and increased utilization of soil P reserves. In addition, the shift of P equilibrium between P pools in the soil encourages more P desorption from soil surfaces (Fink et al., 2016). Furthermore, the added OM may promote microbial activity in the soil, resulting in more microbial P immobilization, increased organic P and reduced adsorbed inorganic P concentrations (Guppy et al., 2005). Nevertheless, added OM can increase soil pH in the short term, thereby decreasing the availability of metal cations such as Fe²⁺ and Al³⁺ by affecting their solubility resulting in decreased P sorption (Borggaard et al., 2005).

On the other hand, the interactions between OM and pedogenic Fe and Al can inhibit the crystallization of Aluminum and iron oxides resulting in increased surface area, thereby increasing o-P adsorption capacity and adsorption sites which consequently reduce the P available for plant uptake (Borggaard et al., 2005). In addition, through metal bridging, OM can adsorb to positively charged sites on the soil surface such as Al³⁺, Fe³⁺, Ca²⁺, creating additional positive sites, which allow further o-P adsorption (Sato, 2003).

7. Conclusion

The influence of OM on P availability is variable. It may increase the availability of P in soil solution and might lead to decreased availability of P in soil solution for plant uptake depending on the created environment after the addition of OM. The role of OM in the availability of P might be influenced by another adsorbent which is known to participate in sorption and desorption possibly this is likely to be the indirect effect of OM to inhibit the crystallization of Fe and Al in the long-term resulting in the formation of less – crystalline pedogenic Al and Fe, with higher SSA which in turn increased P sorption. Thus, the role of OM in P availability in highly weathered tropical soils is still contradictory, any management involving addition of OM should be taken with care as instead of increasing P availability might result to P insufficient for agricultural uptakes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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