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Thèse de Doctorat

*Mention Sciences Ecologiques
Spécialité Ecologie et Biogéochimie*

présentée à l'Ecole Doctorale en Sciences, Technologie, Santé (ED 585)

de l'Université de Picardie Jules Verne

par

Issifou Amadou

pour obtenir le grade de Docteur de l'Université de Picardie Jules Verne

Rôle des formes de phosphore organique, des minéraux du sol, de l'azote et des traits fonctionnels des plantes sur la disponibilité et l'acquisition du phosphore par les plantes

Soutenue le 20 decembre 2022, après avis des rapporteurs, devant le jury d'examen :

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Doctoral thesis

*Honours Ecological Sciences
Specialty Ecology and Biogeochemistry*

Presented to the Doctoral school in Sciences, Technology and Health (ED 585)

of the University of Picardie Jules Verne

by

Issifou Amadou

to obtain the degree of Doctor from the University of Picardie Jules Verne

***Role of organic phosphorus forms, soil minerals, nitrogen,
and plant functional traits on phosphorus availability and
acquisition by plants***

**Defended on December 20, 2022, after the reviewer's opinion, in front of the
examination jury:**

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AVANT-PROPOS

Ce projet de thèse a débuté en octobre 2019 et est financé par FEDER/FSE Picardie 2014-2020 et UniLaSalle (rattaché à l'Université Picardie Jules Verne), basé à Beauvais (France). Le projet est réalisé au sein de l'équipe de recherche AGHYLE (Agroécologie, Hydrogéochemie, Environnements et Ressources) d'UniLaSalle.

Le manuscrit de la thèse est rédigé comme une thèse sur articles en anglais. Les chapitres 1 et 2 ainsi qu'un article de synthèse (présenté dans l'introduction générale) ont été publiés dans des revues internationales et les chapitres 3 et 4 sont en cours de correction pour publication dans une revue internationale. Une liste des publications est disponible à la fin du manuscrit, ainsi qu'un résumé étendu du manuscrit en français.

FOREWORD

This thesis project started in October 2019 and is funded by FEDER/FSE Picardie 2014-2020 and UniLaSalle (attached to the University Picardie Jules Verne), based in Beauvais (France). The project is carried out within the AGHYLE (Agroecology, Hydrogeochemistry, Environments, and Resources) research team of UniLaSalle.

The thesis manuscript is written as a thesis on articles in English. Chapters 1 and 2 as well as a review article (presented in the general introduction) have been published in international journals, and Chapters 3 and 4 are being edited for publication in an international journal. A list of publications is available at the end of the manuscript, as well as an extended abstract of the manuscript in French.

Je dédie ce manuscrit à mon grand-père, qui :

Parmi les conseils qu'il me donna, place ces paroles "Mon fils ! que le coq ne soit pas plus vigilant que toi lorsqu'il chante à l'aurore ; alors que toi, tu dors". Et Voici ces vers :

"Une colombe a gémi, dans la nuit, sur une branche :

Je dormais... Mon père ! ma mère ! Mon amour est un menteur :

Sur un véritable amour, elle n'eût pas pris d'avance...

Je suis l'amant aux yeux secs, mais elle verse des pleurs !"

Mon fils,

'Sache, que celui qui croit toucher au but sans effort est un homme de désir ; et celui qui ne compte que sur l'effort fait acte de présomption".

J'ai alors appris que la clé du succès, à l'origine, était l'amour, le travail assidu et la détermination ; et je me suis contenté de les prendre pour alliés, quitte à faire preuve de beaucoup d'abnégation et à dompter mon âme...

Aussi,

Par ce manuscrit, je rends hommage à tous les enseignants du monde

Voici mes vers :

Sache, lecteur, qu'être enseigné n'est pas un droit, c'est une chance, parce qu'il y en a qui n'en ont pas, malgré de grandes prières ;

Et si les anges ne s'appelaient pas vraiment anges, moi je les aurais appelés enseignants du primaire, du collège, du lycée et des universités ;

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INTRODUCTION

1 INTRODUCTION

1.1 Organic phosphorus sorption in soils: processes, models and implications for sustainable phosphorus management

Phosphorus (P) is a limiting nutrient for agroecosystem productivity (Filippelli, 2008; Jarvie et al., 2019; Withers et al., 2015). The application of phosphate to the soil is necessary to maintain or improve crop yields. However, the depletion of global phosphate rock reserves from which chemical fertilizers are produced is now threatening global food security (Schoumans et al. 2015; Cordell et al. 2009). Therefore, recycling P from organic amendment is becoming a necessity for sustainable P management in agroecosystems (Bennett and Schipanski, 2013). However, P in organic amendment is in various forms of inorganic P (IP) and organic P (OP) that differ in their availability to plants (Faucon et al., 2015). Most research on the fate of P applied to soil has focused on IP, showing that most of it is adsorbed to the soil surface, thus affecting its availability to plants (Huang et al. 2008; Houben et al. 2011; Hinsinger 2001). In contrast, the fate of OP has been understudied to date, and knowledge of their dynamics and contribution to plant nutrition is still lacking (Faucon et al., 2015).

In soils treated with organic amendments, up to 80% of total P is present as OP (Nash et al. 2014; Harrison 1987). Typically, OP compounds include phosphomonoesters, phosphodiesteres, and organic polyphosphates even though their relative proportions in soils vary greatly between studies (Table 1). Among these OP compounds, forms such as inositol hexakisphosphate, IHP (Turner et al. 2002; Vincent et al. 2013; Vestergren et al. 2012), glycerophosphate, GLY (Newman et Tate 1980; Doolette et al. 2009; Doolette et al. 2011), and glucose-6-phosphate, G6P (Vincent et al. 2013; Cui et al. 2007; Hogema et al. 1997) are generally considered major forms. Despite the widely recognized importance of OP forms as a source of P to plants and its essential role in biogeochemical cycling and ecosystem functioning (Nash et al. 2014; Dalai 1977), its chemical nature as well as its transformation is still largely neglected and remains poorly understood compared to IP forms. Organic P forms differ significantly in their behavior and bioavailability in soil (Condron et al. 2005). This is due to their relationship with the soil minerals, but also to their different biochemical properties and chemical nature: P content, type of P bonding and size of the molecules (Ganta et al. 2021; Huang et al. 2017; Turner et Engelbrecht 2011). Moreover, the identification of OP species is still incomplete and much more difficult than that of IP. Therefore, their dynamics among soil properties and during the long-term development of ecosystems is unknown (Huang et al. 2017; Pant et al. 1999; Young et al. 2013). This poor understanding of the sources and types of OP and their transformations in soils not only hinders the optimization of organic amendment and the development of sustainable management practices, but also limits our ability to predict the response of ecosystem processes to changes in nutrient stoichiometry.

Table 1 : Organic P accumulation according to some soil properties

Soil properties	OP forms	Reference
Neutral soils with high organic matter	Phosphate monoesters	(Turner et Engelbrecht 2011 ; Huang et al. 2017)
Acidic soils	DNA; Phosphonates	(Turner et Blackwell 2013; Cheesman, et al. 2014)
Acidic soils with low organic matter	Phosphate diesters	(Turner et Engelbrecht 2011)
Low Fe /Al soils	Phosphate diesters; Polyphosphates	(Vincent et al., 2012)
High Fe /Al soils	Myo-, scyllo- and unknown Inositol phosphates	(Vincent et al., 2012)
Forest soils	Orthophosphates, Inositolhexaphosphate; α -Glycerophosphate	(Vincent et al. 2012 ; Newman et Tate 1980 ; Turner et al. 2002 ; Pant et al. 1999)
Riparian soils	Glycerophosphate (9.4-131.4 mg P kg ⁻¹)	(Young et al., 2013)
Alfisols	Glycerophosphate (45% of OP); Other monoester	(Pant et al. 1999)

Depending on the nature of the OP-containing molecule in organic amendment, there are large differences regarding their affinity to soil particles and mineralisation dynamics (i.e. the corresponding enzyme activity). After supply in soil, the dynamics of OP are greatly influenced by factors and processes such as adsorption and desorption, complexation and precipitation, redox state, and organic matter composition (Lü et al., 2017; Ruttenberg and Sulak, 2011). These physical, chemical, and biological factors are listed as the primary abiotic processes governing the fate of OP in the soil-plant system (Turner et al. 2002; Turner 2008). Furthermore, the size and molecular structure of OP generally affect the rate of their sorption density. Thus, it has been suggested that the higher the degree of phosphorylation of OP compounds, the greater the sorption to the soil solid phase. Since OP fixation in soil is often much higher than that of anionic IP species (Gerke, 2015), their sorption process requires careful study.

Soil minerals such as Fe and Al oxyhydroxides and clay minerals, constitute a major component of soils and sediments and have high P adsorption capacity (Ryan et al. 2001; Bortoluzzi et al. 2015). Their P bonding degree depends on their reactive surface groups as well as on their degree of crystallinity or porosity (Guan et al., 2006; Ruttenberg and Sulak, 2011). Minerals with a high concentration of reactive Fe/Al-OH groups would strongly bind OP forms (Ganta et al. 2019a). Until today, a large part of the main soil minerals is not considered in the OP adsorption processes. Among all soil constituents, the effect of humic substances on P dynamics is often ignored (Borggaard et al., 2005; Gerke, 2010).

However, soil humic substances possess several characteristics that affect the P distribution between the solid phase and the soil solution (Gerke, 2010). As OP is not only bound to minerals surfaces in soil but can also be bound, similar to IP, to humic surfaces via Fe or Al bridges, research on this topic is strongly required. Several surface complexation models that describe phosphate adsorption have been developed and successfully applied to IP adsorption by specific soil minerals and soils (Houben et Kaufhold 2011; Sheals et al. 2002). However, little is known about the OP surface complexation with soil. In addition, conflicting discussions are still present on the nature of the bonding process of the adsorbed OP and IP species and their relative abundance in soil (Olsson et al. 2012; Kim et al. 2011).

Compared to the adsorption process, which is already less well known, the desorbability and mineralization of OP to plant nutrition are difficult to assess, but studies in soil (Stewart and Tiessen, 1987) suggest that this contribution increases with the mineral composition and geological age of the soil as well as the plant community. Because desorption occurs slowly, several authors have suggested that the adsorbed OP complex is not available to plants. The reason for this is that the mineral-OP complexes are formed during the slow reaction of the adsorption process (Ganta et al. 2019a). Factors such as percent of P saturation (Parfitt 1979; He et al. 1994; Celi et Barberis 2002), incubation time, and temperature (Barrow, 1978) may affect the release of P from mineral-OP complexes to the soil solution, and thus the availability of P to plants, but the type of relationship involved is not yet clear. It is also likely that desorbability of phosphate from mineral-OP complexes is influenced by different factors, which, in turn, depend upon the type of soil mineral (Parfitt, 1979). Unfortunately, the impact of different types of minerals has not been sufficiently studied, despite their practical implications for P fate.

Clearly, it is very likely that the potential of organic amendments to improve P use efficiency depends on the forms and biochemical properties of their different forms of OP. Indeed, depending on the nature of the OP molecule, there could be large differences in their affinity to soil particles and mineralization dynamics (i.e., corresponding enzymatic activity). Understanding these dynamics and the differences that can occur between forms of P is necessary to improve P availability from OP compounds. In this paper, we review the dynamics of OP in soil-plant systems as well as differences among OP forms by focusing on their sorption phenomena. We first discuss in detail their adsorption to the surface of soil minerals and their potential availability from the mineral-OP bonding complex. Then, we summarize some knowledge on the molecular characteristics of the main forms of OP in soil as well as recent advances on the nature, mechanisms and bonding strengths of sorbed OP. Finally, we present some open questions that need to be addressed in future studies with emphasis on characteristics and relative proportions of OP derived from organic amendments and their relationship to existing soil OP pools; the establishment of quantitative models for the transformation of mineral-OP bonding complexes and sophisticated models to quantify the relative importance of mechanisms governing the sorption of different forms of OP in soil.

1.1.1 Characteristics and adsorption of the major OP forms in soils

1.1.1.1 Inositol phosphates

Inositol phosphates are a six-carbon cyclohexanehexol (inositol) ring that has phosphate moieties linked by an ester bond. The number of substituted phosphate groups on the inositol ring may vary between one and six, which is indicated by the prefix's mono, bis, tris, tetrakis, pentakis and hexakis (Nomenclature, 1977). Inositol phosphates exist in various states of phosphorylation and isomeric forms (e.g., *myo*, *d-chiro*, *scyllo*, *neo*). The *myo* stereoisomer is the most common in nature, although *neo*-, *scyllo*- and *d-chiro* are also present in terrestrial and aquatic environments (Turner et al. 2002; Cosgrove 1962). In terrestrial environments, Inositol phosphates are synthesized in plants (seeds), almost exclusively as the inositol hexakisphosphate (IHP) stereoisomer (Turner 2008; Nash et al. 2014). The IHP isomer is known under different names: "phytic acid" for the free acid form, and "phytate" for the salt of phytic acid. In older texts, "phytin" is sometimes used to refer specifically to the Ca-phytic acid or Mg-phytic acid salt (Cosgrove, 1963; Peperzak et al., 1959). Inositol hexakisphosphate represents the main OP form in most legumes, cereals and oil seeds (Kasim and Edwards, 1998). It has also been reported in animal wastes (2–60% total OP), bacteria and fungi (Cosgrove, 1963; Peperzak et al., 1959). Between pH 5 and 12 IHP possesses an axial structure and an equatorial structure outside this range (Turner et al. 2002). The chemical structure of IHP is shown in Figure 1.

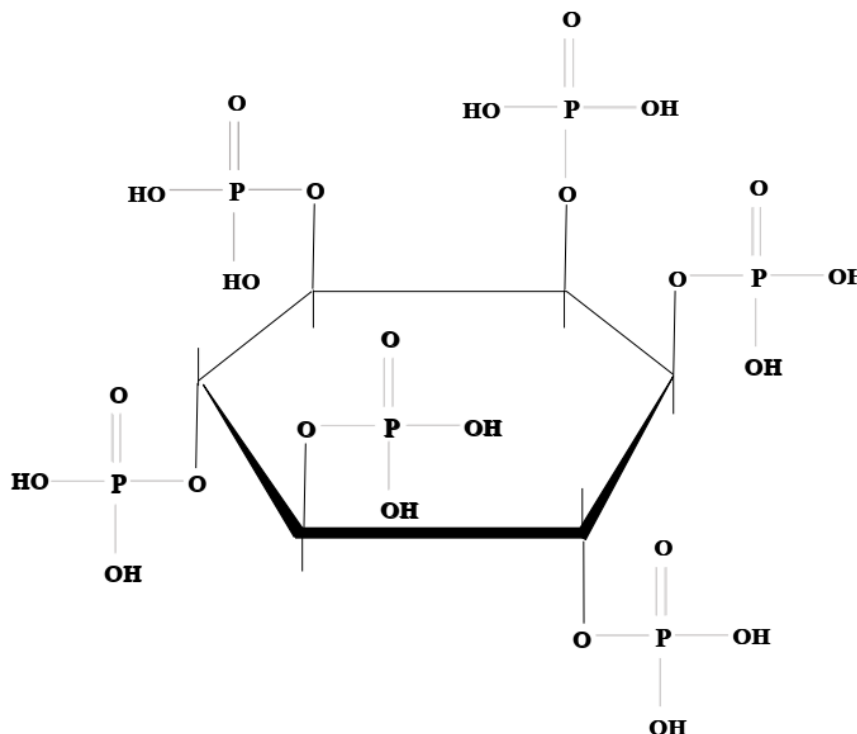


Figure 1: Chemical structure of IHP

In most OP adsorption studies, IHP is found to exhibit the higher adsorption capacity. This strong reaction means that IHP undergoes preferential stabilization, which prevents interaction with hydrolytic enzymes and results in its accumulation to form frequently the dominant fraction of OP in soils (Harrison, 1987). In a study evaluating the affinity of OP forms, Celi et al. (1999) have reported an adsorption ratio of 3:2 between IHP and IP at pH 4.5. Later, Celi et al. (2004) confirmed the greater affinity of IHP than IP on goethite, with maximum values of 3.6 for IHP and IP for 2.4 mmol P m⁻². Similarly, based on Langmuir bonding strength values, Celi et al. (2007) found that goethite shows a higher affinity for IHP than for the other OP and IP forms. Li et al. (2018b) reported a maximum IHP adsorption of 1.95 mmol P m⁻² at pH 5 which is close to the value of 1.20 mmol P m⁻² obtained by Ganta et al. (2021). The details of IHP adsorption on goethite have been extensively studied (Celi et al. 1999; Celi et al. 2007; Celi et al. 2001; Johnson et al. 2012). Comparing the adsorption capacity values of the Freundlich model for IHP and IP, Ganta et al. (2021) showed that the adsorption of IHP was about 1.58 times that of IP, very close to those reported by Celi et al. (1999). The adsorption of IHP generally leads to a faster saturation of the soil mineral surface than that of GLY and IP. This was confirmed on the basis of the order of Freundlich exponent values (IHP < GLY < IP) applied to goethite. This faster saturation is due to the fact that even if IHP binds to goethite via some phosphate groups, the remaining phosphate groups, often deprotonated, would induce a more negative charge on the surface compared to the IP and GLY cases (Xu et al. 2017; Celi et al. 2001). Furthermore, it was found that GLY leads to a more negatively charged surface than IP (Xu et al. 2017). This explains why the Freundlich exponent value for GLY is lower than for IP. The adsorption of IHP onto common soil mineral occurred through ligand exchange at the surface, releasing OH⁻ and H₂O into the solution, and the formation of an inner sphere complex (Lü et al. 2017; Ognalaga et al. 1994). Nevertheless, phosphate groups have been found to also form an outer sphere complex (Yadav et al., 2012). As a predominant mechanism, the binuclear-bidentate complex has been widely suggested to explain OP adsorption on soils (Johnson et al. 2012). The bonding stability between sorbate and sorbent can be expressed by the affinity constant. A high affinity constant means a rapid uptake and strong bonds or associations between P compound and soils components (Ruttenberg and Sulak, 2011). Some of the factors that influence the stability of IHP are soil texture, pH, organic matter content, climate and soil management/land use. The most important soil property controlling the variation in IHP content is the clay type and content in soil. Inositol hexakisphosphate is more strongly sorbed to illite than kaolinite (Celi et al. 1999). The pH significantly affects the stabilization of IHP. Acidic soils are known to accumulate more IHP than alkaline soils, which is due to the higher concentration of Fe and Al in solution at acidic pH (Harrison 1987; Hawkes et al. 1984; Goring 1950; Emsley et al. 1981; Celi et al. 2001). Moreover, in soils rich in constituents with variable charges (Al/Fe oxyhydroxides), its sorption increases with decreasing pH due to the higher positive charge of these constituents (Celi et al. 2001). Laboratory study models have provided a better understanding of the reactions of IHP with soil constituents. The higher adsorption of IHP to Fe and Al oxyhydroxides relative to clays reported in some studies was attributed to the electrostatic association of four of the six

orthophosphate groups, while only two orthophosphate groups bind with clays. Because of the unattached phosphate groups in IHP, the electrochemical properties are altered and the net negative charge on the particle surface is increased (Celi et al. 2000). Adsorption of IHP may also be affected by the type of electrolyte in solution. It has been reported that the adsorption of IHP decreases in KCl solution, but increases with CaCl₂ (Giaveno et al. 2010; Celi et al. 2001). In any case, the highest affinities of IHP like that of ATP to soil constituents have been explained by the fact that their molecules have more phosphate groups that can coordinate with more hydroxyl (OH) groups on the surface of soil minerals. Also, the phosphate groups of IHP and ATP carry higher negative charges, which leads to a stronger electrostatic attraction with the surface of the soil minerals (Celi et al. 2001).

1.1.1.2 Glucose-6-phosphate

Glucose-6-phosphate (Figure 2) is a glucose sugar phosphorylated at the hydroxy group on C six (Adam et al., 2019). It plays an important role in the carbohydrate metabolism of all bacterial and plant organisms (Cui et al. 2007). It acts in several catabolic pathways to generate energy in the form of ATP. In the environment, we also have Glucose-1-phosphate which is only a stereoisomer of G6P. Glucose-6-phosphate level can provide information on the activities of enzymes such as G6P dehydrogenase, phosphoglucosmutase, hexokinase and phosphoglucose isomerase (Coevoet and Hervagault, 1997). Glucose-6-phosphate regulates the activity of certain enzymes, such as glycogen synthase, a protein kinase (Bellaver et al., 2004; Sergeeva and Vreugdenhil, 2002). Glucose-6-phosphate is a "low energy" phosphate compound because its free-hydrolysis energy is only $-13.8 \text{ kJ mol}^{-1}$, which is significantly lower than some other OP forms such as IHP (approximately $-58.5 \text{ kJ mol}^{-1}$) (Katti et al. 1982). There are many studies that focus on intracellular biochemistry of G6P but there is limited information on the availability of P from these organic forms of P in soil. A couple of studies on G6P adsorption on soil minerals reported that G6P is potentially more available than IHP (Goebel et al., 2017; Yan et al., 2014). The G6P sorption density and rate is higher than IHP and ATP as a result of its lower molecular weight (Giaveno et al., 2008; Ruttenberg and Sulak, 2011). At low pH values, boehmite, hematite and goethite preferentially adsorb G6P and glucose-1-phosphate than the other forms of OP (Johnson et al. 2012). Moreover, Olsson et al. (2010) showed that glucose-1-phosphate an isomer of G6P formed three types of surface complexes on goethite in a pH-dependent fashion. Furthermore, G6P was reported exhibit higher adsorption at outer surface sites than IP due to its pore size effects (Goebel et al., 2017).

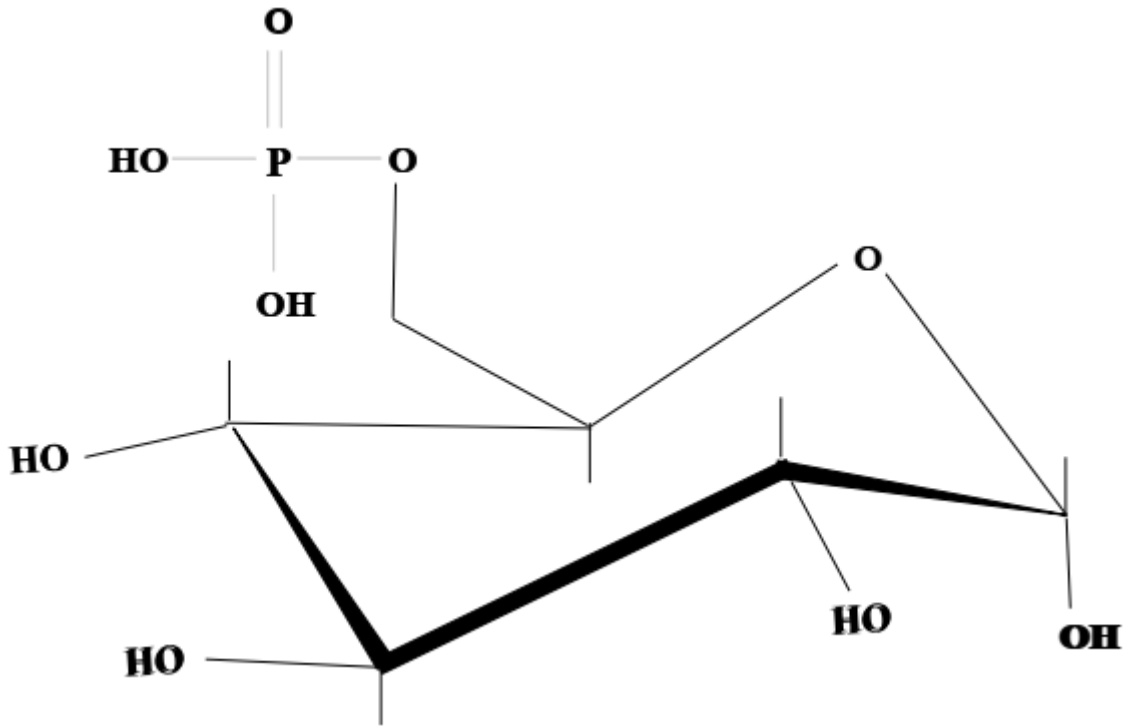


Figure 2: Chemical structure of β -D-Glucopyranose-6-phosphate

1.1.1.3 Glycerophosphate

Glycerophosphate is a phosphoric ester of glycerol. It is a phosphomonoester which is characterized by a single ester bond with the orthophosphate (Figure 3). Glycerophosphate like all the other OP forms acts as a donor of phosphate groups during its mineralization in the soil. In manure-amended soils, GLY is found in its α and β form, but β -glycerophosphate (β -GLY) is generally reported as the most common and important form (Li et al. 2018a; Doolette et al. 2009). β -glycerophosphate is also referred as β -phosphoglycerol, glycerol 2-phosphate, or under the IUPAC name as 1,3-dihydroxypropan-2-yl dihydrogen phosphate. The plant availability of GLY has been established by a few studies and its use as a P source has been tested. Following incubation for 24 h in 5 ml of a solution containing 250 μg GLY at pH 5.1, samples of 18 mycorrhizal roots completely hydrolysed the ester. A second experiment showed that hydrolysis was rapid and that 10 root tips could completely hydrolyse within 90 min 300 μg contained in 2.5 ml at pH 4.8 (Bartlett and Lewis, 1973). Wang et al. (2011) reported that the contribution of GLY as a sole P source supported the growth of different phytoplankton taxa groups more than control with IP, with relative growth between 109% and 165%.

The adsorption of GLY are dependent on the properties of different soils. Li et al. (2018b) suggested that GLY adsorbs onto the goethite surface by forming inner-sphere complexes through the phosphate group. Hori et al. (1985) showed that GLY adsorbs onto hydrated iron (Fe^{+3}) oxide precipitates. In

addition, GLY exhibits strong interaction with boehmite, $\alpha\text{-Al}_2\text{O}_3$ and $\text{Al}(\text{OH})_3$ (Yan et al. 2014) , and also with ferric oxide (Anderson et Arlidge 1962).

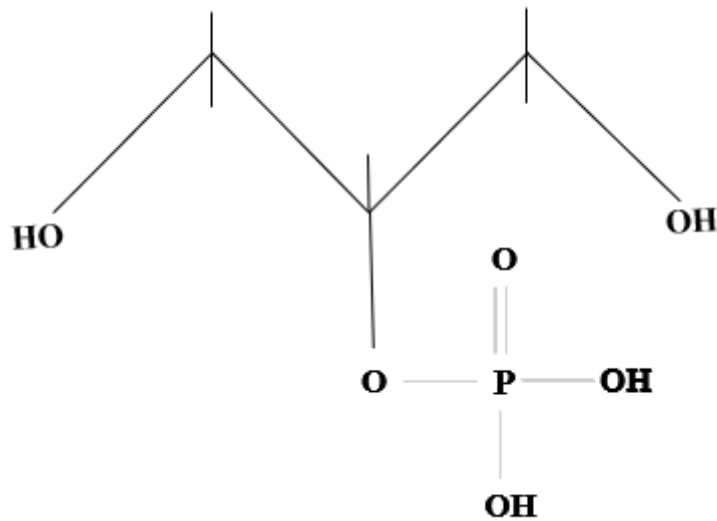


Figure 3: Chemical structure of Glycerol 2-phosphate.

1.1.1.4 Phosphodiester compound: DNA

Deoxyribonucleic acid (DNA) is made up of sugar molecules linked by ester bonds to an orthophosphate. It is found only in the nucleus of the cell, and has multiple charges that are all negative. In soil, DNA of bacterial origin exists as linear chromosomal DNA, as well as supercoiled plasmids (Poly et al., 2000). Like other OP forms, phosphodiester such as DNA can be protected from dephosphorylation by adsorption to the soil matrix, but several factors can affect that process (Levy-Booth et al., 2007). At pH 5 to 7, DNA and RNA are usually negatively charged and their adsorption to minerals is thus facilitated by cationic bridging. However, at a pH below 5, they are positively charged and thus less adsorbed (Cai et al. 2006; Greaves et Webley 1965). Structural changes in DNA molecules adsorbed by soil, sand, humic acids, and mineral or organomineral complexes may result in changes in their bioactivities and affect the degradation of DNA by nucleases (Franchi et al., 1999; Pietramellara et al., 2001). The level of adsorption and protection of DNA by soil particles varied significantly with DNA configuration and the type of the adsorbent (Lorenz et al. 2013; Demanèche et al. 2001). Demanèche et al. (2001) showed that illite provided a lower level of protection for DNA molecules than montmorillonite and kaolinite. Higher level of adsorption and protection of DNA was found with montmorillonite and organic clays compared to kaolinite and clays (Cai et al. 2006). The protection of DNA against nuclease degradation by soil colloids and minerals is apparently not controlled by the adsorption affinity of DNA molecules for the colloids and the conformational change of bound DNA. The higher stability of DNA is likely to be attributed mainly to the presence of organic matter in the

system and the adsorption of nucleases on soil colloids and minerals (Cai et al. 2006). However, the adsorption and protection of DNA by soil particles to enzymatic degradation is not totally understood, as is also the influence of parameters such as mineral constituents, organic matter, and particle size of soil colloids (Paget and Simonet, 1994). This information would be of fundamental significance for the understanding of the behavior of DNA and related P forms in soil environment.

1.1.2 Effect of OP characteristics on relative OP sorption in soils

The accumulation and distribution of OP from soils are greatly influenced by adsorption and desorption (Figures 4 and 5) phenomenon (Xu et al. 2017). In general, the molecular size and structure of OP compounds influence the sorption dynamics in soil (Yan et al., 2014). By using different synthetic soil constituents (goethite and hematite), the results of Lü et al. (2017) suggest that OP sorption rates might be classified as follows: IP > Adenosine monophosphate (AMP) = G6P > ATP, showing a downward trend in sorption levels with increasing molecular weight of the different OP forms. This means that the larger the molecular size, the higher the activation energy is required for desorption (Shang et al., 1996). The lower affinities of AMP and G6P to soil properties than those of IP are thought to be due to the higher steric hindrance effects caused by the C chain and glucose ring of these compounds (Ruttenberg and Sulak, 2011). Steric hindrance at a given atom in a molecule such as P is congestion caused by the physical presence of surrounding ligands, which can slow or prevent reactions to P. Steric hindrance occurs when the volume occupied by one part of a molecule interferes with the approach of a reagent or another part of the molecule.

Conversely, recent studies have shown a trend towards increasing rather than decreasing sorption levels with increasing molecular weight of the different forms of OP. Such as, for example, the work of Ganta et al. (2020) which shows on the basis of the Langmuir and Freundlich model that the adsorption capacity and strength increase in the following order: GLY < IP < IHP. Suggesting that despite the larger molecular size of IHP, the steric hindrance effect due to its large organic molecule would not have occurred. The explanation put forward was that the organic fraction of IHP might not influence the individual phosphate, but only the conformational flexibility of the overall bonding process (Ganta et al. 2019b). This is consistent with the observation of Celi et al. (1999) showing that the phosphate groups of IHP react with the goethite surface in the same way as the IP forms. A more recent additional explanation shows that on goethite, the Fe-P distances observed for IHP are close to the Fe-P distances for IP and suggest that the organic fraction of IHP may not influence the interaction of individual phosphate groups with goethite (Ganta et al. 2019b; Ganta et al. 2021).

1.1.3 Influence of soil constituents on OP sorption

Iron and Al oxyhydroxides (goethite, gibbsite...), clay minerals (kaolinite, montmorillonite...) and humic substances have attracted considerable attention because of their high P sorption capacity (Ryan et al. 2001; Bortoluzzi et al. 2015). Their P bonding degree depends on their surface areas, crystallinity, number of active surface sites, point of zero charge, and concentration of hydroxyl groups (Ruttenberg and Sulak, 2011). It is assumed that at pH 4–10, gibbsite and amorphous Al(OH)₃ would have maximum sorption capacity for IHP (Guan et al., 2006; Yan et al., 2014). Yan et al. (2014) studied sorption of different OP (GLY, ATP and IHP) on aluminium (oxyhydr)oxides. They found that the maximum adsorbed phosphate normalized to the mass of adsorbent increases with decreasing crystallinity of the minerals: Al₂O₃ < boehmite AlO(OH) < amorphous Al(OH)₃. Moreover, they concluded that OP adsorption and phosphate fate in the environment are strongly affected by the degree of crystallinity and crystal structure of mineral surfaces.

Humic substances, such as humic acids (HA), account for 40–90% of organic matter in soil (Hur and Schlautman, 2004). In most studies, the effect of humic substances on P dynamics has often been ignored due to previous results showing that humic substances would have no effect on P adsorption in soil (Borggaard et al., 2005; Gerke, 2010). However, the chemical interaction between soil organic matter and IP or OP forms is an important reaction in the soil solid phase, soil solution and even in natural waters (Gerke, 2010). The adsorption of OP on HA and the effect of the latter on sorption processes have been studied with macroscopic sorption measurements. Large quantities of IHP have been found to be associated with fractions of humic substances in soil (Ruyter-Hooley et al. 2015; Borie et al. 1989). Humic acids can strongly complex metals, mainly by carboxylic and phenolic groups (Ritchie and Perdue, 2008; Tipping, 2002). Humic-Fe and Al oxyhydroxides complexes can adsorb P, thereby forming “humic- Fe and Al oxyhydroxides-P” complexes. The main bonding mechanism of OP is probably via Fe and/or Al-bridges to the humic matrix, similar to the bonding of the IP anion (Gerke 2010; Negrin et al. 1995; Urrutia et al. 2014). A great proportion of OP can be found associated with humic substances (Thomas and Bowman, 1966). The main sorption mechanisms involve electrostatic interaction and ligand exchange (Figure 4 and 5; Tombácz et al., 2004). The presence of HA would be likely to affect the OP available to plants in soil systems (Ruyter-Hooley et al., 2015). However, more knowledge is needed to understand the nature of the interaction between HA and OP or via Fe or Al bridges in soil. Table 2 summarizes a qualitative annotation of the main research on the adsorption of organic forms of P to the surface of the main soil minerals at pH 4 to 6.

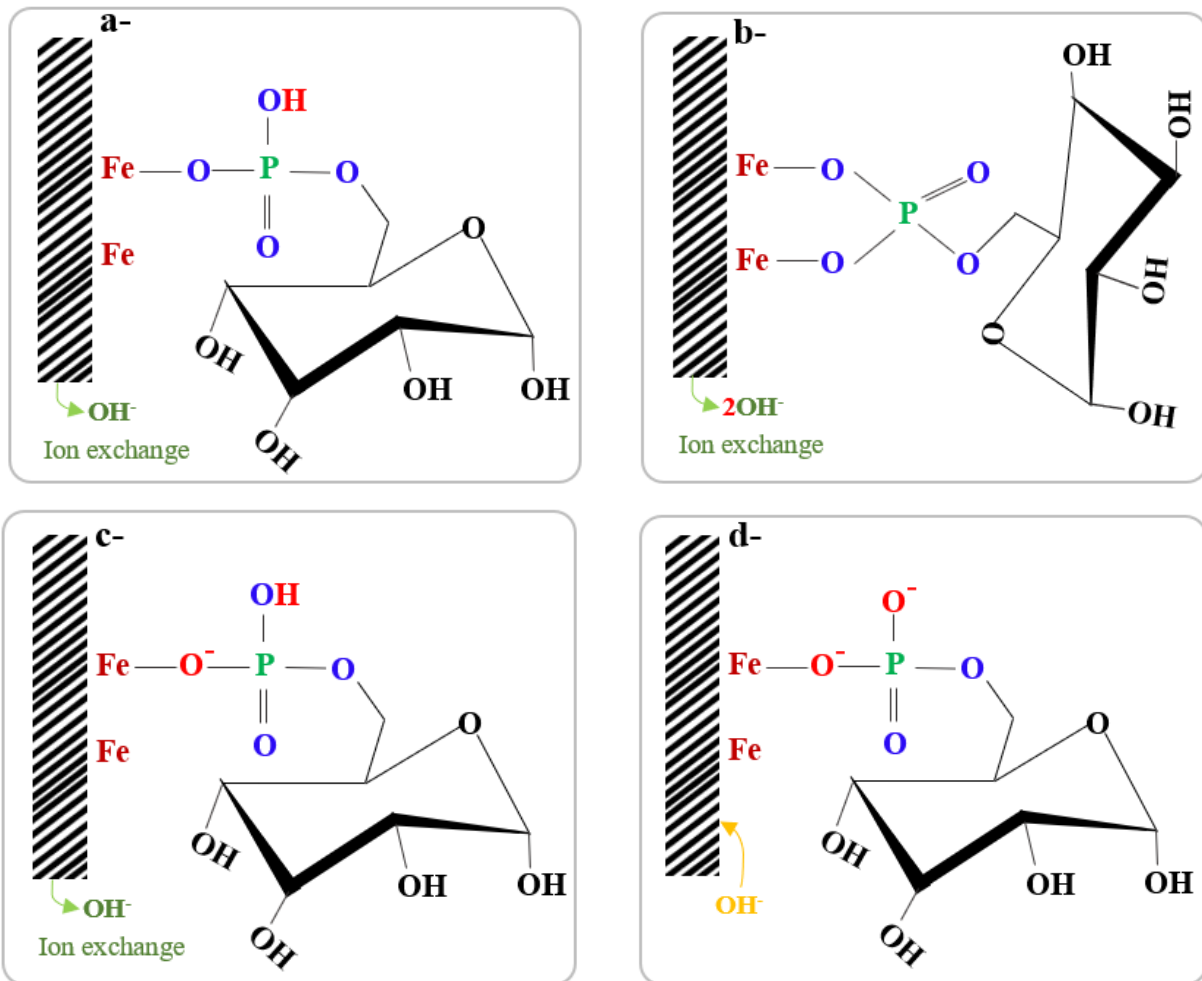


Figure 4 : Plausible surface complexes of OP compounds at soil properties interface.e.g. Inner-sphere complex of β -D-Glucopyranose-6-phosphate with iron (oxy)hydroxides.

(a) Inner-sphere mono-dentate mono-protonated complex pH = 1-7, (b) Inner-sphere bi-dentate complex pH = PZC, (c) mono-dentate mono-protonated complex characterized by Lewis Acid-Base Interaction pH = 8-12 and (d) mono-dentate unprotonated complex characterized by Lewis Acid-Base Interaction pH = 8-12.

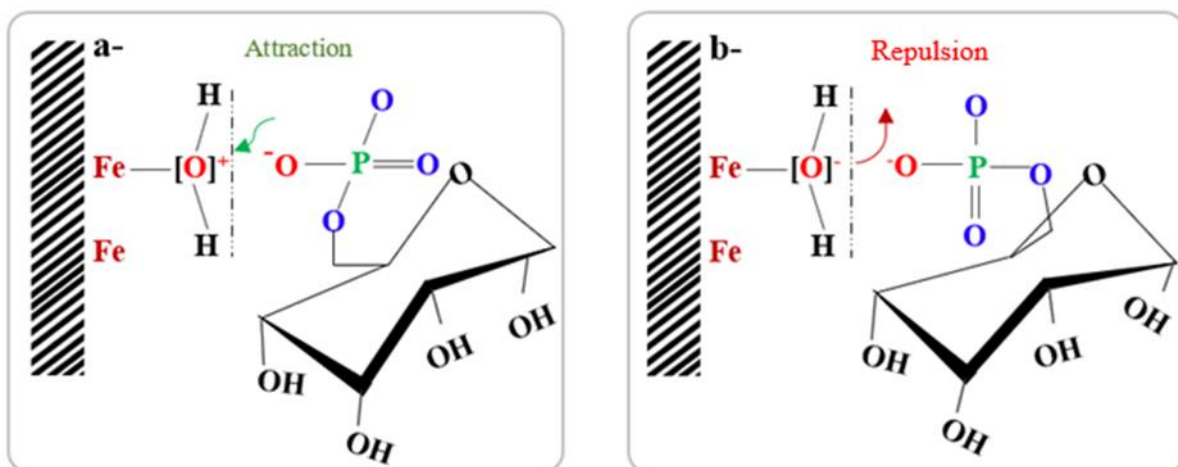


Figure 5 : Plausible surface complexes of OP compounds at soil properties interface.e.g. Outer-sphere complex of β -D-Glucopyranose-6-phosphate with iron (oxy)hydroxides.

(a) Outer-sphere complex electrostatic attraction pH = 1-7, (b) Outer-sphere complex electrostatic repulsion pH = 8-12.

Table 2 : Summary of the main investigations on the adsorption of OP forms on soil minerals under pH 4 to 6.

The sign (+) means that there is an adsorption. The more + signs are present, the greater the adsorption capacity. The sign (0) means that no studies were found concerning the adsorption of the form of P on the mineral. Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate and IP: KH_2PO_4); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals.

Soil minerals	P forms							
	IP	IHP	GLY	G6P	G1P	AMP	ATP	DNA
Goethite	+++++	+++++	++	++++	+++++	+	+++	
Gibbsite	0	+++++	0	0	0	0	0	0
Ferrihydrite	+++++	+++++	0	++++	0	+	+++	
Hematite	+++++	+++	0	++++	0	++++	++	0
Akaganeite	+++++	0	0	0	0	0	0	0
Amorphous Al (OH) ₃	+++	+++++	++	+	0	0	+	0
Maghemite	++++	+++	0	0	0	0	0	0
Magnetite	++++	+++	0	0	0			
GoethiteHumic acid	++++	0	0	0	0	0	0	0
Ferrihydrite Humic acid	+++	0	0	0	0	0	0	0
Boehmite	++++	+	+++++	+++	0	0	++	0
Dolomite	+++	0	0	0	0	0	0	0
Kaolinite	+++	+	0	0	0	0	0	+++++
Montmorillonite	0	0	0	0	0	0	0	.+++
Illite	0	+++	0	0	0	0	0	++++
Humic acid	+++	+++++						

1.1.4 Organic P desorption and availability from mineral-OP bridging complexes

Compared to adsorption, desorption of OP from soil minerals has received less attention. Factors such as P saturation (Parfitt 1979; He et al. 1994), pH and temperature (Barrow, 1978) may affect the release of P from mineral surfaces to the soil solution and thus the availability of P to plants, but the type of relationship involved is not yet clear. Several authors have suggested that the mineral-OP bridging forms are not available to plants because these complexes are formed during the slow reaction phase with soil minerals (Hingston et al. 1974; Barrow et Shaw 1975). Hinsinger (2001a) through physicochemical findings, showed that Fe and Al oxyhydroxides bind very strongly to P via inner sphere complexes. This process has been hypothesized to be a major cause of limiting plant growth (Javaid, 2009). The desorption of OP compounds from mineral surfaces would be much lower than for IP. Therefore, the question of the availability of sorbed OP on soil minerals is still not resolved. Recently, García-López et al. (2020) showed that when IHP was used as P source for plants, P uptake decreased with increasing Fe oxides concentration in the growing media. Bollyn et al. (2017) showed that after several desorption cycles less than 5% P desorbed from IHP. Similar findings by Ruyter-Hooley et al. (2015) showed limited desorption of IHP (<3% of P) on gibbsite, even in the presence of HA as a competing ligand. From goethite, the amount of IHP desorbed was less than 20% of the amount of desorbed IP, which was attributed to the strength of the bonds and the high negative charge of the complex (Nash et al. 2014). In any case, there is a greater affinity of the OP forms for soil minerals than that of the IP forms, indicating the formation of a very stable complex of OP with mineral surfaces. Thus, it can be expected that desorption and plant availability of mineral-OP complexes are more difficult than those of IP forms, although this has never been quantitatively defined (Table 3).

Contrary to the result presented above which suggests that mineral-OP bridging forms are not available for plants, there is also some experimental evidence that most of the P taken up by plants comes from the soil mineral-P bridging complex, although sorbed P is not easily or widely desorbed. This implies that P associated with soil minerals is potentially available to plants, although availability also depends on the type of soil minerals and the P form (Andrino et al., 2019; D'Amico et al., 2020). Recently, D'Amico et al. (2020) exposed mesh bags filled with goethite associated with IP or IHP for 13 months to P-deficient soils in the Italian Alps. More P was lost from the mesh bags, indicating a direct release of P from the mineral surfaces. Parfitt (1979), showed that P sorbed to goethite was available to ryegrass, while Guzman et al. (1994) found that P sorbed to goethite was less available to sunflower than P sorbed to ferrihydrite and hematite. The type of extractor also influences the level of OP desorption. Desorption rates of G6P by KCl and citrate are generally very high compared to those of IHP, ATP and GLY (Yan et al., 2014). However, it was more easily desorbed by citrate than KCl (Table 3). This could be explained by the fact that citrate induces a more important ligand exchange mechanism than KCl. These ligands would compete for sorption sites with sorbed G6P to promote

greater desorption (Johnson et Loeppert 2006; Violante 2013). Up to 32.4% of G6P, adsorbed by goethite could be desorbed from Goethite-G6P complexes.

Beyond the few studies on G6P and GLY desorption in soil, there is still limited information on the biogeochemical cycling of G6P in agroecosystems; most of the available data refers specifically to IP and IHP. It is therefore important to carry out further research to understand all the mechanisms governing the mobility of G6P and GLY in soil systems in order to improve their availability. In addition, in all the above studies, the behavior of some important Fe and Al oxyhydroxides minerals (gibbsite, ferrhydrite...) has not been adequately examined and comparable studies with other main soil components (clay minerals and humic substances) have not been conducted. Since OP can constitute up to 80% of the total P in soils amended with organic amendments (Anderson, 1980), it is likely that the phytoavailability (and desorbability) of the different specific OP compounds in soil surface complexes is influenced by their biogeochemical properties (P content, type of P bonding and molecule size...). Thus, the amount of P available to plants from mineral-OP bridging complexes need to be evaluated and well understood.

Table 3 : Desorption of P from Boehmite with KCl and Citrate and from different mineral surface saturations of 50% and 100%.

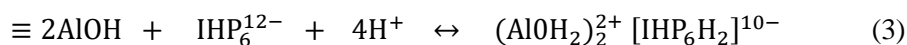
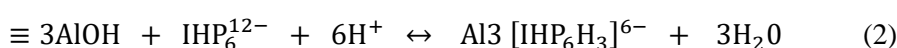
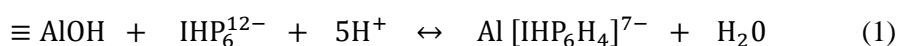
Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate and IP: KH_2PO_4); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

Desorbition of P from boehmite (Yan et al., 2014)			Effect of surface saturation on desorption (He et al. 1994)	
Complex	KCl	Citrate	Complex	Resin extraction
Boehmite-IP	-	-	Montmorillonite-P50	45.5%
Boehmite-IHP	0.93%	4,33%	Montmorillonite-P100	41.4%
Boehmite-GLY	8%	39,50%	Kaolinite-P50	3.6%
Boehmite-G6P	13%	59,68%	Kaolinite-P100	5.4%
Boehmite-ATP	5%	21,33%	Goethite-P50	0%

1.1.5 Nature of bonding between OP and mineral surfaces

The fate of P in the ecosystem is strongly influenced by the mechanisms by which P is bound to soil mineral surfaces, and a good understanding of these mechanisms is a major key for the development of new strategies to increase P application efficiency.(Nash et al. 2007; Martin et al. 2004; Martin et Wicken 1966; Ganta et al. 2020). Recently, Li et al. (2010) and Wang et al. (2017) investigated the sorption of phosphate onto boehmite using ^{31}P MAS NMR techniques. Both studies, concluded the formation of a binuclear inner-sphere complex. In previous studies, IHP sorption was suggested to involve only inner-sphere complexation (Ognalaga et al. 1994; Celi et al. 1999; Guan et al. 2006). Guan

et al. (2006) and Yan et al. (2014) also proposed inner-sphere complexation to be the dominant sorption mechanism for IHP on amorphous Fe and Al oxyhydroxides. In contrast, work by Johnson et al. (2012) showed that IHP sorption to goethite occurs largely through the formation of outer-sphere complexes.. Furthermore, Ruyter-Hooley et al. (2015) investigated the sorption of IHP onto gibbsite using surface complexation modeling. The result indicated that outer-sphere complexation is important in the sorption process at higher pH, while inner-sphere complexation and surface precipitation are dominant at lower pH. The reactions described two inner-sphere surface complexes (1 and 2) and one outer-sphere complex (3) as follows:



The surface complexation mechanism of P with soil components, especially goethite (Cordell et al. 2009), as well as surface complexation models that describe P adsorption have been explored (Ahmed et al., 2015). However, they are not generally successfully applied to the adsorption of OP to soil components and soils (Houben et Kaufhold 2011; Sheals et al. 2002). As a result, little is known about the surface complexation of OP with soil.

The nature of the bonding patterns of the adsorbed OP and IP species is still a matter of conflicting debate. In addition, the relative abundance of monodentate (**Mono**) (Sheals et al. 2002; Olsson et al. 2012) versus bidentate (**Bid**) (Kim et al. 2011; Ganta et al. 2019a) bonding of the soil minerals-P complexes is less known. This was reported in the literature to be related to the presence of different surface planes for soil minerals and multiple bonding motifs for mineral-P complexes. Thus, different views have been put forward to assign mineral-P bonding motifs based on infrared spectroscopy or molecular modeling. Molecular modeling is considered a powerful tool to resolve these conflicting discussions by providing a molecular level description of the nature of the minerals-P complexes formed. By molecular modeling, Kwon et Kubicki (2004) studied the IP-bonding process to goethite and suggested the abundance of the diprotonated **Bid** complex at pH 4-6 and the deprotonated or monoprotinated **Mono** complex at pH 7.5-7.9. Similarly, Ganta et al. (2019a) combined adsorption experiments and molecular dynamics simulations to analyze the adsorption of the major forms of P in forest soil, namely IP, GLY, and IHP, on the surface of goethite. The modeling results show that IP and GLY form stable binuclear **Mono** and **Bid** motifs, **Bid** being more stable than **Mono**, while IHP forms stable **Mono** and **3Mono** motifs. Furthermore, by combining the experimental and modeling results, they showed **Bid** motif dominates for IP, while GLY forms **Mono** and IHP forms a combination of **Mono** and **3Mono** motifs. This study, like others, allows us to understand the mechanisms by which microbes and plants overcome to recover P from the strong IHP-mineral bond. However, despite the

presence of a significant number of studies reporting the bonding pattern of IP, IHP and GLY on the surface of goethite, such an in-depth atomistic investigation for the bonding mechanisms of OP at the interface of all major soil minerals is still lacking (Ganta et al. 2021). A more detailed knowledge of the interaction of P with these components will provide a better understanding of the interaction and availability of P with these soil mineral components.

There is no consensus in the literature on the number of phosphate groups of the IHP that bind to the goethite surface or on the dominant bonding motifs. Ganta (2020) and Ganta et al. (2021) found for goethite-IHP complexes the **Mono** and **3Mono** bonding motifs, which is supported in the literature previously (Arai and Sparks, 2007). However, no clarity on which bonding motif would be dominant. The **3 Mono** (Guan et al. 2006; Ganta, et al. 2019b), **2Mono** (Guan et al. 2006; Ganta et al. 2020) and **1Mono** (Ganta et al. 2019) motifs are already reported for IHP on minerals. In contrast, Johnson et al. (2012) proposed that IHP interacts with goethite by forming outer-sphere complexes, which conflicts with much of the literature. Also, it is surprising to note that none of the above studies concerning IHP suggest that it forms a binuclear **Bid** motif, as suggested in other previous studies (Guan et al. 2006). However, this seems understandable since it was found that the initial **Bid** motif of IHP is not stable.

Compared to IP, the adsorption of GLY on soil minerals has not been extensively studied and, therefore, information on its bonding patterns is limited. Based on the analysis of FTIR spectra, GLY would form inner-sphere complexes with goethite with only **Mono** motifs on the surface (Li et al. 2018). Similarly, studies of the bonding mechanisms of monomethyl phosphate ($\text{CH}_3\text{-H}_2\text{PO}_4$), an organic P with a single phosphate group like GLY and that of glyphosate, have shown that it forms mainly **Mono** units with goethite (Persson et al. 1996; Sheals et al. 2002). It has also been suggested that the phosphate group of GLY interacts with the mineral surface in a very similar way to IP forms. This is because it has been suggested that the Fe-P distances observed in the GLY are in the range of the Fe-P distances observed for IP in the literature (Rose et al., 2010; Tribe et al., 2006). Summarizing this literature data, the **Mono** motif would appear to be the dominant motif for GLY type molecules on the surface of soil minerals, more precisely goethite.

It is very important to keep in mind that the different bonding patterns reported depend very strongly on the properties of the soil, specifically the saturation level of the soil minerals. Tejedor-Tejedor et Anderson (1990) and George Anderson (1980) proposed that the **Bid** motif is the dominant motif, for low surface coverage of IP on goethite in the pH range of 3.6-8.0. In addition, they proposed that the **Mono** motif exists at low surface coverage but as a non-dominant motif. Using Density functional theory (DFT) calculations, Kwon et Kubicki (2004) concluded that the **Bid** motif is dominant between pH 4-6. Recently, a joint approach by Ahmed et al. (2019) involving adsorption experiments and DFT simulations showed that the **Mono** motif is dominant at both extremely low and high pH values, while the **Bid** motif is dominant in the intermediate pH range.

1.1.6 Bonding energy and strength of OP sorption to soil mineral surfaces

A challenge for further studies and application is to understand and explore the mechanisms by which microbes and plants can overcome the strong OP-mineral bonding and incorporate or uptake the phosphate groups into their metabolism. This would require better knowledge of the interaction energy of P and soil minerals. The interaction energy between P and the mineral surface could be calculated by using eq (4) (Ganta et al. 2021; Ganta et al. 2020):

$$E_{int} = E_{S-P_{complex}} - (E_S + E_P) \quad (4)$$

Here, $E_{S-P_{complex}}$ denote the total electronic energies of the soil-phosphate complex, E_P electronic energies of P forms and E_S the soil minerals surface one.

It has been reported that mineral-GLY binding complexes exhibit a higher binding interaction energy for the Bid motif than the Mono motif by a factor of 2.4, probably due to a greater number of deprotonation steps. For the mineral-IHP complexes, the **3Mono** motif of the IHP has a higher interaction energy than the more stable **3Mono** motif, but shows a 1.2-fold lower interaction energy per bond (Ganta et al. 2021; Ahmed et al. 2019). Based on these results, it is clear that if the two species (Gly and IHP) are competing for the same active sites on the soil surfaces, the bonding of IHP will be dominant. Moreover, molecular dynamics simulations on adsorption data have reported total interaction energies measured for goethite-IP and goethite-GLY complexes to range from -20 to -81 kcal mol⁻¹ depending on the type of bond (**Mono** or **Bid**) (Ahmed et al. 2019; Ganta et al. 2021; Kubicki et al. 2012; Rakovan et al. 1999). But the interaction energies per P-bond for the GLY motif is higher than that of IP (Ganta et al. 2021). The difference comes from the glycerol group in GLY. Both IP and GLY interact through one phosphate group, but through the glycerol group, GLY has a higher solvent accessible surface area and shows a stronger interaction with water than IP (Ahmed et al., 2019). A similar observation was made for GLY on the surface of diasporite (Li et al. 2018), which is isomorphic to goethite (Cordell et al. 2009). Moreover, Xu et al. (2019) showed that GLY induces a more negative charge on hematite than IP, which could also influence the strength of Fe-OP covalent bonds. This helps to understand why the desorption of GLY would be under certain conditions more difficult than IP forms. The bonding energies of the IHP to minerals would be between -69 and -85 kcal mol⁻¹, generally higher than IP forms (Ganta et al. 2021; Ganta et al. 2020; Ahmed et al. 2015). Of the three types of the bonding motif reported in the literature for IHP on soil minerals, the **3Mono** has a higher total interaction energy than the **2Mono** due to the additional covalent bonds and proton transfer from IHP to the mineral surface. However, the interaction energy per bond between IHP and goethite for the **3Mono** motif has been reported to be lower than that of the **2Mono** motif. The **Table 4** presents the bonding patterns of P-forms and their interaction energies per number of bonds on goethite and two diasporite surface planes.

In summary, there is still much to be known about the nature, interactions motif and strength of OP forms at all soil mineral surfaces. Therefore, it is important to develop new methods that would

provide a better understanding of these mechanism. Recently, Ganta et al. (2021) suggested that a molecular-level understanding of the mechanisms of P bonding to soil mineral surfaces may be key to developing new strategies for more efficient application of P. Thus, much experimental work has been done to understand P bonding to several reactive and abundant minerals, including goethite (α -FeOOH). From our investigations, atomistic modeling of mineral-P complexes using molecular dynamics simulations is emerging as a new tool, which provides more detailed information on the mechanisms, nature and strength of bonding processes. However, it is mostly applied to IP forms than to OP. Since forms such as GLY, IHP, and G6P are abundant species in forest soils and soils amended with organic amendments, such a detailed atomistic investigation for their bonding mechanisms at the mineral interface needs to be further investigated.

Table 4 : Binding patterns of P-forms and their interaction energies per number of bonds ($E_{int}/bond$) on goethite and two diaspore surface planes.

Diaspore (α -AlOOH) is isomorphous with goethite having an Al^{+3} oxidation state instead of Fe^{+3} . Compared with goethite it exhibits a higher surface energy (Guo and Barnard, 2013; Ganta et al. 2021; Ganta et al. 2019b).

P forms	Binding motif	Binding energy: $E_{int}/bond$ (kcal/mol)		
		Goethite	010 diaspore surfaces	100 diaspore surfaces
IP	Monodentate	-36
	Bidentate	-41
GLY	Monodentate	-48	-63	-23
	Bidentate	-38	-148	-15
IHP	Monodentate	-85	..	-33
	2-monodentate	-69	-170, -115	-18
	3-monodentate	-72	-145	-109

1.1.7 Modeling OP sorption for sustainable P management

The mechanisms that govern the dynamics of the OP forms, even if they are still not well investigated in relation to IP, are in general understood, but we do not know the relative importance of each of these mechanisms on the fate of P in the soil and therefore models are needed in order to understand more. Studies of OP composition across environmental gradients demonstrated that soil properties exert a strong control on the amounts and forms of OP in some Fe and Al oxyhydroxides (McDowell et Stewart (2005). Vincent et al. (2012) found that distribution of OP species in agricultural soil depend on level

of Al and Fe sites, due to the stabilizing effect of these metal oxides. Therefore, sorption of OP on Fe and Al oxyhydroxides have attracted considerable attention (Ryan et al. 2001; Bortoluzzi et al. 2015), however clay minerals (kaolinite, montmorillonite...) effect on OP dynamic is less studied despite it is also a major component of soils and sediments. Of all the soil minerals, the effect of humic substances on OP fate is often ignored because of results showing that humic substances have no or little effect on P adsorption to soil components. However, soil humic substances account for 40–90% of organic matter in soil and the bonding of the IP anion at the humic surface is found to be similar to the bonding to Fe/Al-hydroxides. Therefore, we strongly suggest to include the effect of humic substances on OP sorption process.

It is clear that the number of the P groups in a certain OP compound is determining the stability of its complex with the mineral surface however it depends on the surface plane of soil minerals. Given the lack of knowledge on the surface plane of soil minerals and the chemical nature of OP species, the nature of their bonding is not well understood. Different opinions have been put forward to assign bonding motifs based on infrared (IR) spectroscopy (Tejedor-Tejedor et al. 1990). Molecular modeling is considered as a powerful tool to resolve such conflicting discussions by providing a molecular level description for the nature of the formed mineral–P complexes. However, this model has been generally applied on goethite and IP form (Kubicki et al., 2012). Therefore, we suggest future investigation to introduce a molecular level understanding for the bonding mechanism of OP species via a joint experimental and theoretical approach. Further, simulation of adsorption experiments could be carried out by molecular modeling for the bonding processes of especially major OP forms (IHP, GLY, G6P), by applying hybrid quantum mechanics/molecular mechanics–based molecular dynamics simulations.

Soil minerals-OP transformation and availability in soil comprises a set of interconnected physical, chemical and biological processes such as percent P saturation (Parfitt 1979; He et al. 1994), residence time, pH and temperature. It is characterized by multiple linear or nonlinear responses and thresholds depending on soil minerals. Future advances in P availability from minerals-OP complexes will require careful application of numerical models that quantitatively describe their past and present changes from laboratory studies and forecast their variation trends in the future to field level. The recent development of a numerical modeling approach for data evaluation by Müller et al. (2014) provides new opportunities to study OP transformations in a wide variety of native and agricultural ecosystems (Huang et al. 2013; Turner et al. 2015). However, this model does not include any mineral-OP bridging complexes which are potential sources of P in soil. Similar approaches could therefore be applied to modeling mineral-OP bridging complexes transformation and availability in soil. Moreover, data on rates of P desorption from mineral-OP bridging in the laboratory should be compared to rates derived in the field.

1.1.8 Summary and perspectives

Current knowledge has led to a better understanding and identification of the processes that limit the availability of P to crops and ways to improve it by increasing access to OP. Given the importance of OP for global food security and its critical roles in soil biogeochemical cycling (Vance et al. 2003), its dynamics in natural soils as well as experiments involving comparison of specific forms of OP in agricultural soils need to be studied in combination with the use of state-of-the-art techniques in order to understand better the basic principles and mechanisms governing the sorption process of OP forms with soil mineral surfaces. In addition, the transformation and availability of P from mineral-OP bonding complexes needs to be studied under different land use conditions in order to develop extensive databases to quantitatively model and predict the availability of P from such complexes. This would contribute to optimize the management of P in cropping systems, especially those amended with organic inputs, while limiting negative impacts on the environment.

Despite intensive efforts to understand and characterized the complexity of OP forms dynamics and behavior when they arrive in the soil, the relative proportions, pathways and thresholds of OP species transformation in organic amendments amended soil and especially its interaction or competition with existing OP pools in soils remain largely unknown(Huang et al. 2017). Therefore, it is important to highlight the role of the OP form from organic amendments application in changes in existing soil P forms over time by well characterizing both chemical and soil properties involved in P dynamics. In addition to add different OP species to soil, decomposition of organic amendment may generate humic substances and organic acids that can be adsorbed into soil surfaces, decreasing the potential P adsorption by blocking sites for the formation of complexes with Al, Fe and Ca (Fuentes et al. 2006; Fuentes et al. 2009). Thus, the characteristics of organic amendments that could reduce or increase the sorption strength of the OP on soil minerals need to be further investigated. A thorough understanding of the amount of P in the soil-plant system and the time period during which P adsorbed in soil and organic matter is released for uptake by crops is strongly needed to improve P use in agricultural ecosystems.

In the course of our investigation, we noted that IHP, GLY and G6P mobility and availability for plants is limited due to its strong bonding to the soil solid phase. Moreover, despite several studies on some Fe and Al oxyhydroxides, their relationship with clay minerals and humic substances is scarce. Their use as sole P fertilizer has been tested by some laboratory studies (Wang et al. 2012), but no recent studies have been done to determine its availability in agricultural production conditions. Hence, we strongly suggest that future research could focus on understanding the extent to which these P forms react on soil compounds, how they are used by plants and how this could be improved in the perspective of an efficient organic fertilization. Nevertheless, there has been substantial progress on adsorption rates of total OP or specific OP (IHP) based on incubation experiments. However, the rates measured in the laboratory should be compared to rates derived in the field. Further, studies on the effect soil properties

on the OP residence time and turnover in different soils composition are also required to elucidate the relative importance of biological and biochemical processes in adsorbed OP transformation. There is also a need to investigate rates and changes in different OP forms such as IHP, GLY and G6P across various soil chronosequences in order to formulate numerical models that can predict future major OP forms adsorption and transformations process.

1.2 Unravelling the role of rhizosphere microbiome and root traits in organic phosphorus mobilization for a sustainable phosphorus fertilization. A review

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Abstract: Moving toward more sustainable sources for managing phosphorus (P) nutrition in agroecosystems, organic phosphorus (OP) derived from organic inputs and soil is increasingly considered to complement mineral P fertilizer. However, the dynamics of P added by organic input in soil-plant systems is still poorly understood and there is currently no clear information on how the OP composition of these amendments determines P availability, in particular through their interactions with soil microbiome and root traits. Here, we review the main mechanisms of rhizosphere microbiome and root traits governing the dynamics of organic input/soil derived OP pools in the soil-plant system. We discuss the extent to which the major forms of OP derived from organic input/soil can be used by plants and how this could be improved to provide efficient utilization of organic inputs as potential P source. We provide new insights into how a better understanding of the interactions between OP forms, root traits, and rhizosphere microbiomes can help better manage P fertilization, while discussing recent advances in the mobilization and recovery of OP from organic input. We then develop emerging strategies in agroecology that could be used to improve OP utilization, specifically by better linking plant traits and OP forms and developing new cropping systems allowing a more efficient OP recycling.

Keywords: agroecology; biogeochemistry; cover crops; organic inputs; organic phosphorus; plant traits; rhizosphere soil; rhizosphere microbiomes

1.2.1 Introduction

Phosphorus is a limiting nutrient for the productivity of agroecosystems (Filippelli, 2008; Jarvie et al., 2019; Withers et al., 2015). This is due to its low availability in soil which results from its low solubility

and its strong affinity for mineral surfaces. Phosphorus fertilization is therefore needed to achieve high yields. Most of the P currently used in chemical fertilizers is derived from phosphate rocks (Schoumans et al., 2015). These resources are unevenly distributed at the Earth surface and, in European Union (EU), food production is dependent on imported primary P (Cordell et al., 2009; Schoumans et al., 2015). Because the reserves are located only in a few places on Earth and thus controlled by few countries, the EU's P supply is vulnerable to geopolitical issues with possible problems with the accessibility and price of P fertilizers on the mid-term (Cordell et al., 2009). Additionally, phosphate rock is a strategic resource whose *mining* can lead to occupations and armed conflicts. Moving towards more sustainable sources for managing P in cropping systems, renewable nutrient-rich organic amendments are increasingly considered to complement P fertilizers produced from phosphate rocks, not only by scientists but also by politics and stakeholders (Bennett and Schipanski, 2013). The use of organic inputs represents shifting from a linear use of a limited resource towards a circular economy because it promotes the reduction of fossil fuel use and greenhouse gas emissions (McCormick and Kautto, 2013) while contributing to the development of new green markets (Zulkifli et al., 2019) and jobs by promoting the conversion of waste into value-added products (Bracco et al., 2018; Mohanty et al., 2002; Scarlat et al., 2015). The use of organic inputs could make the transition to sustainable agriculture a priority, focusing on prevention of environmental impacts, through the adoption of innovative technological systems (Zulkifli et al., 2019). The sustainability benefit of using renewable organic P depends on farming systems types associated to a with low carbon emissions from renewable P traffic, such as livestock farming systems using which use effluents or digestates, or other farming systems using which use agro-industriessy coproducts at territory scale, and urban and peri-urban agri-culture systems that valorize sludges. Using organic inputs as a sustainable and renewable resource is a necessity to address the socio-economic and scientific issues that have recently been raised concerning sustainable P management approaches.

Organic inputs cover a large diversity of matters, including raw or treated livestock manure, food industry, urban or domestic sludge from water purification operations or wastewater treatment, raw materials, water and sewage sludge, paper, petroleum, textile, chemical, bio-waste (green waste composts, organic household or domestic waste), the digestates composted or not from mechanization, ashes, in particular, biomass burning, sediments dredged and biochar's (materials resulting from the pyrolysis of certain wastes). The agronomic interests for organic inputs are well documented (Houot, 2018). For instance, in France, 78% and 62% of P and N respectively used in agriculture derive from organic inputs (Houot et al., 2016). However, unlike conventional P fertilizers, such as triple superphosphate, P is present in organic inputs in various inorganic and organic forms which vary in their availability to plants (Faucon et al., 2015). Most research on the fate of P applied to soil has focused on the dynamics of inorganic P (IP). In contrast, the fate of OP forms, that can account for up to 80% of total soil P (Andrino et al., 2019; Harrison, 1987) has been neglected to date, and there is still a lack of knowledge about the contribution of these forms to plant nutrition (Faucon et al., 2015). A study by

Kahiluoto et al. (Kahiluoto et al., 2015) shows that OP from organic inputs would be more available than P from chemical fertilizers. Nevertheless, this availability is affected by rhizosphere microbiome and root traits (Sulieman and Mühlhling, 2021; Sulieman and Tran, 2015; Zogli et al., 2017). Therefore, a better understanding of the interactions between OP forms, root traits, and rhizosphere microbiomes can help to better manage P fertilization.

In its definition, OP is any compound that contains an organic moiety in addition to P. The P atoms are covalently bonded to C via a phosphoester linkage (P–O–C), or phosphodiester linkage (C–O–P–O–C), or directly bonded to C (P–C). In a wider definition, it would include phosphate which is associated with organic matter. Through the utilization of different technologies from sequential extractions to ³¹P NMR spectroscopy, OP compounds have been identified and quantified in various organic inputs. This has been a major step in the better understanding of the different forms of OP, their quantities and dynamics. Globally, both organic input and soil contains numerous OP forms in varying amounts. The notable forms are those belonging to phosphomonoesters, e.g., inositol phosphates, phosphodiesters, e.g., nucleic acids, and organic polyphosphates, e.g., adenosine triphosphate (Nash et al., 2014; Stutter et al., 2015). Among these compounds, specific forms such as inositol hexakisphosphate (IHP) (Turner et al., 2002b; Vestergren et al., 2012; Vincent et al., 2013), glycerophosphate (GLY) (Doolette et al., 2009, 2011; Newman and Tate, 1980), and glucose-6-phosphate (G6P) (Cui et al., 2007; Hogema et al., 1997; Vincent et al., 2013) are generally considered major forms. In addition to these species, several other OP are potentially active but poorly characterized and remain somewhat puzzling (Richardson and Simpson, 2011). Each form differs from the others by its P content, and molecule size. These biochemical properties to which are added their adsorption, desorption and hydrolyzation processes control their fate and thus their availability to plants. The mobilization of each OP to plant is driven by soil microbes and root traits in the soil-plant continuum (Bünemann and Condron, 2007; Lazali et al., 2020). Indeed, soil microbes living freely in the complex plant-soil system (Richardson, 2005), can significantly control the status and turnover of OP and ultimately its availability in the soil (Margenot et al., 2017). Furthermore, in response to P deficiency, plants have developed numerous strategies that allow them to mobilize OP and assimilate IP with greater efficiency in soils. These are morphological, physiological, biochemical and molecular mechanisms (Jain et al., 2007; Skene, 2000). These strategies consist of (i) increased root growth, (ii) the establishment of specialized organs, (iii) the expression of high-affinity IP transporters, (iv) the secretion of root exudates and specific enzymes (Jones et al., 2004; Lazali and Bargaz, 2017) and (v) symbiotic association with rhizosphere microbiome. It is therefore very likely that the potential of recycled P fertilizers to increase plant uptake depends not only on the forms and biochemical properties of the different OP, but also on the mobilization/acquisition process by microbes and strategies (e.g. protons, carboxylates and phosphatase release...) used by plants to increase P availability. Thus, to predict the availability of P in cropping systems, it is very important to consider both the characteristics

of the OP forms applied to soil and the mechanisms governing their mobilization/acquisition for crop plants.

The purpose of this review is to (1) highlight the main mechanisms involved in the potential mobilization of OP from organic inputs and soil in the soil-plant system and (2) to develop the emerging strategies in agroecology which can be adopted to improve the P availability in cropping systems.

1.2.2 Amount and characteristics of OP in soil and organic inputs

Phosphorus in soil comes from both pedogenic and anthropogenic sources, the majority of P being introduced as mineral fertilizers (Fuentes et al., 2008) or organic residues (Scherer and Sharma, 2002). In addition to IP, soil OP are an important P pool (Monbet et al., 2009), especially in soils treated with organic inputs (Ruttenberg and Sulak, 2011). Studies which quantify OP in organic inputs and soils report different values about the amount of OP in soils, ranging from 20 to 90% of the total P pool in soils and sediments (Anderson, 1980; Anderson et al., 1974; Dalai, 1977; Hu et al., 2020; Turner et al., 2002a). A random-effects meta-analysis performed by Darch et al. (Darch et al., 2014) based on different studies showed that contribution of IP and OP to total P varied significantly in organic input or soil (Tables 5 ,6 , 7 and 8): in organic input, the contribution of IP was found to be 5200 mg.kg⁻¹ against nearly 4000 mg.kg⁻¹ for the OP pools. This revealed that OP is as important in amount as IP in soil and organic inputs. The amount of IHP the major forms of OP reaches 1325 mg.kg⁻¹ in organic inputs, one order of magnitude higher than in soil (269 mg.kg⁻¹). Moreover, the percentage contribution of IHP to total OP varied across the sample types, with soil (40%) > organic inputs (30%). This agrees with the idea that IHP is preferentially stabilized in soil compared with other OP forms due to its relative recalcitrance (Turner et al., 2002b), caused by its strong binding to the soil (Ganta et al., 2019). Further ³¹P NMR studies have shown that the pool of labile monoester-P compounds was the largest pool of OP (Granger et al., 2010; Ignatiades and Gotsis-Skretas, 2010; Withers et al., 2015) and that phosphonates were the weakest and generally less quantified group (Jarosch et al., 2015; Zhu et al., 2018). Most individual studies that characterize OP in the environment show that total IP and OP vary with the characteristics of the organic inputs or soil types or properties, with IP being more important than OP, but remaining very close in some samples (Tables 5 and 6). In soils, P forms and amounts vary with soil type (Turner et al., 2003), land use, and fertilizer history (Guggenberger et al., 1996). Given these large pools of OP in soil and fertilizer and the range of values (20-90% of total P) generally carried over in soils and sediments (Anderson, 1980; Hu et al., 2020), it is pivotal to consider OP dynamics along with IP in order to improve P cycles in agroecosystems.

Current knowledge has revealed that OP is as equally important in amount as IP. However, most research on the fate of organic inputs applied to the soil has focused on the dynamics of IP, while the fate of OP has been neglected until now, and there remains a lack of knowledge on its contribution to plant nutrition. Thus, there is a need to define standard methods that can help guide OP research and a

sustainable approach that could be taken to improve soil OP cycling. This can be achieved through a multi-pronged combination of sustainable farming systems, genetically-improved plants, beneficial biota (biofertilizers).

Table 5 : Total IP and OP forms in organic inputs.

Values in parentheses are percentage of total extractable P.

N°	Organic input	Extractant	Analysis	Total IP	Total OP	References
1	Feces (dairy)	NaOH-EDTA	³¹ PNMR	4961 mg.kg ⁻¹ (64)	2650 mg.kg ⁻¹ (36)	(Toor et al., 2006)
2	Manure (dairy)	NaOH-EDTA	³¹ PNMR	4231 mg.kg ⁻¹ (75)	1396 mg.kg ⁻¹ (26)	(Toor et al., 2006, 2005)
3	Dairy manure - dry	NaOH-EDTA	³¹ PNMR	4736 mg.kg ⁻¹ (67)	2342 mg.kg ⁻¹ (30)	(He et al., 2007)
4	Dairy manure - wet	NaOH-EDTA	Enzymatic hydrolysis	3840 mg.kg ⁻¹ (57)	2957 mg.kg ⁻¹ (49)	(He et al., 2009)
5	Dung	NaOH-EDTA	³¹ PNMR	58 mg.kg ⁻¹ (22)	399 mg.kg ⁻¹ (40)	(Bol et al., 2006)
6	Solid manure (dairy)	NaOH-EDTA	³¹ PNMR	5731 mg.kg ⁻¹ (67)	2848 mg.kg ⁻¹ (33)	(Hansen et al., 2004)
7	Lagoon manure (dairy)	NaOH-EDTA	³¹ PNMR	19 mg.kg ⁻¹ (66)	10 mg.kg ⁻¹ (34)	(Hansen et al., 2004)
8	Cattle manure	NaOH-EDTA	³¹ PNMR	3120 mg.kg ⁻¹ (74)	1080 mg.kg ⁻¹ (25)	(Turner, 2004)
9	Dairy manure	Water	³¹ PNMR	1870 mg.kg ⁻¹ (85)	221 mg.kg ⁻¹ (15)	(He et al., 2009)
10	Dairy manure	NaAcNa ₂ S ₂ O ₄	³¹ PNMR	3680 mg.kg ⁻¹ (79)	944 mg.kg ⁻¹ (21)	(He et al., 2009)
11	Dairy manure	NaOH-EDTA	³¹ PNMR	3637 mg.kg ⁻¹ (77)	964 mg.kg ⁻¹ (23)	(He et al., 2009)
12	Animal species (beef and dairy cattle, swine, chicken, turkey, dairy goat, horse, and sheep)	H ₂ O, NaHCO ₃ , NaOH	-	-	500-8800 mg.kg ⁻¹	(Pagliari and Laboski, 2012)
13	Broiler litter	NaHCO ₃	³¹ PNMR	1300 mg.kg ⁻¹ (12)	2800 mg.kg ⁻¹ (25)	(Li et al., 2014)
14	Dairy manure	NaHCO ₃	³¹ PNMR	2400 mg.kg ⁻¹ (35)	890 mg.kg ⁻¹ (13)	(Li et al., 2014)
15	Swine manure	NaHCO ₃	³¹ PNMR	6500 mg.kg ⁻¹ (21)	1600 mg.kg ⁻¹ (5)	(Li et al., 2014)

Table 6: Total IP and OP forms in different soil properties (in mg.kg-1).

Values in parentheses are percentage of total extractable P.

N°	Land use	Extractant	Analysis	Total IP	Total OP	Reference
1	Semi-arid irrigated arable soils (U.S.)	EDTA	³¹ PNMR	141 mg.kg ⁻¹ (72)	57 mg.kg ⁻¹ (27)	(Turner et al., 2003)
2	Semi-arid irrigated arable soils (U.S.)	Bicarbonate	³¹ PNMR	31 mg.kg ⁻¹ (76)	7 mg.kg ⁻¹ (26)	(Turner et al., 2003)
3	Grassland (Australia)	Deionised water	Enzymatic hydrolysis	1.3 mg.kg ⁻¹ (36)	1.5 mg.kg ⁻¹ (48)	(Turner et al., 2002a)
4	Grassland (New Zealand)	NaOH-EDTA	Enzymatic hydrolysis	454 mg.kg ⁻¹ (56)	23 mg.kg ⁻¹ (4)	(McDowell et al., 2008)
5	Clover and arable plots (Australia)	NaOH-EDTA	³¹ PNMR	345 mg.kg ⁻¹ (76)	6 mg.kg ⁻¹ (2.5)	(Bünemann et al., 2006)
6	Grassland (U.S.)	NaOH-EDTA	³¹ PNMR	221 mg.kg ⁻¹ (82)	54 mg.kg ⁻¹ (19)	(Hansen et al., 2004)
7	Grassland (Netherlands)	NaOH-EDTA	³¹ PNMR	406 mg.kg ⁻¹ (56)	207 mg.kg ⁻¹ (44)	(Koopmans et al., 2007)
8	Grassland (Ireland)	NaOH-EDTA	³¹ PNMR	358 mg.kg ⁻¹ (47)	373 mg.kg ⁻¹ (54)	(Murphy et al., 2009)
9	Grassland (New Zealand)	NaOH-EDTA	³¹ PNMR	(32)	(68)	(Newman and Tate, 1980)
10	Grassland (England and Wales)	NaOH-EDTA	³¹ PNMR	275 mg.kg ⁻¹ (40)	480 mg.kg ⁻¹ (70)	(Turner et al., 2003)
11	Grassland (England and Wales)	NaHCO ₃	³¹ PNMR	18 mg.kg ⁻¹ (25)	70 mg.kg ⁻¹ (80)	(Turner, 2005)
12	Grassland (New Zealand)	NaOH-EDTA	³¹ PNMR	500 mg.kg ⁻¹ (50)	20 mg.kg ⁻¹ (3)	(McDowell et al., 2005)
13	Forest, grassland and arable (Germany)	NaOH	³¹ PNMR	52 mg.kg ⁻¹ (30)	149 mg.kg ⁻¹ (56)	(Guggenberger et al., 1996)
14	Grassland (England)	NaOH	³¹ PNMR	224 mg.kg ⁻¹ (50)	140 mg.kg ⁻¹ (40)	(Hawkes et al., 1984)
15	Semi-arid grassland and arable (Canada)	H ₂ O and NaOH	³¹ PNMR	175 mg.kg ⁻¹ (58)	117 mg.kg ⁻¹ (42)	(Condon et al., 2005)
16	Grassland (U.S.)	NaOH-EDTA	³¹ PNMR	23 mg.kg ⁻¹ (20)	66 mg.kg ⁻¹ (67)	(Cheesman et al., 2014)
17	Arable (Canada)	NaOH-EDTA	³¹ PNMR	504 mg.kg ⁻¹ (73)	370 mg.kg ⁻¹ (48)	(Cade-Menun, 2017)
18	Grassland (New Zealand)	NaOH-EDTA	³¹ PNMR	620 mg.kg ⁻¹ (54)	465 mg.kg ⁻¹ (45)	(McDowell et al., 2005)

19	Burkina Faso Arable Lixisol	NaOH-EDTA	³¹ PNMR	19 mg.kg ⁻¹ (23)	-	(Jarosch et al., 2015)
20	Madagascar Arable Ferralsol	NaOH-EDTA	³¹ PNMR	50 mg.kg ⁻¹ (54)	15 mg.kg ⁻¹ (12)	(Jarosch et al., 2015)
21	Australia Grassland Alfisol	NaOH-EDTA	³¹ PNMR	35 mg.kg ⁻¹ (39)	16 mg.kg ⁻¹ (17)	(Jarosch et al., 2015)
22	Germany Arable Luvisol	NaOH-EDTA	³¹ PNMR	249 mg.kg ⁻¹ (74)	35 mg.kg ⁻¹ (13)	(Jarosch et al., 2015)
23	Switzerland 2 Arable Luvisol	NaOH-EDTA	³¹ PNMR	228 mg.kg ⁻¹ (66)	36 mg.kg ⁻¹ (12)	(Jarosch et al., 2015)
24	Switzerland 3 Grassland Cambisol	NaOH-EDTA	³¹ PNMR	121-396 mg.kg ⁻¹ (36- 66)	8-206 mg.kg ⁻¹ (1-17)	(Jarosch et al., 2015)
25	Different soils	-	-	-	(>55)	(Roberts and Johnston, 2015)
26	Caribou soil with conventional cultivation history	NaOH	Enzymatic hydrolysis	1162 mg.kg ⁻¹	330 mg.kg ⁻¹	(He et al., 2004)
27	Caribou soil with manure application history	NaOH	Enzymatic hydrolysis	966 mg.kg ⁻¹	249 mg.kg ⁻¹	(He et al., 2004)
28	Swine manure		Enzymatic hydrolysis	173 mg.kg ⁻¹	235 mg.kg ⁻¹	(He et al., 2004)

Table 7 : Amount of IP and OP species in organic input

N°	Organic input	IP forms			OP forms				
		Orthophosphate Pyrophosphate Polyphosphate	Phosphomonoesters		Phospholipi ds	Phosphodieters			Unidenti fied
			IHP	Labile		DNA/ polynucleotide	Other	Phospha nate	
1	Feces (dairy)	4961mg.kg ⁻¹	1325 mg.kg ⁻¹	624 mg.kg ⁻¹	423 mg.kg ⁻¹	154 mg.kg ⁻¹	113 mg.kg ⁻¹	73 mg.kg ⁻¹	-
2	Manure (dairy)	4231mg.kg ⁻¹	496 mg.kg ⁻¹	503 mg.kg ⁻¹	210 mg.kg ⁻¹	108 mg.kg ⁻¹	83 mg.kg ⁻¹	55 mg. kg ⁻¹	-
3	Dairy manure dry	4736 mg. kg ⁻¹	268 mg.kg ⁻¹	204 mg.kg ⁻¹	-	24 mg.kg ⁻¹	-	-	1842 mg. kg ⁻¹

4	Dairy manure wet	3840 mg.kg ⁻¹	678 mg.kg ⁻¹	608 mg.kg ⁻¹	-	434 mg.kg ⁻¹	-	-	1237 mg.kg ⁻¹
5	Dung	5-24 mg.kg ⁻¹	61-106 mg.kg ⁻¹	-	40-103 mg.kg ⁻¹	58-90 mg.kg ⁻¹	-	0-2 mg.kg ⁻¹	-
6	Solid manure (dairy)	5731 mg.kg ⁻¹	1338 mg.kg ⁻¹	1236 mg.kg ⁻¹	154 mg.kg ⁻¹	77 mg.kg ⁻¹	-	231 mg.kg ⁻¹	43 mg.kg ⁻¹
7	Lagoon manure (dairy)	19.1 mg.kg ⁻¹	3.2 mg.kg ⁻¹	5.9 mg.kg ⁻¹	0.3 mg.kg ⁻¹	0.3 mg.kg ⁻¹	-	-	-
8	Cattle manure	3120 mg.kg ⁻¹	500 mg.kg ⁻¹	140 mg.kg ⁻¹	220 mg.kg ⁻¹	220 mg.kg ⁻¹	-	-	-
9	Dairy manure	1870 mg.kg ⁻¹	0	136 mg.kg ⁻¹	-	18 mg.kg ⁻¹	67 mg.kg ⁻¹	85 mg.kg ⁻¹	-
10	Dairy manure	3680 mg.kg ⁻¹	444 mg.kg ⁻¹	369 mg.kg ⁻¹	-	51 mg.kg ⁻¹	81 mg.kg ⁻¹	131 mg.kg ⁻¹	-
11	Dairy manure	3637 mg.kg ⁻¹	444 mg.kg ⁻¹	385 mg.kg ⁻¹	-	45 mg.kg ⁻¹	90 mg.kg ⁻¹	-	-

Table 8: Amount of IP and OP species in soil

	Soil types	IP forms		OP forms				Unidentified
		Orthophosphate Pyrophosphate Polyphosphate	Phosphomonoesters		Phospholipids	DNA/ polynucleotide	Other P forms Phosphanate	
			IHP	Labile				
1	Semi-arid irrigated arable soils (U.S.)	150 mg.kg ⁻¹	45 mg.kg ⁻¹	10 mg.kg ⁻¹	1 mg.kg ⁻¹	0.3 mg.kg ⁻¹	1.3 mg.kg ⁻¹	-
2	Semi-arid irrigated arable soils (U.S.)	31 mg.kg ⁻¹	1.6 mg.kg ⁻¹	1.4 mg.kg ⁻¹	0.1 mg.kg ⁻¹	0.9 mg.kg ⁻¹	1 mg.kg ⁻¹	2.2 mg.kg ⁻¹
3	Grassland (Australia)	1.3 mg.kg ⁻¹	0.28 mg.kg ⁻¹	0.04 mg.kg ⁻¹	0.2 mg.kg ⁻¹	0.03 mg.kg ⁻¹	0.23 mg.kg ⁻¹	0.8 mg.kg ⁻¹

4	Grassland (New Zealand)	454 mg.kg ⁻¹	221 mg.kg ⁻¹	100 mg.kg ⁻¹	5 mg.kg ⁻¹	5 mg.kg ⁻¹	9.5 mg.kg ⁻¹	.
5	Clover and arable plots (Australia)	345 mg.kg ⁻¹	40 mg.kg ⁻¹	14 mg.kg ⁻¹	3 mg.kg ⁻¹	2.5 mg.kg ⁻¹	-	-
6	Grassland (U.S.)	221 mg.kg ⁻¹	37 mg.kg ⁻¹	11 mg.kg ⁻¹	0.1 mg.kg ⁻¹	1.8 mg.kg ⁻¹	0	-
7	Grassland (Netherlands)	406 mg.kg ⁻¹	150 mg.kg ⁻¹	56 mg.kg ⁻¹	0.3 mg.kg ⁻¹	0.1 mg.kg ⁻¹	-	-
8	Grassland (Ireland)	353 mg.kg ⁻¹	239 mg.kg ⁻¹	100 mg.kg ⁻¹	-	16.4 mg.kg ⁻¹	3.2 mg.kg ⁻¹	-
9	Grassland (New Zealand)	-	-	-	-	-	-	-
10	Grassland (England and Wales)	271 mg.kg ⁻¹	142 mg.kg ⁻¹	102 mg.kg ⁻¹	21 mg.kg ⁻¹	17 mg.kg ⁻¹	6.8 mg.kg ⁻¹	22.6mg.kg ⁻¹
11	Grassland (England and Wales)	18 mg.kg ⁻¹	-	12.4 mg.kg ⁻¹	0.8 mg.kg ⁻¹	3.6 mg.kg ⁻¹	-	39mg.kg ⁻¹

1.2.3 Organic phosphorus dynamics in rhizosphere

Rhizosphere microbiomes and roots traits involved in P acquisition are known to affect the dynamics of OP in the rhizosphere and, ultimately, its availability to the plant (Figure 6). Although studies showed that OP can be significantly depleted within the rhizosphere (Chen et al., 2004; Gahoonia and Nielsen, 2004), the interaction between rhizosphere microbiomes in the rhizosphere, root traits, and their contribution to OP release to plants are not fully elucidated so far (Jakobsen et al., 2015). Here we summarize and discuss the role of soil microbial processes, root mechanisms and their interactions in the fate of OP forms in the organic input-soil-plant system.

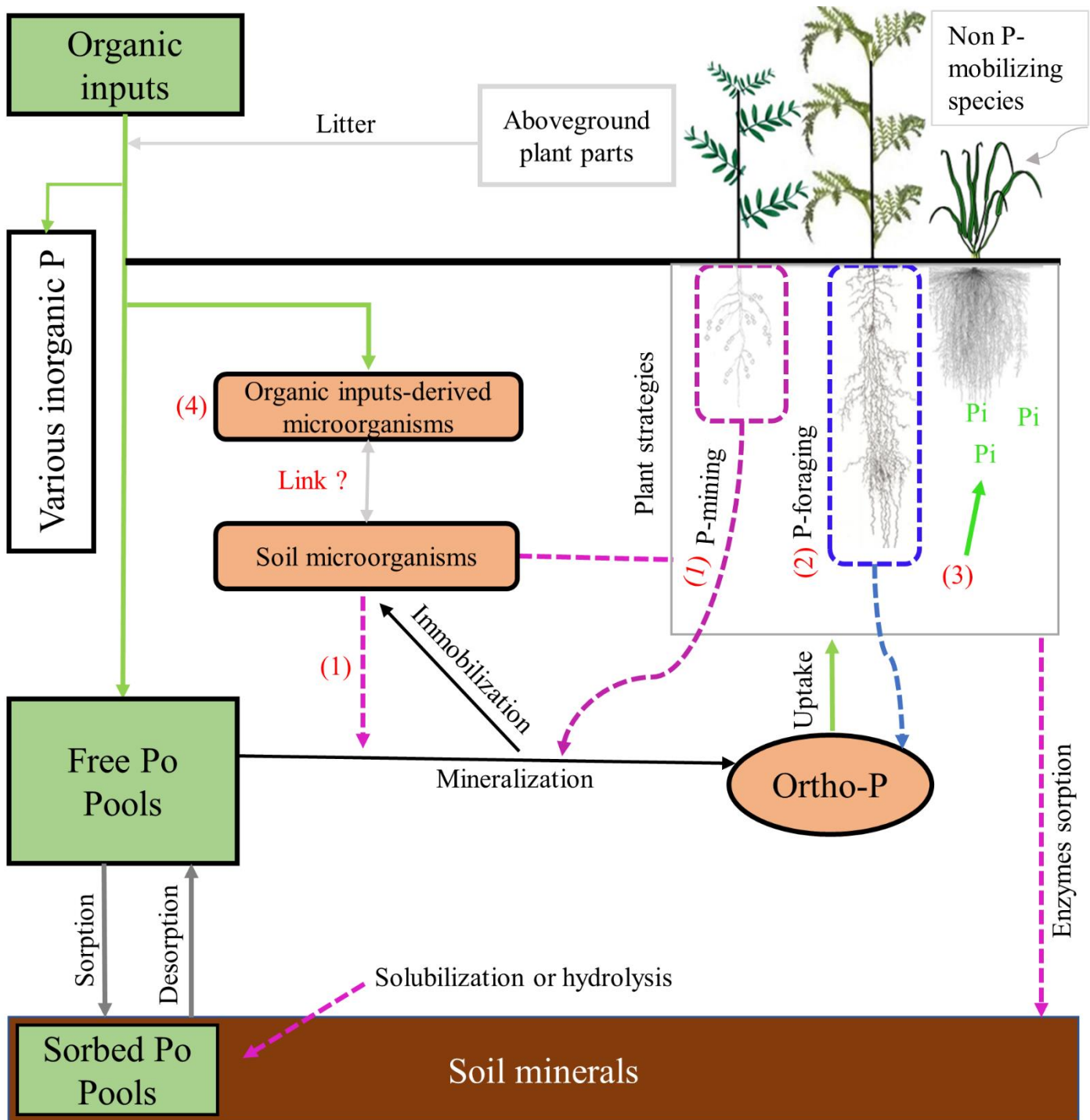


Figure 6: Organic input-soil-plant system-related biogeochemical processes that may ultimately modify the dynamics of the OP pool in the rhizosphere.

(1) and (2) are the plants *P mining* and *foraging* strategies respectively (see Section 3.2 for more details); (3) P-mobilizing crop species improve OP utilization for non-P-mobilizing species, (4) refers to the microorganisms coming from organic input. Indeed, organic inputs involve the addition of carbon sources and often even contain their own microbiota. System modified from (Hinsinger et al., 2015) and (Suliman and Mühling, 2021).

1.2.3.1 Soil microbial processes involved in OP mobilization

In organic inputs-amended soils and P-depleted environments, there is generally a proliferation of free rhizosphere microbiome and symbiotic associations with mycorrhizal fungi which have the potential to mobilize and mineralize different forms of available and unavailable OP (Suliman and Mühling, 2021; Tian et al., 2021) (Table 9). Phyla involved in OP mineralization include the dominant phyla *Proteobacteria* followed by *Acidobacteria* and *Actinobacteria* (Annaheim et al., 2010; Gaiero et al., 2018). The order *Xanthomonadales* of *Xanthomonadaceae* family is known to contain several OP mineralizing genes. To obtain P from OP compounds, *Streptomyces* uses an extracellular alkaline phosphatase encoded by the *phoA* gene. Other alkaline phosphatase genes, *phoD* and the *phoC*, were initially described in the *Streptomyces avermitilis* and *Streptomyces coelicolor* genomes, respectively (Tian et al., 2021). *Stenotrophomonas spp.* has been shown to be an important contributors of OP solubilization. Controlled experiments using plant inoculated with rhizosphere microbiome provided further evidence for microbially mediated OP bioavailability to plants. Richardson et al. (Richardson et al., 2011) showed that both grasses and legumes exhibited an improved ability to utilize IHP-P when inoculated with bacteria isolates with high phytase activity. *Bacillus spp.* and *Trichoderma spp.* may be able to increase the use of IHP as P source by plants due to the production of organic anions and phytase (Garcia-Lopez et al., 2015; Garcia-Lopez and Delgado, 2016). Nevertheless, there are little evidences on how these rhizosphere microbiomes may act in the presence of soil minerals that can immobilize both OP and hydrolytic enzymes. Soil minerals such as Fe, Al oxides, and clay minerals are known to considerably reduced the efficiency of applied P. It is assumed that adsorbed OP on Fe and Al oxides are protected from enzymatic hydrolysis leading to its accumulation in soil (Stutter et al., 2015) and its decreased use as P source by plants. However, García-López et al. (2020) recently showed that *Bacillus subtilis* improved hydrolytic activity of IHP even in the presence of high Fe oxide concentration. This led the conclusion that rhizosphere microbiome could contributes to an increased hydrolyzing capacity in soil with high OP sorption capacity (Table 9). Current work is insufficient to understand the extent to which rhizosphere microbiomes are actually able to access sorbed forms of P. Future work must be conducted by inoculating microorganisms with sorbed P complexes on major soil minerals such as goethite, gibbsite, and major clays under laboratory conditions and even further in the field. Thus, as most of the legacy P is poorly available to plants, especially the important part corresponding to OP pools (Stutter et al., 2012), the impact of rhizosphere microbiomes in mobilizing this legacy P is a crucial issue to reduce the dependence on mined P fertilizers (Giles et al., 2011). Moreover, it is important to keep in mind that hydrolysis of adsorbed OP depends to some extent on the release of organic anions or citrate by plant and rhizosphere microbiomes; this promotes the desorption and dissolution of OP making it available for hydrolysis (Celi et al., 2020).

Different enzymes released by the rhizosphere microbiome that are involved in OP hydrolysis, such as phytases and alkaline and acid phosphatases, act specifically on particular OP substrates

(Annaheim et al., 2010). Several studies using soil-specific enzyme additions have been published over the past decades (George et al., 2008; Turner et al., 2002b). Their results show that OP mineralization would be explained by the specificity of enzymatic activities on OP forms. For example, Scyllo-IHP was found to be most resistant to phytase activity (Cosgrove, 1963) while IHP hydrolysis has been reported for bacterial acid phosphomonoesterases (Lung et al., 2008). Other phytases from *Aspergillus spp.* (EC 3.1.3.8) have also been reported to hydrolyze IHP, simple monoesters (G6P, GLY), and phosphoanhydrides, but their ability to hydrolyze diester bonds in nucleic acids (George et al., 2007; Turner et al., 2002b) is contradicted by the result of various studies (Annaheim et al., 2013). Monoesterase enzymes have been found to hydrolyze diester phosphates. However, the release of phosphates from DNA is generally very low. This could be because monoesterases hydrolyze only the 5' and 3' phosphate residues of DNA (Annaheim et al., 2010), while the other phosphate groups are not accessible (George et al., 2007). It has previously been shown that acid and alkaline phosphatase and phytase are not active on nucleotide pyrophosphate that contains nucleotide pyrophosphate bonds, nor on RNA and DNA that contain phosphodiester bonds (He and Honeycutt, 2001). In organic input, nucleotide pyrophosphatase, which hydrolyzes nucleotide pyrophosphate to nicotinamide mononucleotide and AMP, and a P1 nuclease, which cleaves RNA and DNA to produce 5-phospho-monoesters, were used to assess the presence of OP forms. The result showed that both enzymes (nucleotide pyrophosphatase and P1 nuclease) acted only on their own substrate (nucleotide pyrophosphate, RNA and DNA). Therefore, it has been suggested that these enzymes could be used to release specific forms of phosphorus when present in the soil (He and Honeycutt, 2001).

Soil properties may influence the conversion of OP into IP by rhizosphere microbiome. Among the soil properties, soil pH is an especially important factor that affects the efficacy and biochemical availability of enzymes that hydrolyze the OP forms in the soil. For instance, at a pH of 7.5, *Aspergillus niger* phytases remained in solution, but at a pH of 5.5, it is unavailable (George et al., 2007). But, optimal pH varies according to the soil microorganism species and the associated plant. Fungal phytases have a pH between 4.5 and 6.5, such as *Aspergillus fumigatus*, where 80% of the activity takes place (Wyss et al., 1999). Species such as *Rhizoctonia sp.* and *Fusarium verticillioides* can produce phytases at optimal pH of 4.0 and 5.0, respectively (Marlida et al., 2010), while in bacterial phytases the maximum activity was observed at an optimal pH of 6.0-8.0, as in *Bacillus sp.* (Kim et al., 1998). Most of the phytases are acidic and have an optimal pH between 4.5 and 6.0 (Konietzny and Greiner, 2002), whereas alkaline phytases in legume seeds (Scott, 1991), lily pollen and cattail pollen have been reported to have an optimal pH of 8.0 (Azeem et al., 2015). For example, at pH 7.5, phytases from *Aspergillus niger* remain available in solution, but at pH 5.5 they are not available (George et al., 2007). It is clear that phosphatases produced by rhizosphere microbiomes are more sensitive to pH. This pH dependence would even be superior to that of plant phosphatases. However, the optimal pH for OP mobilization varies among rhizosphere microbiome species. In addition, it is also important to understand how microorganisms could facilitate P mobilization from organic inputs or soil organic matter within a given

pH range. Consequently, we conclude that the determination of the optimal pH for OP mobilization by microbes and root traits requires careful judgment in future research.

In addition to pH, soil temperature has a strong effect on OP availability even though studies showed divergent results on the influence of temperature on P solubilization by microbes. White et al. (White et al., 1997) found 20-25°C to be the optimal temperature for maximum microbial solubilization of P while 28°C was reported by Chauhan et al. (Chauhan et al., 2014) and Alori et al. (Alori et al., 2017). In addition, others recorded 30 °C as the best temperature for solubilization and mineralization of OP (Fasim et al., 2002; Kim et al., 1998). Nautiyal et al. (Nautiyal et al., 2000) reported solubilization and hydrolysis of P at an extreme temperature of 45°C in desert soil while Johri et al. (Johri et al., 2015) reported a low temperature of 10 °C. The optimum temperature for phytate-degrading enzymes ranges from 35 to 77°C. In general, plant phytases, such as those from cereals, show maximum activity at lower temperatures than microbial phytases (Konietzny and Greiner, 2002). The phytase from *Fusarium verticillioides* showed an optimal temperature of 50°C and stability up to 60°C (Azeem et al., 2015). The optimal temperature for phytase activity towards magnesium phytate (Mg-IHP) has been reported to reach 40°C without and 50°C with 5 mM Ca²⁺ (Park et al. 2012). Most plant phytases have an optimal temperature of 45-60°C, as reported by Johnson et al. (Johnson et al., 2010). The lowest temperature has been reported to be 10°C (Johri et al., 2015). However, it is generally assumed that higher temperature (> 30°C) has a better effect on OP solubilization and availability as shown by the higher OP solubilization by *Bacillus megaterium* at 36°C than at 21°C. Like pH, phosphatases produced by rhizosphere microbiomes are thermostable. Therefore, changes in the interactions between microbes and root traits as a result of temperature variations and how this could affect OP mobilization processes must be considered in the soil-plant system. Furthermore, understanding the optimal activity of microorganisms as a function of soil temperature is an important challenge for improving biofertilizer management practices and their positive effects on OP hydrolysis and P availability. However, given the challenge of controlling soil temperature, it is nonetheless possible to identify the dates and seasons to apply the biofertilizer to maximize its effect. The effectiveness of microbial enzymatic activity is also influenced by different cations and other constituents in the soil solution. Model studies have shown that three classes of phytases, histidine acid phosphatases, β-propellant phytases, and purple acid phosphatases, would be unable to hydrolyze Al³⁺, Fe²⁺, Fe³⁺, Cu²⁺ salts of IHP, but were able to hydrolyze Ca²⁺, Mg²⁺, and Mn²⁺ salts (Lim et al., 2007; Tang et al., 2006). This implies that P mobilization will depend on the nature of the cation that precipitates OP. Thus, the accessibility of precipitated OP by enzymes and its mobilization for plants will be largely different depending on the nature and concentration of electrolytes in the soil.

In summary, the hydrolysis of OP and its release by enzymatic activity is generally affected by the biochemical nature of OP and its ability to interact with soil properties and rhizosphere microbiomes. A wide variety of bacteria, fungi, and endophytes can therefore solubilize OP through the production of organic acids (Adhya et al., 2015). This solubilization is very important because most forms of OP are

high molecular weight compounds that are generally resistant to chemical hydrolysis. However, the mechanisms associated with the transformation of OP to IP are poorly understood, and further work is needed, especially under field conditions. In most studies, the experimental conditions have suppressed interactions between system components. Therefore, these studies generally only indicate what is possible, but they do not necessarily indicate what is likely (Lung and Lim, 2006; Zimmermann et al., 2003). Indeed, knowledge of OP transformations must be a prerequisite for understanding the potential contribution of lesser-known forms of OP in the organic input-soil-plant system. In any case, it is clear that OP mineralization occurs in the rhizosphere and could contribute significantly to the requirements for plant growth. Factors affecting rhizosphere microbiome are likely to influence the lability and stability of their enzymes. Some enzymes become stable through interactions with soil minerals and humic substances, and retain some enzyme activity (Allison et al., 2007). In general, microbial activity is affected by biological (the amount and type of substrate, concentration of enzyme, ect.) and physicochemical processes (interactions with soil constituents pH, temperature, ect.). The former cause changes in enzyme production rates and microbial community composition, while the latter cause changes in adsorption/desorption reactions, substrate diffusion and enzyme degradation rates (Wallenstein et al., 2009). Critical factors affecting microbes and their enzyme activities include the amount and type of OP (Fitriatin et al., 2008), interactions with soil constituents, pH, temperature, and concentration of enzyme and product (Sarapatka, 2002). In addition, because OP adsorbs rapidly and strongly on-to soil particles, the binding processes involved also play a crucial role in the activity of rhizosphere microbiomes (Fierer, 2017; Qu et al., 2020). To date, there are relatively few studies that explore the enzymatic hydrolysis of adsorbed OP. It has been reported that mineral surfaces protect the majority of adsorbed phosphate esters from enzymatic hydrolysis, but whether this is a general finding remains open (Jones et al., 2004). Furthermore, the mechanism of this process is largely unknown in the case where the enzyme is able to access the adsorbed OP forms. The results of Olsson et al. (Olsson et al., 2012) on the hydrolysis of G1P on α -FeOOH surfaces showed the role of interactions at mineral surfaces with respect to the stabilization of OP molecules in soils (Bian et al., 2012). These authors provided a mechanistic explanation of how P can be mobilized via enzymatic activity despite strong interactions with soil minerals. This sheds light on previous results showing that microbial stimulation and the resulting enzymatic activity can mobilize adsorbed OP from soil minerals (Tang et al., 2006). However, a question is whether the enzyme acts only on the soluble fraction that is reconstituted by desorption of the substrate or whether the hydrolysis reaction occurs at the interface between the aqueous solution and solid particles. We therefore suggest future studies on these issues to understand better the effect of rhizosphere microbiomes on OP dynamics.

Apart of the rhizosphere microbiome, organic inputs-derived microorganisms also play a major role in the mobilization of OP. Organic inputs imply the addition of carbon sources and often even contain their own microbiota, like an inoculation of microbes and this is a very important issue that needs more study. Amendment of organic inputs generally increases the diversity of rhizosphere

microbiomes and their enzymatic activities in the soil (Francioli et al., 2016). These positive reactions highlight the role of organic inputs-derived microorganisms in OP availability and on the other hand their high content of organic matter (Li et al., 2010) which is the main substrate of most microorganisms (Li et al., 2014). However, complex questions remain about how the addition of organic inputs alters the soil microbial community and especially how this relates to soil OP mineralization. Then to successfully manage organic inputs, there is a need to develop a consistent procedure to quantitatively compare the potential of these different microorganisms to release orthophosphate from different sources of OP (Li et al., 2014). As organic input-soil-plant continuum consists of various forms of OP with different chemical properties, their solubilization and hydrolysis rates would be strongly related to the diversity of soil microbial communities. Therefore, it is crucial to develop and utilize more advanced approaches to support the roles soil microbes especially the phosphate solubilizing microorganisms-derived enzymes in releasing free IP from OP forms in the soil (Alori et al., 2017; Liang et al., 2020). In sum, the main microbial processes involved in P dynamics that are synthesized and highlighted in this section, and the factors that influence them, greatly affect soil P mobilization processes. They could therefore, if well understood, contribute to increase the P use efficiency of organic wastes and those accumulated in agricultural soils. Furthermore, it is known that plant roots inoculated with commercial microorganisms can express synergistic effects to solubilize IP in the soil. In contrast, little is known about their effect on OP pools. Therefore, further research is needed to evaluate the application and efficacy of commercial microorganisms on various crops with contrasting root traits and fertilized with different P sources under field conditions.

Current cropping models often focus on understanding competition for light and the effects of N or P fertilization, but do not consider interactions with the rhizosphere microbiome and how it affects soil OP forms. Thus, the development of cropping models that consider more OP dynamics is needed to determine the efficiency of OP use in multi-species cropping systems and to manage P sustainably in the agroecosystem. Furthermore, it is important to note that current decision support tools do not consider OP spation, its mineralization kinetics, and the effect of root trait and rhizosphere microbiome interactions on its dynamics. Therefore, for future research aimed at assisting farmers in organic input management, these parameters that govern OP dynamics, should be further studied and integrated into decision support tools. This will not only improve the decision support tools but also make them more focused on OP mobilization in the organic input-soil-plant system.

Another important factor is the effect of rhizosphere microbial populations on OP mineralization. Some studies have shown that soils taken from the rhizosphere slowed the sorption of phytate or phytase into the rhizosphere, suggesting that rhizosphere soils alter the adsorption of phytase and thus the release of orthophosphate from soils. This is an important observation because OP dynamics are altered in the rhizosphere, so it is possible that OP from organic inputs is more available around plant roots. Therefore, we strongly suggest that, along with the mobilization process by soil microbes, root mechanisms/traits can be exploited to facilitate soil OP mobilization at the field scale.

The hydrolysis of OP and its release by enzymatic activity is influenced by the biochemical nature of OP and its ability to interact with soil properties and rhizosphere microbiomes. However, current work is insufficient to understand the extent to which rhizosphere microbiomes are actually able to access sorbed forms of P from both soil constituents and organic matter. Furthermore, the potential of microbes to mobilize OP has been conducted on cultivable microbes, yet most root-associated rhizosphere microbiomes are not cultivable. We recommend future investigations to screen rhizosphere bacteria in the presence of different forms of OP and different soil properties, to identify those that are effective in OP mobilization.

Table 9: Possible root traits and microbial activity involved in OP mobilization (solubilization and mineralization).

Organic phosphorus forms	Mode of action that root traits and microbes act to mobilize the OP.	Associated microorganisms	Reference
Glycerophosphate and phytate	Alkaline phosphatase and acid phosphatase; phytase	<i>Bacillus coagulans</i>	(Yadav et al., 2012)
Ca-phytate	pH reduced; phytase	<i>Bacillus altitudinis</i> WR10	(Yue et al., 2019)
OP pools	Alkaline phosphatase	<i>Aphanothece halophytica</i>	(Kageyama et al., 2011)
Na-phytate	pH reduced; phytase	<i>Tetrathibacter</i> sp. PB-03 and <i>Bacillus</i> sp. PB-13	(Kumar et al., 2013)
Phytic acid	Phytase	<i>Bacillus amyloliquefaciens</i> US573 <i>Acromobacter</i> sp. PB-01	(Boukhris et al., 2015)
Total OP pools	Alkaline phosphatase and acid phosphatase	<i>Bacillus pumilus</i> strain JPVS11	(Kumar et al., 2021)
beta-Glycerophosphate	pH reduced; acid phosphatase	<i>Agrobacterium</i> sp. and <i>Bacillus</i> sp.	(Barua et al., 2012)
5-bromo-4-chloro-3-indolyl phosphate (BCIP)	pH reduced; phosphatase	<i>Pantoea agglomerans</i> strain P5 <i>Microbacterium laevaniformans</i> strain P7 and <i>Pseudomonas putida</i> strain P13	(Malboobi et al., 2009)
p-nitrophenyl phosphate (pNPP) and guanosine 5-triphosphate (GTP)	Alkaline phosphatase/phosphodiesterase activity	<i>Cobetia amphilecti</i>	(Noskova et al., 2019)

Lecithin	pH reduced; organic acid	<i>Kushneria sp.</i> YCWA18, <i>Bacillus megaterium</i>	(Xiang et al., 2011; Zhu et al., 2011)
Total OP pools	pH reduced, oxalic acid, citric acid, malic acid, succinic acid and acetic acid; alkaline phosphatase	<i>Alcaligenes faecalis</i>	(Bikash Chandra Behera et al., 2017)
p-nitrophenyl phosphate	Malic acid, lactic acid and acetic acid; acid phosphatase, pH reduced, oxalic acid, citric	<i>Serratia sp.</i> , <i>Alcaligenes faecalis</i>	(B. C. Behera et al., 2017)
Fe-OP, and lecithin	pH reduced	<i>Ensifer sesbaniae</i> , <i>Gordonia terrae</i> , <i>Bacillus sp.</i> , <i>Acinetobacter Sp.</i>	(Jiang et al., 2020)

1.2.3.2 Root mechanisms involved in the fate of OP forms

The contribution of plants to OP availability is known since many decades. Most plants have developed strategies to increase P acquisition in P-deficient soil or to specifically access different forms of OP and IP in the soil (Simpson et al., 2011). These strategies cover a wide range of morphological, architectural and physiological traits (Robles-Aguilar et al., 2019). In general, these traits could be categorized into three types of P acquisition strategies: *foraging*, *mining* and collective *microbial-root* strategy (Figure 6 and Table 9).

The plant P-*foraging* strategy is the acquisition of P in the soil solution through morphological and architectural traits by maximizing soil exploration. Through this strategy, plants can induce a diffusion gradient which in turn would favour the desorption process of the different adsorbed OP forms (Fang et al., 2019; White and Hammond, 2008). Phosphorus *foraging* strategy would also improve the efficiency of P uptake by slowing the rate at which OP moves from the free or moderately adsorbed form to the strongly adsorbed form on soil compounds (Simpson et al., 2011). *Foraging* strategy involves morphological traits such as specific root length, diameter and radius, and architectural traits including root length density, root biomass, root hairs, and the formation of clustered roots or arbuscular mycorrhizal symbioses that allow plants to increase their *foraging* capacity (Haling et al., 2018). These traits alter the C cost of soil exploration by regulating the extent of competition within and between root systems (Ge et al., 2000; Rubio et al., 2003). Among morphological trait, root radius is considered important in the efficiency of P use. Plants with finer/thinner roots favoured the exploration and contact of a greater volume of soil per unit root area. Gahoonia et Nielsen (Gahoonia and Nielsen, 2004) reported that plant species with finer roots may be more effective in mobilizing OP and absorption of IP from the soil. Very recently, trade-offs between thicker and thinner roots have been observed by Honvault et al. (Honvault et al., 2020). Thicker roots are reported to have greater carboxylate release and phosphatase

activity in the rhizosphere, which are involved in the desorption and mineralization of OP (Honvault et al., 2020). In contrast, the thinner exhibit the morphological traits (*foraging*) that favoured the exploration and contact of a larger volume of soil to permit P mobilization process (Hammond et al., 2009; Lynch, 2015). These observations are consistent with other results showing that species with finer fibrous roots express higher levels of morphological traits to access more OP in the soil (Haling et al., 2018; Lambers et al., 2006; Wen et al., 2019). However, since fine roots (root hairs, small root radius) tend to renew faster than large roots (Ge et al., 2000), the cost of C to produce fine roots could be higher, since they would also need to be replaced more frequently (Rubio et al., 2003). In addition to root radius, the formation of root groups such as the proteoid and dauciform root groups commonly found in plant species belonging to the families *Proteinaceae* and *Fabaceae* (Lambers et al., 2006) and others is very strongly related to the dynamics of OP in soil. These roots cover a very dense mat of root hairs and also specialize in the efficient synthesis and secretion of citrate and malate (organic anions) and phosphatases, which help solubilize insoluble OP resources and hydrolyze OP for plant uptake (Pearse et al., 2006). Various effects of root growth and variation in root hair length on OP dynamics and contribution to P uptake have been reported in several species including maize, wheat, barley, beans, soybean and white clover (Wang et al., 2004; Zhu et al., 2005). Higher root length density in the upper soil layers was shown to be the most important root trait of wheat for OP mobilisation in response to organic input (Lamont, 2003). Moreover, the variation in root growth angle and root hairs might have a significant impact on the total mobilisation of P in the soil (Trachsel et al., 2011). In closely related maize genotypes, the effects of root growth and root hair length variation reportedly led to a 100% increase in total mobilized P and in other genotypes to as much as a 600% increase in P mobilization (Zhu et al., 2005). Such increases are due to the fact that root growth maximizes soil exploration and can induce a diffusion gradient and modify soil properties to promote P desorption. Root hairs are smaller in diameter than roots and grow perpendicular to the root axis and can form up to 77% of the root surface (Fort and Freschet, 2020) of soil/field crops (Parker et al., 2000; Raghothama, 1999). The presence of root hairs can be very important for the effectiveness of OP mobilization through a considerable increase of root area in the soil. It has been reported that root hairs can contribute up to 70% of OP uptake (Gahoonia and Nielsen, 2004; Smith, 2002). Root hair length and density are highly controlled by P bioavailability. Geometric modeling indicates that root hair responses to P availability interact synergistically to enhance OP and IP acquisition (Ma et al., 2018). Root hairs also aid in the dispersal of root exudates such as organic acids into the rhizosphere, which improve OP bioavailability in many soils (Ryan et al., 2001). Root morphological traits reveal a much more significant influence on OP acquisition generally in winter wheat genotypes than at biochemical transformation by acid phosphatases (Nobile et al., 2019; Wang et al., 2004). These biochemical and morphological changes can vary considerably between and within plant species (Sulieman and Mühling, 2021; Zogli et al., 2017). Admittedly, the potential ability of plants root traits to utilize poorly available OP sources is greatly determined by its genetic makeup.

The plant P *mining* strategy, is the acquisition of P in the soil solution through physiological traits that are released into the soil from the roots, including carbohydrates, organic and amino acids, phenolic compounds, proteins, fatty acids, sterols, enzymes, polysaccharides and phospholipids (Guppy et al., 2005; Weiskopf et al., 2006). Among these compounds, carboxylic acids, PME activity, phenolic and mucilage compounds, and protons are the main physiological traits involved in P *mining* strategies for OP mobilization (Carminati et al., 2013). Through this strategy, plants increase the turnover of poorly available OP pools (Lambers et al., 2006; Richardson, 2005) by desorption, solubilization and mineralization process. Before any hydrolysis process by the enzymes, OP, if not free, must first be desorbed or dissociated from soil minerals or organic matter. The secretion of organic acids by P-mobilizing species improves the availability of OP forms by promoting their desorption from soil constituents to the soil solution in which they are subsequently mineralized by phosphatases (Li et al., 2004). Organic acids are generally expected to be strongly linked to OP mobilization in the soil-plant system (Neumann et al., 1999). Plant roots have the ability to produce organic acids, particularly short-chain organic acids such as lactate, acetate, oxalate, succinate, fumarate, malate, citrate, isocitrate, and aconitate which can mobilize both OP and IP (Damon et al., 2014). Among the organic acids, malic and citric acids are the most widespread and abundant detected in root exudates (Aziz et al., 2011). Given the highest affinities between OP forms and soil components, chelation between organic acids in root exudates and soil constituents would be the main mechanism for OP solubilization by organic acids in soil (Oburger et al., 2011). Citrate has been shown to chelate Fe and Al oxyhydroxide and Mn and Ca-carbonates, which could actively displace adsorbed OP towards free forms (Ryan et al., 1985). Low molecular weight organic acids generally carry one or more negative charges. By complexolysis, negatively charged organic acids are able to release OP from insoluble forms of OP. These reactions lead to the solubilization of insoluble forms of OP such as Ca-OP, Na-OP etc. (Courty et al., 2010). The impact of direct chelation in the solubilization of OP by citrate exudation has for instance been demonstrated in rice (Kirk et al., 1999). In general, citrate and oxalate have a higher potential for mobilization of OP compared to other organic anions (Neumann et al., 1999; Ryan et al., 2001). After OP desorbed from soil minerals by organic acids, the improvement of phosphatase and phytase activity released by roots can contribute to its efficiency use by plant (Hallama et al., 2019; Hayes et al., 2000). Chickpea, which appears to produce both phosphomonoesterases and diesterases, is thought to improve its P nutrition, probably through mining and mineralization of OP forms in soil (Darch et al., 2018; Pang et al., 2018). Various studies have demonstrated that plants have limited ability to access P in the form of IHP (the main form of OP) due to its low availability in soil solution and low level of extracellular phosphatase or phytase (George et al., 2007; Richardson and Simpson, 2011). It has also been shown that wheat and many other species are able to utilize P from G6P, GLY and phosphodiesteres (DNA and RNA) due to the *mining* capacity, but are limited to acquiring P directly from IHP, although it is abundant in many soils (George et al., 2008). This suggests that the biological importance of the different forms of OP will be driven by their turnover rates. Therefore, it was considered that plants with optimal

mining strategies for phytase release could potentially be used to improve the efficiency of inositol phosphate mobilization. The challenges are to understand the functioning of root-derived phytase activities on OP forms, and the chemical nature, soil properties, and root traits of crop species, to increase OP desorption and hydrolysis.

The collective *microbial-root* strategy refers to the investment of resources by plants to interact with the microbial community to access OP in soil. Many plants have developed a symbiotic association with vesicular arbuscular mycorrhizal fungi (AMF) that grow out from the root into the surrounding soil, extending the capacity of the root to mineralize OP and take up IP in soil solution (Tinker, 1984). The association of roots with arbuscular mycorrhizae is thought to be much more related to the mobilization of total P than root hairs and root length activity (Gashaw Deressa and Schenk, 2008). The symbiotic association of plant roots with mycorrhizae is reported to extend further from the roots than root hairs, and is also active in areas where P forms are adsorbed onto soil components (Graham and Eissenstat, 1994; Sattelmacher et al., 1994). A significant contribution of AMF to the uptake of P by plants has been reported, particularly in soils with high OP binding capacity. It is also accepted that AMF store OP in their vacuoles, which can be hydrolyzed and transported as IP in the host plant (Smith and Gianinazzi-Pearson, 1988). In addition, they also hydrolyze OP by releasing acid phosphatase in the soil. However, the relative contribution of root-derived extracellular phosphatases in the use of OP is still unclear, as the number and activity of bacteria and fungi are higher in the rhizosphere than in the soil in general (Richardson, 2005).

Overall, the traits of the *P mining*, *foraging* and collective *microbial-root* strategies are known and their indirect and sometimes even direct effects on OP dynamics/mobilization have been demonstrated (Ma et al., 2018; Nobile et al., 2019). The processes differ according to the nature of OP forms (phosphate mono or diester), the structure and function of soil microbial communities, and the physicochemical properties of the soil and climate. For instance, the availability of IHP, G6P, GLY and phosphodiester (DNA and RNA) as a direct effect of the *P mining*, *foraging* and collective *microbial-root* strategies remains unclear. Although the release of organic acids can make G6P, GLY and phosphodiester (DNA and RNA) available to plants, it is less efficient to solubilize IHP (Gerke, 2015) probably due to its strong binding to soil. Interactions between plant traits in the mobilization of P have been studied but remain poorly understood and unconfirmed. To this end, when developing new crop varieties or cultivars, selection should be based on crops with high OP use efficiency to promote greater P availability. Thus, in future crop breeding programs, traits involved in OP use efficiency should be identified and recorded. Specifically, efficient cultivars with genes and traits that produce strong phosphatase/phytase activities should be identified for better mobilization of the major OP form (IHP). There may also be trade-offs between physiological and morphological traits (Honvault et al., 2020; Lambers et al., 2006). These trade-offs have been examined very recently in different crop families and species (Honvault et al., 2020). Trade-offs between thicker and thinner roots were observed (Honvault et al., 2020), with thicker roots showing greater carboxylate release or phosphatase activity in the

rhizosphere. Trade-offs and coordination between traits were strongly influenced by soil type. However, their effect on the availability of OP forms must still be elucidated (Wen et al., 2019). Thus, we suggest that these strategies can be exploited using combinations of species with contrasting strategies or using a single species to understand better their actual effects on OP forms in agroecosystems.

Both plant functional traits and organic input characteristics strongly interact to modulate OP dynamic. However, it is still unclear to what extent these contribute to the mobilization of sparingly-available OP forms. Challenges and perspectives should focus on understanding the relationships between plant functional traits, OP nature and organic input properties in order to characterize the dynamics of OP, model its fate in the soil-plant system and better understand its consequences on P availability. Further, crop models to estimate total soil OP reserves and at least its specific forms (IHP, G6P, GLY, etc.) in a multi-species cropping system can be developed based on plant traits (shoot and root morphological and chemical characteristics), including inter- and intraspecific trait variability and soil properties. This trait-based approach to modeling P mobilization can be developed and would therefore be potentially useful in different climates.

1.2.4 Approaches/strategies to improve OP-use efficiency

1.2.4.1 Understand and manage plant traits, root-associated microorganism and OP pool interactions to characterize P dynamics and P availability

In agroecosystems amended with organic inputs, it is pivotal to grow crops able to mobilize and release OP from both soil constituents and organic input. Several direct and innovative approaches have been identified to improve the mobilization of OP forms by plants (Table 10). These include the identification and selection of crop species/genotypes based on their functional traits (Faucon et al., 2015). This approach uses morphological, architectural (Lynch, 2005; Nielsen et al., 1998) and physiological traits (Nielsen et al., 1998; Zhu et al., 2005; Zhu and Lynch, 2004), microorganisms or a combination of both to access sparingly available OP forms (Figure 6). Several plant species are presumed to be relatively efficient in OP utilization without assistance from rhizosphere microbiome. Some barley species with long root hairs (up to 1.0 mm) could easily access and mobilize twice as much OP as zita species (*Prunus laurocerasus*) in low P soil (Bates and Lynch, 2000). More importantly, allocating C to root hair growth would represent a minor metabolic cost to achieve greater P use efficiency (Bates and Lynch, 2000; Fang et al., 2019). Numerous plant species belonging to the family *Fabaceae* have been classified as efficient OP solubilizers (Schneider et al., 2019). For instance, legumes (72%) are more efficient than grain or oil crops (22%) in terms of extracellular acid phosphatase activity (Yadav and Tarafdar, 2007, 2003). Compared with non-nodulated legumes, N₂-fixing species possess a high level of functional plasticity to assist plants in facilitating OP mobilization (Zogli et al., 2017). Since N₂ fixation is highly expensive in terms of IP and energy expenditure, it is likely that this group of plants can promote OP

bioavailability. A wide range of biochemical, physiological, and molecular mechanisms can give nodulating plants a superior dynamic capacity to utilize soil OP more effectively. Simultaneously, most legumes have a high potential capacity to establish double symbiosis with AMF and rhizobia (Sulieman and Tran, 2015). This tripartite symbiosis can provide an additional potential advantage that might assist in OP mobilization. Unfortunately, it is still unclear to what extent these symbiotic associations contribute to the mobilization of sparingly-available OP forms. Other approaches aim at stimulating rhizosphere microbiomes that would improve plant OP acquisition and thus meet the overall goal of reducing the amount of chemical fertilizer from non-renewable mineral rocks (Li et al., 2019; Strock et al., 2018). It is therefore necessary to focus on these innovative approaches to optimise the management of organic input in the agricultural system.

Briefly, a better understanding of the impact of OP mobilization and acquisition strategies by plants, which are related to the multiple morphological and physiological traits and the interactions between them, is key in the management of OP availability. Compared to IP, the impact of these strategies in soil amended with various OP forms has received much less attention. Crop species trait might be used to increase OP mobilization, helping thereby rethink P fertilization, sustain production and recycle more OP in organic amended soil but this requires to elucidate the relationship among the various OP forms in organic inputs and root traits. In addition, understanding the trade-offs and effects of combining traits would allow us to unravel the complexity of the P form acquisition strategies and provide new knowledge for designing cultivated crop communities (i.e. multi-species crops) such as cover crops or intercrops to improve P acquisition and availability (Raven et al., 2018; Wen et al., 2019).

The strategies of P-acquisition by plants and the impact of root-associated microorganisms in P mobilization are quite well understood and are currently the focus of much research. However, it is still unclear to what extent they may interact with organic input to mobilize the sparingly-available OP forms. Several plant species belonging to the family *Fabaceae* are presumed to be relatively efficient in OP utilization without assistance from soil microorganisms. Therefore, future research should test these species under controlled conditions or at the field scale to identify specific plants that are strongly involved in to the mobilization of specific forms of OP.

Table 10 : Case studies used to promote and improve OP-use efficiency in the soil-plant system

Case studies	Observation/concept	OP forms	Test plant	Reference
Sewage sludge application in an agroecosystem (long-term (> 20 years) cropland field in northern France	Sludge is as effective as TSP to improve soil P availability. Sludge promotes soil enzymatic activities (phosphatases) for OP hydrolysis	OP forms, Apatite-P, Nonapatite-P	Oilseed rape– winter wheat – winter barley rotation	(Houben et al., 2019)

Measured of ten morphological and physiological traits involved in P acquisition across species in two contrasting soils with moderate P limitation.	There is Tradeoffs between thicker and thinner roots. Thicker roots exhibiting greater carboxylate release or phosphatase activity in the rhizosheath	Total P	Thirteen species of diverse phylogenetic lineages	(Honvault et al., 2020)
Placement of phytase in the vicinity of roots using mesoporous silica nanoparticle materials.	Phytases are stable and resistant to soil degradation	Phytate/IHP	<i>Medicago truncatula</i>	(Trouillefou et al., 2015)
Intercropping of P-mobilizing and non-P-mobilizing crop species	P-mobilizing crop species (legume) improve OP utilization for non-P-mobilizing species (non-legume) Phytase activity and organic anions concentration increased with increased Fe oxides in the media.	Phytate	Wheat/chickpea	(Li et al., 2004)
Contribution of phytate to plant nutrition is affected by Fe oxides and phosphohydrolases releasing microorganisms in the growing medium.	Phytate supplied was recovered as inorganic P at the highest Fe oxide concentration. Inoculants of <i>B. subtilis</i> promoted an enhanced hydrolytic activity at the highest Fe oxide concentration.	Phytate/IHP	Cucumber plants	(Garcia-Lopez et al., 2015)
Application of phytase to the root medium of plants	Phytase increases OP hydrolysis	IHP (phytin)	Maize	(Findenegg and Nelemans, 1993)
Inoculation of plants with soil isolates/microorganisms that possess efficient phytase activity	Mineralization of complex organic substrates by phytases	IHP	Pasture legume (subterranean clover, white clover, alfalfa) and pasture grass (wallaby grass, <i>Phalaris</i>) species	(Richardson, 2001)
P-acquisition strategies of three main crops are affected by the application of sewage sludges, compared with a mineral P fertilizer.	Wheat and barley had a greater root carboxylate release. Canola had higher root released acid phosphatase activity which promoted the mineralization of sludge-derived OP	OP forms, Apatite-P, Nonapatite-P	wheat, barley and canola	(Nobile et al., 2019)
Inoculation of plants with arbuscular mycorrhizal fungi	Mycorrhizal colonization contributes to OP cycling and plant IP acquisition	Phytate, RNA, lecithin	Red clover	(Fang et al., 2019)

Application of bacterial grazer (nematodes) together with mycorrhiza and P-solubilizing bacteria	Interaction of bacterial grazers with mycorrhiza and phosphobacteria promotes P org solubilization	Phytate	Maritime pine	(Irshad et al., 2012)
Biochar addition to agricultural soils	Biochar enhances IP-solubilizing bacteria	OP and IP forms	Ryegrass	(Anderson et al., 2011)
Genetic transformation of plants to overexpress extracellular phytases in root cells	Transgenic lines display better IP nutrition owing to the efficient release of extracellular root phytases	Phytate	<i>Arabidopsis</i> Subterranean clover Potato Tobacco	(Mudge et al., 2003; Richardson, 2001; Zimmermann et al., 2003)

1.2.4.2 Development of new cropping systems to recycle P from OP pools

1.2.4.2.1 Cover crops and OP availability

Cover crops offer the opportunity to improve OP recycling in agroecosystems by reducing P losses through runoff attenuation and improving P availability through P hydrolysis (Table 10), P release from crop residues, and decreased P sorption (Hallama et al., 2019; Honvault et al., 2020). As such, in soils amended with organic input with high levels of OP and/or superphosphate, several cover crop species have been effective in utilizing more of the OP and IP pool not only by promoting different root traits for soil exploration, but also developing mechanisms to release various OP species from organic input and soil (Huang et al., 2008; Richardson et al., 2011). The use of ryegrass as a cover crop and P fertilizer applications resulted in a decrease in soil IHP stock (Menezes-Blackburn et al., 2016). In addition, several cover crop species are thought to be able to significantly contribute to the desorption and redistribution of sorbed forms of P from the upper soil layer to the subsoil (Franchini et al., 2004). Species such as common vetch (*Vicia sativa*) and radish (*Raphanus sativus*) are generally identified as effective for these desorption and redistribution mechanisms (Pavinato et al., 2008). For example, in a high P-fixing soil, the dynamics of various forms of P from different organic inputs were studied in the presence of five cover crop species: vetch, white lupin, forage radish, ryegrass, and black oat for 5 years in a no-till system. These species were able to mobilize labile and less labile OP and increase the proportion of IP in the soil solution. Considering the literature on cover crop species, white lupine is widely suggested to be the most efficient for extracting OP and IP forms and could be considered a P-mobilizing species, although this may depend on the characteristic of the organic input applied (Calegari et al., 2013; Soltangheisi et al., 2020). Furthermore, though there is little information available in the literature, it is also pointed out that cover crops could specifically increase the dissolution of resistant OP associated with fulvic acid and highly resistant OP associated with humic acid (Bowman and Cole, 1978; Cui et al., 2015). Of the forms of soil OP, IHP can account for more than 70% of soil stoks because

of its strong binding to soil minerals. For its more efficient mobilization, Gerke (2015), suggests that future research considering P acquisition from IHP should focus on its mobilization from the surface of soil components by root exudates of cover crop species, primarily di- and tricarboxylic acids, which can increase IHP solubility. In sum, cover crops can be an innovative technique to improve the mobilization of OP pools from the organic input-soil-plant system. However, their effects are mixed and depend on the concentration of P available in the soil and thus on the added P fertilizer (Slazak et al., 2010). The perspective is to examine the role of cover crops on desorption, mineralization of OP forms and consequences on P availability with a view to model their potential effect on P availability in soils amended with organic input. Studies on the impact of cover crops on OP availability are generally conducted over a short evaluation period. Thus, as observed by Calegari et al. (Calegari et al., 2013), long-term studies are needed, as OP mobilization from applied organic input may depend on the cover crop species and their ability to desorb and redistribute fixed P. Most studies on the impact of cover crops on P dynamics are descriptive studies in which plant traits and OP forms are generally not characterized. Therefore, we suggest that future studies are needed to quantify species traits that may influence key forms of OP. This is to manage the relationship between cover crops and OP and more broadly between cover crops and organic input. The wide variability in potential contributions of OP pools in cover crop systems, their possible interactions with IP from crop residues for subsequent crop nutrition suggest a strong need to integrate soil OP dynamics into crop models in order to select cover crop traits that provide optimal utilization of OP from organic fertilization in cropping systems.

Cover crops have a wide range of P acquisition traits, and thus potentially different P acquisition strategies exploiting different P pools and probably OP pools. An outstanding question is whether P forms and soil type influence the expression of trade-offs and OP acquisition strategies in cover crops. To answer this question, future research should measure morphological, architectural, and physiological traits of different cover crop species from various phylogenetic lineages in different contrasting agricultural soil types. This may help to characterize the relationships among traits involved in P acquisition to explore tradeoffs and the main P-acquisition strategies and their mediation by soil type.

1.2.4.2.2 Management of OP inputs in crop rotations

The ability of crop species to mobilize OP of organic inputs and soil constitutes an opportunity to define an OP management at the crop rotation scale (Table 10). Many *Brassicaceae* crop species (e.g. canola, cabbage, radish...) that produce more acid phosphatase than wheat, oats, maize, beans and chickpeas in response to P deficiency (Nobile et al., 2019; Wang et al., 2017), can benefit from the fertilization with organic inputs. Brassicaceae with different P acquisition strategies mineralize OP and improve P availability that would be beneficial to the next crop (Haling et al., 2018; Pang et al., 2010)(Figure 6). The large differences in the efficiency of the P uptake strategy of canola, cabbage and radish on the one hand, and wheat, oats and barley on the other hand, can provide a tool to optimize the combination

between the rotation crop and the organic input to be applied. In practice, since organic inputs slowly increase the soil P content available to plants after incorporation into the soil (Houben et al., 2019), *Brassicaceae* crop species should be the first choice in the crop rotation to improve the P content of crops from poorly available forms of OP. For crop species such as wheat and barley that have high specific root length and relatively high carboxylate release, they could be more effective in releasing different forms of P adsorbed and/or precipitated on soil constituents, such as IHP which are very strongly adsorbed on soil. From an agronomic perspective, the most efficient system would be to apply organic input to the *Brassicaceae* species, while the following cereals will benefit from the residual OP. But, this will require more investigation in the future. Another interesting effect of rotational crops for organic input management is the particular ability of legumes to affect soil P levels. Indeed, legumes significantly decrease soil IP/OP ratio values (Lazali et al., 2020). Thus, linking the efficiency of legumes to mobilize OP to the type of organic input is an essential step to know and optimize the combination of the crop species in relation to the P fertilizer type, thus allowing a more sustainable P fertilization.

It is now known that the application of organic input in rotations would affect soil OP reserves and their dynamics over time (Houben et al., 2019; Lazali et al., 2020; Lemming et al., 2017). In general, as Glæsner et al. (Glæsner et al., 2019) point out, organic inputs, due to their OP content, have an impact on labile P in crop rotations system, which remains highly available to plants in the soil after long-term application. However, most of the studies do not generally consider how other forms of soil P (already available soil P) are affected in the rotation. In addition, the ability of rotational crops to mobilize OP from organic inputs remains poorly understood. Indeed, recent work suggests that P availability in rotations may change over time due to changes in the dynamics of soil-bound OP pools, which in turn are mediated by the type of crop in rotation (mobilization/acquisition strategies), concentrations, and forms of OP in organic input. Further studies are needed to determine the relative contribution of rotational crops with contrasting OP acquisition strategies on increasing labile P using isotope labeling techniques. As an innovative perspective to better manage short- or long-term OP inputs in agrosystems, fertilization management models need to evolve at the rotational scale by integrating plant traits, organic waste forms of OP, and soil properties to model microbial activities and their effects on available P.

1.2.5 Future Prospects

From the importance of OP mobilization processes by roots and rhizosphere microbiome, several suggestions and avenues of research can be deduced as well as promising approaches and innovative techniques that could improve the cycling of OP in the soil for use by plants. This includes a multi-pronged combination of beneficial biota, agronomic management practices and genetically-improved plants:

An important first direction for future research would be to focus on developing new cropping systems to recycle P from OP pools. To this end, understanding the impacts of cropping strategies, whether in rotation or intercropping systems, on mobilized OP could be promising for managing P availability for agroecological development. With this knowledge, crop species/genotypes (with specific morphological and physiological traits) which can enhance OP use efficiency could easily be identified and selected to improve plant P acquisition and thus reduce the amount of P fertilizer needed to maximize production. For this purpose, we suggest that future researches studies could test plants with different P mobilization/acquisition traits in monospecific treatment or in multispecies treatment under different sources of OP. This would allow not only to evaluate the overall P uptake between these different treatments (multi-species and monospecific), but also to better determine their higher P use efficiency. Inclusion of multi-species or single-species with different P-uptake strategies in P-uptake efficiency as cover crops or in crop rotation can help to develop new cropping system to recycle more OP and reduce the use of mineral P fertilizer. Other practices include better use of organic input as an alternative source of P by its better management in crop rotations, or of biofertilizers (microbial inoculants). The combination of these different practices deserves to be further explored and developed.

Since P availability depends on the interactions between OP and crop traits, the timing of application, the influence of both OP and the type of organic input and plants on microbial communities, it is necessary to start from the characterization of OP species in organic inputs and then study their relationship with soil properties and plant traits to really understand the P cycle and manage P availability. Furthermore, the direct contribution of OP to plant nutrition also needs to be well understood by quantifying the availability of readily available forms of OP to plants and by better understanding the dynamics of those adsorbed on soil minerals (sol-OP bonding complex). This knowledge will be useful to predict P availability as a function of the form that is applied and to better model P behavior as a function of soil properties and organic input characteristics.

At present, it is not known how the application of organic input can have an impact on the structure of the rhizosphere microbiome-root traits interaction on OP mobilization in the rhizosphere. Furthermore, the pathways and thresholds of transformation of OP species in soils amended with organic inputs, and especially their interaction or competition with existing OP pools in soils, and all this in relation to mobilization processes by rhizosphere microbiomes and root traits, remain largely unknown. Therefore, it is important for future research to highlight the role of OP forms from organic inputs in the changes of existing soil P forms over time by well characterizing the effect of rhizosphere microbiomes and root traits involved in their dynamics and how they relate to soil properties. The identification of these factors is a crucial step in fostering the utilization of soil OP by crop plants. Simultaneously, elucidating the plant uptake system to acquire OP can provide a strong complement to these efforts. Apart from adding different OP species to the soil, the decomposition of organic inputs can activate exogenous microorganisms and organic acids that can influence OP dynamics (mobilization process), but these aspects are very poorly considered in the literature.

The N-P interactions play a major role in the C and P cycles (co-limiting or synergistic effects depending on their concentrations) and, accordingly, organic fertilization is jointly managed in the cropping system. Since organic inputs differ in terms of N concentration and organic carbon composition (e.g. cellulose, hemicellulose, lignin) which in turn impact microbiome-root trait interactions (protons, pH reduced, organic acid, phosphatase), one hypothesis is that forms of OP would have different response times to changes in nutrient status (C and N levels) in agricultural ecosystems. Thus, to confirm or refute the hypothesis, future research is needed to evaluate the actual effect of these compounds on OP mobilization in the organic input-soil-plant system.

Most research on the potential of microbes to mobilize OP has been conducted on culturable microbes. Because most rhizosphere microbiomes associated with plant roots are not culturable, further research on these microbes in the plant rhizosphere is needed, which will improve knowledge of the microbial community and microbe-plant roots traits interactions in OP mobilization. Furthermore, since the ability of rhizosphere microbiomes to mobilize OP varies with the forms of OP and their chemical properties, in order to better take advantage of these soil organisms or even select and introduce them, it is recommended that screening of these bacteria in the presence of different forms of OP and different soil properties be investigated, since in most studies, these bacteria have been screened under conditions where neither the forms of OP nor the soil properties are highlighted.

It is known that plant roots associated with rhizosphere microbiome can express synergistic effects to increase IP uptake by mobilizing more OP in the soil. Therefore, further research is needed to evaluate the actual effectiveness of beneficial rhizosphere microbiome associations with various crops with contrasting root traits and fertilized with different P sources under field conditions, as well as how the mechanisms by which they mobilize OP, are hampered by competition with endemic microorganisms and soil properties (P sorption capacity, soil P status, pH, etc.).

Sustainable agricultural systems are expected to enhance the diversity of functional microorganisms in the soil, especially those actively involved in P mobilization from organic inputs or soil organic matter. However, given the lack of data about the link between sustainable agricultural systems and OP mobilization, it is important for future research to characterize both direct and indirect effect of such systems on OP mobilization in the organic input-soil-plant continuum.

1.2.6 Conclusion

Organic inputs and soil, can be used as a primary or supplementary source for plant P nutrition. This is because OP is as important in amount as IP in soil and organic inputs. However, the present review highlights that OP present in organic inputs and soil is in various chemical forms which differ in their ability to be mobilized and their availability to plants. These forms of OP tend to be scarcely available in agroecosystems because of their strong affinity for soil mineral surfaces. Rhizosphere microbiomes have the potential to mobilize and mineralize different forms of available and unavailable OP. Various

controlled experiments using plants inoculated with the rhizosphere microbiome provide evidence for this. Rhizosphere microbiomes solubilize OP through the production of organic acids and then mineralize it via enzymes. However, the mechanisms associated with this mineralization are poorly understood, and in most studies, the experimental conditions suppress interactions between the components of the system. Furthermore, there is little evidence on how these rhizosphere microbiomes can act in the presence of soil minerals that can immobilize both OP and hydrolytic enzymes. Future work should be conducted by inoculating microorganisms with sorbed OP complexes on key soil minerals under laboratory conditions and even further in the field. Root traits may alter rhizosphere characteristics to enhance reactions of OP dissolution, desorption, chelation and mineralization. These traits are related to root *P foraging* strategy and may include alterations in root structure such as plasticity in low P stress responses and spatial arrangement of roots to induce a diffusion gradient that will in turn promote the process of OP desorption and thus P availability. Expansion of fine roots and longer, denser root hairs promotes OP acquisition by roots via increased root surface area. Physiological characteristics related to *P mining* strategy may alter pH and/or release carboxylates and phosphatases to increase turnover of sorbed OP pools. These rhizosphere microbiome and root traits processes are continuously interacting to modulate the stock of OP in agricultural soils. An alternative approach to P limitation would be to use crop species/genotypes with specific traits, inoculated naturally by rhizosphere microbiomes with suitable OP forms and soil properties, at crop and rotation scales, to increase OP mobilization from organic inputs. Thus, under conditions of P-deficient or soils amended with organic inputs, root traits and soil microbes will be effective in increasing plant growth especially by mobilizing highly-binding OP forms. The present work reinforces the need to develop future research to understand the trade-offs between root traits, their relationship to microbes, and their direct effect on OP mobilization and P availability. These mechanisms/processes could be integrated into models and decision support tools for estimating soil P availability and managing P fertility from organic waste.

OBJECTIVES

2 PhD OBJECTIVES

This Ph.D. project aims to understand better the role of organic phosphorus forms (OP), soil minerals, nitrogen (N), and crop functional traits and their interactions on P availability and acquisition by plants for optimizing organic fertilizer management in agrosystems. To address this general objective four chapters were produced to examine the central and still pending questions involved (Figure 7).

Chapter 1 examined the sorption and desorption of OP on goethite, gibbsite, kaolinite, and montmorillonite. The goal of this chapter was to elucidate the adsorption and desorption dynamics of several forms of OP on several representative soil minerals. Specifically, the objective was to determine the factors underlying the adsorption and desorption of OPs onto and from soil minerals. It is assumed that the selected Fe, Al oxides, and clay minerals abundant in soils will exhibit various adsorption and desorption capacities due to their contrasting chemical properties.

Chapter 2 studied the role of soil minerals on organic phosphorus availability and P uptake by plants. The objective was to elucidate the extent to which OP bound to Fe and Al oxyhydroxides and clay mineral complexes contributes to plant P acquisition. Specifically, we determined P availability to plants from several IHP, G6P, and GLY complexes that were adsorbed onto Fe and Al oxyhydroxides (goethite and gibbsite) and clay minerals (kaolinite and montmorillonite). The following three main hypotheses were discussed: (1) P from adsorbed OP compounds is available to ryegrass and varies with soil mineral properties; (2) the relative P uptake of various OP-mineral complexes depends on their binding strength; and (3) adsorbed OP compounds are less available than adsorbed IP because it desorbs less and requires not only desorption but also enzymatic cleavage before being taken up by ryegrass. These aims could open up possibilities for utilization of renewable nutrient-rich organic amendments based on various soil mineral properties.

Chapter 3 aimed to understand better how N and soil mineralogy determine phosphorus limitation and plant P uptake from inorganic and organic forms of P. It focuses on assessing the independent and interactive effects of N and P forms and their interaction with soil minerals on P limitation in plants, to unravel biogeochemical processes involved in P limitation by characterization the role of N and P forms and their interaction with soil minerals in P availability and uptake by plants. The following assumptions were made: (1) addition of N in various specific forms would increase P limitation under conditions with low P availability, i.e. with OP forms and soil minerals, (2) plants shift from N limitation to P limitation would be due to the beneficial effect of N addition on rhizosphere processes involved in P mobilization/acquisition by plants, and (3) the degree of both P limitation and total plant P uptake would vary significantly by mineral type and P forms because of the contrasting physicochemical properties of the minerals used and the biochemical nature of the P sources. The results of this chapter are needed not only to enable ecosystem models to accurately predict plant N-P limitation and its impacts, but also to develop robust ecosystem models with fully coupled N-P or C-N-P interactions.

Chapter 4 aimed at estimating the role of phosphorus-acquisition strategies on organic P mobilization and acquisition. The objective of this chapter was to examine the response of P acquisition strategies toward P forms (IP and OP) in interactions with soil minerals and their consequences on OP availability and acquisition. The general hypothesis was that P-acquisition strategies (i.e. *foraging* and *mining*) differ in their responses to P sources, and this would promote greater OP availability and P acquisition from soil minerals. More specifically, (1) morphological traits involved in *P-foraging* strategy will increase P availability and uptake from OP. These traits would induce a diffusion gradient which, in turn, will favor the desorption process of the different forms of adsorbed OP, and thus the availability of P and (2) physiological traits involved in *P-mining* strategy will increase P availability and uptake by modifying the pH and/or release carboxylates and phosphatases allowing to increase the turnover of the pools of sorbed OP via desorption, solubilization and mineralization processes; (3) the acquisition of P from OP will be more significant under strategies involving *P-mining* than under those involving *P-foraging*, because OPs will be hydrolyzed by the strong activities of phosphatase, and finally (4) regardless of the strategy, the acquisition of P from OPs will be lower than that of IPs due to their strong sorption on minerals. This chapter can offer insight into how phosphorus acquisition strategies could be utilized to increase OP mobilization, which would help rethink P fertilization, sustain production, and recycle more OP into soils amended with organic amendments.

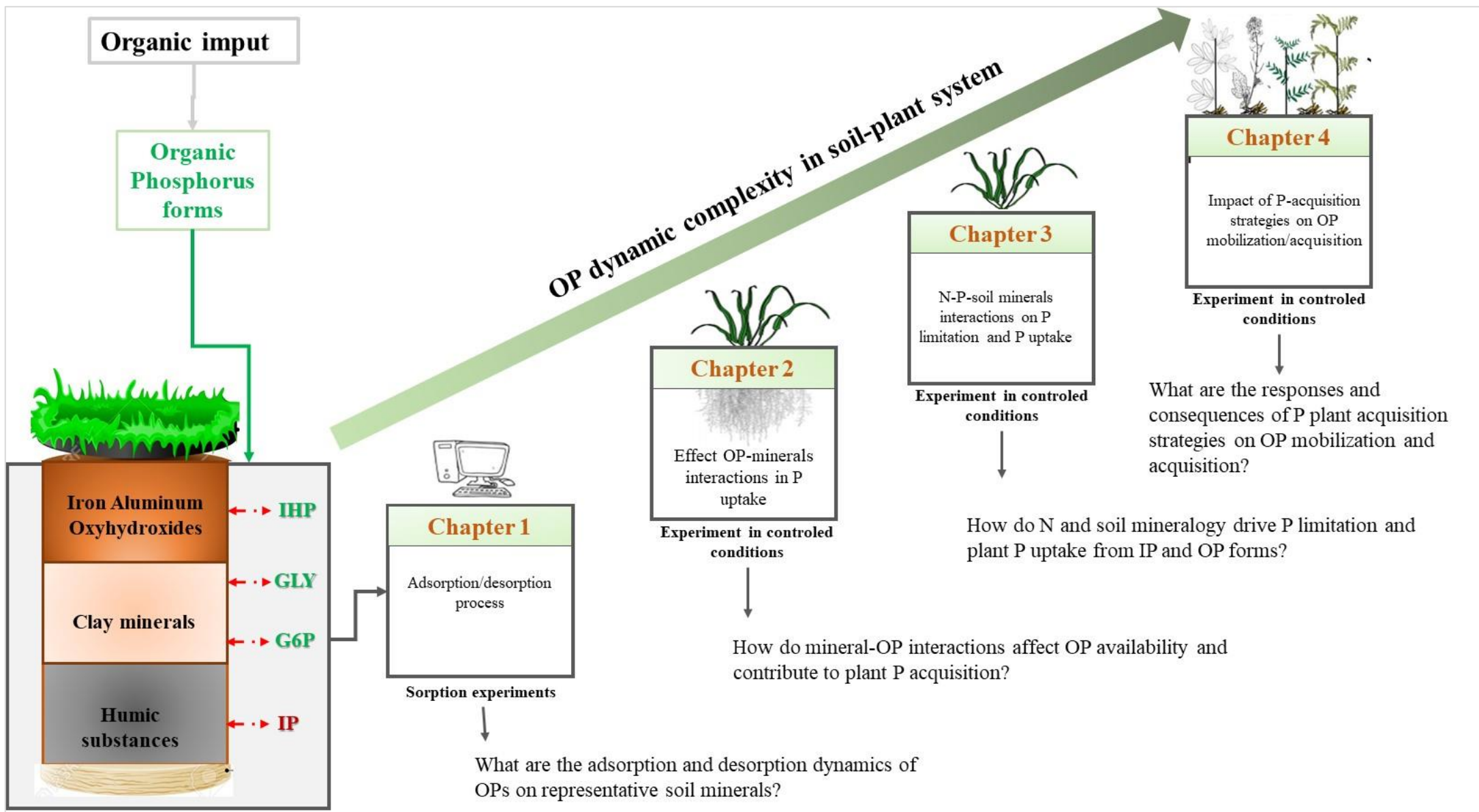


Figure 7: The main objectives of the thesis project. OP: Organic P, IHP: Myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate, and IP: Inorganic P; N: nitrogen

Phd METHODS

3 Phd METHODS

Four complementary approaches were used to investigate the overall objective of this thesis. The first approach, addressing the objectives described in Chapter 1 (Figure 7), was to determine the factors underlying the adsorption and desorption of OPs onto and from soil minerals. After adsorption, both desorption and availability of OP forms to plants are still not elucidated. Therefore, the approach in Chapter 2 aims to investigate the extent to which OPs bound to Fe and Al oxyhydroxides and clay mineral complexes contribute to P acquisition by plants. Furthermore, since renewable P fertilizers differ in terms of nitrogen (N) concentration, which can impact the physicochemical and biological properties of the soil and thus the dynamics of OPs, the third approach, addressing the objectives described in Chapter 3, was to characterize the role of N and P forms and their interaction with soil minerals in the availability and uptake of P from OPs by plants. The fourth and final approach, addressing the objectives described in Chapter 4, examines the response of P acquisition strategies to OP forms interacting with soil minerals and their consequences on organic P availability and acquisition, before modeling the expected impacts on phosphorus uptake. In this step, plants with various P mobilization/acquisition characteristics were tested alone (single species treatment) (Figure 7).

3.1 Characterization of factors governing the dynamics of OP adsorption and desorption onto and from soil minerals

Moving toward more sustainable sources for managing P nutrition in agroecosystems, OP derived from organic inputs and soil is increasingly considered to complement mineral P fertilizer (Amadou et al., 2021; Sulieman and Mühling, 2021). However, enhancing OP cycling and availability in soils while reducing OP loss into the environment requires a better understanding of OP adsorption/desorption processes on soil minerals (Amadou et al., 2022; Wang et al., 2017). Factors related to soil properties and OP molecular characteristics directly affect the reactions of OP and its release into the soil. Extensive research has evaluated the adsorption of different individual sources of organic and inorganic P to soils or to individual soil minerals (Amadou et al., 2022). However, no study has evaluated and compared P desorption from the main OP compounds that were adsorbed onto the main soil minerals. Deciphering the interactions between soil minerals and the predominant forms of OP in soils could provide new insights for the sustainable management of P in agroecosystems.

Triplicate batch experiments were conducted to understand the interactions between OP forms and soils minerals at different P concentrations. We used standard P adsorption procedure proposed by Nair et al. (1984). Three organic P (OP) compounds, IHP, GLY, G6P and one IP (KH_2PO_4) were selected based on their predominance in organic wastes and soils and their contrasted properties (type of P bonds, different molecular sizes). The individual soil minerals were selected to be representative of the

predominant soil minerals involved in P adsorption in soils. Four individual soil minerals were used. Goethite [FeO(OH)] and gibbsite [Al (OH)₃] were chosen as representative of Fe and Al oxides; kaolinite and montmorillonite were selected as clay minerals, particularly 1:1 phyllosilicate and 2:1 phyllosilicate respectively. The minerals used have different specific surface areas (SSA) and points of zero charge (PZC). The SSA of the minerals used are as follows: goethite (46 m² g⁻¹), gibbsite (120-364 m² g⁻¹), kaolinite (19 m² g⁻¹) and K-montmorillonite (83 m² g⁻¹) and their PZCs were: goethite (7.04), gibbsite (9.3), kaolinite (4.5) and montmorillonite (2.5), as previously reported by other authors (He et al., 1994; He and Zhu, 1997; Ruttenberg and Sulak, 2011; Shang et al., 1990; Yan et al., 2014). Inorganic P was determined colorimetrically (Ohno and Zibilske, 1991). Organic P compound samples was hydrolyzed to IP form before colorimetric determination by using the persulfate oxidation method (Peters and Van Slyke, 1932). The quantity of P adsorbed was calculated as the difference between the initial amount of P added and the remaining P amount in solution at the end of the adsorption experiment. Total P concentration in a subsample of each P-loaded was also determined using the procedure by Ostrofsky (2012) and showed very similar values compared to the ones determined as the difference between the initial and the final P amount in the supernatant (differences were in the range of 3-5.5% for the organic mineral-P complexes and 1.5-5% for the inorganic mineral-P complexes). Adsorption maxima, capacity and other adsorption parameters were determined by fitting data to the non-linear form of the Langmuir (1) and Freundlich (2) isothermal model (Crini et al., 2007; Langmuir, 1918). Desorption maxima and rate were determined by fitting data to the non-linear form of the Elovich kinetic model (Bulut et al., 2008) (3). More specific details are described in the methodology section of Chapter 1.

3.2 Assessment of P availability to plants from several mineral-OP complexes

Organic phosphorus (OP) represents a significant fraction of the total P pool in soils. With the increasing use of organic resources to substitute mineral P fertilizers and the need to recover P from the soil, it is pivotal to gain insight into the interactions between various OP forms and soil minerals and their consequences on P availability. Overall, our understanding of the dynamics of the major OP pools in the soil-plant system is very limited. Most research has focused on the dynamics of IP forms (Sulieman and Mühling, 2021), suggesting that soil characteristics control their availability to plants (Gómez-Suárez et al., 2020). However, OP forms may strongly differ from each other's and have therefore different biogeochemical processes controlling their availability and uptake by plants (Anderson et al., 2011). To date, it is not known how the chemical forms of OPs, and their interactions with soil minerals, influence the uptake of OPs by plants in ecosystems. The paucity of research significantly limits our ability to understand the overall dynamics of P cycling in ecosystems and to optimize the use of

renewable P fertilizers which often contain various forms of OP (Kelessidis and Stasinakis, 2012; Mininni et al., 2015).

After gaining more insight into the sorption and desorption dynamics of OPs in Chapter 1, this chapter aims to determine the extent to which adsorbed OPs are available to plants. Four soil minerals were loaded with the three OP compounds or inorganic P to serve as a P source for ryegrass (Chapter 2). The four minerals were selected to be representative of the predominant minerals in soils: Goethite [Fe(OH)O] and gibbsite [Al(OH)₃] were chosen as representative of Fe and Al oxyhydroxides; kaolinite and montmorillonite were selected as clay minerals, particularly 1:1 phyllosilicate and 2:1 phyllosilicate respectively. The three OP compounds, include myo-inositol hexakisphosphate (IHP), glycerophosphate (GLY) and glucose-6-phosphate (G6P), and one inorganic P (KH₂PO₄). Organic P compounds were initially selected based on their predominance in organic inputs and soils, the types of P bonds and their different molecular sizes. The inorganic P form was chosen for comparison with organic P compounds. We used the RHIZOtest device (MetRHIZlab, France) (Figure 8) designed by Bravin et al. (2010) which consists in separating plant roots from soil with a 30-mm polyamide mesh to facilitate the collection of roots and rhizosphere (Houben and Sonnet, 2015). Prior to the experiment, the substrates were sterilized by autoclaving at 121 °C for 2 h (Gómez-Suárez et al., 2020) to eliminate potential microorganisms, allowing therefore to attribute the results to the only effect of root activity. To avoid any P limitation for plants during the experiment, we supplied a total amount of P which was previously found to sufficiently meet the plant requirement in such RHIZOtest devices (Gómez-Suárez et al., 2020). The RHIZOtest devices were placed in controlled conditions (phytotron) under a photoperiod of 12h, constant temperature (25 °C), and relative humidity (80%). Unplanted control treatments, in which the quartz - mineral-P complex had been incubated in similar devices without plants (hereafter called the bulk substrate), were also conducted. In total, 128 such devices were implemented: 4 P compounds (IHP, GLY, G6P, and IP) x 4 soils minerals (goethite, gibbsite, kaolinite and montmorillonite) x 2 crop conditions (ryegrass and bulk soil) x 4 replicates. The concentration of P in shoots and roots was determined colorimetrically (Ohno and Zibilske, 1991) after mineralization by 65% HNO₃ digestion directly in a microwave Teflon vessel (Lange et al., 2014). The amount of P taken up by shoot and root from the P-mineral complexes was calculated as the difference between the amount of P in plant parts at the end of the experiment minus the average amount of P in plants at the end of the preculture period. Total plant P uptake from P-minerals was calculated by summing P uptake from P-minerals by roots (i.e., root P concentration multiplied by root dry mass) and P uptake from P-minerals by shoot (i.e., shoot P concentration multiplied by shoot dry mass). The percentage of P recovered by ryegrass was determined. To assess the factors that determine OP availability to the plant, desorption dynamics, rhizosphere and bulk soil P availability and Phosphomonoesterase activities were evaluated.



Figure 8 : RHIZOtest device experiment setting

3.3 Unraveling the biogeochemical processes involved in OP availability and P limitation by characterization the role of N and P forms and their interaction with soil minerals

Ecosystem N and P cycling consists of multiple pools and biogeochemical processes that are interrelated and interdependent, jointly controlling soil P availability, plant P uptake and its limitation (Vitousek et al., 2010). To date, it remains unclear how N forms, P chemical forms, and their interactions with soil minerals influence both P limitation and P uptake by plants within ecosystems. The paucity of research on the effect of these important biogeochemical processes (N-P-soil minerals), severely limits our ability to understand ecological processes underlying the alteration of ecosystem P cycling with N additions. More importantly, it limits our ability to incorporate the actual impact of P limitation into ecosystem models used to analyze the effects of potential future climate change on overall ecosystem productivity (Deng et al., 2017; Goll et al., 2012).

In Chapter 2, the availability of OPs was strongly determined by OP forms and mineral types. However, to date, it remains unclear how N forms contained in organic fertilizers and their interactions with soil minerals influence OP dynamics, i.e., OP availability, P limitation, and P uptake by plants in ecosystems.

To attempt to answer this question in this chapter, two minerals (goethite and kaolinite) were loaded with the three compounds P (IHP, GLY, and IP) to serve as a source of P for ryegrass. The two minerals were chosen on the basis of their contrasting characteristics, as shown in Chapter 1. The procedure for preparing the mineral-OP complexes was similar to that described in Chapter 2. The two forms of nitrogen used were ammonium ($\text{NH}_4\text{-N}$) provided as $(\text{NH}_4)_2\text{SO}_4$ and nitrate ($\text{NO}_3\text{-N}$) provided as $\text{Ca}(\text{NO}_3)_2$. We used a device whose principle is very similar to the RHIZOtest except that here, the roots of the plants are not separated from the soil but remain separated from the nutrient solution (Figure 9). Non-planted control treatments, in which the quartz-mineral-P complex was incubated without plants (hereafter called bulk substrate), were also performed. A total of 96 such devices were implemented: 3 P compounds (IHP, GLY and IP) x 2 soil minerals (goethite and kaolinite) x 2 forms of nitrogen ($\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$) x 2 cropping conditions (ryegrass and bulk soil) x 4 replicates. The concentration of P in shoots and roots was determined calorimetrically (Ohno and Zibilske, 1991) after mineralization by 65% HNO_3 digestion directly in a microwave Teflon vessel (Lange et al., 2014). In addition to P analysis, the N elemental concentrations were determined. We calculated N:P ratios by dividing leaf N concentration by leaf P concentration (both as percentage nutrient in the sample) within each plant tissue sample. Total plant P uptake was calculated by summing P uptake by roots. After defrosting some samples, acid phosphomonoesterase activity in the rhizosheath (PME) was measured with a modified buffer at pH 6.5 (Tabatabai and Bremner 1969).

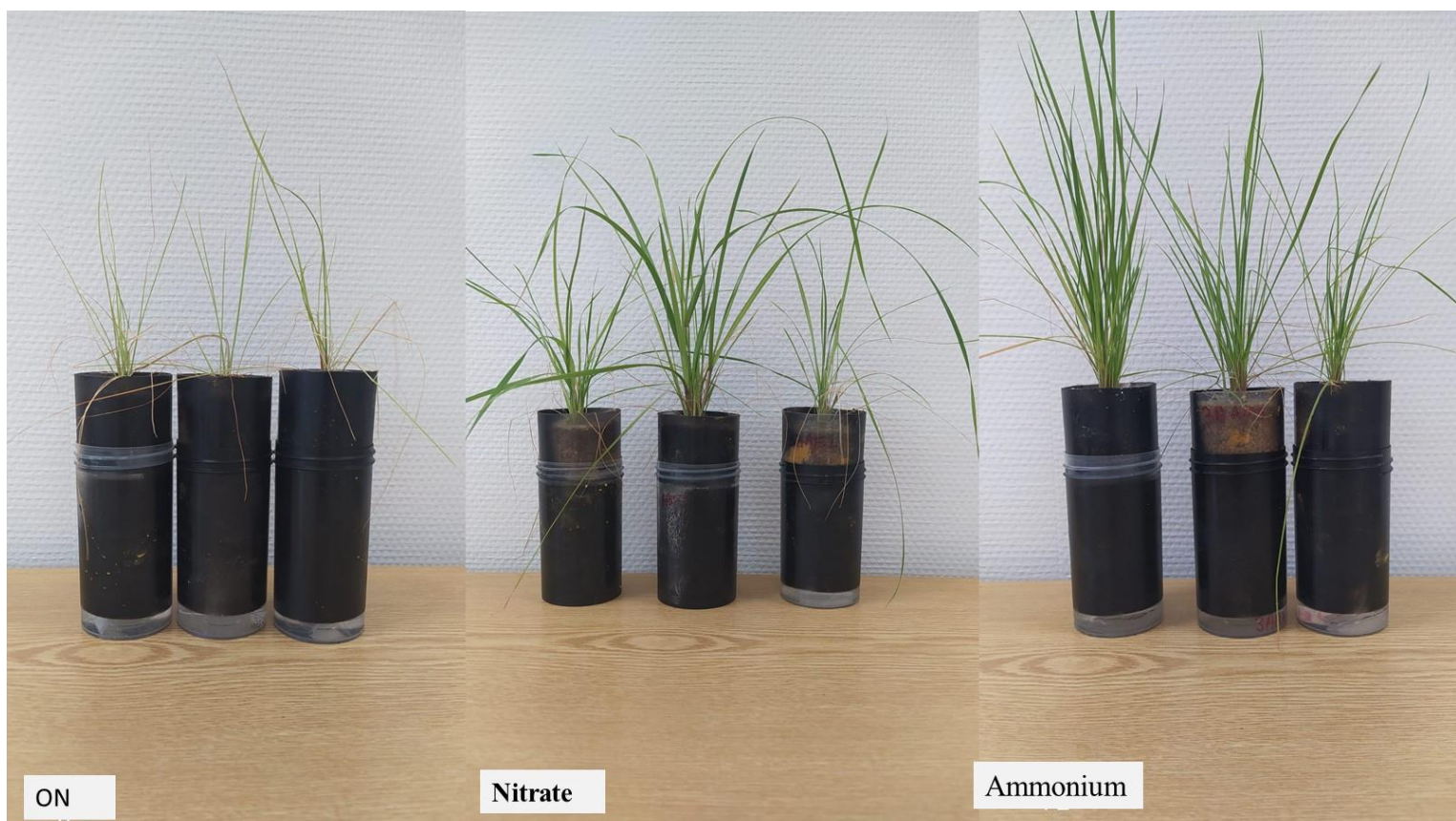


Figure 9 : Experiment setup

1.1. Analyzing the response of P acquisition strategies to OP forms in interaction with soil minerals and their consequences on OP availability and acquisition.

The plant P acquisition traits are known and their indirect and sometimes even direct effects on P acquisition/mobilization have been demonstrated (Ma et al., 2018; Nobile et al., 2019). The processes differ according to the nature of IP or OP forms (phosphate mono or diester) and the physicochemical properties of the soil. For instance, the availability of the different OP forms (IHP, G6P, GLY, DNA and RNA) as a direct effect of P acquisition strategies (*P mining* and *foraging*) remains unclear. Although the release of carboxylates can make some OP (G6P, GLY) available to plants, it is less efficient to solubilize IHP (Gerke, 2015) probably due to its strong binding to soil. Interactions between plant functional traits in the mobilization/acquisition of both OP and IP have been studied but remain poorly understood and unconfirmed. Thus, it has been suggested that plant strategies can be exploited using combinations of species with contrasting strategies or using a single species to understand better their actual effects on OP mobilization and acquisition in agroecosystems. A better understanding of the impact of P-acquisition strategies on OP mobilization and acquisition by plants, which are related to the multiple morphological and physiological traits and the interactions between them, is key in the management of OP availability.

In order to examine the response of P acquisition strategies toward P forms (IP and OP) in interactions with soil minerals and their consequences on OP availability and acquisition, a wide range of traits were measured for their recognized role in phosphorus acquisition (Lynch, 2005). Measured traits included morphological and architectural traits (root length density, root surface area, specific root length, finer root percentage) involved in plant phosphorus *foraging* capacity (Haling et al., 2018) and physiological traits or indicator thereof (phosphomonoesterase activity in the rhizosphere, change in rhizosphere pH, carboxylate exudation rate) involved in plant phosphorus mobilizing capacity (Sun et al., 2009). Two OP compounds, including inositol hexakisphosphate/phytate (IHP) and glycerophosphate (GLY), as well as inorganic P (KH_2PO_4), were selected for the experiments. Organic P compounds were initially selected because of their ubiquity in organic inputs and soils, the nature of phosphorus bonds, and their variable molecular sizes. Inorganic P forms were selected for comparison with organic P compounds. Two minerals were chosen because of their contrasting properties and as representatives of the major soil minerals: goethite [$\text{Fe}(\text{OH})\text{O}$] was chosen as representative of iron oxyhydroxide, and kaolinite as a clay mineral. The two soil minerals were loaded with the two OP compounds or inorganic P to serve as a P source for the different species. Eight (sub)species of diverse phylogenetic lineages (*Poaceae: Hordeum vulgare, Lolium perenne; Fabaceae: Lens culinaris* Medik., *Pisum sativum subsp. arvense* L., *Trifolium alexandrinum* L., *Vicia faba* L., *Lupinus albus*; *Hydrophyllaceae: Phacelia tanacetifolia* Benth.) were selected for their diverse morphologies, P-

acquisition traits and relevance for the local context. Species selection is central in order to observe enough diversity in trait attributes to produce generalisable results (Duarte et al., 1995). Species from different phylogenetic families (*Poaceae*, *Fabaceae* and *Hydrophyllaceae*) were selected in order to ensure we would observe varied trait values and phosphorus acquisition strategies. *Fabaceae* have been observed to have high phosphorus *mining* capacity (Maltais-Landry, 2015) and often incorporated in cover crops for their ability to fix atmospheric N. *Poaceae* species were selected due their phosphorus-*foraging* strategy. Finally, *Hydrophyllaceae* were selected for their capacity to mine phosphorus and capacity to forage large soil volumes respectively. To construct the experimental mesocosms, we filled 120×120 mm square polymer Petri dishes with sterilized coarse quartz sand (Figure 10), which is extremely poor in soil nutrients. The various P-mineral complexes prepared were then added to each square Petri dish and mixed with acid-washed quartz. Prior to the experiment, the substrates were sterilized by autoclaving at 121 °C for 2 h (Gómez-Suárez et al., 2020) to eliminate potential microorganisms, thus allowing the results to be attributed to the effect of root activity alone. The procedure for preparing the mineral-OP complexes was similar to that described in Chapter 2 and 3. To avoid any P limitation for the plants during the experiment, we provided a total amount of P that was found to be sufficient to meet the plants' needs (Gómez-Suárez et al., 2020). A total of 480 such devices were implemented: 8 species x 3 P compounds (IHP, GLY and IP) x 2 soil minerals (goethite and kaolinite) x 2 cropping conditions (ryegrass and bulk soil) x 5 replicates. A multivariate clustering approach was employed to identify plant phosphorus acquisition strategies based on the array of phosphorus acquisition trait measured.



Figure 10: Experimental mesocosms, with square petri dishes

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CHAPTER 1

4 New insights into sorption and desorption of organic phosphorus on goethite, gibbsite, kaolinite and montmorillonite

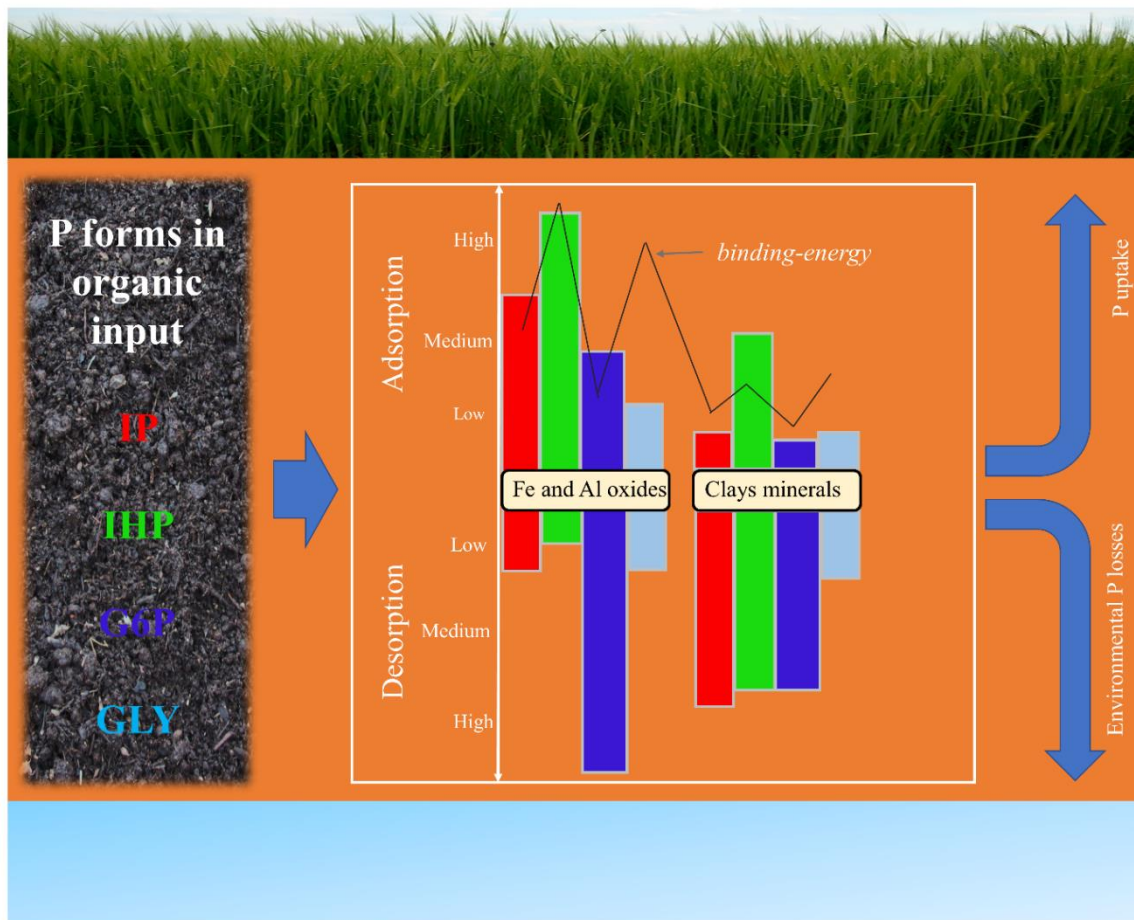
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Highlights

- Mineral properties and organic P (OP) characteristics affected OP (de)sorption
- Myo-inositol hexakisphosphate had higher adsorption than the other OP forms
- Organic P showed contrasted adsorption capacities relative to inorganic P forms (IP)
- Fe and Al oxides exhibited highest adsorption capacity compared to clay minerals
- Organic P was more desorbed from clays minerals than from Fe and Al oxides

Graphical abstract



Abstract

With the increasing use of organic resource for P fertilization, the adsorption and desorption dynamics of various organic phosphorus (OP) forms remain an important gap of knowledge to bridge in order to improve P availability. In this study, we examined the adsorption and desorption dynamics of various OP (myo-inositol hexakisphosphate, IHP; glycerophosphate, GLY; and glucose-6-phosphate, G6P) compounds to and from several soil minerals including Fe and Al oxides (goethite and gibbsite, respectively) and clays minerals (kaolinite and montmorillonite). Overall, IHP was the most adsorbed form followed by G6P and then GLY which reflected that OP adsorption increased according to the number of phosphate groups and/or the size of the organic molecule. Fe and Al oxides showed higher OP adsorption capacity than clays, as adsorption followed the trend kaolinite < montmorillonite < goethite <<<< gibbsite.

Desorption experiments revealed that the adsorption was not fully reversible as only 30% could easily desorb. On Fe and Al oxides, G6P and GLY were more desorbed than IHP while the opposite trend was found on clay minerals. In addition, OP desorption from soil minerals followed the trend gibbsite < goethite < kaolinite << montmorillonite. The clay-OP complex released P rapidly but over a short period of time, whereas the Fe- and Al-OP complex released P slowly but over a longer period of time. The comparison between the P adsorption and desorption properties of montmorillonite and other soil minerals are only valid for the K-saturated montmorillonite used here. The results could be different if the montmorillonite were saturated with Al or Ca. By deciphering the interactions between soil minerals and the predominant forms of OP in soils and organic fertilizers, our results provide new insights for the sustainable management of P in agroecosystems.

Keywords: Adsorption; desorption; organic phosphorus; phosphorus availability; soil fertility

4.1 Introduction

Phosphorus (P) is one of the essential nutrients required for plant growth and an important driver of agroecosystem productivity (Hu et al., 2020a; Ruttenberg and Sulak, 2011). Due to its low solubility and high affinity for mineral surfaces (Roy et al., 2017; Tisdale and Nelson, 1966), P availability is limited in agricultural soils and rarely sufficient for optimum growth and development of crops. On the other hand, accumulation of P in the soil increases the risk of P leaching and runoff, consequently leading to eutrophication of surface waters (Hansen et al., 2002). Therefore, with the increasing use of organic resources as P fertilizers (Amadou et al., 2021), a sustainable and efficient use of organic P (OP) fertilizers is of utmost importance to secure future crop production and reduce environmental hazard (Faucon et al., 2015). However, most of the research investigating the fate of P applied to the soil

has focused on inorganic P (IP) so far, showing that most of it was adsorbed onto iron (Fe) and aluminum (Al)-oxides and clays minerals (Celi et al., 2000, 1999) or precipitated with Ca (Houben et al., 2011; Urrutia et al., 2013). In contrast, the fate of OP has been disregarded so far even though it is now clear that these forms of P can be at least as available as IP (Amadou et al., 2021; Kahiluoto et al., 2015). Organic P can be mineralized along with plant uptake and/or be protected by organic substances from adsorption, even in the long term (Huang and Zhang, 2012). However, the adsorption mechanisms of OP and the factors that affect sorbing processes remain poorly understood (Yan et al., 2014) and there is still a lack of knowledge about their contribution to plant nutrition (Faucon et al., 2015).

Organic P in soil-plant-system comes from both soil and organic waste sources (e.g. manure, compost, sludge, biochar, ...) (Fuentes et al., 2006). The major OP compounds from soil and organic wastes include IHP (Turner et al., 2002; Vincent et al., 2013), GLY (Doolette et al., 2011; Newman and Tate, 1980) and G6P (Deiss et al., 2018; Giles et al., 2011). Each form differs from the others by its P content, P bond type and molecular size. They may constitute large fractions of the total P in soils (Monbet et al., 2009), especially in organic waste-amended soils (Khare et al., 2004). It has been shown that adsorption of OP compounds increases with the number of P groups. Therefore, with six phosphate groups, IHP has a high charge density and would undergo a strong interaction with the soil (Anderson and Arlidge, 1962; Celi et al., 1999). This higher accumulation of IHP through adsorption limits P acquisition by plants from this source. The size and molecular structure of OP forms generally affect their adsorption capacity. The G6P adsorption density and rate is higher than IHP and adenosine triphosphate (ATP) as a result of its lower molar mass (Giaveno et al., 2008). However, Goebel et al., (2017) reported that G6P is potentially more available than IHP and ATP.

After adsorption, the ability of soil minerals to release P in soil solution determines P availability for plants but also loss of P in both surface runoff and subsurface flow (Sharpley et al., 2001). Several authors have suggested that P from mineral-P complexes is not available to plants because of their very limited desorption (Barrow, 1986; Bollyn et al., 2017; Guzman et al., 1994; Lagos et al., 2016). For instance, Bollyn et al., (2017) showed that after several cycles of desorption, less than 5% P desorbed from IHP-goethite complexes. Similar results by Lagos et al., (2016) showed limited desorption of IHP (<3% P) from gibbsite. On the other hand, there is also experimental evidence that P can desorb significantly from minerals to be available to plants and runoff (Andrino et al., 2019; Parfitt, 1979). However, in all of these studies cited above, the form of P used was exclusively IP with very limited consideration for important OP pools such as IHP, GLY or G6P. Furthermore, the soil minerals used were in most cases Fe oxides (namely goethite) while Al oxides and clay minerals were much less investigated. To our knowledge, no study has evaluated and compared P desorption from the main OP compounds (IHP, GLY, and G6P) that were adsorbed onto the main soil minerals (Fe and Al oxides, and clay minerals). There is a need to bridge this gap of knowledge to identify the properties that govern OP adsorption and desorption processes and gaining insight into the behavior of OP compounds at the surface of soil minerals.

In sum, extensive research has evaluated the adsorption of different individual sources of organic and inorganic P to soils or to individual soil minerals. However, no study has evaluated and compared P desorption from the main OP compounds that were adsorbed onto the main soil minerals. The aim of our study was to elucidate the dynamics of adsorption and desorption of several forms of OP on several representative soil minerals. More specifically, we aimed at determining the drivers of adsorption and desorption of OP on soil minerals. For this purpose, we studied the adsorption of three OP compounds, myo-inositol hexakisphosphate (IHP), glycerophosphate (GLY) and glucose-6-phosphate (G6P) and one inorganic compound (KH_2PO_4 , IP) on Fe and Al oxides (goethite and gibbsite, respectively) and on clay minerals (kaolinite and montmorillonite). Organic P sources were chosen based on their predominance in both soils and organic inputs and their contrasted chemical properties. We assume that the selected Fe, Al oxides and clay minerals, abundant in the soils, will present different capacities of adsorption and desorption due to their chemical properties.

4.2 Materials and methods

4.2.1 Organic P forms and individual soil minerals

Three organic P (OP) compounds, IHP, GLY, G6P and one IP (KH_2PO_4) (Figure 11) were selected based on their predominance in organic wastes and soils and their contrasted properties (type of P bonds, different molecular sizes). The individual soil minerals were selected to be representative of the predominant soil minerals involved in P adsorption in soils. Four individual soil minerals were used. Goethite [$\text{FeO}(\text{OH})$] and gibbsite [$\text{Al}(\text{OH})_3$] were chosen as representative of Fe and Al oxides; kaolinite and montmorillonite were selected as clay minerals, particularly 1:1 phyllosilicate and 2:1 phyllosilicate respectively. The minerals used have different specific surface areas (SSA) and points of zero charge (PZC). The SSA of the minerals used are as follows: goethite ($46 \text{ m}^2 \text{ g}^{-1}$), gibbsite ($120\text{-}364 \text{ m}^2 \text{ g}^{-1}$), kaolinite ($19 \text{ m}^2 \text{ g}^{-1}$) and K-montmorillonite ($83 \text{ m}^2 \text{ g}^{-1}$) and their PZCs were: goethite (7.04), gibbsite (9.3), kaolinite (4.5) and montmorillonite (2.5), as previously reported by other authors (He et al., 1994; He and Zhu, 1997; Ruttenberg and Sulak, 2011; Shang et al., 1990; Yan et al., 2014). All minerals were obtained from Sigma-Aldrich Chemie S.a.r.l. and VWR (France) for experimentation (see supplementary data references in supplementary data (Appendix A, Table S1) for mineral references).

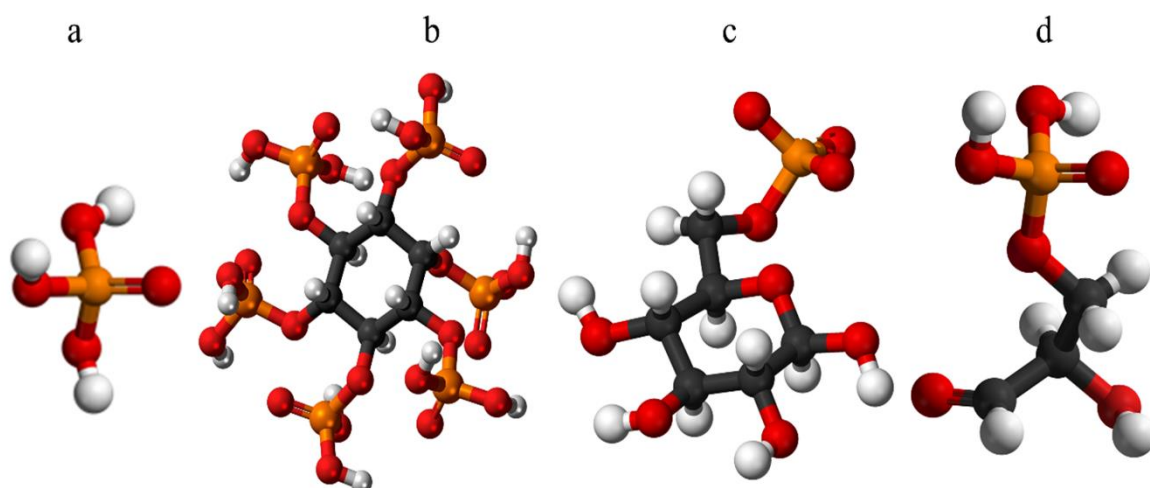


Figure 11 : Chemical structure of potassium dihydrogen phosphate, IP (a), myo-inositol hexakisphosphate, IHP (b), β -D-Glucopyranose-6-phosphate, G6P (c) and Glycerol phosphate, GLY(d)

4.2.2 Adsorption Experiments

Triplicate batch experiments were conducted to understand the interactions between OP forms and soils minerals at different P concentrations. We used standard P adsorption procedure proposed by Nair et al., (1984). Prior to adsorption, 80mg of each soil mineral were weighed and transferred to 50 mL polypropylene centrifuge tubes. Then, 20 ml of 0.1 M KCl were added and the tubes were shaken for 24 hours at 25°C to sufficiently hydrate the adsorption sites on the minerals. The pH was maintained at 5.5 ± 0.05 by adding 0.1 M HCl or NaOH solution. Six P concentrations (0, 4, 8, 16, 40, 75 and 100 mg L⁻¹) were used for each P forms. Phosphorus stock solutions of each OP were prepared under the same conditions of 0.1 M KCl at pH 5.5. KCl was used as electrolyte to mimic the environmental condition and adjust ionic strength of the solution. To start the adsorption, 20 ml of solution containing each concentration of P were pipetted into tubes containing the soil particles. The control experiment was the same but without P. The final volume was 40 mL and the concentration of particles in this final volume was 2 g L⁻¹. In each tube, some drops of hexanol were added to suppress microbial activities. The final samples were shaken on a mechanical shaker for 24 hours at 25°C and then centrifuged (3000 g for 15 minutes). After centrifugation, samples were immediately filtered through a 0.22- μ m membrane syringe filter. The filtrates were stored in a cold room until the P content was analyzed. Inorganic P was determined colorometrically (Ohno and Zibilske, 1991). Organic P compound samples was hydrolyzed to IP form before colorimetric determination by using the persulfate oxidation method (Peters and Van Slyke, 1932). The quantity of P adsorbed was calculated as the difference between the initial amount of P added and the remaining P amount in solution at the end of the adsorption experiment. Adsorption

maxima, capacity and other adsorption parameters were determined by fitting data to the non-linear form of the Langmuir (1) and Freundlich (2) isothermal model (Crini et al., 2007; Langmuir, 1918):

$$Q_{\text{ads}} = Q_m K_L [C_e / (1 + K_L C_e)] \quad (1);$$

where C_e is the concentration of P in the equilibrium solution (mg L^{-1}), Q_{ads} is the total amount of P adsorbed, K_L is the affinity constant or binding energy (L mg^{-1}), and Q_m is the P adsorption maxima ($\mu\text{g g}^{-1}$). The ability of soil minerals to resist a change in solution P concentration was measured as the maximum adsorption buffer capacity: $\text{MBC} = K_L \times (Q_m)$; where K_L and Q_m are the binding-energy related constant and maximum adsorption, respectively, in the Langmuir equation.

$$Q_{\text{ads}} = K_F C_e^{1/n_F} \quad (2);$$

where Q_{ads} ($\mu\text{g g}^{-1}$) is the total amount of P adsorbed, C_e is the adsorbate equilibrium concentration in solution, K_F ($\mu\text{mol L}^{-1}$) is adsorption capacity, and n_F (mmol L^{-1}) is Freundlich exponent.

4.2.3 Desorption kinetics experiments

Prior to desorption, the four soil minerals were loaded with the three OP compounds or IP. Solutions containing 1 g P L^{-1} in 0.1 M KCl at pH 5.5 were prepared using the different P compounds. Goethite, gibbsite, kaolinite and montmorillonite was weighed in portions of 100 g into 1L bottles containing. Then, 200 ml of 0.1 M KCl were added and the bottles were shaken for 24 hours at 25°C to sufficiently hydrate the adsorption sites on the minerals. The pH was maintained at 5.5 ± 0.05 by adding 0.1 M HCl or NaOH solution. To start the complex formations, each of the 1L bottles containing the soil minerals was filled with 800 ml of P solutions. This was done in order to obtain all the mineral-P complexes, for example for goethite we will have: goethite-IP, goethite-IHP, goethite-G6P and goethite-GLY and similarly for the other minerals. In each 1L bottles containing both the soil minerals and P compounds, some drops of hexanol were added to suppress microbial activities. The final samples containing in the bottles were shaken on a mechanical shaker for 24 hours at 25°C and then centrifuged (3000 g for 15 minutes). The 1L bottles were distributed into several small 250-mL bottles, centrifuged, and the supernatants were collected. Centrifugation was repeated until the maximum volume of supernatants was removed. The produced P-loaded minerals was agitated in deionized water and frozen at -20°C . The amounts of adsorbed P were determined using the same procedure as described in Section 4.3. The amounts of adsorbed P ($\mu\text{gP g}^{-1}$) were similar to the Q_m values (Table 11) of the adsorption data (Section 2.2) that were predicted by the Langmuir model.

Desorption kinetics experiments were initiated by adding 40 ml of 0.1 M KCl adjusted to pH 5.5 to 0.5g of the different minerals-P complex. Samples were shaken on a mechanical shaker at 25°C at regular intervals (24h, 48h, 72h, 96h). After the first cycle (24h), the entire suspension was removed

and immediately filtered through a 0.22- μm membrane filter. A fresh 40 ml solution of 0.1 M KCl was added to start the second cycle (48h). The same process was applied for the remaining cycles. The P concentration in the supernatant was determined as described above. Desorption maxima and rate were determined by fitting data to the non-linear form of the Elovich kinetic model (Bulut et al., 2008) (3):

$$Q = A + B * \text{Ln}t \quad (3);$$

where q is the amount of P desorbed at time t , and A and B are the constants with $A = \frac{1}{\beta}$ and $B = \frac{1}{\beta} \text{Ln}\alpha\beta$ (α and β are the constants in the original formula of Elovich equation). The A value (mgP kg^{-1}) in the Elovich equation is the amount of P desorbed in the first day of desorption ($q = A + B * \text{Ln}t$, $A = q$ when $t = 1$) and that B (mgP day^{-1}) is positively related with the P desorption rate as demonstrated in the studies of (He and al. 1994). A and B values have been used to compare P release rate in different soils (He and Zhu, 1997). The maximum desorption amount (D_m) was calculated as total amount P desorbed.

4.2.4 Statistical analysis

All the Langmuir, Freundlich and Elovich model's parameters were evaluated by non-linear regression method using function *nls* from *Package 'nlstools'* in R software. Nonlinear parameter estimates can be obtained using different methods (Archontoulis and Miguez, 2015; Bates and Watts, 1988); the most common is ordinary least squares, which minimizes the sum of squared error between observations and predictions (Brown, 2001). The determination coefficient (R^2) for each parameter was used to measure the goodness-of-fit. Apart from R^2 , standard errors (S.E.) were also used to determine the best-fitting isotherm to the experimental data. The conceptual framework was performed using *correlate* and *network plot* function in the latest development version of the *corr package* (Ahmed et al., 2021). This generates a network graph of a correlation data frame in which variables that are more highly correlated appear closer together and are connected by stronger paths. The proximity of points is determined using multidimensional clustering.

4.3 Results

4.3.1 Dynamics of Organic Phosphorus Adsorption

4.3.1.1 Effect of OP forms on adsorption dynamics

Organic P adsorption differed for each specific OP compounds (Table 11). The strongest differences in OP adsorbed among the different isotherms occurred with the greatest initial OP concentrations (Figure

12). In addition, the magnitude of OP adsorption increased rapidly when the initial OP concentration was low ($< 25 \text{ mg L}^{-1}$), but became relatively slow with increasing concentration (up to 40 mg L^{-1}). Each OP compound had different adsorption characteristics onto the various soil minerals. The Q_m , i.e. maximum OP adsorption capacity from the Langmuir equation (Table 11) ranged from $1045 \mu\text{g g}^{-1}$ to $56697 \mu\text{g g}^{-1}$, indicating marked variations in the amount of OP adsorbed. Among the OP compounds, IHP was the most adsorbed form ($3742\text{-}56697 \mu\text{g g}^{-1}$) followed by G6P and then GLY ($1045\text{-}6237 \mu\text{g g}^{-1}$) (Figure 12 and Table 11). The adsorption maxima of OP increased with increasing molar mass in this order: GLY (172 g mol^{-1}) $<$ G6P (260 g mol^{-1}) $<$ IHP (660 g mol^{-1}), which showed that the size of the molecule would have favored the adsorption of OP compounds.

Compared to IP, a contrasted adsorption behavior of OP compounds was observed. The adsorption dynamics followed the trend $\text{IHP} > \text{IP} > \text{G6P} > \text{GLY}$, showing that IHP was more adsorbed than IP, which in turn was more adsorbed than the G6P and GLY forms (Figure 12 and Table 11). The K_L value, i.e. the binding energy between OP and minerals surfaces were highly variable. With the exception of montmorillonite, GLY or G6P showed higher or equal binding strength compared IHP (Table 11). Our results showed that the adsorption dynamics of OP was strongly controlled by their biogeochemical properties in the soil. The IHP, GLY and G6P form showed a different adsorption process from each other as well as from the IP form. In general, IHP was found to be the most adsorbed P form and GLY the least adsorbed form.

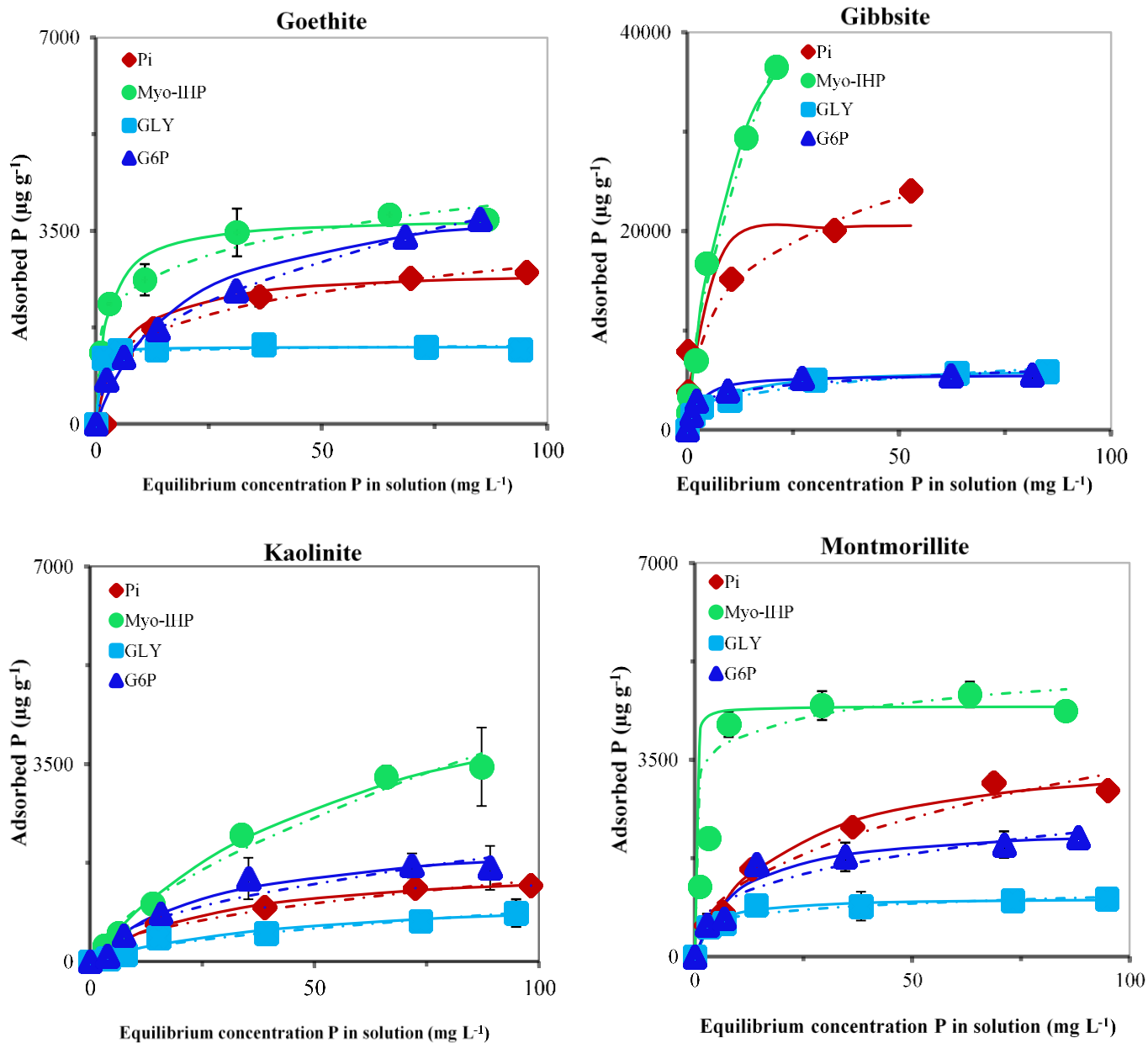


Figure 12 : Adsorption isotherms of OP forms by different soil minerals in 0.1 M KCl at pH 5.5

Symbols are data points, solid lines are Langmuir isotherms, and dashed lines are Freundlich isotherms. Gibbsite was different from other minerals because of the large difference in the maximum adsorption amount. Values of adsorbed quantities (Q_{ads}) and error bars (Se) are also provided as supplementary data (APPENDIX A Table S2).

Table 11 : Isotherm parameters of the Langmuir and Freundlich models for P adsorption

Soil components	P Forms	Langmuir equation				Freundlich equation		
		Q _m (μg g ⁻¹)	K _L (L mg ⁻¹)	R ²	MBC (L Kg ⁻¹)	K _F	n	R ²
Goethite	IP	2810	0.16	0.97	450	848	3.77	0.99
	myo-IHP	3742	0.4	0.97	1497	1584	4.88	0.98
	GLY	1398	3.31	0.99	4626	1228	9.7	0.99
	G6P	4337	0.05	0.98	217	561	2.35	0.99
Gibbsite	IP	20949	0.99	0.91	20740	7158	3.31	0.96
	myo-IHP	56698	0.08	0.99	4536	5703	1.62	0.99
	GLY	6237	0.14	0.97	873	1584	3.26	0.98
	G6P	5588	0.4	0.98	2235	2254	4.58	0.96
Kaolinite	IP	1736	0.04	0.99	69	157	2.08	0.98
	myo-IHP	6082	0.02	0.99	122	197	1.53	0.98
	GLY	1222	0.02	0.96	24	57	1.68	0.96
	G6P	2295	0.04	0.98	92	198	2.01	0.92
Montmorillonite	IP	3709	0.05	0.99	185	465	2.34	0.97
	myo-IHP	4857	0.32	0.97	1554	1966	4.82	0.87
	GLY	1045	0.28	0.98	293	477	5.71	0.96
	G6P	2338	0.1	0.96	234	521	3.1	0.92

Q_m: maximum adsorption capacity, K_L: binding-energy related constant, R²: model fitting degree, MBC: maximum buffer capacity (ability of soil minerals to resist a change in solution P concentration).

4.3.1.2 Adsorption dynamics as affected by soil minerals

Isotherms of OP adsorption for the four tested minerals demonstrated that OP adsorption patterns of the Fe and Al oxides (goethite and gibbsite, respectively) were very similar but quite different from that of clays minerals (montmorillonite and kaolinite) (Figure 12). Fe and Al oxides rapidly adsorbed OP and their adsorption maximum was reached at a lower initial concentration than for clays. All tested minerals fitted the Langmuir and Freundlich equation (Table 11). Adsorption capacity (K_F) of OP by soil minerals followed the trend kaolinite < montmorillonite < goethite << Gibbsite (Table 11), showing a marked variability between the adsorption capacities of the tested soil minerals. The Fe and especially Al oxides exhibited the highest maximum adsorption capacity for all OP forms. The specific surface area (SSA) of soil minerals may differently affect their ability to sorb OP compounds. Our result showed that the larger the SSA of soil minerals, the greater their ability to sorb IP forms. However, this was not consistent for the OP compounds. For instance, kaolinite showed greater IHP adsorption than goethite and montmorillonite despite its smaller specific surface area.

The K_L value, i.e. the binding-energy-related constant obtained from the Langmuir equation varied in the following order clays \ll Fe and Al oxides (Table 11). The highest binding energy for adsorbed OP was observed with goethite and the lowest with kaolinite. In addition, the maximum buffering capacity of adsorption (MBC) of the Fe and Al oxides was much larger than for the clay mineral (Table 11). Compared to IP, goethite and montmorillonite are more strongly bonded to OP; however, the opposite was found on gibbsite and kaolinite, which bond IP more strongly than OP. Therefore, despite the highest OP adsorption capacity of gibbsite, its interaction with OP would be less strong than with IP. The results for the adsorption capacity and binding energy of montmorillonite are only valid for the K-saturated montmorillonite used in this study. Al or Ca saturated montmorillonite would result in different adsorption mechanisms. Figure 16 illustrates a conceptual framework showing the relationship between soil mineral properties (PZC, SSA) and Langmuir model adsorption parameters (K_L and Q_m). A positive relationship was found between the ability of soil minerals to adsorb and strongly bind OP and the chemical and physical properties of the soil minerals (PZC, SSA).

4.3.2 Dynamics of Organic Phosphorus Desorption

4.3.2.1 Role of OP compounds in desorption dynamics

In general, OP desorption by KCl was well fitted with Elovich equation, with determination coefficient from 0.91 to 0.99 (Table 12). In this study, KCl was found to desorb a variable portion of adsorbed OP from the tested OP-mineral complexes. The portion of OP desorbed from all soil minerals was lower than the initially adsorbed OP (Figure 13 and Table 12) which indicates that the adsorption was not fully reversible, as a large amount remained adsorbed. Overall, P desorption was high on the first day (up to 30%) and then slowed down from the second to the fourth day (Figure 13 and Table 12).

The D_m values refer to the predicted maximum desorption capacity of OP obtained from the Elovich model (Table 12). Organic P compounds showed different D_m trends by mineral type. Both G6P and GLY showed higher D_m values (13%-56%) than IHP (3%-14.44%) on Fe and Al oxides. On clay minerals, the pattern was rather opposite, with IHP desorption being higher than other OP forms (Table 12). The desorption maxima of all of the OP compounds were 4%-56%, lower than those of IP which were between 13 % to 70% (Table 12 and Figure 13), showing a general lower desorption of OP relative to IP. However, there were some exceptions with G6P and/or GLY which showed higher desorption than IP on Fe and Al oxides. The amount of OP desorbed could be related to the strength with which it was bound to soil minerals (adsorption parameter K_L). The Figure 16 showed negative correlations between D_m and K_L , indicating that the amount of OP desorbed tends to decrease with increasing OP binding energy to the soil minerals.

The rate of OP desorbed per day (A) predicted by the Elovich model varied widely for each OP-mineral complex (Table 12). Most of OP-minerals complexes showed lower desorption rates per day

than IP-minerals. In addition, the different OP-mineral complexes can be classified according to desorption rates into three categories (Figure 14): low desorption rate complexes (<5% per day) which include all the OP desorbed from gibbsite and kaolinite; medium desorption rate complexes (10-20% per day) including IHP and G6P from montmorillonite and high desorption rate complexes (20% > per day) which include only G6P from goethite (Figure 14).

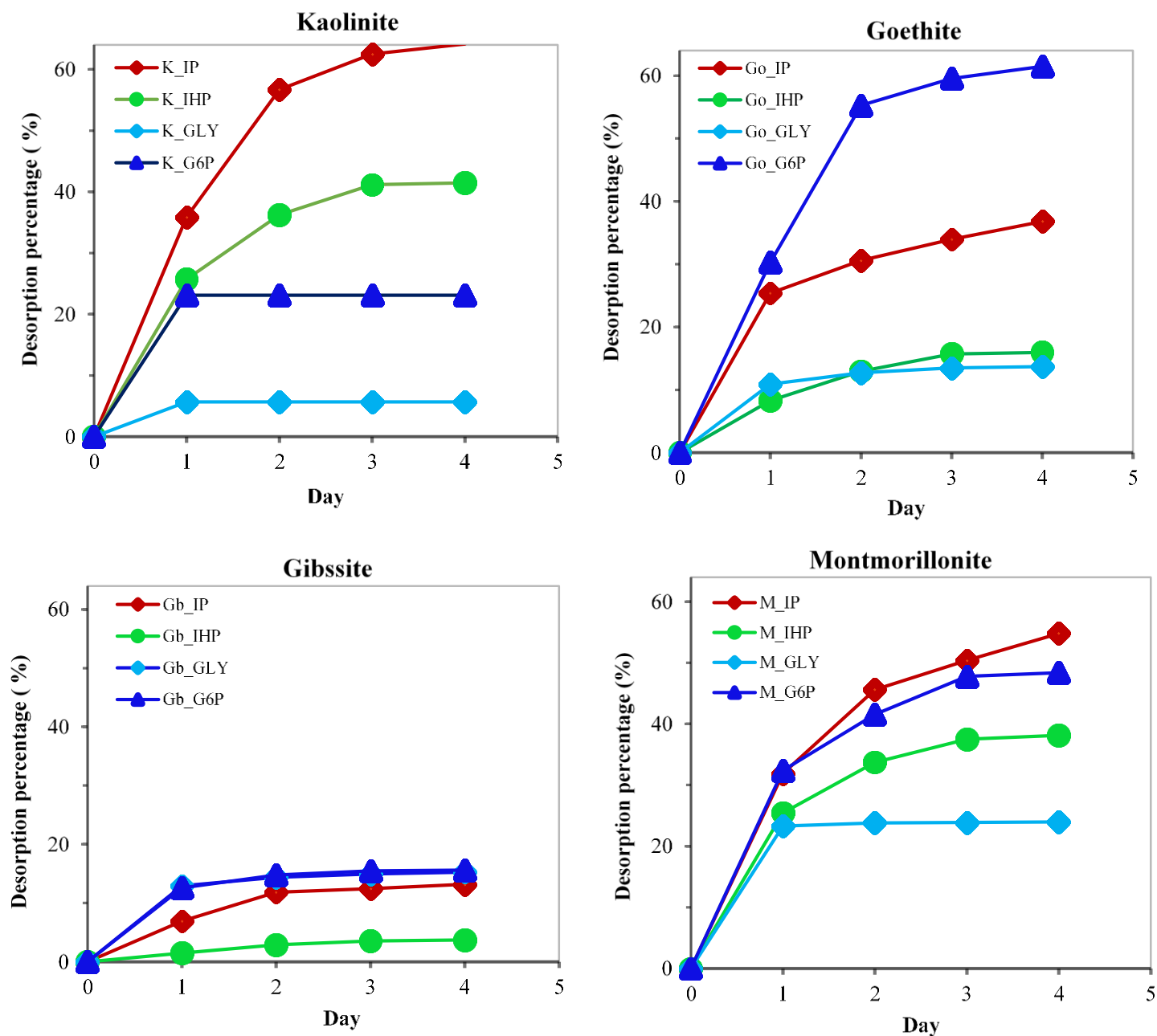


Figure 13 : Desorption kinetics of IHP, GLY and G6P by 0.1 M KCl at pH 5.5 and at 25°C

Table 12 : Organic P desorption isotherm parameters of the Elovich model

Soil components	P Forms	Elovich equation			
		Dm (%P g ⁻¹)	A (%P day ⁻¹)	B (%P g ⁻¹)	R ²
Goethite	IP	33	8	25	0.99
	myo-IHP	14	6	9	0.97
	GLY	13	2	11	0.97
	G6P	56	23	33	0.90
Gibbsite	IP	12	5	7	0.91
	myo-IHP	3	2	2	0.97
	GLY	15	2	13	0.98
	G6P	15	2	13	0.94
Kaolinite	IP	59	21	38	0.94
	myo-IHP	39	12	27	0.95
	GLY	6	0.01	6	0.98
	G6P	23	0.01	23	0.98
Montmorillonite	IP	49	16	33	0.99
	myo-IHP	36	10	26	0.96
	GLY	24	0	23	0.92
	G6P	45	12	33	0.97

Dm: maximum P desorption capacity, A: P desorption rate, B: amount of P desorbed in the first day of desorption in this study ($q = A + B * \ln t$, $B = q$ when $t = 1$), R²: model fitting degree.

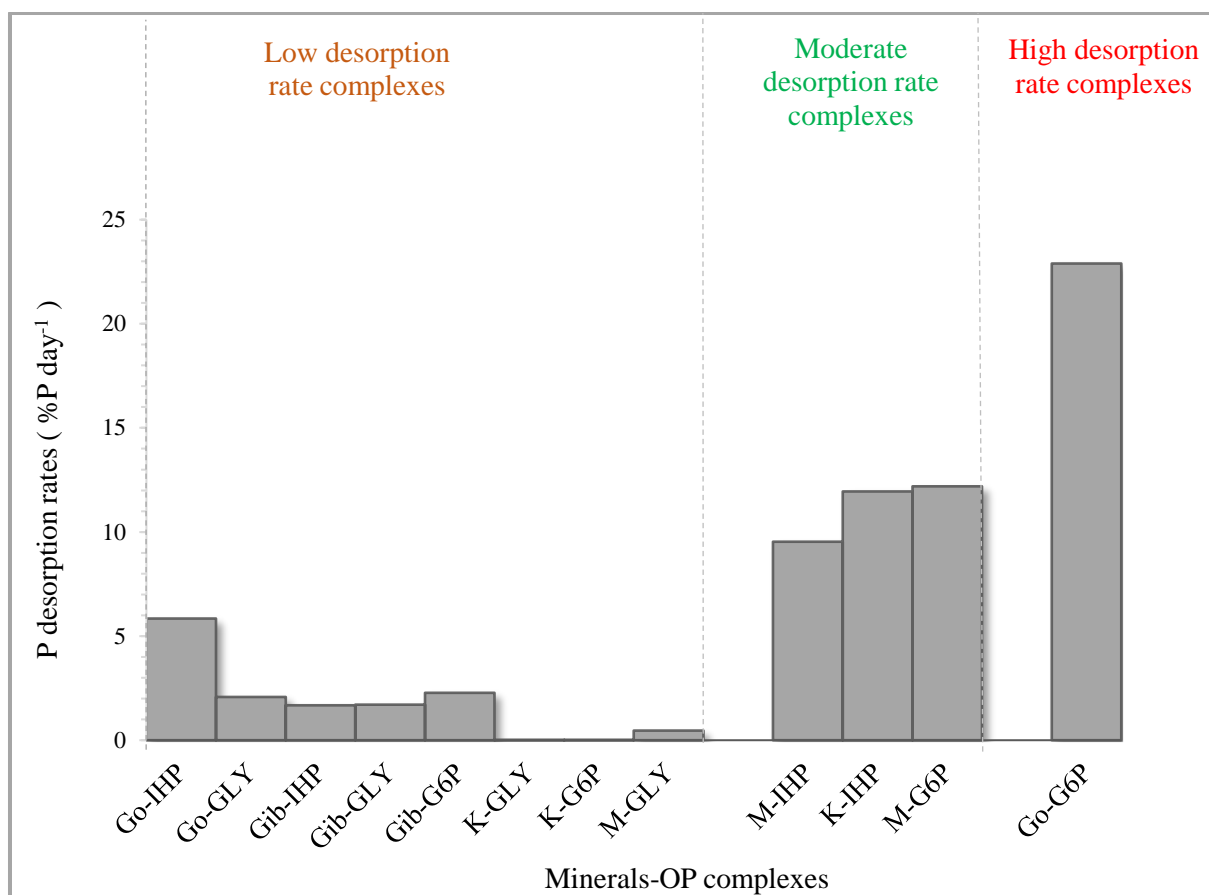


Figure 14 : Variation in P desorption rates of mineral-OP complexes

4.3.2.2 Role of soil minerals in desorption dynamics

There was a large difference between Fe and Al oxides minerals and clays mineral with respect to desorption properties (Table 2 and Figure 13). Phosphate desorption from Fe and Al oxides was very rapid, and equilibrium was attained within 2 days. Except for G6P on goethite, OP desorption from soil minerals at the end of the experiment could be ranked as gibbsite (3-14%) < goethite (13-14%) < kaolinite (5-39%) << montmorillonite (23-45%) (Table 2, Figure 13). Organic P desorption from clays minerals was thus much higher than from Fe and especially Al oxides. This large difference in the capacity of soil minerals to release OP would be related to the physicochemical properties of the soil and the OP. Indeed, our results showed strong negative correlation between the desorption capacity (Dm) and the properties of the soil minerals (PZC and SSA), and the correlation appears to be stronger with PZC (Figure 16).

Successive desorption (Figure 15) using KCl showed that more than 25% of the adsorbed OP (IHP, G6P, GLY) on montmorillonite was desorbed in the first cycle and there was no desorption after 4 cycles. Compared to the clays-IHP complex, P desorbed from Fe, Al oxide- IHP was lower but declined more slowly with increasing number of cycles (Figure 15). The same trends were observed with the Fe and Al oxide-GLY complexes. For instance, at the first cycle, more IHP and GLY was

desorbed from the clay minerals than from the Fe and Al oxides, but from the second cycle, Fe and Al oxides had desorbed almost as much IHP and GLY as the clays. At the fourth cycle, the amount of IHP and GLY desorbed from the clay minerals was lower or equal to that from Fe and Al oxides. This suggests that the clays-IHP and GLY complex supplied P rapidly but over a short period whereas the Fe and Al oxide-IHP and GLY complex supplied P slowly but over a long period. With slight differences, the soil mineral-G6P complexes appeared to show the same trend as mineral-IHP or GLY. As mentioned above for the results of the adsorption mechanisms of montmorillonite, the desorption properties (kinetics, amount and rate of desorption) are also only valid for K-saturated montmorillonite.

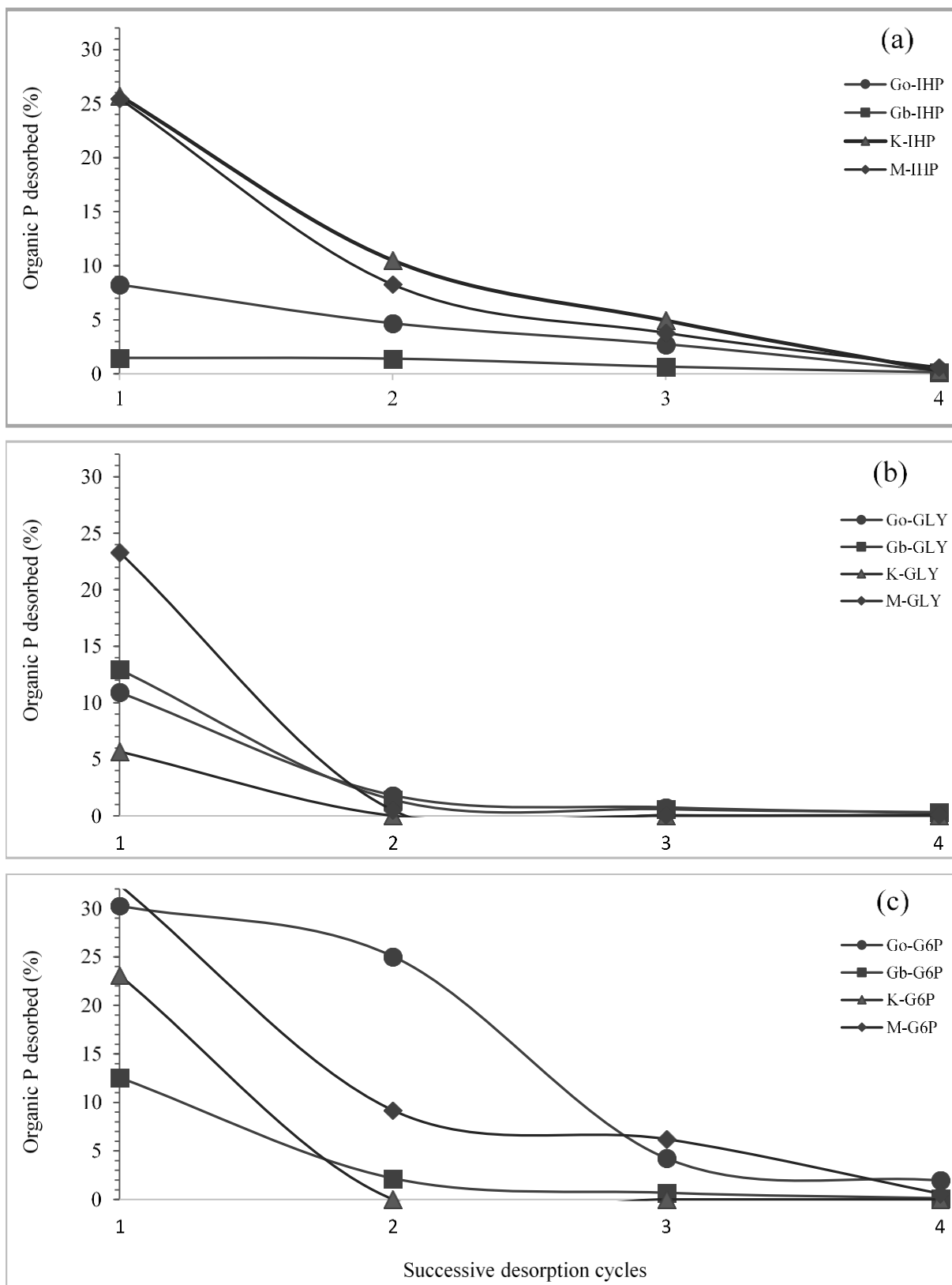


Figure 15 : Successive desorption of (a) IHP, (b) GLY and (c) G6P from OP-mineral complexes by KCl

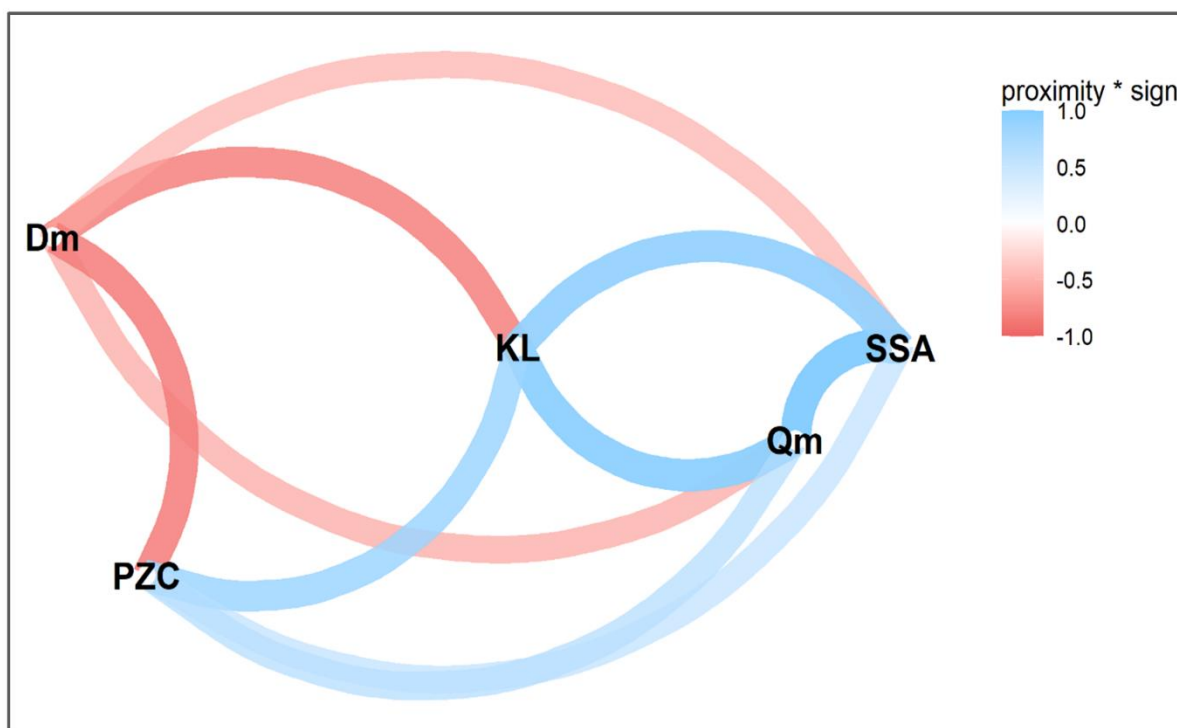


Figure 16 : Conceptual framework showing the linkage among soil minerals properties (PZC, SSA) and adsorption/desorption parameters (bonding strength, KL; adsorption capacity, Qm, and desorption capacity, Dm).

The linkage is based on the relationships between different variables. The color of each line refers to the degree of relationship between the variables. $R^2 > 0.5$

4.4 Discussion

4.4.1 Influence of organic phosphorus properties on adsorption and desorption dynamics

Adsorption dynamics of OP compounds play an important role in the potential reactivity of OP in soils amended with organic input. Our results showed the positive relationship between OP adsorption dynamics and the number of phosphate groups of the organic molecule. The higher phosphate group number, the higher the adsorption. Thus, IHP, which has six orthophosphates per C moiety, was adsorbed in larger quantities than the orthophosphate monoesters (G6P and GLY) because it can coordinate with more hydroxyl (OH) groups on the surface of soil minerals (McKercher and Anderson, 1968). The sizes of the C moiety, may be also responsible for the difference in adsorption amount of each OP compounds. Our results about molecular mass effects on OP adsorption dynamics were in disagreement with most studies that found decreases in OP adsorption with increasing molecular mass due to steric hindrance effects (Lü et al., 2017; Ruttenberg and Sulak, 2011). They specifically disagree with those of Lü et al., (2017) who observed that the adsorption maxima of OPs on goethite and hematite were classified as follows: IP > Adenosine monophosphate (AMP) = G6P > ATP, showing a decreasing trend in sorption levels with increasing molecular mass of the different forms of OP. Our results also

contrast with those of Yan et al., (2014) where the maximum sorption densities of three Al (oxyhydr)oxides (amorphous Al(OH)₃, boehmite and α -Al₂O₃) increased with decreasing molecular masses follows IHP < ATP < G6P < GLY < IP. However, the results obtained agree with the work of Berg and Joern, (2006), which showed a trend of increasing rather than decreasing sorption levels with increasing molecular mass of different forms of OP (IHP > G6P > ATP > IP). Similarly, recent work by Ganta et al., (2020) and Ahmed et al., (2021) also supported our results. They demonstrated that the organic fraction of the OP may not influence the interaction of individual phosphate groups with the soil and thus the effect of molecular mass steric hindrance may be insignificant.

After adsorption, the ability of OP compounds to desorb depends not only on their chemical properties but also on the degree of energy with which they are adsorbed onto soil minerals (Ganta et al., 2021, 2019). A general weaker or equal binding strength of IHP compared to GLY or G6P was found. This disagrees with recent results that reported total interaction energies (in absolute value) measured for goethite-IHP complexes (-72 to -85 kcal mol⁻¹) higher than those for GLY (-38 to -48 kcal mol⁻¹) (Ganta et al., 2019; Kubicki et al., 2012; Rakovan et al., 1999). In addition, this finding also contradicts the extensive literature that associates the large amount of IHP adsorbed with its strong binding to minerals (Celi et al., 2000; Giaveno et al., 2008; Guan et al., 2006; Johnson et al., 2012; Xu et al., 2017). However, this indicates that the higher adsorption of IHP relative to other OP compounds did not necessarily imply that its binding capacity is always strong and stable under all environmental conditions. Thus, we suggest that despite the higher accumulation of IHP reported in most soils (Amadou et al., 2021; Gerke, 2015), its desorption may be easier than that of the GLY or G6P forms, although this depends greatly on the soil minerals and experimental conditions. Furthermore, our results indicated that if both GLY and G6P species compete with IHP for the same active sites on soil minerals, the binding energy of GLY or G6P would be higher than that of IHP. Therefore, one could expect easier desorption of IHP from soil compared to GLY and G6P even though this would be highly dependent on soil minerals.

4.4.2 Influence of soil mineral characteristics on adsorption and desorption dynamics

The tested soil minerals presented a different capacity to sorb OP compounds due to their contrasting physicochemical properties. Fe and Al oxides showed very different OP adsorption mechanisms compared to clays, as the adsorption capacity ranked as follows: kaolinite < montmorillonite < goethite <<< gibbsite. This can be explained by their contrasting types of surface charge. At pH 5.5 (pH used for this study), kaolinite has a small net negative charge, goethite has a small net positive charge and gibbsite is positively charged while montmorillonite is negatively charged according to their PZC values (He et al., 1994; He and Zhu, 1997). Gibbsite exhibited the greatest adsorption maximum, which was probably

related to the combined effect of its high surface positive charge and greater SSA ($120\text{-}364\text{ m}^2\text{ g}^{-1}$), as well as the abundance of active adsorption sites, as noted by Shang et al., (1990) and Yan et al., (2014). Manning and Goldberg, (1996) found that gibbsite and goethite adsorbed roughly 23 times more P than kaolinite and up to 53.5 times more IP than montmorillonite and illite. However, despite the highest OP adsorption capacity of gibbsite, its interaction energy with OP would be less strong than IP. The order of the K_L value, i.e., binding energy (clays \ll Fe and Al oxides), suggests a much higher binding energy between OP and Fe and Al oxides than between OP and clays. These results suggest that the mechanism of OP adsorption on Fe and Al oxides is quite different from that on clay minerals. In sum, soil minerals had diverse adsorption mechanisms, specifically Fe and Al oxides compared to clay minerals. The changes in their adsorption and binding capacity to OP compounds were the result of their contrasting physicochemical properties. This may result in different behavior in the desorption of adsorbed OP. However, since it is well known that the number of positive charges of variably charged minerals (especially Fe and Al oxyhydroxides and kaolinite) decreases with increasing pH, we speculate that their adsorption may decrease at higher pH than that of our study (i.e. $\text{pH} > 5.5$) (Hu et al., 2020b). In addition, it is also known that cations in solution can affect the P sorption potential of certain minerals, e.g., Al or Ca saturated clay minerals (Ellis Jr and Truog, 1955; Pissarides et al., 1968; Prietzel et al., 2016). The next challenge will be therefore to elucidate the role various cations on OP retention by minerals. This could also allow to feed surface complexation models to gain in robustness on the understanding of the adsorption and desorption mechanisms while better predicting P behavior in soils.

The desorption dynamics of the adsorbed OP was markedly affected by both OP and soil minerals characteristics. OP was more desorbed from clays minerals (montmorillonite and kaolinite) than from Fe and Al oxides. Since clays have also been shown to have a lower OP retention capacity, it can be expected that OP will be more available when organic inputs are applied to soils dominated by phyllosilicates, e.g. subtropical and temperate soils (Bortoluzzi et al., 2015; He et al., 1994). Furthermore, with time, OP desorption kinetics and rate differed between soil minerals. Our findings showed that clays-OP complex released P rapidly but over a short period whereas the Fe and Al oxide-OP complex released slowly but over a longer period. In the clay-OP complexes, the binding energy would be unstable and its distribution would have varied remarkably with time, probably from loosely-bound fraction to tightly-bound fraction. In contrast, Fe and Al oxide-OP complexes were stable with time. These results indicated that each complex would have presented a different binding mechanism, e.g. the inner sphere versus the outer sphere complex with different types of bonds e.g. bidentate versus monodentate (Ganta et al., 2019). Our results highlighted the central role of OPs and their interactions with soil minerals on P availability and potential P loss to water. Better knowledge of these interactions constitutes an important challenge to model OP dynamics and predict P release to plants and waters in soil amended with OP fertilizers. Despite the overall low desorption of OP from Fe and Al complexes, G6P and GLY were however more desorbed from goethite and gibbsite than IP. This weaker retention of these OP forms by Fe and Al oxides suggests that both G6P and GLY could be used in Fe/Al oxide-

rich soils to improve P nutrition of plants. This has therefore great implication for P fertilization in highly weathered soils of tropical regions in which Fe and/or Al oxides are dominant. Taken together, our results indicate that both Fe and Al oxides and clay minerals in soil could be either OP sinks or OP sources, depending on their properties, binding energy and adsorption saturation.

It must be noted, however, that soils may contain a much wider variety of Fe and Al oxides than those used in this study, namely goethite and gibbsite respectively. For example, many soils contain significant amounts of ferrihydrite, which was reported to have a higher P sorption than goethite (Prietz et al., 2016; Ruttenberg and Sulak, 2011; Prietz and Klysubun, 2018). As an outlook, we strongly suggest studies to understand better the involvement of a wide range of iron oxides in the dynamics of OP forms. More generally, though our results provide a mechanistic understanding of the sorption processes of various OP forms on selected soil minerals, the role of other soil minerals alone or in combination needs still to be investigated to generate a better overview of OP dynamics in real complex soil systems. In addition, it is also important to point out that our results regarding the comparison between the P (de)sorption properties of montmorillonite and other soil minerals are only valid for the K-saturated montmorillonite used here. For Al- or Ca-saturated montmorillonite, a much stronger P sorption or less pronounced P desorption would be expected compared to K-saturated montmorillonite. Furthermore, in agroecosystems, with the exception of periods immediately following heavy K fertilization, K-saturated montmorillonite, which was used here as the montmorillonite type, is rare in most soils. Thus, the results must be considered in light of the type of clay used (K-saturated montmorillonite in this study).

4.4.3 Adsorption and desorption dynamics of OP relative to IP

Compared to IP, IHP was generally more strongly adsorbed whereas the opposite was observed for G6P and GLY. This result showed that specific forms of OP, depending on their characteristics, had contrasting adsorption dynamics with respect to IP. Therefore, the weaker retention of OP compared to IP which is generally suggested in the literature (Anderson et al., 1974; Condon et al., 2015, 2005) did not apply to all organic P compounds as higher inositol phosphate esters can be strongly retained in soil. Berg and Joern, (2006) found that soils pretreated with IHP or having combinations of IHP and IP in solution had reduced IP adsorption by successfully competing for binding sites, indicating that there was a preference in the adsorption of IHP over IP. This preference may either lead to the release of already adsorbed IP or prevent further adsorption of IP, leading to an increase in both available IP for plants and soluble IP for runoff (Leytem et al., 2002). Furthermore, in the presence of different OP forms in soils, the preferential adsorption of IHP or IP over both G6P and GLY may increase G6P and GLY availability and promote their mineralization. Thus, this contrasting adsorption dynamics of OP versus IP have important implications for P management from organic input in soils because IHP, GLY and G6P can comprise up to 80% of total P in some organic input (Amadou et al., 2021; Darch et al., 2014; George

et al., 2018), and many animal manures, notably those from monogastrics (pigs, poultry), contain substantial quantities of inositol phosphates (Hu et al., 2020a; Peperzak et al., 1959). Application of these manures to agricultural land could, therefore, promote the solubilization of IP and/or reduce the adsorption of G6P and GLY which would then be available for uptake by plants but also released into runoff water (Reid et al., 2018). On most soil minerals, the amount of desorbed OP and the desorbed rate of OP were generally lower than those of IP. After several desorption cycles, (Roy et al., 2017) found that 20% of IP desorbed from goethite while it only accounted for less than 5% for OP. Similar findings were reported by (Ruyter-Hooley et al., 2016) with limited desorption of OP (<3% of total amount) on gibbsite, even in the presence of humic acids as competing ligands for sorption sites. Huang and Zhang, (2012) showed that OP compounds added by organic input may desorb slowly and mineralized in step with plant uptake, even in the long term. However, our results showed that this did not apply to all OP compounds.

4.5 Concluding remarks

Moving toward more sustainable sources for managing P nutrition in agroecosystems, OP derived from organic inputs and soil is increasingly considered to complement mineral P fertilizer. However, enhancing OP cycling and availability in soils while reducing OP loss into the environment requires a better understanding of OP adsorption/desorption processes on soil minerals. Factors related to soil properties and OP molecular characteristics directly affect the reactions of OP and its release into the soil. The IHP, GLY and G6P form showed different adsorption processes from each other as well as from the IP form. Our results demonstrated contrasted adsorption capacities between IHP and the other organic P forms (G6P and GLY) relative to IP form, with IHP exhibiting the greatest adsorption capacities. The adsorption capacity of each OP compounds is determined by the number of orthophosphate groups associated with the C moiety in each compound and its size. The general idea of a lower adsorption of OP relative to IP suggested by the literature does not match for all OP compounds since, even though IHP was more strongly retained relative to IP, G6P and GLY were more weakly retained. In general, OP compounds showed less desorption and slower desorption rate per day than IP forms. Fe and Al oxides showed very different OP adsorption mechanisms compared to clays regarding their binding energy and adsorption amount, which were related to different in properties (SSA and PZC). The Fe and especially Al oxides (gibbsite) exhibited the highest maximum adsorption capacity for all OP forms.

The desorption dynamics of the adsorbed OP was markedly affected by both OP and soil minerals characteristics. Montmorillonite showed the highest desorption for OP suggesting higher OP release when organic inputs are applied soils dominated by 2:1 phyllosilicate. However, the results are very dependent on the specific type of montmorillonite used in this study. In fact, the results related to the comparison between the P (de)sorption properties of montmorillonite and other soil minerals are

only valid for the K-saturated montmorillonite used here. If Al- or Ca-saturated montmorillonite, which are the most common types of montmorillonite in soils, had been used, much higher P sorption and lower P desorption would be expected compared to K-saturated montmorillonite. Finally, despite their overall high adsorption, the higher desorption of G6P or GLY relative to IP from Fe and Al oxides indicated that G6P and GLY release would be less affected than IP by such soil compounds, which are especially abundant in highly weathered soils. However, since the P concentration used in our study may be higher than that of real soil systems, it would be interesting to investigate the effect of P concentration on adsorption processes by performing sorption experiments at different (and lower) P concentrations.

By simultaneously analyzing the interactions between various OP forms and various soil minerals, this study provides new insight into the OP adsorption and desorption dynamics on soil minerals which is important to optimize the use of organic input as fertilizer and to improve or develop prediction model of OP release in agroecosystems.

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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CHAPTER 2

5 Role of soil minerals on organic phosphorus availability and phosphorus uptake by plants

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Highlights

- Organic P (OP) availability is strongly driven by OP forms and mineral types
- Ryegrass was able to take up about 3-18% of OP adsorbed to soil minerals
- Adsorbed glycerophosphate was more available than the other OP forms
- Montmorillonite-OP showed the highest P uptake and kaolinite-OP the lowest one
- The binding strength of OPs to the mineral surface did not explain P availability

Abstract

Organic phosphorus (OP) represents a significant fraction of the total P pool in soils. With the increasing use of organic resources to substitute mineral P fertilizers and the need to recover P from the soil, it is pivotal to gain insight into the interactions between various OP forms and soil minerals and their consequences on P availability. Here, we aim at elucidating the extent to which OP compounds adsorbed onto major soil minerals may be available to plants. Ryegrass (*Lolium multiflorum*) plants were grown in RHIZOtest devices in the presence of OP including myo-inositol hexakisphosphate (IHP), glycerophosphate (GLY), and glucose-6-phosphate (G6P) and inorganic P (IP) compounds that were previously adsorbed onto Fe and Al oxyhydroxides (goethite and gibbsite, respectively) and clay minerals (montmorillonite and kaolinite). Phosphorus availability and P uptake were then determined through rhizosphere and plant characterization. Irrespective of the type of mineral, ryegrass was able to take up about 3-18% of adsorbed OP compounds. The magnitude of availability and uptake depended on the OP compounds and the type of soil minerals. The potential availability of OP adsorbed by different minerals was strongly mediated by mineral-OP interaction types and properties. The P uptake increased in the following order: kaolinite-OP << gibbsite-OP ≤ goethite OP << montmorillonite-OP. Phosphorus uptake from adsorbed OP compounds showed contrasting patterns compared to adsorbed IP and depended more on available P concentration in the rhizosphere rather than on the binding strength of OPs to the mineral surface.

Keywords: Adsorption; desorption; organic phosphorus; phosphorus availability; phosphorus acquisition

5.1 Introduction

Phosphorus (P) is a limiting nutrient in both natural and agricultural ecosystems due to its strong sorption with soil particles which limits its availability for plants (Fan et al., 2020; Hou et al., 2020). The depletion of the world's phosphate rock reserves used to produce mineral fertilizers threatens food security (Filippelli, 2008; Reijnders, 2014; Yu et al., 2022). Recycling P from organic input becomes thus a necessity for sustainable P management in agroecosystems (Elser and Bennett, 2011; Houben et al., 2017; McGrail, 2021). However, P contained in organic input and soil occur under various inorganic and organic forms that differ in their availability to plants (Faucon et al., 2015; Kahiluoto et al., 2015). The predominant organic P (OP) forms in organic input include myo-inositol hexakisphosphate (IHP), glycerophosphate (GLY) and, glucose-6-phosphate (G6P) (Giles et al., 2011; Vincent et al., 2013). Each compound differs from the others in its P content, type of P bond, and size of the molecule (Amadou et al., 2021; Xu and Arai, 2022). These biochemical properties are likely to impact the availability of OP forms to plants as they govern their interactions with the solid phases. Most research on the fate of P applied to soil has focused on inorganic P (IP) compounds, showing that most of it is adsorbed at the surface of soil particles, which in turn influences its availability to plants (Grenon et al., 2021; Hinsinger, 2001; Houben et al., 2011). In contrast, the dynamics of OP forms and their availability have been understudied to date and the contribution of these compounds to plant nutrition is poorly known (Faucon et al., 2015; Haygarth et al., 2018; Mezeli et al., 2019).

Soil minerals such as iron (Fe) and aluminum (Al) oxyhydroxides (e.g. goethite and gibbsite, respectively) and clay minerals (e.g., kaolinite, montmorillonite) are major components of soils (Xu and Arai, 2022). They have received considerable attention due to their high P adsorption capacity (Bortoluzzi et al., 2015; Ryan et al., 2001; Xu et al., 2021) which may cause an OP utilization efficiency in soils as low as 5-10% (He et al., 1994). This leads to poor utilization of OP sources in agroecosystems (Amadou et al., 2021; Sulieman and Mühling, 2021). Organic P compounds adsorbed on minerals were found to be the most stable P forms in different soil types (Martin et al., 2002; Montalvo et al., 2015). This has been attributed to their specific binding mechanism. Indeed, it was found that the number of the phosphate groups in a certain OP compound determines the stability of its complex with the mineral surface (Anderson and Arlidge, 1962; Li et al., 2021). For instance, IHP with its six phosphate groups generally exhibits a strong binding and high stability as compared with other OP or IP compounds which have a smaller number of phosphate groups (Gerke, 2015). Ognalaga et al. (1994) showed that up to four phosphate groups of IHP interact with the goethite surface, leading to the formation of inner-sphere complexes between the IHP phosphate groups and the goethite surface. A similar mechanism has been suggested for other P-mineral complexes. Desorption of P from mineral surfaces would be more limited

for OP compounds compared to IP (Bai et al., 2021; Gerke, 2015; Ruttenberg and Sulak, 2011). However, the extent to which OP compounds adsorbed to soil minerals can desorb remains poorly known and their availability to plants is still debated.

Several authors have suggested that the mineral-OP bridging compounds are not available to plants because these complexes are formed during the slow reaction phase with soil minerals (Hingston and Quirk, 1974; Barrow and Shaw, 1975). This process has been hypothesized to be a major cause of plant growth limitation (Javaid, 2009). After several desorption cycles, Martin et al. (2002) found that 20% of IP desorbed from goethite while it only accounted for less than 5% for IHP. Similar findings were reported by Ruyter-Hooley et al. (2015) with limited desorption of IHP (<3% of total amount) on gibbsite, even in the presence of humic acids as competing ligands for sorption sites. In addition, Gerke (2015) proposed that the presence of Ca in soil solution further reduces IHP solubility and availability due to the formation of Ca-IHP precipitates. These studies suggest that the availability of OP is probably mainly limited by its solubility and not by enzymatic activity (Gerke, 2015; Lung and Lim, 2006). This is corroborated by plant growth tests in the presence of synthetic goethite (Martin et al., 2002) and in P-fixing soils (Adams and Pate, 1992) where sorption and/or precipitation also lowered both IHP solubility and availability. In any case, there was a greater affinity of the OP compounds for soil minerals than that of the IP compounds, indicating the formation of a very stable complex of OPs with mineral surfaces. Thus, it can be expected that desorption and plant availability of mineral-OP complexes are lower than those of IP compounds. However, the very few studies on OP do not adequately quantify their potential contribution to P availability in the organic fertilizer-soil-plant system (Amadou et al., 2021; Klotzbücher et al., 2020; Sulieman and Mühling, 2021). For example, although some studies consider IHP as a source of available P, its availability in the presence of the major soil minerals remains poorly understood (Garcia-Lopez et al., 2015; Martin et al., 2002). Moreover, these studies did not consider other important P pools such as GLY or G6P which, together with IHP, nevertheless represent an important part of the total P in the soil (Darch et al., 2014; Gérard, 2016). Furthermore, the soil minerals used were in most cases goethite while Al oxyhydroxides and clays were much less considered (Amadou et al., 2022; Gérard, 2016). To our knowledge, there are no study that evaluates and compares the availability of P to plants from the major OP compounds (IHP, GLY, and G6P) that were adsorbed onto the major soil minerals (Fe and Al oxyhydroxides and clay minerals). It is therefore crucial to understand the complex mechanisms that control the dynamics of important compounds of OP in major soils fertilized with organic inputs and the efficiency of the OP-minerals interaction in supplying P to crops.

Overall, our understanding of the dynamics of the major OP pools in the soil-plant system is very limited. Most research has focused on the dynamics of IP forms (Sulieman and Mühling, 2021), suggesting that soil characteristics control their availability to plants (Gómez-Suárez et al., 2020). However, OP forms may strongly differ from each others and have therefore different biogeochemical processes controlling their availability and uptake by plants (Amadou et al., 2021; Condon et al., 2005).

To date, it is not known how the chemical forms of OPs, and their interactions with soil minerals, influence the uptake of OPs by plants in ecosystems. The paucity of research significantly limits our ability to understand the overall dynamics of P cycling in ecosystems and to optimize the use of renewable P fertilizers which often contain various forms of OP (Kelessidis and Stasinakis, 2012; Mininni et al., 2015). The goal of this study was to elucidate the extent to which OP bound to Fe and Al oxyhydroxides and clay minerals complexes contributes to plant P acquisition. This could open up possibilities for the use of renewable nutrient-rich organic amendments according to different soil mineral properties. Specifically, we determined the plant P availability from several complexes of IHP, G6P, and GLY that were adsorbed onto Fe and Al oxyhydroxides (goethite and gibbsite) and clay minerals (kaolinite and montmorillonite). Mineral-IP complexes with KH_2PO_4 were also carried out for comparison. The P uptake for each compound was determined using ryegrass grown in an RHIZOtest device. The three main following hypotheses were addressed: (1) P from adsorbed OP compounds is available to ryegrass and varies with soil mineral properties; (2) the relative P uptake of the different complexes OP-minerals are dependent on their binding strength and (3) adsorbed OP compounds are less available than adsorbed IP because it desorbs less and requires not only desorption but also enzymatic cleavage before being taken up by ryegrass.

5.2 MATERIALS AND METHODS

5.2.1 Organic P compounds and individual soil minerals

Three OP compounds, including myo-inositol hexakisphosphate (IHP), glycerophosphate (GLY) and glucose-6-phosphate (G6P), and one inorganic P (KH_2PO_4) were selected for experiments. Organic P compounds were initially selected based on their predominance in organic inputs and soils, the types of P bonds and their different molecular sizes. The inorganic P form was chosen for comparison with organic P compounds. Four minerals were selected to be representative of the predominant minerals in soils: Goethite [$\text{Fe}(\text{OH})\text{O}$] and gibbsite [$\text{Al}(\text{OH})_3$] were chosen as representative of Fe and Al oxyhydroxides; kaolinite and montmorillonite were selected as clay minerals, particularly 1:1 phyllosilicate and 2:1 phyllosilicate respectively. All mineral powders were obtained from Sigma-Aldrich Chemie and VWR (France) for experimentation.

5.2.2 Preparation of minerals-P Adsorption Complexes

The four soil minerals were loaded with the three OP compounds or inorganic P to serve as a P source for ryegrass. Solutions containing 1 g P L^{-1} in 0.1 M KCl at pH 5.5 were prepared using the different P compounds. Goethite, gibbsite, kaolinite, and montmorillonite was weighed in portions of 100 g into 1-L bottles. Then, 200 mL of 0.1 M KCl were added and the bottles were shaken for 24 hours at $25 \text{ }^\circ\text{C}$ to

sufficiently hydrate the adsorption sites on the minerals. The pH was maintained at 5.5 ± 0.05 by adding 0.1 M HCl or NaOH solution. To start the formation of OP-mineral complexes, each of the 1 L bottles containing the soil minerals was filled with 800 mL of each P solution. In each bottle containing both the soil minerals and P compounds, some drops of hexanol were added to suppress microbial activities. Bottles were shaken on a mechanical shaker for 24 hours at 25 °C and then centrifuged (3000 G for 15 minutes). The 1 L bottles were distributed into several 250-mL bottles, centrifuged, and the supernatants were collected and removed. The produced P-loaded minerals were agitated in deionized water and frozen at -20 °C. To determine the amounts of adsorbed P, a certain volume of supernatants was immediately filtered through a 0.22- μ m membrane syringe filter for P analysis. The concentration of P in the supernatants was determined colorimetrically (Ohno and Zibilske, 1991) after hydrolyzing OP to IP using the persulfate oxidation method (Peters and Van Slyke, 1932). The quantity of P adsorbed was calculated as the difference between the initial amount of P added and the remaining P amount in the supernatant at the end of the experiment. Total P concentration in a subsample of each P-loaded was also determined using the procedure by Ostrofsky (2012) and showed very similar values compared to the ones determined as the difference between the initial and the final P amount in the supernatant (differences were in the range of 3-5.5% for the organic mineral-P complexes and 1.5-5% for the inorganic mineral-P complexes). The P loadings of the mineral-P complexes produced are shown in Table 13. All minerals were loaded to reach their adsorption maxima.

Table 13 : P adsorption capacity of the produced minerals-P adsorption complexes.

Go: goethite; Gib: gibbsite; K: kaolinite; M: montmorillonite; IP: inorganic P; IHP: Myo-inositol hexakisphosphate, GLY: glycerophosphate and G6P: glucose-6-phosphate.

Mineral-P complexes	Quantity of P adsorbed ($\mu\text{g g}^{-1}$)
Go-IP	2810
Go-IHP	3742
Go-GLY	1398
Go-G6P	4337
Gib-IP	20949
Gib-IHP	56698
Gib-GLY	6237
Gib-G6P	5588
K-IP	1736
K-IHP	6082
K-GLY	1222
K-G6P	2295
M-IP	3709
M-IHP	4857
M-GLY	1045
M-G6P	2338

5.2.3 Characterization of OP desorption

The desorption ability of various P compounds from soil minerals was characterized using a 0.1 M KCl extraction. Briefly, 40 mL of 0.1 M KCl adjusted to pH 5 were added to 0.5g minerals-P complex. Samples were then shaken on a mechanical shaker at 25 °C for 24h. After centrifugation for 10 minutes, 5 mL of the supernatant was taken for the measurement of desorbed P concentration by colorimetry (Ohno and Zibilske, 1991). In addition, we carried out two additional desorption steps by successively desorbing P at 48h and 72h using the same extractant to further characterize the desorption dynamics of the P forms.

5.2.4 Experimental Setup and Plant growth

We used the RHIZOtest device (MetRHIZlab, France) (Figure 17) designed by Bravin et al. (2010) which consists in separating plant roots from soil with a 30-mm polyamide mesh to facilitate the collection of roots and rhizosphere (Houben and Sonnet, 2015). As described by Gómez-Suárez et al. (2020), in a first step (preculture period), 0.20 g of ryegrass (*Lolium multiflorum*) seeds were grown for 14 days in hydroponics in a cylinder closed at the bottom with a 30 μm polyamide mesh allowing the development of a dense, planar root mat with a nutrient solution: $\text{Ca}(\text{NO}_3)_2$ (2 mmol L^{-1}), MgSO_4 (0.5 mmol L^{-1}), K_2SO_4 (0.7 mmol L^{-1}), KCl (0.1 mmol L^{-1}), KH_2PO_4 (0.1 mmol L^{-1}), MnSO_4 (0.5 $\mu\text{mol L}^{-1}$), CuSO_4 (0.5 $\mu\text{mol L}^{-1}$), ZnSO_4 (0.5 $\mu\text{mol L}^{-1}$), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (0.01 $\mu\text{mol L}^{-1}$) and Fe-EDTA (100

$\mu\text{mol L}^{-1}$). After this preculture period, 15 plants were removed from the experiment and the roots and shoots were kept for analysis to determine the amount of P in plants before the cultivation period.

In a second phase (cultivation period), the two-week-old seedlings, showing a dense root mat, were transferred to a thin layer of substrate made of different mineral-P complexes previously prepared and acid-washed quartz. Prior to the experiment, the substrates were sterilized by autoclaving at 121 °C for 2 h (Gómez-Suárez et al., 2020) to eliminate potential microorganisms, allowing therefore to attribute the results to the only effect of root activity. To avoid any P limitation for plants during the experiment, we supplied a total amount of P which was previously found to sufficiently meet the plant requirement in such RHIZOtest devices (Gómez-Suárez et al., 2020). Thus, the amount of mineral-P complex added to the mixture was calculated to supply 40 mg of P in each treatment while the amount of quartz was calculated to reach a final mass of 10 g, which corresponded to a 1.5-mm thick soil layer. The soil layer was then connected to a 500 mL nutrient solution with a filter paper wick. The composition of this nutrient solution was the same as that used for the preculture period except that P was not added. The RHIZOtest devices were placed in controlled conditions (phytotron) under a photoperiod of 12h, constant temperature (25 °C), and relative humidity (80%). Unplanted control treatments, in which the quartz - mineral-P complex had been incubated in similar devices without plants (hereafter called the bulk substrate), were also conducted. In total, 128 such devices were implemented: 4 P compounds (IHP, GLY, G6P, and IP) x 4 soils minerals (goethite, gibbsite, kaolinite and montmorillonite) x 2 crop conditions (ryegrass and bulk soil) x 4 replicates.

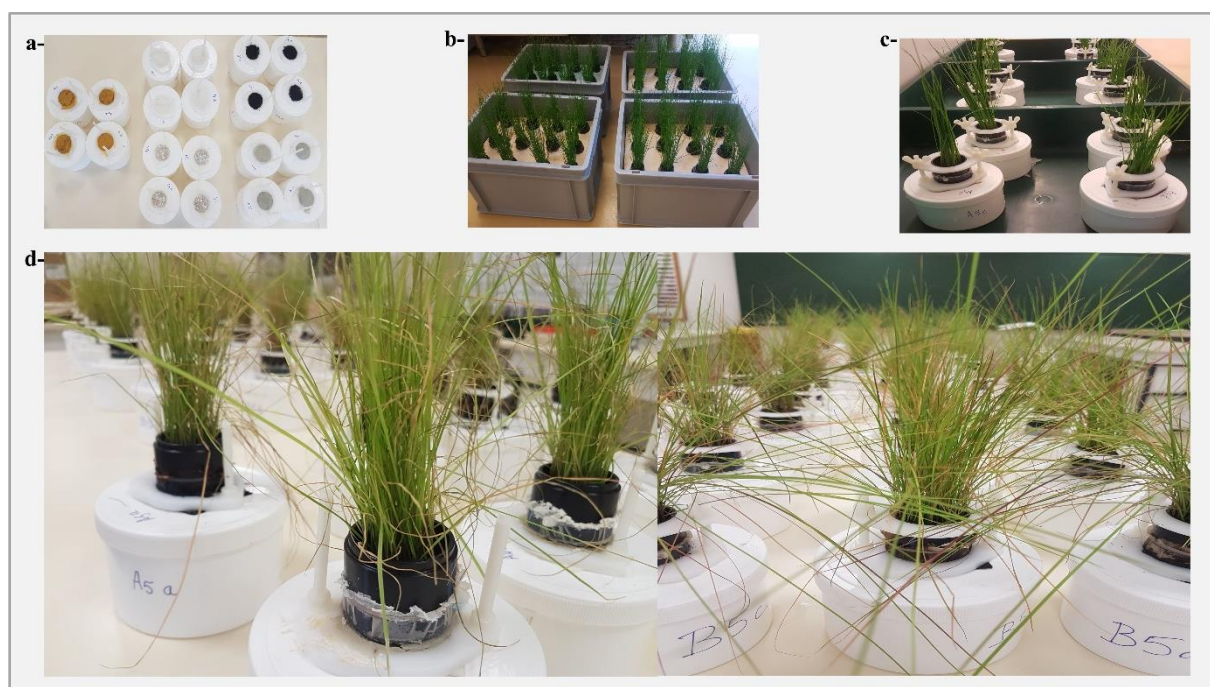


Figure 17: Picture of the experimental Setup and Plant growth using the RHIZOtest device.

a- soil layer of quartz - mineral-OP complex; b- preculture period; c- contact between the soil and plant device; d- result at the end of the experiment.

5.2.5 Plant sampling and analysis

The plants were harvested after 15 days of contact with mineral-OP complexes. At harvest, shoots and roots were separated and roots were gently rinsed with deionized water. Shoots and roots were then dried at 60 °C for 72 h, weighed, and crushed before analysis. The concentration of P in shoots and roots was determined colorimetrically (Ohno and Zibilske, 1991) after mineralization by 65% HNO₃ digestion directly in a microwave Teflon vessel (Lange et al., 2014). The amount of P taken up by shoot and root from the P-mineral complexes was calculated as the difference between the amount of P in plant parts at the end of the experiment minus the average amount of P in plants at the end of the preculture period. Total plant P uptake from P-minerals was calculated by summing P uptake from P-minerals by roots (i.e., root P concentration multiplied by root dry mass) and P uptake from P-minerals by shoot (i.e., shoot P concentration multiplied by shoot dry mass). The percentage of P recovered by ryegrass was determined by the following equation:

$$\text{P recovered (\%)} = \frac{\text{Amount of P uptake per pot (mg P)}}{40 \text{ (Amount of P supplied per pot, mg P)}} * 100$$

5.2.6 Rhizosphere and bulk soil analyses

The availability of P in the rhizosphere and the bulk soil collected at the end of the RHIZOtest experiment was assessed by anion exchange membrane (Nobile et al., 2019). Briefly, 0.5 g (mineral-P + quartz) of the collected mineral-P complexes were added to 50 ml bottles with 30 mL deionized water and two strips of anion exchange membrane. The whole set was mixed and stirred for 16 h. The membranes were then removed and rinsed in deionized water and the P recovered by shaking for 1 h in 20 mL of 0.5M HCl. Phosphorus concentrations were analyzed by colorimetry using a spectrophotometer (610 nm). Just after the harvest, alkaline phosphatase activity in the rhizosphere was determined by measuring the amount of p-nitrophenol (PNP) released from the addition of 5 mM p-nitrophenyl phosphate according to Tabatabai and Bremner (1969).

5.2.7 Data processing and analysis

Data were statistically analyzed with R software (R version 4.1.3). The impact of factors (P compounds, soil minerals, and their combined effect) on P availability and uptake was modeled by generalized linear models (GLM) using the "FactomineR" package. The GLM model was used to avoid mathematical transformation of the variables and to get rid of the strict assumption that "the residuals will follow a conditionally normal distribution" (McCullagh and Nelder, 2019; Warton et al., 2016) and allow the use of a variety of other distributions of the exponential family for the residuals (Cohen et al., 2014). All factors were tested individually and the models were compared based on second-order Aikake

information (AICc), with the lowest relative value being considered the best fit. The ANOVA of the best-fit GLM model with a chi-square test generated the deviance analysis table that gave the significance level of all factors. Statistical analyses to compare the average results of percent P recovered, enzyme activities, and biomass were performed using a one-way analysis of variance (ANOVA) followed by Tukey's honest significant difference (HSD) test ($p < 0.05$).

5.3 RESULTS

5.3.1 Biomass Production

Total biomass varied slightly between treatments (Table 14). Although there was a significant difference between goethite and gibbsite for IHP forms, total biomass did not vary significantly between treatments. Some weak differences were observed between soil mineral types. The lowest biomass was observed with the Gib-OP complex and the highest with the K-OP complex. In general, except on gibbsite, the mineral-OP complexes produced equal or slightly more total biomass than the mineral-IP complexes.

Table 14: Effect of different P-mineral complexes on the root, shoot, and whole plant biomass (root + shoot biomass). Results are mean \pm standard error. Means with a different letter were significantly different according to Tukey's HSD test at $P < 0.05$. Comparisons of means were made for each mineral category. Soil minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); Phosphorus compounds (IHP: Myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate, and IP: KH_2PO_4); Dashes (-) identify mineral-phosphorus complexes produced by adsorption of forms of P onto soil minerals. The example Go-IHP refers to goethite and Myo-inositol hexakisphosphate complexes.

	Root Biomass (g)	Shoot Biomass (g)	Total Biomass (g)
Go-IP	0.27 \pm 0.01 a	0.55 \pm 0.10 a	0.82 \pm 0.11 a
Go-IHP	0.27 \pm 0.03 a	0.85 \pm 0.11 b	1.12 \pm 0.13 b
Go-GLY	0.33 \pm 0.03 a	0.64 \pm 0.09 ab	0.96 \pm 0.12 ab
Go-G6P	0.27 \pm 0.09 a	0.54 \pm 0.09 a	0.81 \pm 0.19 ab
Gib-IP	0.26 \pm 0.03 a	0.60 \pm 0.12 a	0.86 \pm 0.16 a
Gib-IHP	0.17 \pm 0.09 a	0.42 \pm 0.16 a	0.60 \pm 0.25 a
Gib-GLY	0.19 \pm 0.03 a	0.43 \pm 0.08 a	0.62 \pm 0.12 a
Gib-G6P	0.21 \pm 0.01 a	0.45 \pm 0.06 a	0.66 \pm 0.07 a
K-IP	0.22 \pm 0.03 ab	0.83 \pm 0.15 a	1.05 \pm 0.15 a

K-IHP	0.18 ± 0.02 a	0.61 ± 0.14 a	0.79 ± 0.16 a
K-GLY	0.28 ± 0.01 c	0.85 ± 0.19 a	1.13 ± 0.20 a
K-G6P	0.27 ± 0.004 bc	0.75 ± 0.13 a	1.02 ± 0.13 a
M-IP	0.21 ± 0.03 a	0.72 ± 0.09 a	0.93 ± 0.12 a
M-IHP	0.19 ± 0.04 a	0.68 ± 0.15 a	0.87 ± 0.20 a
M-GLY	0.23 ± 0.02 a	0.72 ± 0.20 a	0.95 ± 0.22 a
M-G6P	0.27 ± 0.09 a	0.71 ± 0.06 a	0.98 ± 0.19 a

5.3.2 Combined effects of organic P and soil minerals on P uptake

The impact of P compounds, soil minerals, and their combined effect on total P uptake by ryegrass was modeled by GLM (Table 15). Variations in P uptake by ryegrass were significantly affected by P compounds and their interaction with soil minerals. As shown by the lower AIC values (Table 15), the variation was more dependent on the interaction between minerals and P compounds. During the growing season, P recovered by ryegrass was 21-28% from adsorbed IP, 0-5% from adsorbed IHP, 4-18% from adsorbed GLY, and 2-9% from adsorbed G6P, depending on the mineral type (Table 16).

Table 15: The GLM model results testing the impact of factors (P compounds, soil minerals, and their combined effect) on total P uptake

Variables effects	P uptake	
	<i>p-value</i>	<i>AIC</i>
P forms	<0.001	268-329
Minerals: P forms	<0.001	156-199
Soil minerals	<0.001	314-388
R ²	0.92	

Table 16 : Effect of different P-mineral complexes on the percentage of P recovered by ryegrass from adsorbed OP compounds.

Results are mean ± standard error. Means with a different letter were significantly different according to Tukey's HSD test at $P < 0.05$. Comparisons of means were made for each mineral category. Soil minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate, and IP: KH_2PO_4); Dashes (-) identify mineral-phosphorus complexes produced by adsorption of forms of P onto soil minerals. The example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

Mineral-P complexes	P recovered by ryegrass (%)
Go-IP	21 ± 1.62 d
Go-IHP	1 ± 0.08 a
Go-GLY	11 ± 0.62 c
Go-G6P	4 ± 0.62 b
Gib-IP	3 ± 1.09 b
Gib-IHP	0 ± 0.01 a
Gib-GLY	9 ± 1.66 c
Gib-G6P	3 ± 0.39 b
K-IP	22 ± 3.97 b
K-IHP	4 ± 0.61 a
K-GLY	4 ± 0.32 a
K-G6P	2 ± 0.18 a
M-IP	28 ± 2.37 c
M-IHP	5 ± 1.05 a
M-GLY	18 ± 2.70 b
M-G6P	9 ± 2.58 a

5.3.3 Effect of OP compounds on P uptake by ryegrass

Except for kaolinite, P uptake by ryegrass varied significantly between the adsorbed OP compounds (Table 17; Figure 18). Differences in total P uptake between OP compounds decreased in the order GLY >> G6P > IHP (Table 16; Figure 18). Phosphorus concentrations in roots and shoots were higher in the presence of adsorbed GLY compound compared to the other OP compounds (Table 16; Figure 18). Of all OP compounds, adsorbed IHP was the lowest supplier of P to ryegrass. Compared to IP, P uptake from adsorbed OP compounds was highly contrasted and dependent on the specific compounds of OP. Phosphorus uptake from adsorbed IHP and G6P was significantly lower than that from adsorbed IP, with the order being: IP >> G6P > IHP (Table 16; Figure 18). However, the trend was different for the adsorbed GLY compound, which, depending on the minerals, was in this order IP = GLY (goethite and montmorillonite) or in this order GLY >> IP (gibbsite). Thus, P uptake from GLY adsorbed on goethite and montmorillonite was similar to the adsorbed IP compound while P uptake from GLY adsorbed on gibbsite was significantly higher than IP. Moreover, P uptake was highly variable and strongly dependent on the characteristics of the OP compounds. Successive desorption of the different mineral-P complexes with KCl (see supplementary data Appendix B Figure S1) also indicated that, in general, the percentage of OP desorption at all cycles was in the order GLY >> G6P > IHP, which was similar to the trend observed for OP availability and uptake by the plant (Figure 18). In addition, the forms of P significantly impacted phosphatase activity in the rhizosphere (Figure 19). Irrespective of the soil minerals, treatments might be ranked according to their phosphatase activity as follows: GLY >> G6P > IHP (Figure 19). In sum, OP adsorbed on soil minerals was available to ryegrass since the plant was

able to take up a certain amount of it even if it was relatively low from certain mineral-OP complexes, e.g., mineral-IHP complexes.

Table 17: One-way ANOVA results testing the effects of OP compounds by soil minerals on total P uptake, P availability, and dry weight.

Soils minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); OP: Organic Phosphorus.

Variables effects	P uptake	P availability	Dry weight
	<i>p-value</i>	<i>p-value</i>	<i>p-value</i>
Go-OP	< 0.001	< 0.001	0.07
Gib-OP	< 0.001	< 0.001	0.92
K-OP	0.05	< 0.05	0.08
M-OP	<0.001	< 0.01	0.72

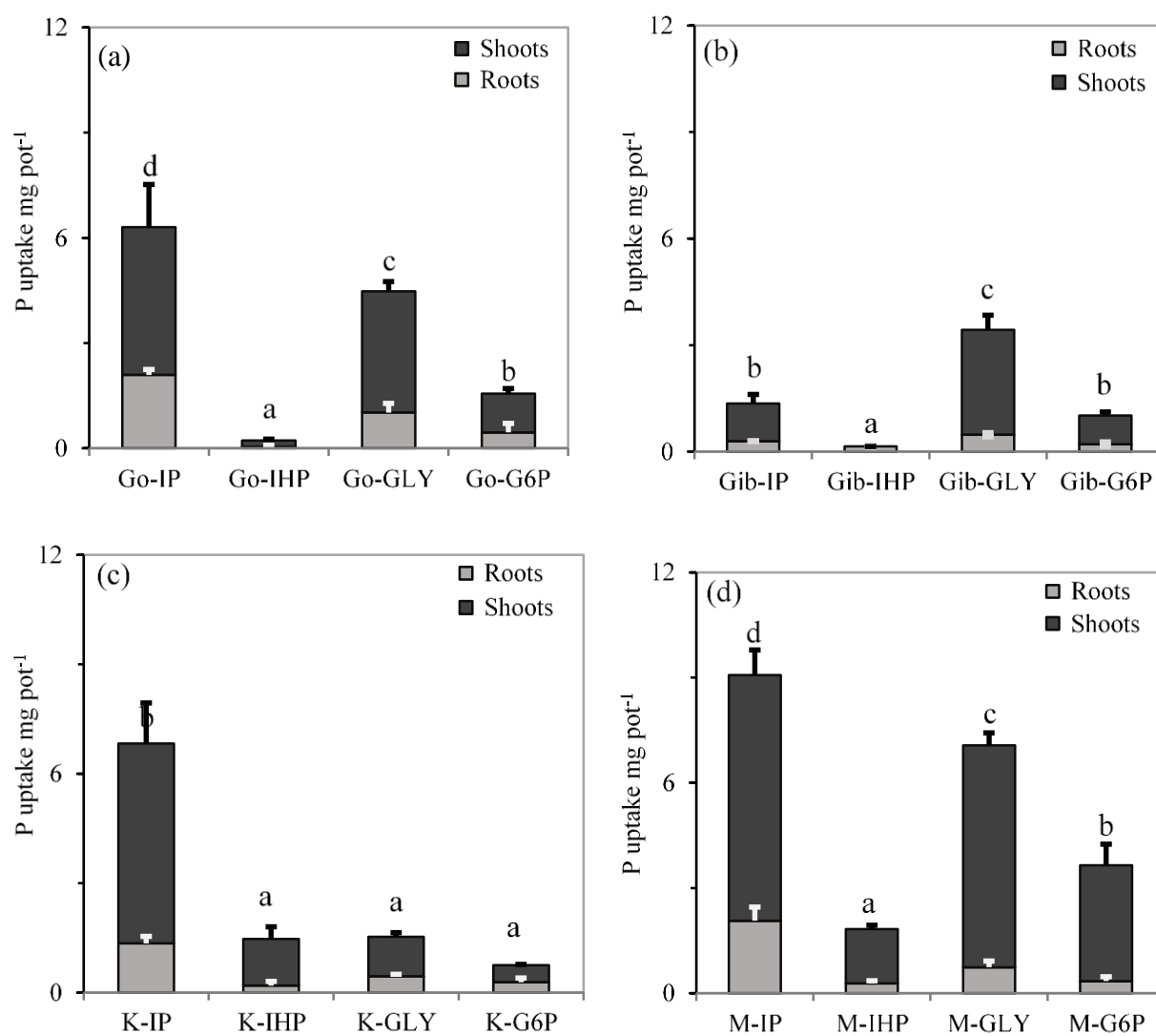


Figure 18: Phosphorus uptake by root and shoot ryegrass plants with different P sources.

The effect of P compounds, soil minerals, and their combined effect on total P uptake was significant ($P < 0.0001$) according to GLM model results testing the impact of factors (P compounds, soil minerals, and their combined effect) on total P uptake. Means with different letters were significantly different according to Tukey's HSD test at $P < 0.05$. Error bars indicate standard error. Soils minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate and IP: KH_2PO_4); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

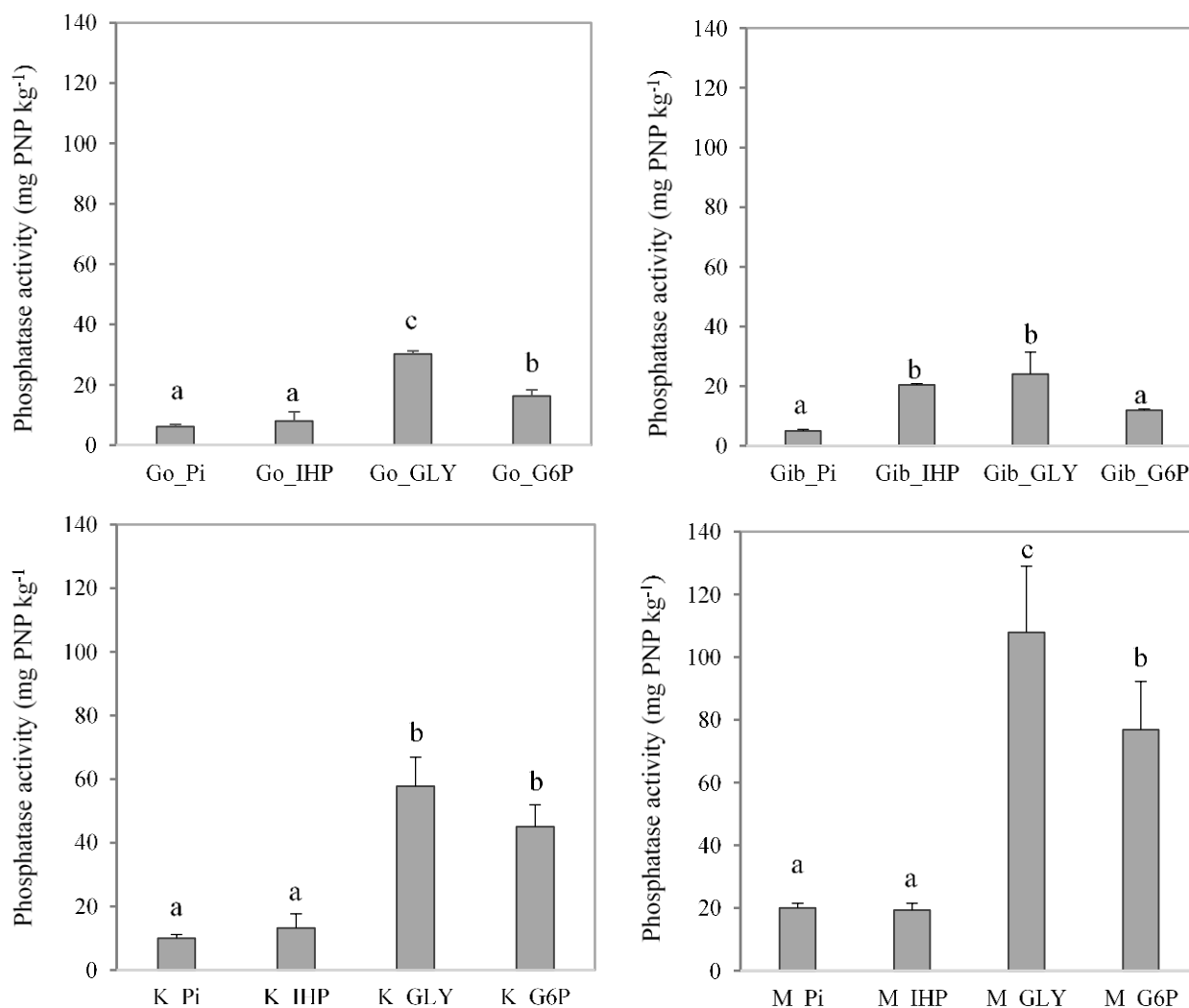


Figure 19: Phosphatase activity in the rhizosphere at the end of the experiment.

Means with different letters were significantly different according to the Tukey's HSD test at $P < 0.05$. Error bars indicate standard error. Soils minerals (Go: goethite, Gib: gibbsite, K: kaolinite, and M: montmorillonite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate and IP: KH_2PO_4); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

5.3.4 Relationships between P uptake, soil minerals-OP interaction and P availability

The P uptake was influenced by the soil mineral-OP interactions. Phosphorus uptake from OP adsorbed onto the four tested minerals increased in the following order: kaolinite-OP << gibbsite-OP ≤ goethite OP << montmorillonite-OP. A large difference was observed among kaolinite, Fe and Al oxyhydroxides and montmorillonite in their ability to release P for plant uptake (Figure 18). The amount of P taken up from montmorillonite-OP complexes was the highest. On the other hand, P uptake from goethite-OP, gibbsite-OP, and kaolinite-OP (especially gib-IHP or G6P) was low. Overall, less than 4% of the initial adsorbed P was desorbed and mineralized for plant uptake (Table 16).

Phosphorus uptake by ryegrass from mineral complexes was positively correlated with ΔP resin ($R = 0.73$, $p < 0.01$) (Figure 20). However, no correlation was found between P uptake, resin-extracted P concentration in the rhizosphere (Resin P), and KCl-extractable P concentration. In addition, the ΔP resin values of the majority of the mineral-OP were generally negative (Figure 21) even though some complexes, e.g., GLY-mineral complexes, showed almost nil ΔP resin values, i.e., no variation between resin P concentration in bulk soil and resin P concentration in the rhizosphere (Figure 21).

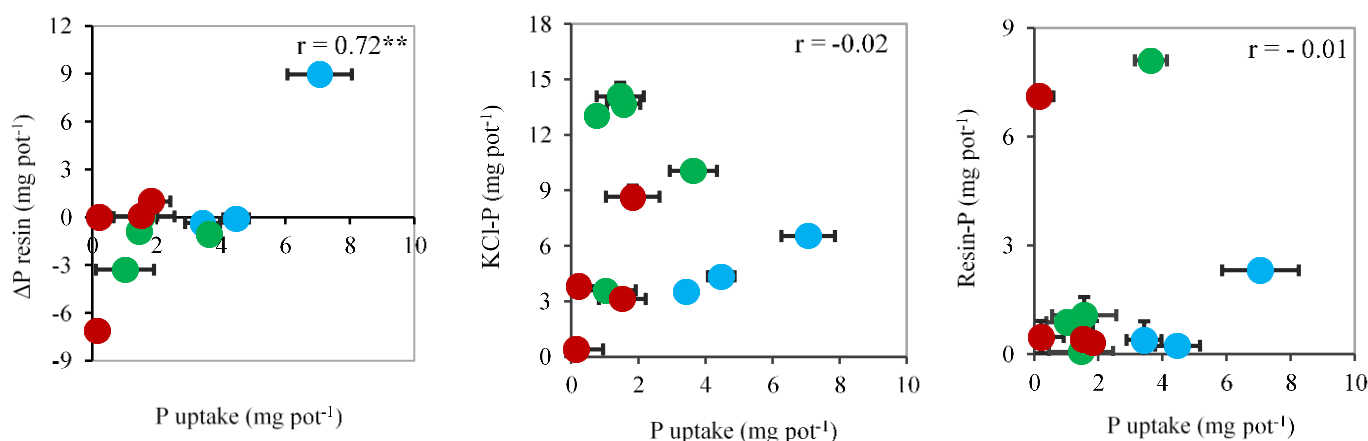


Figure 20 : Relationship between P uptake and the different methods of P extraction (ΔP resin: difference in resin P concentration between bulk soil and rhizosphere).

KCl.P: KCl extracted P). Values are average ($n = 4$) \pm standard deviations. All values are means ($n = 4$) \pm standard deviations. The marked correlation coefficient r is the Pearson's correlation coefficient. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$. Dots colors distinguish the forms of P. Red dots correspond to myo-inositol hexakisphosphate (IHP), green to glucose-6-phosphate (G6P) and blue to glycerophosphate (GLY). Dots colors distinguish the forms of P. Red dots correspond to myo-inositol hexakisphosphate (IHP), green to glucose-6-phosphate (G6P) and blue to glycerophosphate (GLY).

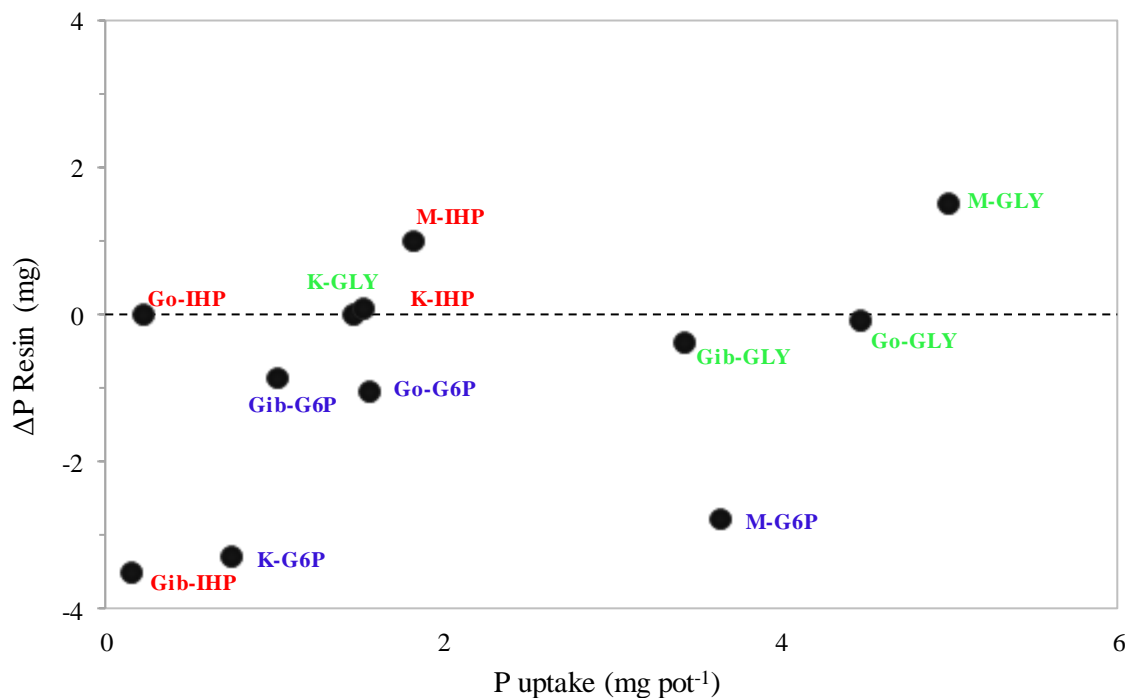


Figure 21: Relationship between Δ resin P (difference in resin P concentration between bulk soil and rhizosphere) and P uptake.

Soils minerals (Go: goethite, Gib: gibbsite, K: kaolinite and M: montmorillonite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate and IP: KH_2PO_4); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

5.4 DISCUSSION

5.4.1 Phosphorus from adsorbed OP compounds is available to plants

Our first hypothesis that P from adsorbed OP compounds is available to ryegrass and varies with soil mineral properties was confirmed in our experiment. The two main findings supporting the hypothesis are: (i) the ryegrass was able to take up about 3-18% of OP adsorbed to soil minerals; (ii) OP compounds as well as their interactions with soil minerals significantly affected P uptake for ryegrass.

The amount of P recovered by ryegrass reached 5% from adsorbed IHP, 9% from G6P and 18% from adsorbed GLY (Table 16). In general, P uptake decreased in the order $\text{GLY} \gg \text{G6P} > \text{IHP}$. Taken together, these results indicate that, irrespective of the soil mineral, adsorbed OP was at least partially available to plants. The magnitude of this availability depended on the OP compounds and the types of soil minerals. By comparing several of the main soil mineral-OP complexes, our work indicates that

some amount of P can be available from the adsorbed OP compounds demonstrating, therefore that adsorbed OPs can act as a source of P for plants.

The availability of P from adsorbed OP differed between OP compounds. The P uptake from the adsorbed GLY compound was much higher than that of adsorbed G6P which was more available than adsorbed IHP. It appears that the difference in availability between adsorbed OP compounds was determined by the adsorption/desorption capacity more than their binding strength. The trend in availability (GLY >> G6P > IHP) would be mainly explained by the distinct desorption dynamics of the different minerals, leading to the lowest desorption for IHP-P, followed by G6P-P and then GLY-P (Amadou et al., 2022). This is also corroborated by the results of desorption dynamics (see supplementary data Appendix B Figure S1). Yan et al. (2014) similarly showed lower desorption of IHP from different structures of aluminum (oxyhydr)oxides compared to other OP compounds. In addition, the trend in availability (GLY >> G6P > IHP) could also be related to their different degrees of hydrolysis by enzymatic activity (Annaheim et al., 2010; Bünemann, 2008) as phosphatase activity was the highest in the presence of GLY and the lowest in the presence of IHP (Figure. 19). Basically, we expected G6P to be more available than GLY due to its higher desorption and its likely instability on soil minerals due to its higher molecular weight than GLY (Annaheim et al., 2013; Park et al., 2022; Yan et al., 2014). The opposite result we found may be the consequence of its more negatively charged surface compared to GLY (Giaveno et al., 2008; Qin et al., 2020; Ruttenberg and Sulak, 2011). These reasons would also explain why the binding energy of G6P predicted from the Langmuir model is often higher than that of GLY or IP (Bai et al., 2021; Goebel et al., 2017). Finally, adsorbed GLY was the higher source of P for plant uptake compared to other compounds, consistently with Adams and Pate (1992). In conclusion, the availability of OPs for plant nutrition from organic inputs and soil would be determined by the stability of OP-mineral complexes or by their (de)sorption dynamics as well as their hydrolysis by enzymes.

5.4.2 Effect of mineral-OP interactions on P uptake by ryegrass

The potential availability of P adsorbed by different minerals was strongly affected by mineral-OP interaction properties. Except for the IHP, the P uptake from OP forms increased in the following order: kaolinite-OP << gibbsite-OP \leq goethite OP << montmorillonite-OP (Tableau 4). Montmorillonite-OP complexes showed the highest P uptake, with a maximum of up to 18%. On the other hand, P uptake from kaolinite-OP was the lowest. Less than 4% of the initially adsorbed P was desorbed and mineralized for plant uptake. These results indicated that regardless of the type of mineral and its OP sorption strength and stability, plants are able to take up at least a small portion of it for their nutrition. This agrees with laboratory and greenhouse studies indicating that specifically adsorbed P was potentially available to plants although it was very difficult to desorb (Bollyn et al., 2017; D'Amico et

al., 2020; Montalvo et al., 2015). Even under conditions where the root-associated microbiomes that can help mobilize P are limited, OP-mineral complexes still have potential for supplying P to plants.

Montmorillonite-OP complexes, in particular, montmorillonite-GLY or G6P were found to serve as sources of P in soils more than the other complexes. Organic P adsorbed on kaolinite released the lowest amount of P to the plants. Overall, there was a marked difference in P uptake between the tested minerals. Montmorillonite-OP complexes would provide more P due to the negative charges of montmorillonite (He et al., 1994) causing its weak binding to OP, resulting in the formation of unstable OP-montmorillonite complexes (He and Zhu, 1998; He et al., 1994; Hingston et al., 1974; Lang et al., 2017). The low P uptake from kaolinite-OP agrees with previous observations showing that kaolinite-P is an inner-sphere surface and bidentate complex below pH 6 (Hu et al., 2020; Ruyter-Hooley et al., 2015), and the adsorbed P on kaolinite is difficult to desorb (Kafkafi et al., 1988; Manning and Goldberg, 1996; Xiong et al., 2022). Hence, our result emphasized that Fe and Al oxyhydroxides were less responsible for limiting OP availability than kaolinite despite their general higher adsorption capacity in soil. Apart from the nature of the OP compounds, the characteristic of the minerals are an important factor responsible for the difference in P uptake between the tested OP-mineral complexes. Thus, it is important to further quantify the interaction of OP with soil minerals in order to characterize and subsequently model P availability.

No correlation was found between P uptake and resin-extracted P (Figure 20). In addition, rhizosheath resin P concentration for most mineral-OP complexes was higher than that of the bulk soil. These results suggest that plants have induced additional desorption of OP. According to Le Chatelier's principle (Law of Mass Action), the sink effect of roots caused an OP depletion in the solution, which in turn induced further OP desorption dissolution to replenish the solution (Houben and Sonnet, 2012; Penn and Camberato, 2019). In addition, mobilization of OP by ryegrass roots might also have contributed to OP depletion. As shown by Martin et al. (2002), high efficiency of ryegrass in displacing strongly bounded P may be due to the fact that the plant can react to P deficiency by extending the root surface and utilizing more than one mechanism of extraction at the same time. Thus, the effect of plant uptake may result in additional mobilization of OP forms from soil minerals.

It is generally accepted that P extraction with KCl is negatively correlated with the binding energy of the P compounds to soils. Thus, the more P can be extracted with KCl to become available to plants, the lower its binding energy (Martin et al., 2004; Yan et al., 2014). However, our results showed no correlation between P uptake and P extracted with KCl. The lack of correlation in our case may imply that the P taken up by plants did not depend on the strength or energy with which OP compounds are bounded to soil minerals. Nevertheless, this lack of correlation between P taken up by plants and P extracted by KCl could also mean that OP compounds may have been released from the soil minerals but remained in organic form without being mineralized for uptake by plants. Therefore, we hypothesize that although OP was desorbed from some minerals, it may not have been absorbed because it was not readily hydrolyzable by the enzyme released by plant roots. This supports our earlier explanation of the

resistance of some of OP compounds to enzymatic hydrolysis because of their chemical properties. Therefore, the availability of adsorbed OPs to plants does not depend on their binding strength to soil minerals but rather on their degree of hydrolysis by soil and root enzymes.

Finally, P uptake by ryegrass was positively correlated with ΔP resin ($R = 0.73$, $p < 0.01$), suggesting that the variation of available P in the rhizosphere determined the P uptake by plant (Figure 21). The ΔP resin values of the majority of the mineral-OP complexes were generally negative, showing that in addition to the spontaneously released P, there would have been a subsequent release of P from soil minerals that would occur in response to plant-induced depletion of available P in the rhizosphere. This means that plant roots mobilized additional P from minerals. However, this finding did not apply to all OP-minerals complexes. For instance, GLY-mineral complexes (Figure 21) showed almost no variation in ΔP resin, i.e. no variation between P resin in the bulk soil and P resin in the rhizosphere, suggesting that plant absorbed only the spontaneously available P without any other mobilization. This confirms that GLY was sufficiently available from soil minerals. Thus, when the plant was in the presence of soil minerals associated with GLY, there was little or no additional P mobilization.

5.4.3 Phosphorus uptake from adsorbed OP relative to adsorbed

IP

Our third hypothesis was that P derived from adsorbed OP would be less available than P derived from adsorbed IP because it desorbs less and requires also enzymatic cleavage before being taken up by ryegrass. Our results support only partially this hypothesis as they showed that the different adsorbed OP compounds led to contrasted P uptake compared to the adsorbed IP compound. Phosphorus uptake from adsorbed IHP and G6P was significantly lower than that of adsorbed IP, whereas P uptake from adsorbed GLY, depending on the mineral, was slightly equal or higher than that of IP. Several studies have shown lower plant availability of adsorbed OP compounds compared to IP compounds (Andrino et al., 2019; D'Amico et al., 2020; Klotzbücher et al., 2019), probably due to the specific binding mechanisms of OP and its low desorption from soil (Bollyn et al., 2017; Ruyter-Hooley et al., 2015). However, in all of these studies, "organic P" refers only to IHP. In addition to IHP, GLY and G6P are also commonly found in soils, soils treated with organic inputs, sediments and wetlands (Missong et al., 2016; Vincent et al., 2013) but these OP forms have not been considered potential sources of P for plants, except in a few studies (Adams and Pate, 1992). Here, our results highlight the relative availability of these major OP forms compared to that of IP. In agreement with previous studies (Andrino et al., 2019; D'Amico et al., 2020; Ruttenberg and Sulak, 2011), IHP was less available than IP. Similar to IHP, we also found that adsorbed G6P was less available than IP. This would be due to the fact that, unlike IP, both IHP and G6P forms must be hydrolyzed after desorption to be available (D'Amico et al., 2020). In the present study, the phosphatase activity measured for IHP was very low

compared to GLY, suggesting that the hydrolysis of IHP to an available IP form was very limited (Figure 19). Finally, we found that the adsorbed GLY compound, depending on the minerals, was almost equivalent or more available than the IP compound. This high availability of GLY could be attributed to its low affinity for soil minerals and especially to its high desorption in soil. Soil amendment with organic inputs with high concentration of GLY would allow the efficient P fertilization from organic waste. This improving of knowledge on OP adsorption by soil minerals therefore reinforces the applications of OP for sustainable alternative to mineral P fertilizer. More importantly, we showed that on Al oxyhydroxides, GLY was significantly more available than IP. Thus, based on comparisons of different P compounds, our results showed that in soil, unlike IHP, another major compound of OP such as GLY can be equal or superior to IP in terms of plant availability.

5.5 Conclusion

Our results demonstrate that adsorbed OP compounds may be a source of P for plants irrespective of the type of mineral and its sorption capacity. Higher use efficiency of OP adsorbed on montmorillonite than on other minerals indicates that soils rich in 2:1 phyllosilicate might have greater P availability than soils rich in Fe and Al oxyhydroxides or 1:1 mineral. In addition, GLY would be less affected by Al oxyhydroxides that limit P availability in highly weathered soils in tropical regions. The binding strength of OPs to the mineral surface does not necessarily affect P availability to plants and plant uptake may result in additional P mobilization in the rhizosphere. Finally, the wide range of P uptake and availability in the presence of different mineral-OP complexes emphasized the importance of considering the chemical nature of OP and its ability to interact with soil minerals when attempting to improve soil OP cycling for plant use. As a further step, the role of OP-soil minerals interactions on P availability should be unraveled according to the main plant P acquisition strategies (e.g. *mining*, *foraging* and *intermediates* strategies) to design sustainable P cropping system.

Statements & Declarations

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CHAPTER 3

6 Nitrogen and soil mineralogy drive phosphorus limitation and P uptake by plants from inorganic and organic P forms

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Abstract

Nitrogen and phosphorus cycles in ecosystems are composed of multiple biogeochemical forms and processes that jointly control P uptake and limitation by plants. To date, it remains unclear how the chemical forms of N, organic P (OP), and their interactions with soil minerals influence both P limitation and plant uptake in ecosystems. The paucity of research on the effect of these important biogeochemical processes (N-P-soil minerals) severely limits our ability to understand the ecological processes underlying the alteration of P cycling in ecosystems with N additions. The aims of this study were to evaluate the irrespective and interactive effects of N and P forms and their interaction with soil minerals on P uptake and limitation in plants. We characterized the N:P ratio, P uptake, and rhizosphere properties of ryegrass grown under several complexes of IP and OP (IHP, and GLY) adsorbed on Fe oxyhydroxides (goethite) and clay minerals (kaolinite) with and without the addition of N. We hypothesized that the addition of N in various specific forms would increase P limitation under conditions of low P availability, i.e., with OP forms and soil minerals, and that the shift of plants from N limitation to P limitation would be due to the beneficial effect of N addition. We found that interactions between N forms, P forms, and soil minerals strongly modified P dynamics, relative to individual effects. These interactions increased plant P limitation and P uptake via modification of rhizosphere chemistry. The degree of P limitation was strongly dependent on the degree of availability of P sources, so we found that the interaction between P forms and soil minerals was a major determinant of P limitation. Therefore, we found that the interaction of N with IP forms led to greater P uptake and a marked reduction in P limitation compared to the interaction of N with OP forms. Thus, we inferred that in addition to the degree of P availability, the characteristics and biochemical nature of P sources determine the degree of P limitation in plants. Furthermore, we found that with the addition of N, more P was recycled from clay minerals and P limitation was delayed compared to iron oxides. This study therefore provides important information on ecosystem P cycling under N addition and the biogeochemical properties involved, which will allow ecosystem models to accurately predict plant N-P limitation and its impacts, and will also help build robust ecosystem models with fully coupled N-P or C-N-P interactions.

6.1 Introduction

Phosphorus (P) limitation and its co-limitation with nitrogen (N) represent a main ecological driver of ecosystem functioning (Hou et al., 2020; Vitousek et al., 2010). The interactions of P with N is a key factor in managing plant P acquisition and agroecosystem productivity. These interactions determine whether plants are limited by P, or N and P together (Long et al., 2016), which in turn influences ecosystem productivity and functioning (Achat et al., 2016; Peñuelas et al., 2013). Worldwide, 32% of the cropland and 43% of the pasture are estimated to be P deficient and require increased P availability and fertilization to improve yields and ensure global food security (Lun et al., 2018). As a result, the increasing global demand for P in a world where soils are enriched with N is creating an N: P imbalance that can lead to significant changes in ecosystems and limit the development of natural ecosystems and agricultural production in the future. According to the theory of ecological stoichiometry, plant growth rate is determined by a specific ratio of RNA to protein which is reflected by the plant N:P ratio (Elser et al., 2010). This ratio is usually recognized as an indicator of P or N (co-)limitation (Vitousek et al., 2010). For instance, extensive researches have shown that P limitation occurring under N addition is reflected by an increased plant N:P ratio which is due to the enhanced production of N-rich protein compared to P-rich ribosomal RNA (Peng et al., 2019). Nevertheless, multiple mechanisms depending on soil properties (Craine and Jackson, 2010), N and P chemical forms, their availability and uptake by plants can mediate the N-induced P limitation. Nitrogen addition affects P uptake by plants directly by promoting plant growth and the production of protein (Sardans et al., 2017; Yue et al., 2017), but also indirectly by interacting with P pools in soil (Long et al., 2016; Schleuss et al., 2020). In particular, it is well known that depending on its inorganic form in the soil solution (i.e. $\text{NH}_4\text{-N}$ or $\text{NO}_3\text{-N}$), N may increase or decrease P solubility, resulting in changes in P limitation and availability (Lü et al., 2013; Peng et al., 2019). For instance, plant-induced decrease in soil pH caused by $\text{NH}_4\text{-N}$ nutrition increases the solubility of poorly soluble P pools in alkaline soils, resulting in greater P availability compared to the supply of $\text{NO}_3\text{-N}$ (Gómez-Suárez et al., 2020; Wang et al., 2012) while the opposite occurs in acidic soils (Hinsinger, 2001). Overall, it has been stated that plants could trade N for P by adjusting N and P acquisition rates from the soil, potentially explaining the synergistic growth responses to N and P addition (Long et al., 2016; Peng et al., 2019; Schleuss et al., 2020). Furthermore, depending on P availability, the effect of N may be more or less pronounced, resulting in differential P limitation between IP and OP forms.

Benefits of N addition on P cycling are highly dependent on characteristics of the minerals involved (Deng et al., 2017; Hou et al., 2020; Vitousek et al., 2010). For example, it is shown that in Luvisols and Calcisol (soil rich in calcium, with neutral or basic pH), P mobilization increases with $\text{NH}_4\text{-induced}$ pH decrease, whereas $\text{NO}_3\text{-induced}$ pH increase had no effect. In contrast, in Oxisols (soil rich in Fe and Al oxides, with acidic pH), a similar decrease in pH caused by $\text{NH}_4\text{-N}$ nutrition had no effect, whereas the increase in pH caused by $\text{NO}_3\text{-N}$ markedly increased soil P mobilization (Gahoonia et al., 1992;

Wang et al., 2012). Thus, it was concluded that in Luvisols P would be dissolved by acidification, whereas in Oxisols adsorbed P would be mobilized by ligand exchange. This suggests that the interaction between N forms and soil minerals is also crucial in the mobilization process of P forms. In brief, current major research has studied the effect of N on P uptake and P limitation by focusing mainly on inorganic P. However, in the soil, there are also pools of organic P that can contribute significantly to plant nutrition, but this depends in particular on the mineralogy of the soil (Amadou et al., 2022, 2021).

Ecosystem N and P cycling consists of multiple pools and biogeochemical processes that are interrelated and interdependent, jointly controlling soil P availability, plant P uptake and its limitation (Vitousek et al., 2010). To date, it remains unclear how N forms, P chemical forms, and their interactions with soil minerals influence both P limitation and P uptake by plants within ecosystems. The paucity of research on the effect of these important biogeochemical processes (N-P-soil minerals), severely limits our ability to understand ecological processes underlying the alteration of ecosystem P cycling with N additions. More importantly, it limits our ability to incorporate the actual impact of P limitation into ecosystem models used to analyze the effects of potential future climate change on overall ecosystem productivity (Deng et al., 2017; Goll et al., 2012). A better understanding of ecosystem P cycling under N additions and the biogeochemical properties involved are needed not only to enable ecosystem models to accurately predict plant N-P limitation and its impacts, but also to develop robust ecosystem models with fully coupled N-P or C-N-P interactions.

The aims of this study were to assess the independent and interactive effects of N and P forms and their interaction with soil minerals on P limitation in plants, to unravel biogeochemical processes involved in P limitation by characterization of the role of N and P forms and their interaction with soil minerals in P availability and uptake by plants. We hypothesized that (1) addition of N in various specific forms would increase P limitation under conditions with low P availability, i.e. with OP forms and soil minerals, (2) plants shift from N limitation to P limitation would be due to the beneficial effect of N addition on rhizosphere processes involved in P mobilization/acquisition by plants, and (3) the degree of both P limitation and total plant P uptake would vary significantly by mineral type and P forms because of the contrasting physicochemical properties of the minerals used and the biochemical nature of the P sources.

6.2 MATERIALS AND METHODS

6.2.1 Organic P compounds, soil minerals and N forms

Two organic P compounds, IHP, GLY, and an IP form (KH_2PO_4) were chosen for the experiments. These OP compounds were selected based on their prevalence in most soils and organic wastes. Each selected form differed from the others in P content and molecular size. The minerals were chosen to be representative of the predominant minerals in the soils. Two contrasting individual minerals were used. Goethite [$\text{Fe}(\text{OH})\text{O}$] was chosen as representative of Fe oxyhydroxides; kaolinite was chosen as the

clay mineral, specifically the 1:1 phyllosilicate. All minerals were obtained from Sigma-Aldrich Chemie S.a.r.l. and VWR (France) for the experiment. The two forms of nitrogen used were ammonium (NH₄-N) provided as (NH₄)₂SO₄ and nitrate (NO₃-N) provided as Ca (NO₃)₂.

6.2.2 Preparation of Goethite-P and Kaolinite-P Adsorption Complexes

The minerals (goethite and kaolinite) were loaded with the three compounds (IHP, GLY, and IP) to serve as a source of P for ryegrass. Solutions containing 1g L⁻¹ P in 0.1 M KCl at pH 5.5 were prepared using the individual P compounds. The minerals were weighed in 100g portions into 1-liter bottles. Then, 200 ml of 0.1 M KCl was added and the bottles were shaken for 24 hours at 25°C to sufficiently hydrate the adsorption sites. The pH was maintained at 5.5 ± 0.05 by adding 0.1 M HCl or NaOH solution. To begin the formation of P-mineral complexes, each of the 1-L bottles containing the soil minerals was filled with 800 mL of each P solution. Then, a few drops of hexanol were added to suppress microbial activities. The bottles were shaken on a mechanical shaker for 24 hours at 25°C and then centrifuged (3000 G for 15 minutes). The 1-L bottles were divided into several 250-mL bottles, centrifuged, and the supernatants were collected and disposed of. The P-laden minerals produced were shaken in deionized water and frozen at -20°C. To determine the amounts of adsorbed P, a certain volume of supernatants was immediately filtered through a 0.22-µm membrane syringe filter for P analysis. The concentration of P in the supernatants was determined by colorimetry (Ohno and Zibilske, 1991) after hydrolysis of IHP and GLY to IP by the persulfate oxidation method (Peters and Van Slyke, 1932). The amount of P adsorbed was calculated as the difference between the initial amount of P added and the amount of P remaining in the supernatant at the end of the experiment. The P loadings of the mineral-P complexes produced are shown in Table 18. All minerals were loaded to reach their adsorption maxima.

Table 18 : P adsorption capacity of the produced minerals-P adsorption complexes

Go: goethite; K: kaolinite; IP: inorganic P; IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate and G6P: glucose-6-phosphate.

Mineral-P complexes	Quantity of P adsorbed (µg g ⁻¹)
Go-IP	2810
Go-IHP	3742
Go-GLY	1398
K-IP	1736
K-IHP	6082
K-GLY	1222

6.2.3 Experimental Setup and Plant growth

We used a device whose principle is very similar to the RHIZOtest (**Figure 22**) except that here, the roots of the plants are not separated from the soil but remain separated from the nutrient solution. In a first step (preculture period), 0.20 g of ryegrass (*Lolium multiflorum*) seeds were grown for 14 days in hydroponics in a cylinder closed at the bottom by a screen allowing the development of the roots with a nutrient solution: $\text{Ca}(\text{NO}_3)_2$ (2 mmol L⁻¹), MgSO_4 (0.5 mmol L⁻¹), K_2SO_4 (0.7 mmol L⁻¹), KCl (0.1 mmol L⁻¹), KH_2PO_4 (0.1 mmol L⁻¹), MnSO_4 (0.5 μmol L⁻¹), CuSO_4 (0.5 μmol L⁻¹), ZnSO_4 (0.5 μmol L⁻¹), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ (0.01 μmol L⁻¹) and Fe-EDTA (100 μmol L⁻¹). In a second phase (culture period), the two-week-old seedlings were transplanted into polystyrene cylinder pots (125 ml volume) containing the growth media. The growing media consisted of a mixture of the previously prepared P-mineral complexes mixed with acid-washed quartz. Before the experiment, the quartz was sterilized by autoclaving (Gómez-Suárez et al., 2020) at 121 °C for 2 h in order to eliminate potential microorganisms, thus allowing the results to be attributed to the effect of root activity alone. In addition, to avoid any P limitation for the plants during the experiment, we provided a total amount of P that was previously found to be sufficient to meet the plants' needs (Gómez-Suárez et al., 2020). Thus, the amount of mineral-P complex added to the growing medium was calculated to provide 10 mg of P in each treatment while the amount of quartz was calculated to reach a final mass of 100 g in each pot. Then the pots containing the plants and growing medium were nested into other 250 ml cylinder pots containing a nutrient solution with a filter paper wick. The composition of this nutrient solution was the same as that used for the preculture period, except that P was not added and N was added as $\text{Ca}(\text{NO}_3)_2$ (4 mmol L⁻¹) or $(\text{NH}_4)_2\text{SO}_4$ (4 mmol L⁻¹). To make the amounts of Ca equal between the $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ treatments, CaCl_2 was added to the $\text{NH}_4\text{-N}$ treatment. The devices were placed under controlled conditions (phytotron) under a 12h photoperiod, constant temperature (25 °C) and relative humidity (80%). Non-planted control treatments, in which the quartz-mineral-P complex was incubated without plants (hereafter called bulk substrate), were also performed. A total of 96 such devices were implemented: 3 P compounds (IHP, GLY and IP) x 2 soil minerals (goethite and kaolinite) x 2 forms of nitrogen ($\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$) x 2 cropping conditions (ryegrass and bulk soil) x 4 replicates.

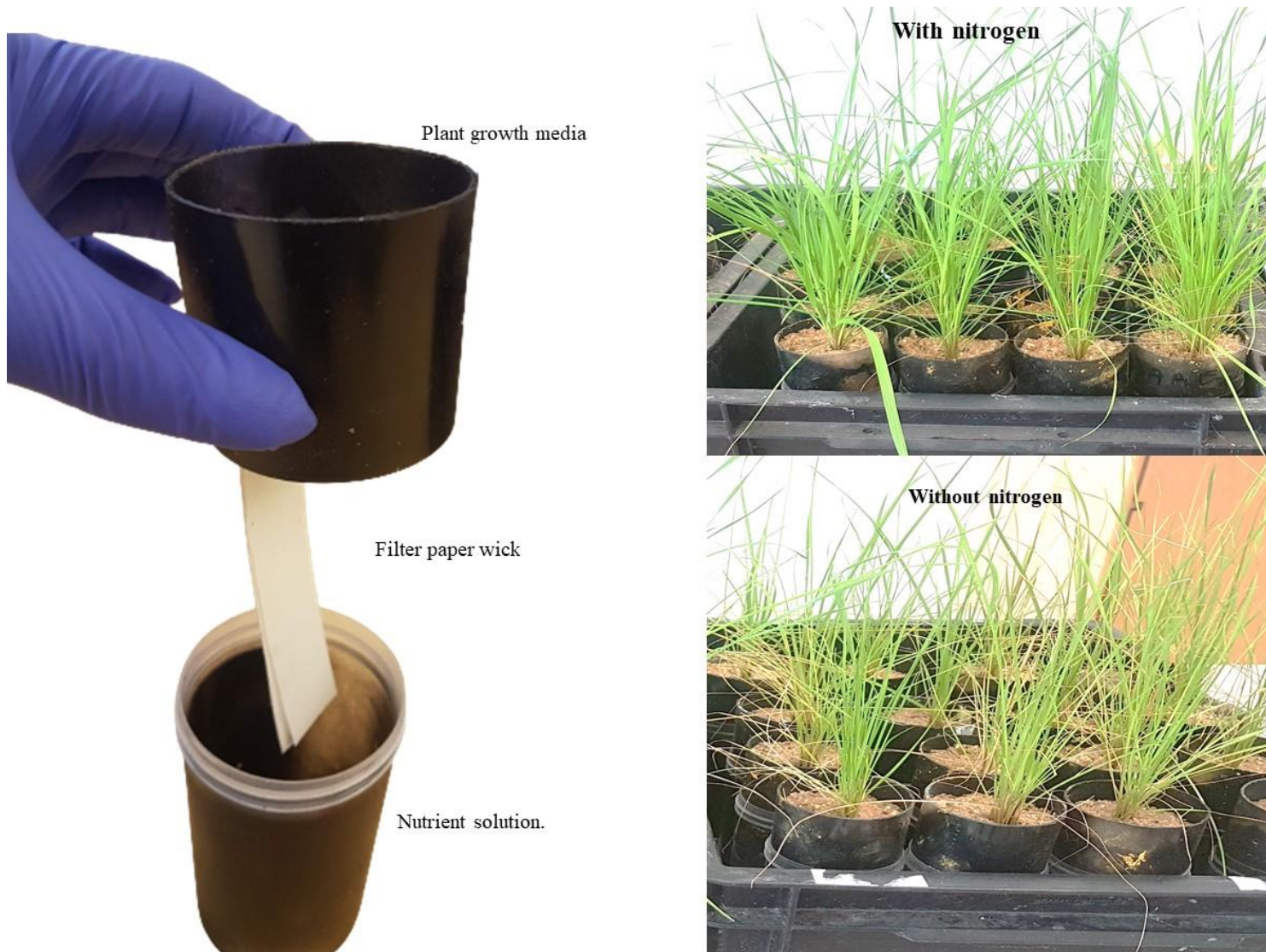


Figure 22: Picture of the experimental Setup and Plant growth

6.2.4 Plant sampling and analysis

The plants were harvested after 20 days of contact with mineral-P complexes. At harvest, shoots and roots were separated and roots were gently rinsed with deionized water. Shoots and roots were then dried at 60 °C for 72 h, weighed and crushed prior to N and P analysis. The concentration of P in shoots and roots was determined calorimetrically (Ohno and Zibilske, 1991) after mineralization by 65% HNO₃ digestion directly in a microwave Teflon vessel (Lange et al., 2014). In addition to P analysis, the N elemental concentrations were determined. We calculated N:P ratios by dividing leaf N concentration by leaf P concentration (both as percentage nutrient in the sample) within each plant tissue sample. Total plant P uptake was calculated by summing P uptake by roots (i.e., root P concentration multiplied by root dry mass) and P uptake by shoot (i.e., shoot P concentration multiplied by shoot dry mass).

6.2.5 Soil Analyses

At the completion of the experiment, cropped soil (i. e., rhizosphere) and the uncropped soil (i. e., bulk soil) were collected and dried at ambient temperature. In accordance with the scheme proposed by DeLuca et al. (2015), each soil sample was subjected to CaCl_2 extraction (0.01 mol L^{-1}), which extracts soluble and weakly adsorbed inorganic P and emulates accessible P by interception and root diffusion. One g of soil was transferred to a polypropylene centrifuge tube to which 20 mL of $0.01 \text{ mol L}^{-1} \text{ CaCl}_2$ was added and shaken for 3 h in a reciprocal shaker at 200 rpm at $20 \text{ }^\circ\text{C}$. After shaking, the pH (pH- CaCl_2) was measured in the suspension and the extract was separated from the solid residue by centrifugation at 3000g for 15 min. In the extract, P concentrations were analyzed colorimetrically (Murphy et al., 2009) using a spectrophotometer (610 nm). ΔpH between rhizosphere and bulk soil from unplanted pots postgrowth was then calculated.

After defrosting some samples, acid phosphomonoesterase activity in the rhizosphere (PME) was measured with a modified buffer at pH 6.5 (Tabatabai and Bremner 1969). Briefly, phosphatase activity was assessed via production of p-nitrophenol from sodium p-nitrophenyl phosphate during a 1 h incubation at $37 \text{ }^\circ\text{C}$ with 0.5 g dry soil, 0.2 mL toluene, 4 mL modified buffer and 1 mL substrate. p-Nitrophenol release was determined spectrophotometrically at 410 nm after stopping the reaction with 4 mL 0.5 M NaOH and 1 mL 0.5 M CaCl_2 and filtering.

6.2.6 Data processing and analysis

All statistical analyses were performed using R software version 3.5.0 and the package Rcmdr. The impact of factors (soil minerals, P compounds, N forms, and their combined effect) on P availability and uptake was modeled by generalized linear models (GLM) using the "FactomineR" package. The GLM model was used to avoid mathematical transformation of the variables and to get rid of the strict assumption that "the residuals will follow a conditionally normal distribution" (McCullagh and Nelder, 2019; Warton et al., 2016) and allow the use of a variety of other distributions of the exponential family for the residuals (Cohen et al., 2014). All factors were tested individually and the models were compared on the basis of second-order Aikake information (AIC), with the lowest relative value being considered the best fit. The anova of the best-fit GLM model with a chi-square test generates the deviance analysis table that gives the significance level of all factors. Statistical analyses to compare the average results of N:P mass ratio, P uptake, enzyme activities, and biomass were performed using a one-way analysis of variance (ANOVA) followed by Tukey's honest significant difference (HSD) test ($p < 0.05$). As recommended by Schabenberger and Pierce, (2001), the results of ANOVA were presented by showing the degree of freedom (Df), F-ratio (F, i.e., the between-group variance divided by the within-group variance) and p-value (i.e., the lowest probability level at which the means are considered significant).

6.3 Results

The best model fit that most affected N:P ratio, total P concentrations, and total ryegrass biomass were obtained with the interaction of all factors, i.e., N x minerals x P forms, rather than their separate effects (Table 19, highest LR Chisq of 20.9 for N:P and lowest AICc values of -35 and -172 for P uptake and total biomass, respectively).

Total biomass increased with N addition to an extent dependent on the mineral-P complexes (Figure 23). The N:P ratio values varied markedly among treatments, ranging from a minimum value of 2.5 ± 0.42 to a maximum value of 32.31 ± 2.00 (Figure 24). Except for K-Gly, the N:P ratio was below 12 without N addition, reflecting N limitation (Figure 24). With N addition, the N:P ratio increased irrespective of the mineral-P complex. It shifted from N limitation to N and P co-limitation in the presence of mineral-IP complexes (N:P = 14.8-15.8) and to P limitation in the presence of mineral-OP complexes (N:P = 19.12-32.2). The addition of both N forms increased the N:P ratio in a similar way except in the Go-IHP treatment where $\text{NO}_3\text{-N}$ significantly increased the N:P ratio compared to $\text{NH}_4\text{-N}$ (Figure 24). Between minerals, the N-induced increase in N:P ratio was significantly higher on goethite than on kaolinite (Figure 24 and Table 19). Similar to N:P, total P uptake differed markedly between mineral-P complexes (Figure 25 and Table 20). With N addition, more P was absorbed by the plant and P in mineral-IP complexes was significantly more available than mineral-OP sources (Table 20). This was evidenced by the discrepancy between the percentage of P recovered without N ($\leq 12\%$) and with N ($\leq 25\%$). In the presence of mineral-IP complexes, the addition of $\text{NO}_3\text{-N}$ significantly increased P uptake compared to $\text{NH}_4\text{-N}$ (Figure 25); however, no significant difference was found between the two N forms for mineral-OP complexes (except on Go-GLY). The mineral type had little influence on N-induced P uptake, except for K-GLY which showed significantly higher P uptake than Go-GLY. In general, P uptake from mineral-P complexes after N addition showed the following trend: mineral-IP >>> mineral-IHP > mineral-GLY (Figure 25 and Table 20). Furthermore, we found that foliar N (Figure 26a) and P (Figure 26b) increased significantly with the N addition, and varied with the mineral-P complexes.

Rhizosphere properties were affected by N forms and their interactions with mineral-P complexes. Rhizosphere pH showed a significant increase with $\text{NO}_3\text{-N}$ but decreased significantly with $\text{NH}_4\text{-N}$ (Figure 26c). The addition of N significantly increased soil phosphatase activities, the highest activities being detected in the presence of mineral-OP complexes (Figure 27). However, the available P pool in the rhizosphere was significantly decreased with N addition (Figure 26d). Plant N:P ratio showed a positive correlation with soil phosphatase activities and foliar N and a negative correlation with soil available P concentration (Table 21). Total P uptake was positively related to available P concentration, phosphatase activity, and foliar N. Foliar P was also positively correlated with foliar N. Overall, no parameter was correlated with rhizosphere pH (Table 21).

Table 19 : GLM model results testing the impact of factors: N form (NO₃-N or NH₄-N), minerals (goethite and kaolinite), and P forms (IP, IHP, and GLY) on N: P ratio, total P uptake, and total biomass.

Explanatory factor	N : P ratio			P uptake			Total biomass		
	LR Chisq	Df	Pr	F	Pr	AICc	F	Pr	AICc
N forms	4.1	2	0.12	65.03	< 0.001	84	34.5	< 0.001	-149
Minerals	5.3	1	< 0.05	18.08	< 0.001	98	2.1	0.1	-121
N forms x Minerals	5.3	2	< 0.05	3.24	< 0.05	87	3.1	< 0.05	-146
P forms	11.5	2	< 0.01	131.38	< 0.001	62	10.5	< 0.001	-126
N forms x P forms	19.5	4	< 0.001	11.09	< 0.001	31	4.7	< 0.01	-161
Minerals x P forms	21.1	2	< 0.001	26.98	< 0.001	53	11.7	< 0.001	-129
N forms x Minerals x P forms	20.9	4	< 0.001	13.3	< 0.001	-35	2.5	< 0.05	-172

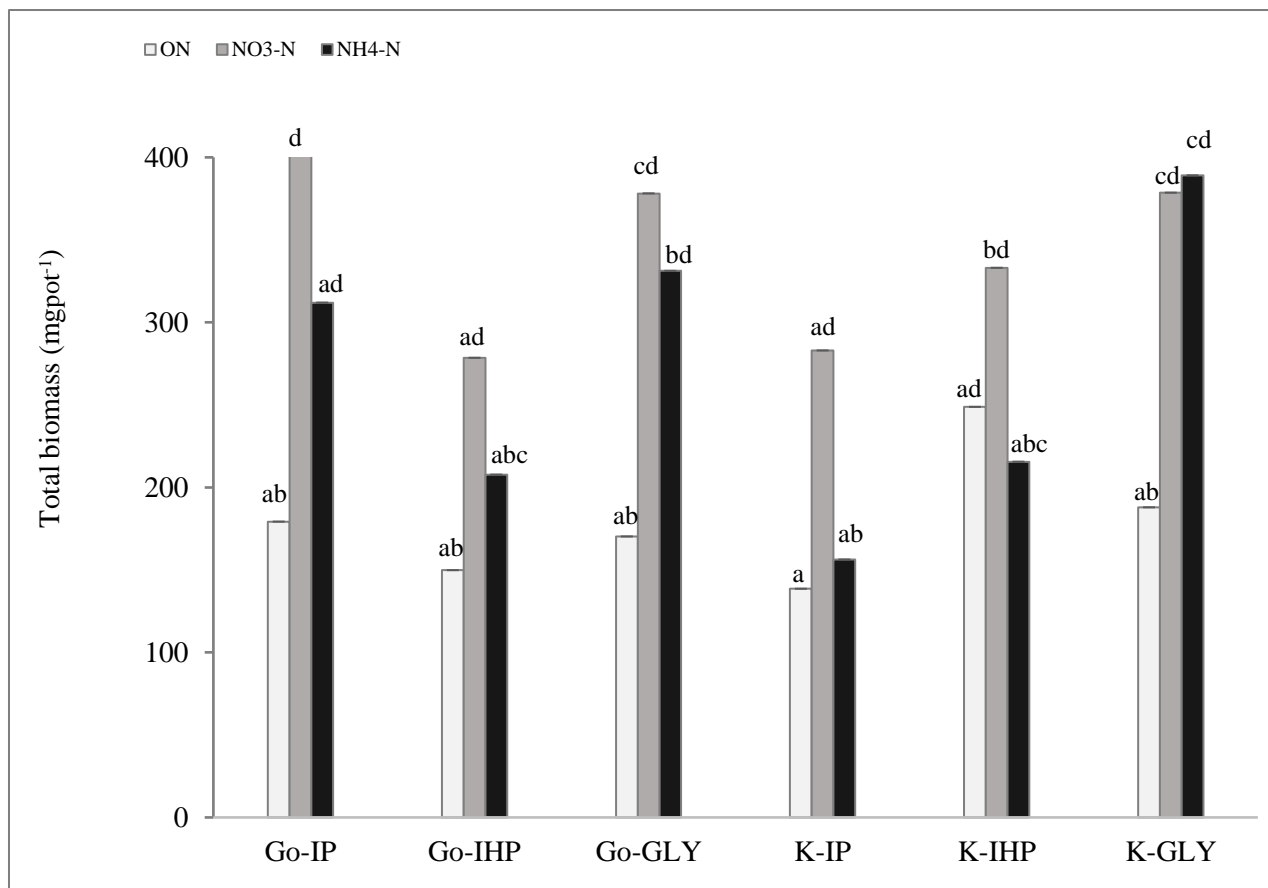


Figure 23 : Effect of N, P and soil mineral interactions on total biomass production by ryegrass.

The interaction effect of N forms, P compounds and soil minerals on total biomass was significant ($P < 0.05$) according to GLM model results testing the impact of factors (N forms, P compounds, soil minerals, and their combined effect) on total biomass. Means with different letters were significantly different according to Tukey's HSD test at $P < 0.05$. Error bars indicate standard error. Soils minerals (Go: goethite and K: kaolinite); N forms (NO₃-N: nitrate and NH₄-N: Ammonium); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate and IP: KH₂PO₄); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

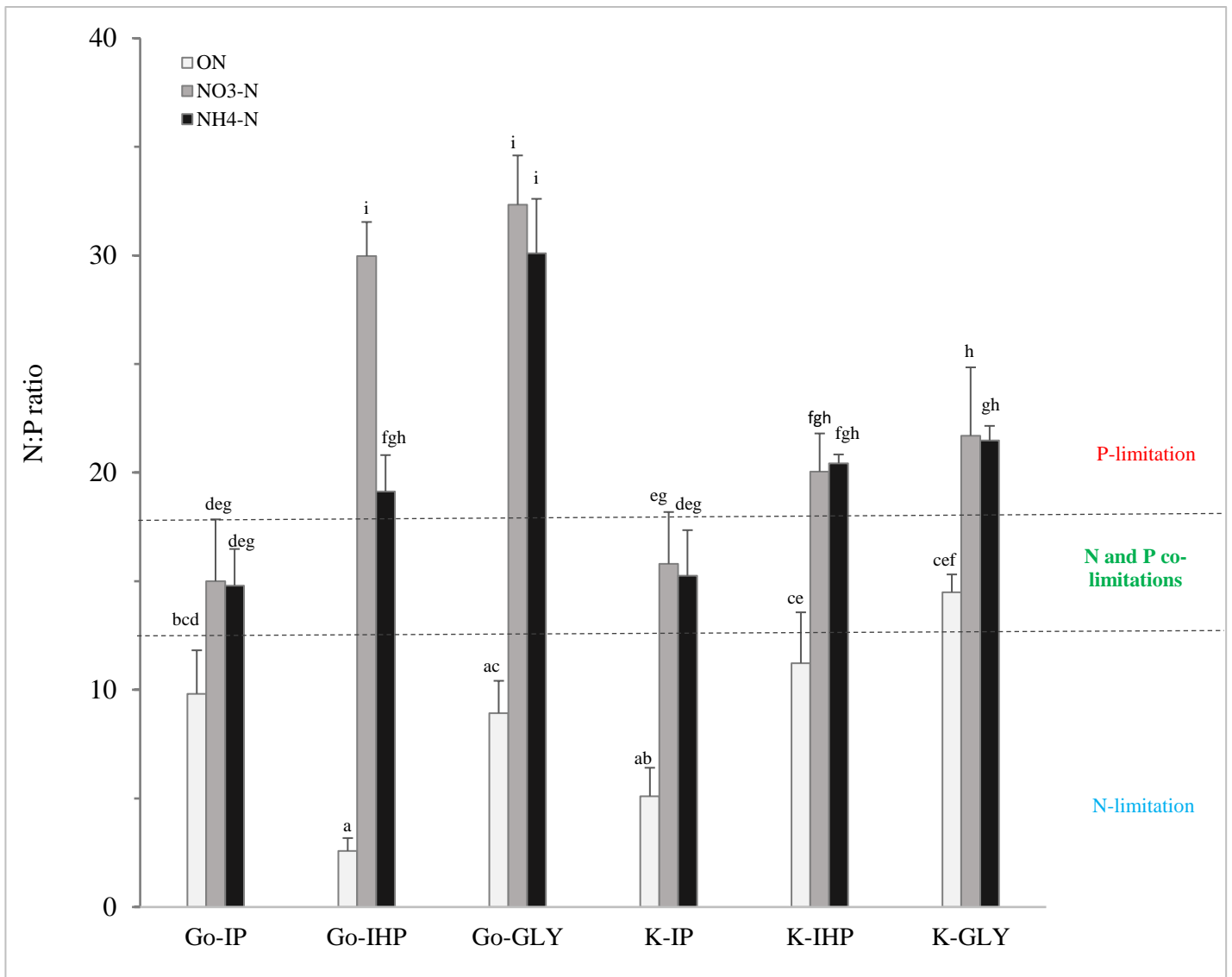


Figure 24: Effect of N forms, and their interactions with minerals-P complexes on N:P ratios.

The interaction effect of N, P compounds, soil minerals on N:P ratios was significant ($P < 0.001$) according to GLM model results testing the impact of factors (N forms, P compounds, soil minerals, and their combined effect). Means with different letters were significantly different according to Tukey's HSD test at $P < 0.05$. Error bars indicate standard error. N forms (NO₃-N: nitrate and NH₄-N: Ammonium); Soils minerals (Go: goethite and K: kaolinite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate and IP: KH₂PO₄); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes. The N:P ratio has been used to indicate plant N or P limitation conditions i.e., N limitation when $N:P < 12$, P limitation when $N:P > 16$ or 20 and NP co-limitation between 12 and 16 or 20 (He et al., 2014; Koerselman and Meuleman, 1996; Zheng et al., 2017).

Table 20 : Percent of P recovered by ryegrass from adsorbed OP complexes with the addition of N forms.

Complexes	N Forms		
	ON	NO ₃ -N	NH ₄ -N
Go-IP	12%	25%	15%
Go-IHP	5%	10%	10%
Go-GLY	1%	6%	2%
K-IP	12%	24%	13%
K-IHP	5%	10%	12%
K-GLY	7%	9%	9%

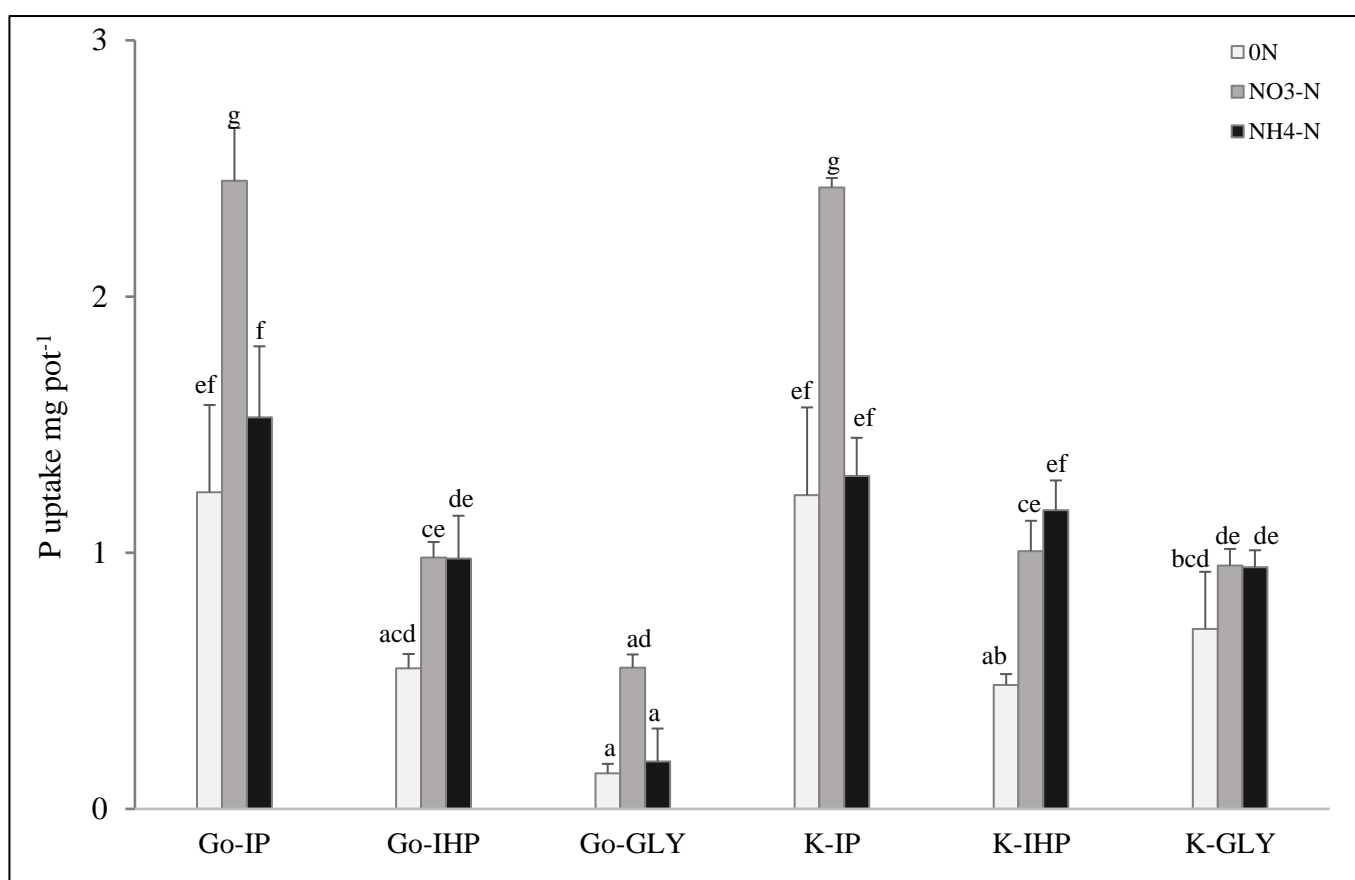


Figure 25: Effect of N, P and soil mineral interactions total P uptake by ryegrass plants with different mineral-P complexes.

The interaction effect of N, P compounds, soil minerals on total P uptake by ryegrass was significant ($P < 0.001$) according to GLM model results testing the impact of factors (N forms, P compounds, soil minerals, and their combined effect). Means with different letters were significantly different according to Tukey's HSD test at $P < 0.05$. Error bars indicate standard error. N forms (NO₃-N: nitrate and NH₄-N: ammonium); Soils minerals (Go: goethite and K: kaolinite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate and IP: KH₂PO₄); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes; The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

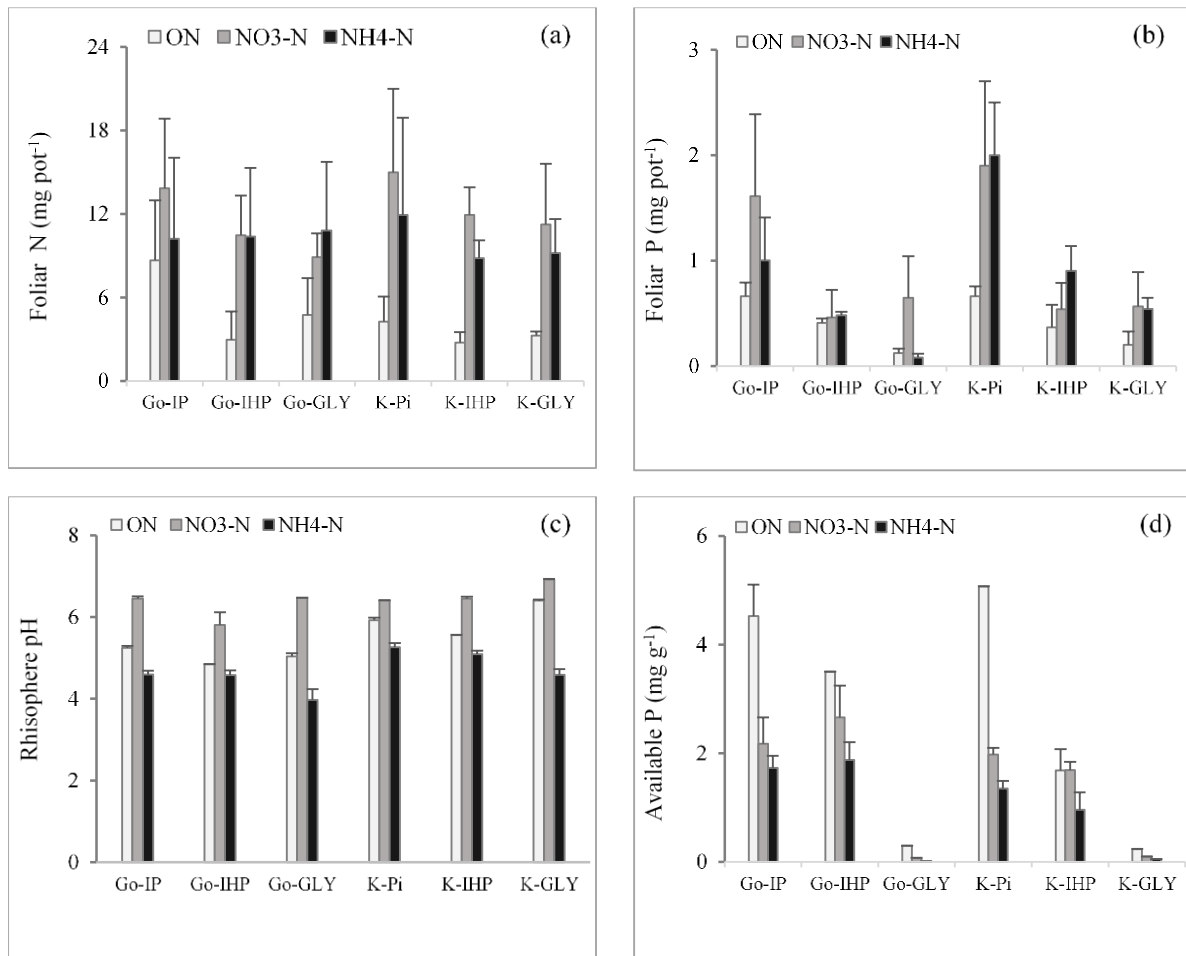


Figure 26 : Changes in foliar N (c), P (c), rhizosphere pH (c) and available P (c) in response to N addition

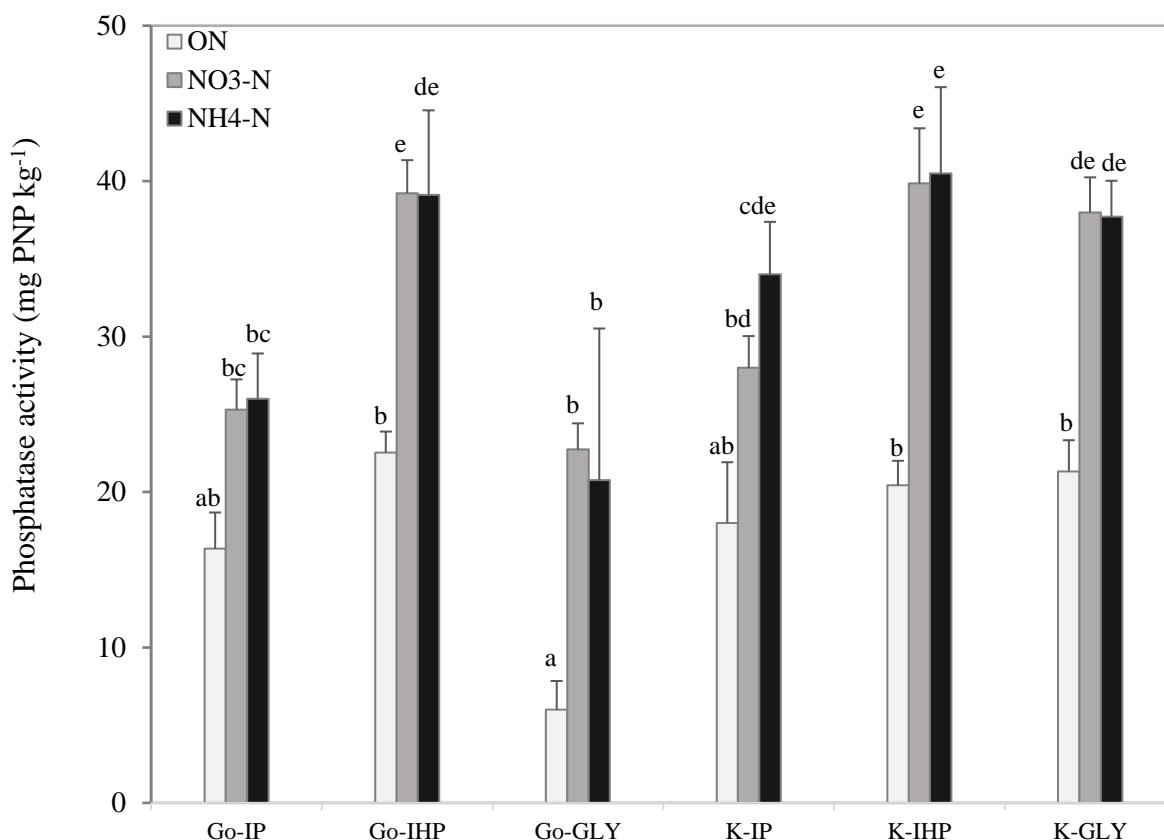


Figure 27: Effect of N, P and soil mineral interactions on phosphatase activity.

Means with different letters were significantly different according to Tukey's HSD test at $P < 0.05$. Error bars indicate standard error. N forms (NO₃-N: nitrate and NH₄-N: Ammonium); Soils minerals (Go: goethite and K: kaolinite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate and IP: KH₂PO₄); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes; The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals.

Table 21: Spearman product-moment correlation (r-values) between total P uptake, foliar N and P and rhizosphere properties.

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

	N:P	Total P uptake	Foliar N	Foliar P
Rhizosphere pH	-0.036	0.159	0.063	0.182
Available P	-0.209 *	0.537***	0.037	0.404***
Phosphatase activity	0.381***	0.463***	0.363***	0.282
Foliar N	0.640***	0.359***	-	0.362**

6.4 Discussion

6.4.1 Effect N forms and P forms on plant P limitation and P uptake

The N:P ratio is a common indicator of P or N (co-)limitation. Usually, $N:P < 12$ and $N:P > 16$ indicate N and P limitation, respectively while co-limitation occurs between 12 and 16 (He et al., 2014; Koerselman and Meuleman, 1996; Zheng et al., 2017). Here, we have shown that interactions among N forms, P forms, and soil minerals strongly influence plant N:P ratio and P uptake of ryegrass as compared to individual effects (Table 19). The range in plant N:P ratio (2.5 to 32.31) was consistent with those reported in other studies (Güsewell, 2004; von Oheimb et al., 2010; Yang et al., 2019). The increase in N:P ratio when N was added to the different mineral-P complexes (Figure 24) suggests that a clear shift from N limitation to P limitation occurred (Sardans et al., 2017; Yang et al., 2019). This supports our first hypothesis that N addition under conditions of low P availability would lead to increased P limitation for plant growth (Harpole et al., 2011; Vitousek et al., 2010). In general, with N addition, the N:P ratio of plants grown on mineral-IP sources was between 14.8 and 15.8 which was lower than that observed for plants grown on mineral-OP sources (i.e. between 19.12 to 32.2) (Figure 24). This suggests that, regardless of soil minerals, when N is added the plant becomes N and P co-limited in the presence of IP, whereas the plant switches to P limitation in the presence of OP forms. These results strengthen our expectation that the type and biochemical nature of P sources determine the degree of nutrient limitation in plants (Amadou et al., 2022; Long et al., 2016). The N-induced plant P limitation in the presence of OP forms (IHP, GLY) is likely related to the lower availability and uptake of OP compared to IP forms (Figure 25 and 26d). This low availability has been widely demonstrated (Bollyn et al., 2017; Lagos et al., 2016) and would be the result of the high affinity and low desorption of OP forms onto and from soil minerals (Amadou et al., 2022; Ganta et al., 2019). Here, the trend in available P after N addition (mineral-IP > mineral-IHP > mineral-GLY, Figure 26d) resulted in a respective decrease in N:P ratio (Figure 24). Similarly, there was a negative correlation between available P and N:P ratio (Table 21). This means that the degree of P limitation would be strongly dependent on the available P (Long et al., 2016; Zheng et al., 2017), with P limitation being less pronounced under IP forms due to their greater availability to the plant (Figure 25 and Figure 26d). Thus, in systems where P is very highly sorbed (such as OP forms), N additions can indeed lead to rapid depletion of available P (Figure 26d) and thus very high P limitation (Figure 24), but in systems where P is relatively more available (such as IP forms), N additions do not lead to systematic P limitation but rather to colimitation of N and P.

6.4.2 Rhizosphere biogeochemical processes involved in P limitation and uptake under different soil minerals, P and N forms.

There is evidence from literature that N addition may increase plant P demand which, in turn, promotes soil P mobilization (Schleuss et al., 2020; Yue et al., 2017; Zhan et al., 2017). This highlights the ecological importance of the beneficial effect of N on P use efficiency by plants (Vitousek et al., 2010). Our results suggest that N addition increased plant P limitation in all treatments (Figure 24), as well as a further increase in plant P uptake (Figure 25) via altered rhizosphere chemistry (Figure 26c, d). The addition of $\text{NH}_4\text{-N}$ or $\text{NO}_3\text{-N}$ resulted in a decrease or increase in pH, respectively (Figure 26c). Accordingly, the shift of plants from N limitation to N and P co-limitation or P limitation (and the associated increase in P uptake) would result from the impact of N addition in stimulating rhizosphere processes involved in P mobilization/acquisition (Schleuss et al., 2020; Zhan et al., 2017), which is consistent with our second hypothesis.

Our results regarding the trend of N:P ratio without N (mineral-IHP < mineral-GLY) and with N (mineral-IHP > mineral-GLY) suggest that the addition of N would promote the mobilization of IHP (main forms of OPs) and make it less plant-limiting compared to other forms of OPs, highlighting the pivotal role of the interaction between N, P, and minerals on the OP cycle (Craine and Jackson, 2010; Hou et al., 2021). In addition, these results highlight a new mechanism by which N inputs could accelerate the cycling of OPs, particularly by increasing the availability of IHP (the most accumulated OP in the soil), and thus delay the onset of P limitation of this form for plant growth. In conclusion, the benefits of N addition on P limitation depend strongly on its interaction with P forms and the characteristics of the minerals involved. With the addition of N, more P can be recycled from the clay minerals (kaolinite) and thus delay P limitation as compared to iron and aluminum oxides (goethite). The magnitude of P limitation resulting from the interaction of N with OP forms relative to that with IP forms provides insight into the consequences of organic fertilization on P cycling dynamics in some OP-rich tropical soils and in N-fertilized agroecosystems. The increase in plant P uptake with the addition of N, particularly with the $\text{NO}_3\text{-N}$ forms (Figure 25), highlights the synergistic effects of N and P and their interactions with minerals on P dynamics, i.e., P availability and limitation. High phosphatase activity (Figure 27), and the availability of P in the rhizosphere (Figure 26d) with N addition likely contributed to plant P uptake, as both increase the possibility that a phosphatase enzyme meets an OP compound and catalyzes its hydrolysis from the minerals (Craine and Jackson, 2010; Long et al., 2016). Consistently, correlations indicated that total P uptake was positively related to available P and phosphatase activity (Table 21). Most likely, the addition of N allowed plants to synthesize N-costly phosphatases (Schleuss et al., 2020), which then made OP available for plant uptake (Helfenstein et al., 2019). Thus, it seems likely that with the addition of N, P is more intensively recycled from the IP and

OP pools, irrespective of the soil minerals (Widdig et al., 2019). However, the lower P uptake found in the presence of mineral OP complexes in spite of the addition of N, (Figure 25) could be a result of their low desorption rate relative to IP (Amadou et al., 2021; Amadou et al., 2022) (Figure 26d) and because once desorbed, OPs require enzymatic cleavage before being taken up by the plant (Klotzbücher et al., 2020). The correlations between plant N and P nutrition, available P and phosphatase activity (Table 21) indicated that increases in N:P ratio and P uptake may be accounted for by the significant changes in soil properties. In this study, N addition increase phosphatase activity (Figure 27) and decreased available P (Figure 26d) and, both were significantly related to plant N:P ratio and P uptake (Table 21), suggesting that in OP sources, available P and phosphatase activity influences plant P uptake and P limitation. The decrease in available P with N addition in the rhizosphere (Figure 26c) may result from greater P uptake and probably lower replenishment of the available P pool from the mineral-P complexes (Lund et al., 2009; Sardans and Peñuelas, 2012). Recent studies also showed that the addition of N has influence on rhizosphere properties (Marklein and Houlton, 2012; Zheng et al., 2017), and in low P ecosystems, the available P could decrease leading to more P limitation for plant primary productivity (Lü et al., 2013). Thus, our results suggest that N supply to plants has the potential to increase P uptake from both mineral-IP and OP complexes, thereby altering plant P limitation. We found that supplying the $\text{NO}_3\text{-N}$ form to plants increased plant P uptake and availability and, to some extent, greater P limitation compared to supplying $\text{NH}_4\text{-N}$ (Figure 24 and 25). This suggests that it was not through alterations in rhizosphere pH that the form of N affected P uptake by the plant.

6.4.3 Key role of soil minerals in P limitation under different N forms additions

Our results showed no significant variation in the N:P ratio of plants between the two N forms, i.e. $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, although $\text{NO}_3\text{-N}$ seems to induce a greater P limitation on some complexes (Figure 24). In the presence goethite-P complexes, the plant was significantly more P-limited (higher N:P ratio) than in kaolinite-P mineral complexes (Figure 24). These results agree with our third hypothesis that the degree of P limitation would vary significantly between mineral types and P forms due to the contrasting physicochemical properties of the minerals used (Bai et al., 2021; Yan et al., 2014) and the biochemical nature of the P sources (Amadou et al., 2021; Anderson, 1980; Condrón et al., 2005). In agreement with the literature, we found in a recent study that, compared to kaolinite, goethite had very low P desorption dynamics (Amadou et al., 2022). Similarly, other studies found greater P limitation in the presence of iron and Al oxides than in the clay minerals (Bortoluzzi et al., 2015; Celi et al., 1999).

6.5 Conclusions

In this study, we tried to unravel the biogeochemical processes involved in P limitation by characterizing the role of N and P forms and their interaction with soil minerals on P availability. Interactions between N forms, P forms, and soil minerals strongly altered P dynamics, as compared to individual effects. These interactions increased plant P limitation and P uptake via modification of rhizosphere chemistry. The extent of P limitation was strongly dependent on the degree of availability of P sources. Therefore, we found that the interaction of N with IP forms led to greater P uptake and a marked reduction in P limitation compared with the interaction of N with OP. Thus, we inferred that in addition to the degree of P availability, the characteristics and biochemical nature of the P sources determine the degree of P limitation in plants. Furthermore, we found with the addition of N, more P was recycled from clay minerals and P limitation was delayed compared to iron oxides.

Our results highlight the ecological importance of the benefit of N and its interaction with soil minerals on P use efficiency by plants. This study, therefore, provides important information on ecosystem P cycling under N addition and the biogeochemical properties involved, which will allow ecosystem models to accurately predict plant N-P limitation and its impacts, and will also help build robust ecosystem models with fully coupled N-P or C-N-P interactions. Future perspectives will be to understand the effects of N-P-mineral interactions on P limitation in other plant species with contrasting P acquisition strategies (*Fabaceae*, *Brassicaceae*...). Then, the scale could be extended to plant communities and ecosystems based on the trait approach of plants and minerals, and N and P chemical forms.

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CHAPTER 4

7 Role of phosphorus-acquisition strategies on organic P mobilization and acquisition

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Abstract

Plant P acquisition strategies (i.e., *foraging* and *mining*) are generally considered to have access to legacy P pools in the soil. However, compared to inorganic P, the impact of these strategies in soil amended with various forms of organic P (OP) has received much less attention. The purpose of this study was to examine the response of P acquisition strategies toward forms of P (IP and OP) in interactions with soil minerals and their consequences for OP availability and P acquisition. We characterized P acquisition strategies in eight plant species from diverse phylogenetic lineages known with contrasting P acquisition traits that were cultivated under several complexes of IP and OP (IHP, and GLY) adsorbed on Fe oxyhydroxides (goethite) and clay minerals (kaolinite). Results showed an important plasticity of root traits in response to IP and OP forms. P acquisition traits of the species changed between application of the OP forms and application of the IP form. A difference in trait responses was also observed between the specific OP forms, i.e. IHP and GLY. Phosphorus-acquisition traits were generally more prominent on the OP forms than on the IP form. The positive response of P acquisition strategies to OP sources resulted in greater availability and acquisition of P from OPs. Species were found to have contrasting responses between P forms. *Vicia faba* and *Pisum sativum* had significantly higher P acquisition from the OP forms, while *Lolium perenne* had a higher overall P uptake on the IP form. On the other hand, *Lens culinaris*, *Hordeum vulgare* and *Trifolium alexandrinum* had an overall equivalent P acquisition between P forms. Compared to strategies involving P *foraging*, those involving P *mining* resulted in greater P acquisition from OPs. Crops employing intermediate strategies (involving both P acquisition strategies) also showed important P acquisition. Nevertheless, modeling results showed that phosphorus uptake was better predicted by root morphological traits than root physiological traits. This study showed that the positive response of P acquisition strategies to OP forms led to P acquisition from OPs, thus potentially improving the use of renewable OP resources via optimization of crop combinations and the type of P fertilizer applied.

7.1 Introduction

Soil phosphorus (P) deficiency limits the productivity of many agroecosystems (Filippelli, 2008; Jarvie et al., 2019). Modern agricultural practices depend heavily on mineral fertilizer derived from mined phosphate rock, a finite and steadily declining resource (Sulieman and Mühling, 2021). To meet plant P

requirements and sustain the growing population and food needs, new strategies that can provide available P for plants while limiting the use of mineral P fertilizers are urgently needed (Faucon et al., 2015; Houben et al., 2019). One solution is to recycle P from P-rich organic wastes (Amadou et al., 2021; Sulieman and Mühling, 2021). However, P in organic wastes is a mixture of organic and inorganic P forms, in various proportions depending on their characteristics. Major organic (OP) compounds found in soil and organic waste include inositol hexakisphosphate, IHP (Turner et al., 2005; Vincent et al., 2013), glycerophosphate, GLY (Doolette et al., 2011; Newman and Tate, 1980), and glucose-6-phosphate, G6P (Deiss et al., 2018). Inorganic forms of P (IP) include calcium phosphates and amorphous P bound to aluminum or iron. These forms have been found to be unavailable to plants due to their strong adsorption to soil minerals (Amadou et al., 2022; Barrow, 1983), which is considered one of the main causes of P limitation for plants (Javaid, 2009). However, these poorly available forms of P in soil or organic wastes can be mobilized by some plants in P-deficient soils (Amadou et al., 2021; Honvault et al., 2020).

Several direct and innovative approaches have been identified to improve the mobilization and acquisition of OP forms by plants. These include the identification and selection of crop species/genotypes based on their functional traits (Faucon et al., 2015; Nobile et al., 2019). This approach uses morphological, architectural (Lynch, 2015; Nielsen et al., 1998) and physiological traits (Richardson et al., 2009; Yadav et al., 2015; Zhu et al., 2005), microorganisms or a combination of both to access sparingly available OP forms. In general, these traits could be categorized into three types of P acquisition strategies: *foraging*, *mining* and collective microbial-root strategy (Amadou et al., 2021). The plant *P-foraging strategy* is the acquisition of P in the soil solution through morphological and architectural traits by maximizing soil exploration. Through these strategies, plants can induce a diffusion gradient which in turn would favor the desorption process of the different adsorbed OP forms (Fang et al., 2017; White and Hammond, 2008). *Foraging strategy* involves morphological traits such as specific root length, fine root percentage and root surface area, and architectural traits including root length density, root biomass, and the formation of clustered roots or arbuscular mycorrhizal symbioses that allow plants to increase their *foraging* capacity (Haling et al., 2018). The plant *P mining* strategy, is the acquisition of P in the soil solution through physiological traits that are released into the soil from the roots, including carbohydrates, organic and amino acids, phenolic compounds, proteins, fatty acids, sterols, enzymes, polysaccharides, and phospholipids (Guppy et al., 2005; Weisskopf et al., 2006). The collective microbial-root strategy refers to the investment of resources by plants to interact with the microbial community to access OP in soil.

Different P-mobilization and -acquisition strategies in crop species and cultivars have been highlighted, but their efficiency to acquire P from different OP and IP forms remains poorly studied (Lambers et al., 2008; Turner, 2008). A recent study of Ceulemans et al. (2017) showed that some grassland species had preferential P acquisition from a P source over another, either OP or IP, while others showed equal P acquisition of both P sources. These authors also showed that P acquisition of

some grassland species was more efficient when multiple P sources were added to the soil, the addition of both OP and IP to the soil inducing a higher shoot P content than the addition of one form only. There may also be trade-offs between physiological and morphological traits (Lambers et al., 2006). These trade-offs have been examined very recently in different crop families and species (Honvault et al., 2020). Trade-offs between thicker and thinner roots were observed (Honvault et al., 2020), with thicker roots showing greater carboxylate release or phosphatase activity in the rhizosphere. Trade-offs and coordination between traits were strongly influenced by soil type. However, their effect on the availability of OP forms must still be elucidated (Honvault et al., 2020; Wen et al., 2019).

Several plant species are presumed to be relatively efficient in OP utilization without assistance from rhizosphere microbiome. Some barley species with different root traits could easily access and mobilize twice as much OP as *Prunus laurocerasus* in low P soil (Bates and Lynch, 2000). Numerous plant species belonging to the family *Fabaceae* have been classified as efficient P solubilizers (Schneider et al., 2019). Chickpea, which appears to produce both phosphomonoesterases and diesterases, is thought to improve its P nutrition, probably through *mining* and mineralization of OP forms in soil (Darch et al., 2018; Pang et al., 2010). Various studies have demonstrated that plants have limited ability to access OP in the form of IHP (the main form of OP) due to its low availability in soil solution and low level of extracellular phosphatase or phytase (George, 2007; Richardson et al., 2009). It has also been shown that wheat and many other species are able to utilize P from G6P, GLY and phosphodiesteres (DNA and RNA) due to the *mining* capacity, but are limited to acquiring P directly from IHP, although it is abundant in many soils (George et al., 2008). This suggests that the biological importance of the different forms of IP and OP will be driven by their turnover rates. The challenges of OP mobilization and acquisition are to understand the response of plant functional traits depending on OP forms and soil properties to improve P acquisition and mobilization of crop species.

Overall, the plant P acquisition traits are known and their indirect and sometimes even direct effects on P acquisition/mobilization have been demonstrated (Ma et al., 2018; Nobile et al., 2019). The processes differ according to the nature of IP or OP forms (phosphate mono or diester) and the physicochemical properties of the soil. For instance, the availability of the different OP forms (IHP, G6P, GLY, DNA and RNA) as a direct effect of P acquisition strategies (*P mining* and *foraging*) remains unclear. Although the release of carboxylates can make some OP (G6P, GLY) available to plants, it is less efficient to solubilize IHP (Gerke, 2015) probably due to its strong binding to soil. Interactions between plant functional traits in the mobilization/acquisition of both OP and IP have been studied but remain poorly understood and unconfirmed. Thus, it has been suggested that plant strategies can be exploited using combinations of species with contrasting strategies or using a single species to understand better their actual effects on OP mobilization and acquisition in agroecosystems. Briefly, a better understanding of the impact of P-acquisition strategies on OP mobilization and acquisition by plants, which are related to the multiple morphological and physiological traits and the interactions between them, is key in the management of OP availability. Compared to IP, the response of P

acquisition strategies to OP compounds and their impact on P acquisition from soils amended with various forms of OP have received much less attention. Crop species traits could be used to increase OP mobilization, helping to rethink P fertilization, sustain production, and recycle more OP in soils amended with organic amendments, but this requires a better understanding of the response of P-acquisition strategies to P sources, and their effect on OP mobilization and acquisition from soil minerals. In addition, understanding the trade-offs and effects of combining traits would allow us to unravel the complexity of the P form acquisition strategies and provide new knowledge for designing cultivated crop communities (i.e. multi-species crops) such as cover crops or intercrops to improve P acquisition and availability (Raven et al., 2018; Wen et al., 2019).

The aim of this study was to examine the response of P acquisition strategies toward P forms (IP and OP) in interactions with soil minerals and their consequences on OP availability and acquisition. We measured P-acquisition strategies in eight major plant species from various phylogenetic lineages grown on several complexes of IP and OP (IHP, and GLY) adsorbed on Fe oxyhydroxides (goethite) and clay minerals (kaolinite). We hypothesized that P-acquisition strategies (i.e. *foraging* and *mining*) differ in their responses to P sources, and this would promote greater OP availability and P acquisition from soil minerals. More specifically:

- (i) morphological traits involved in *P-foraging* strategy will increase P availability and uptake from OP. These traits would induce a diffusion gradient which, in turn, will favor the desorption process of the different forms of adsorbed OP and thus the availability of P and,
- (ii) physiological traits involved in *P-mining* strategy will increase P availability and uptake by modifying the pH and/or release carboxylates and phosphatases allowing to increase the turnover of the pools of sorbed OP via desorption, solubilization and mineralization processes;
- (iii) the acquisition of P from OP will be more significant under strategies involving *P-mining* than under those involving *P-foraging*, because OPs will be hydrolyzed by the strong activities of PME, and finally
- (iv) regardless of the strategy, the acquisition of P from OPs will be lower than that of IPs due to their strong sorption on minerals.

7.2 Materials and methods

7.2.1 Crop species, organic P compounds, and individual soil minerals

Two OP compounds, including inositol hexakisphosphate/phytate (IHP) and glycerophosphate (GLY), as well as inorganic P (KH_2PO_4), were selected for the experiments. Organic P compounds were initially selected because of their ubiquity in organic inputs and soils, the nature of phosphorus bonds, and their variable molecular sizes. Inorganic P forms were selected for comparison with organic P compounds.

Two minerals were chosen because of their contrasting properties and as representatives of the major soil minerals: goethite [Fe (OH)O] was chosen as representative of iron oxyhydroxide, and kaolinite as a clay mineral, particularly the 1:1 phyllosilicate. All mineral powders were purchased from Sigma-Aldrich Chemie and VWR (France) for the experiments. Eight (sub)species of diverse phylogenetic lineages (*Poaceae*: *Hordeum vulgare*, *Lolium perenne*; *Fabaceae*: *Lens culinaris* Medik., *Pisum sativum* subsp. *arvense* L., *Trifolium alexandrinum* L., *Vicia faba* L., *Lupinus albus*; *Hydrophyllaceae*: *Phacelia tanacetifolia* Benth.) were selected for their diverse morphologies, P-acquisition traits and relevance for the local context.

7.2.2 Preparation of minerals-OP Adsorption Complexes

The two soil minerals were loaded with the two OP compounds or inorganic P to serve as a P source for the different species. Solutions containing 1 g P L⁻¹ in 0.1 M KCl at pH 5.5 were prepared using the different P compounds. Goethite, and kaolinite was weighed in portions of 100 g into 1-L bottles. Then, 200 mL of 0.1 M KCl were added and the bottles were shaken for 24 hours at 25 °C to sufficiently hydrate the adsorption sites on the minerals. The pH was maintained at 5.5 ± 0.05 by adding 0.1 M HCl or NaOH solution. To start the formation of OP-mineral complexes, each of the 1 L bottles containing the soil minerals was filled with 800 mL of each P solution. In each bottle containing both the soil minerals and P compounds, some drops of hexanol were added to suppress microbial activities. Bottles were shaken on a mechanical shaker for 24 hours at 25 °C and then centrifuged (3000 G for 15 minutes). The 1 L bottles were distributed into several 250-mL bottles, centrifuged, and the supernatants were collected and removed. The produced P-loaded minerals were agitated in deionized water and frozen at -20 °C. To determine the amounts of adsorbed P, a certain volume of supernatants was immediately filtered through a 0.22-µm membrane syringe filter for P analysis. The concentration of P in the supernatants was determined colorimetrically (Ohno and Zibilske, 1991) after hydrolyzing OP to IP using the persulfate oxidation method (Peters and Van Slyke, 1932). The quantity of P adsorbed was calculated as the difference between the initial amount of P added and the remaining P amount in the supernatant at the end of the experiment. Total P concentration in a subsample of each P-loaded was also determined using the procedure by Ostrofsky (2012) and showed very similar values compared to the ones determined as the difference between the initial and the final P amount in the supernatant (differences were in the range of 3-5.5% for the organic mineral-P complexes and 1.5-5% for the inorganic mineral-P complexes). The P loadings of the mineral-P complexes produced are shown in table 22. All minerals were loaded to reach their adsorption maxima.

Table 22 : Maximum P adsorption capacity of the produced minerals-P adsorption complexes.

Go: goethite; K: kaolinite; IP: inorganic P; IHP: Myo-inositol hexakisphosphate and GLY: glycerophosphate

Mineral-P complexes	Quantity of P adsorbed ($\mu\text{g g}^{-1}$)
Go-IP	2810
Go-IHP	3742
Go-GLY	1398
K-IP	1736
K-IHP	6082
K-GLY	1222

7.2.3 Experimental Setup and Plant growth

To construct the experimental mesocosms, we filled 120×120 mm square polymer Petri dishes with sterilized coarse quartz sand, which is extremely poor in soil nutrients (Figure 28). The various P-mineral complexes prepared previously were then added to each square Petri dish and mixed with acid-washed quartz. Prior to the experiment, the substrates were sterilized by autoclaving at 121 °C for 2 h (Gómez-Suárez et al., 2020) to eliminate potential microorganisms, thus allowing the results to be attributed to the effect of root activity alone. To avoid any P limitation for the plants during the experiment, we provided a total amount of P that was found to be sufficient to meet the plants' needs (Gómez-Suárez et al., 2020). Thus, the amount of mineral-P complex added to the mixture was calculated to provide 40 mg of P in each treatment while the amount of quartz filled was approximately 100 g. The eight species were seeded one individual per square Petri dish per species and watered four times per week with water and a mixture of solution without P: Ca (NO₃)₂ (2 mmol L⁻¹), MgSO₄ (0.5 mmol L⁻¹), K₂SO₄ (0.7 mmol L⁻¹), KCl (0.1 mmol L⁻¹), MnSO₄ (0.5 $\mu\text{mol L}^{-1}$), CuSO₄ (0.5 $\mu\text{mol L}^{-1}$), ZnSO₄ (0.5 $\mu\text{mol L}^{-1}$), (NH₄)₆Mo₇O₂₄ (0.01 $\mu\text{mol L}^{-1}$) and Fe-EDTA (100 $\mu\text{mol L}^{-1}$). The devices were placed under controlled conditions (phytotron) with a 12h photoperiod, constant temperature (25 °C) and relative humidity (80%). Non-planted control treatments, in which the quartz-mineral-P complex had been incubated in similar devices without plants (hereafter referred to as the bulk substrate), were also performed. A total of 480 such devices were implemented: 8 species x 3 P compounds (IHP, GLY and IP) x 2 soil minerals (goethite and kaolinite) x 2 cropping conditions (ryegrass and bulk soil) x 5 replicates.



Figure 28 : Picture of the experimental Setup

7.2.4 Plant traits measurement

At harvest (25 days) plants were manually separated from the bulk soil with special care given to ensure minimum damage. Rhizosheath adhering to the roots up to a maximum of 2 mm after shaking was collected and stored at $-20\text{ }^{\circ}\text{C}$ for further analysis. Roots were then immersed in 0.20 mM CaCl_2 for 1 h, after removing any remaining soil particles by quickly rinsing with CaCl_2 . The CaCl_2 volume was adjusted to ensure a complete immersion of the root system. The solution was then sampled and stored at $-20\text{ }^{\circ}\text{C}$ before measuring carboxylic acid exudation by reversed phase column liquid chromatography (RPLC) (Cawthray 2003; Yacoumas et al. 2020). Briefly, an acid mobile phase (93% $25\text{ mM KH}_2\text{PO}_4$ at pH 2.5 and 7% methanol) allowed a good resolution of five acids (citric, fumaric, maleic, malic, malonic) on a C18 column with a 15 min elution time and a 1 mL min^{-1} flow rate. Total carboxylate release rate was later calculated as the sum of all previously mentioned acids (see Table 23 for abbreviations).

7.2.5 Morphological traits

Aboveground biomass and roots were separated by cutting the stem 1 cm above the first visible root. Roots were then scanned while being immersed in deionised water using an Epson Scanner perfection V800 (Regent Instruments Inc., Québec, Qc, Canada) to produce a 600-dpi image. The image was analysed using WinRHIZO Regular software V.2016a (Regent Instruments Inc., Québec, Qc, Canada) to determine root traits including root surface area (RSA), the percentage of fine root (FR), defined here as length of roots with a diameter < 0.5 mm, and root length density (RLD). After 48 h drying at 55 °C, scanned roots were weighed to calculate specific root length (SRL).

7.2.6 Nutrient uptake

Shoots and roots were then dried at 60 °C for 72 h, weighed, and crushed before analysis. The concentration of P in shoots and roots was determined colorimetrically (Ohno and Zibilske, 1991) after mineralization by 65% HNO₃ digestion directly in a microwave Teflon vessel (Lange et al., 2014). The P concentrations in the seeds of the different species were also measured. The amount of P in seeds and plants (mg) was then calculated as the concentrations multiplied by their biomasses, respectively. Finally, the amount of P taken up by plants (mg) was calculated after deducting the amount of P supplied by seeds (mg).

7.2.7 Rhizosphere and bulk soil analyses

After defrosting, acid phosphomonoesterase activity in the rhizosphere (PME) was measured with a modified buffer at pH 6.5 (Tabatabai and Bremner 1969). Briefly, phosphatase activity was assessed via production of p-nitrophenol from sodium p-nitrophenyl phosphate during a 1 h incubation at 37 °C with 0.5 g dry soil, 0.2 mL toluene, 4 mL modified buffer and 1 mL substrate. p-Nitrophenol release was determined spectrophotometrically at 410 nm after stopping the reaction with 4 mL 0.5 M NaOH and 1 mL 0.5 M CaCl₂ and filtering. Rhizosphere pH was measured on 2 g equivalent dry soil with a 1:10 soil to solution ratio. Δ pH between rhizosphere and bulk soil from unplanted pots postgrowth was then calculated.

7.2.8 Data analysis

Data were statistically analyzed with R software (R version 4.1.3). The impact of factors (Species, P compounds, soil minerals, and their combined effect) on all measured morphological/architectural and physiological traits as well as P uptake and total biomass production was modeled by generalized linear models (GLM) using the "FactomineR" package. The GLM model was used to avoid mathematical

transformation of the variables and to get rid of the strict assumption that "the residuals will follow a conditionally normal distribution"(McCullagh and Nelder, 2019; Warton et al., 2016) and allow the use of a variety of other distributions of the exponential family for the residuals (Cohen et al., 2014). All factors were tested individually, and the models were compared based on second-order Aikake information (AICc), with the lowest relative value being considered the best fit. The ANOVA of the best-fit GLM model with a chi-square test generated the deviance analysis table that gave the significance level of all factors. Statistical analyses to compare the average results of percent P recovered, enzyme activities, and biomass were performed using a one-way analysis of variance (ANOVA) followed by Tukey's honest significant difference (HSD) test ($p < 0.05$). As multiple differences were observed between minerals, further analysis was performed separately for each soil minerals type. To identify the main covariation in P-acquisition traits and rhizosphere processes, a principal component analysis (PCA) was performed using the "FactomineR" package on log-transformed data (Lê et al. 2008). The number of components was selected to represent more than 75% of the total variability. Relation between traits were confirmed with Spearman correlation tests as some data did not fulfil the condition of normality. Classification of species on principal components (HCPC) was then performed to define groups species with similar patterns of P-acquisition traits and influence on the rhizosphere. Classification was performed with a confidence level of over 80%. Differences between clusters/groups for each individual factor were then investigated, either with tests of variance (ANOVA and post-hoc test of Tukey) or non-parametric tests (Kruskall-Wallis test + post-hoc test of Mann Whitney). The selection of the combinations of traits that give the best model fits to predict P uptake was performed in R software with the *stepAIC* () and *bestglm* () functions, which are based on the stepwise and best subset approaches. The best-fitting models have a lower AICc and a Δ AICc closer to zero. Differences between models were tested with ANOVA as well as the criteria Δ AICc. Complementary to GLM regression, partial square path modelling (PLS) was performed to underline the relative ability of trait combinations and type for predicting P uptake. The main goal of PLS was to characterize the contribution of each strategy to P uptake and highlight the main traits involved in these strategies for P acquisition, and how this varies especially with P form. Three clusters of variables, or "latent variables" were defined, respectively, the "morphological traits" variables encompassing root surface area, SRL, fine root percentage, root length density, the "physiological traits" variables encompassing PME activity, carboxylate release and change in rhizosheath pH and the "intermediate traits" variables encompassing foliar [P] and mixed of the previous variables. To ensure the condition of positively correlated variables in a latent variable, the sign of some variables was changed. Variables and components were selected based on their loading and correlation as suggested in Sanchez (2013). Overall model quality was evaluated with the Goodness of Fit (GoF) index. Analyses were performed with the package "plsrm" version 0.4.9. All tests were performed in R version 3.6.0 with a significance level of 0.05.

Table 23: List of abbreviations and associated units

Variable	Abbreviation	Unit
Change in rhizosheath	ΔpH	-
Percentage roots with diameters less than 0.5 mm	FR	-
Foliar phosphorus concentration	Leaf[P]	mgPpot ⁻¹
Acid phosphomonoesterase activity	PME	$\mu\text{g nitrophenol g}^{-1} \text{h}^{-1}$
Root length density	RLD	cm cm^{-3}
Root surface area	RSA	cm ²
Specific root length	SRL	m g^{-1}
Total carboxylate release rate	TCE	$\mu\text{mol g root}^{-1} \text{h}^{-1}$
Inositol hexakisphosphate	IHP	-
Glycerophosphate	GLY	-
P uptake (mg/pot) and (g).		mgPpot ⁻¹
P available		mgPpot ⁻¹
Biomass		g

7.3 Results

7.3.1 Highlighting phosphorus acquisition strategies among P forms in crop species

Figure 29 shows the results of the principal components analysis (PCA) performed on P-acquisition strategies and leaf [P] concentration in IP and OP forms. The two principal components extracted by PCA accounted for 54.9% and 56.2% of the variance in IP and OP respectively. In both P forms, the PC1 was negatively associated with fine root percentage and SRL, and positively related to root length density, root surface area and total carboxylate release rate (Figure 29). The PC2 was negatively correlated by leaf [P] concentration and root length density, and positively related to rhizosheath pH change. Overall, on both forms of P, species clustered into four groups of P acquisition strategies (Figure 29). The first "physiological/ exudation" group C1 included *Vicia faba*, *Pisum sativum*, and *Lupinus albus*. It had positive values on PC1 and showed the greatest exudation of carboxylic acids, an important activity of PME in the rhizosheath, as well as the lowest fine root percentage and SRL. The second "intermediate/morphological" group C2 encompassed *Hordeum vulgare*. This group were spread on negative values on PC1 and 2. It presented the lowest carboxylate release while presenting the highest leaf [P] concentration and RLD and an important fine root percentage compared with other groups. The third "intermediate" group C3 encompassed *Lens culinaris*. It presented intermediate values of all measured morphological/architectural and physiological traits, and important leaf [P] content. Finally, the fourth "morphological" group C4, encompassing *Lolium perenne*, *Trifolium alexandrinum*, and *Phacelia tanacetifolia*, presented low to the intermediate expression of P mining traits, a high fine root percentage and the highest SRL observed in all groups. It had negative values on PC1.

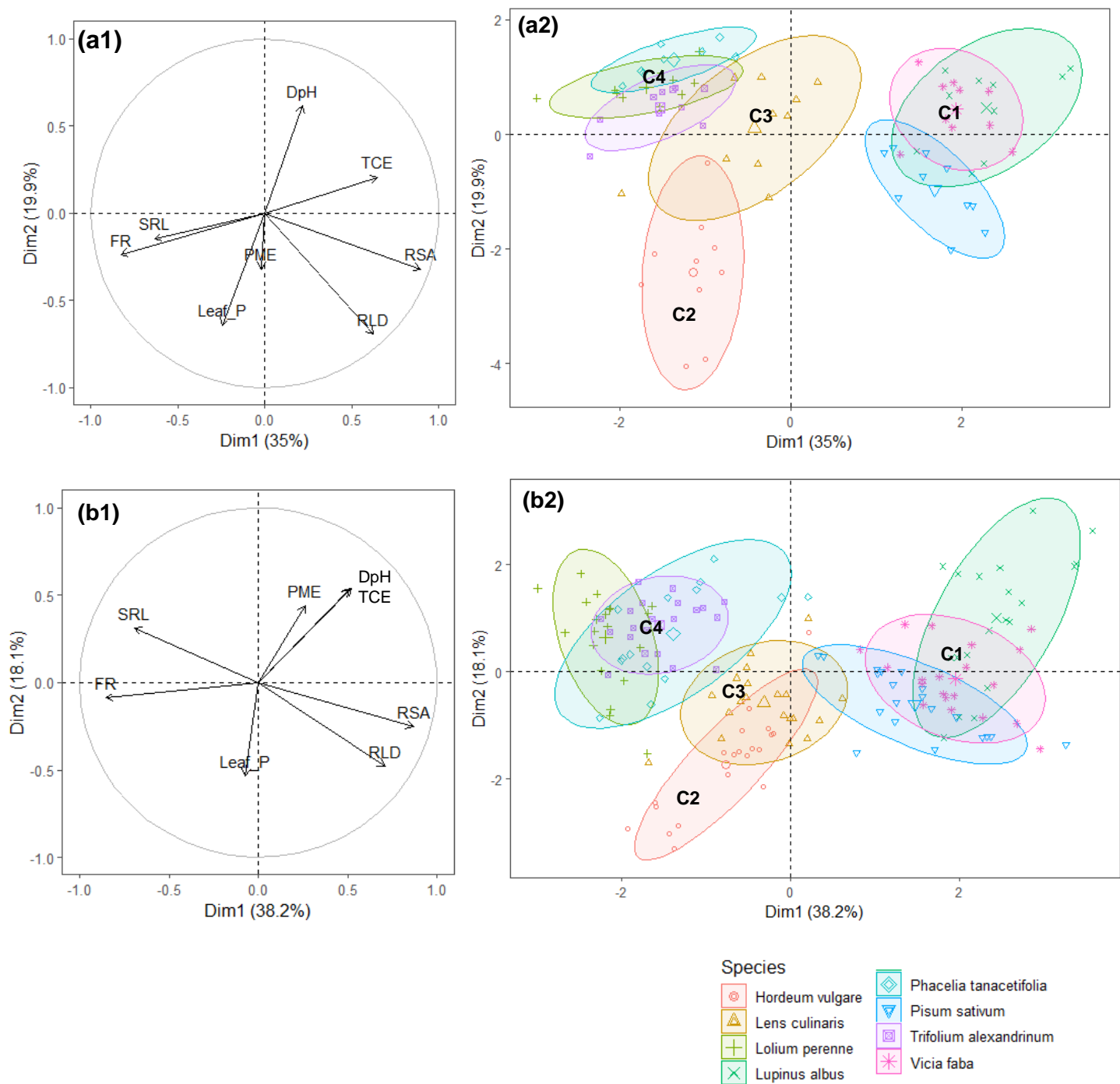


Figure 29 : Principal component analysis (PCA) of P-acquisition strategies involved in phosphorus acquisition from inorganic P form (a) and organic P forms (IHP and GLY) (b).

Analysis was performed irrespective of minerals. (1) Variable covariation along first two components, (2) groups/clusters formed with classification on PCA. Abbreviations: DpH: change in rhizosheath pH; FR: percentage roots with diameters less than 0.5 mm; Leaf[P]: foliar phosphorus concentration; PME: acid phosphomonoesterase activity; RLD: root length density; RSA: root surface area; SRL: specific root area; TCE: total carboxylate release rate.

7.3.2 Influence of species, P forms and soil minerals f and their interactions on P acquisition traits

All measured morphological/architectural and physiological traits as well as P acquisition and total biomass production were significantly affected by species ($P < 0.0001$) and their interaction with P forms ($P < 0.01$) (Table 24). Mineral-species interactions had a significant effect on all measured traits ($P < 0.001$) except for fine roots percentage and total carboxylate release. Interactions between all factors (Species x Minerals x P forms) also affected the majority of plant traits ($P < 0.0001$).

Table 24 : The generalized linear models (GLM) results testing the impact of factors (species, P compounds, soil minerals, and their combined effect) on P-acquisition traits, total P uptake, and biomass production.

Abbreviations: Δ pH: change in rhizosheath pH; FR: percentage roots with diameters less than 0.5 mm; Leaf_P: foliar phosphorus concentration; PME: acid phosphomonoesterase activity; RLD: root length density; RSA: root surface area; SRL: specific root area; TCE: total carboxylate release rate; AICc second order Aikake's information. $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

		Minerals		P forms		Species		Minerals x P forms		Species x Minerals		Species x P forms		Species x Minerals x P forms	
		<i>P</i>	<i>AICc</i>	<i>P</i>	<i>AICc</i>	<i>P</i>	<i>AICc</i>	<i>P</i>	<i>AICc</i>	<i>P</i>	<i>AICc</i>	<i>P</i>	<i>AICc</i>	<i>P</i>	<i>AICc</i>
Morphological/ architectural traits	RSA	**	2201	Ns	2203	***	1687	Ns	2209	*	1686	Ns	1711	Ns	1739
	RLD	***	752	Ns	755	***	342	Ns	759	**	335	*	357	Ns	378
	SRL	*	2409	Ns	2411	***	2155	Ns	2416	***	2150	***	2131	Ns	2150
	FR	Ns	-8.3	Ns	-6.5	***	-393	*	-1.4	Ns	-379	***	-418	***	-420
Physiological traits	Δ pH	***	-210	***	-271	***	-332	***	-281	***	-499	***	-361	***	-686
	PME	**	74.7	Ns	80.2	***	30	Ns	80.8	***	5.17	***	31	Ns	23
	TCE	Ns	2682	**	2681	***	2403	Ns	2687	Ns	2418	***	2392	***	2424
	Leaf [P]	Ns	-853	**	-855	***	-1012	***	-856	***	-1017	*	-1007	***	-1026
P acquisition	P uptake	Ns	-515	Ns	-513	***	-7716	***	-515	**	-714	***	-729	**	-736
	Available _P	***	-123	***	-130	***	-173	**	-139	*	-175	***	-212	***	-228
	Biomass	Ns	-187	Ns	-185	***	-782	Ns	-179	***	-790	***	-795	***	-807

7.3.3 Response of P acquisition traits and strategies to P forms

The P acquisition traits of species within the P acquisition strategy groups varied among P forms, with significant responses for some traits (Tables 25 and 26). In *Lolium perenne* (group C4) and *Phacelia tanacetifolia* (C4), only total carboxylate release and fine roots percent differed significantly among P forms, and their values were significantly greater under OP forms. Total carboxylate release was found to be significant with *Lolium perenne*, and fine root percentage with *Phacelia tanacetifolia* in both OP forms. PME activity and other traits were also significant under OP forms but not significant from IP

forms. Traits were significantly higher in the IHP form than in the GLY form. *Pisum sativum* (C1) and *Hordeum vulgare* (C2) species showed significant variation of rhizosheath pH and total carboxylate release as well as SRL and fine root percentage in response to P forms. However, unlike the previous species, these traits were significantly higher on IP form than on OP forms. Finally, the remaining species, *Lupinus albus* (C1), *Vicia faba*(C1), *Lens culinaris* (C3), and *Trifolium alexandrinum* (C4) showed different physiological (Rhizosheath pH change, total carboxylate release and PME activity) and morphological (SRL, fine root percentage, RLD) traits between the IP and OP forms. Rhizosheath pH change was significantly elevated on the IP form, however, on the OP forms (IHP and GLY), it was mainly total carboxylate release, PME activity, and morphological traits (SRL, fine root percentage, RLD) that were significantly higher. Within these species, *Lens culinaris* (C3) and *Trifolium alexandrinum* showed more physiological and morphological traits in the IHP source, while in the GLY source it was rather *Lupinus albus* (C1) and *Vicia faba*(C1). In general, these species showed only physiological traits on goethite, whereas on kaolinite, we observed the expression of both morphological and physiological traits. Furthermore, for some species, the expression of traits differed between minerals but was generally not significant.

7.3.4 Effect of crop species and their P acquisition strategies on OP availability and P acquisition

The response of P acquisition strategies to P forms affected species P acquisition, which depended strongly on P forms for some species and on the interaction between P form and mineral for others (Table 25 and 26). We found that irrespective of soil minerals, the P acquisition traits of two of the eight species: *Vicia faba*(C1) and *Pisum sativum*(C1) resulted in significantly high P acquisition and available P from OP forms ($P < 0.01$) and also some significantly high biomass productions (Table 25 and 26). Specifically, among the OP forms, the acquisition of P and available P in these species was higher from the IHP as compared to GLY forms and the biomass produced higher on GLY form. By contrast *Lolium perenne*(C4) had a globally higher P uptake on IP form compared to OP forms. Conversely, compared with previous species, *Lens culinaris* (C3), *Hordeum vulgare* (C2) and *Trifolium alexandrinum* had a globally equivalent P uptake between P forms even though the available P was slightly higher on the IP form. The species *Phacelia tanacetifolia*, *Lupinus albus* had a highly soil mineral dependent P acquisition. On goethite, the P acquisition strategies expressed by these species led to significantly high P acquisition from IP forms ($P < 0.05$), whereas on kaolinite, P acquisition was significantly high from OP forms. Among OP forms, available P content and P uptake were higher in GLY forms than in IHP forms. In general, the biomass produced was higher on the IP form for these species and Available P was not different between P forms and minerals.

Table 25 : Mean values ± standard error and P-acquisition strategies by species among different P forms on goethite.

FR Fine root percentage (<0.5 mm diameter), Leaf [P] Leaf phosphorus concentration (mg P g⁻¹), PME Phosphomonoesterase activity (µg nitrophenol g⁻¹ hour⁻¹), RLD Root length density (cm cm⁻³), SRL Specific root length (m g⁻¹), TCE Total carboxylate release rate (µmol g root⁻¹ hour⁻¹), ΔpH Change in rhizosheath pH, P uptake (mgPpot⁻¹), P available (mgPpot⁻¹) and biomass (g).

Species/Clusters	P forms	RSA	RLD	SRL	FR	ΔpH	PME	TCE	Leaf [P]	Available P	P uptake	Biomass
C1: Physiological/exudation												
<i>Lupinus albus</i>	IP	67,52±	2,62±	26,62±7	0,41±	-0,42±	18,82±	445,5±	0,05±	0,29±	0,20±	0,65±
		18,32	0,61	33	0,09	0,066	0,137	155,9	0,04	0,15	0,06	0,04
	IHP	74,37±	2,86±	23,96±	0,36±	-0,15±	18,83±	269,5±	0,13±	0,06±	0,14±	0,65±
		9,159	0,15	4,877	0,05	0,040	0,142	89,24	0	0,06	0,00	0,02
	GLY	67,64±	2,69±	35,97±	0,39±	-0,06±	19,01±	551,2±	0,02±	0,03±	0,10±	0,54±
		17,69	0,73	10,26	0,03	0,020	0,053	160,0	0,00	0,00	0,08	0,11
<i>p-value</i>		<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	0.001	0.04	0.02	0.0001	0.01	<i>Ns</i>	<i>Ns</i>
<i>Pisum sativum</i>	IP	112,1±	5,22±	63,99±	0,61±	-0,23±	18,82±	144,4±	0,04±	0,17±	0,23±	0,40±
		6,805	0,98	44,43	0,05	0,013	0,047	22,74	0,01	0,09	0,03	0,10
	IHP	132,1±	4,38±	41,56±	0,61±	-0,15±	18,79±	102,1±	0,05±	0,24±	0,26±	0,41±
		57,29	0,77	11,93	0,09	0,017	0,128	20,35	0,01	0,08	0,01	0,06
	GLY	79,97±	2,84±	10,83±	0,52±	-0,27±	18,65±	110,9±	0,02±	0,20±	0,20±	0,56±
		12,57	0,47	6,136	0,04	0,092	0,219	28,02	0,00	0,09	0,09	0,18
<i>p-value</i>		<i>Ns</i>	0.01	0.02	<i>Ns</i>	0.01	<i>Ns</i>	0.03	0.01	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>
<i>Vicia faba</i>	IP	70,93±	2,16±	8,152±	0,21±	-0,20±	18,52±	145,3±	0,05±	0,18±	0,06±	0,62±
		17,32	0,57	1,257	0,05	0,021	0,157	19,26	0,01	0,28	0,01	0,08
	IHP	72,93±	2,29±	8,102±	0,22±	-0,15±	18,50±	111,7±	0,03±	0,16±	0,28±	0,67±
		15,55	0,43	1,664	0,04	0,017	0,240	25,57	0,00	0,03	0,06	0,28
	GLY	84,67±	2,75±	9,450±	0,29±	-0,14±	18,72±	128,5±	0,03±	1,21±	0,07±	0,70±
		30,25	1,29	3,652	0,06	0,013	0,241	78,25	0,00	0,80	0,05	0,25
<i>p-value</i>		<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	0.001	<i>Ns</i>	<i>Ns</i>	0.01	0.0001	<i>Ns</i>	
C2 : intermediate / morphological												
<i>Hordeum vulgare</i>	IP	32,72±	3,18±	88,77±	0,81±	-1,02±	18,91±	11,70±	0,15±	0,35±	0,16±	0,08±
		11,62	1,18	29,68	0,03	0,134	0,037	7,766	0,05	0,56	0,04	0,01
	IHP	33,25±	3,22±	87,67±	0,81±	-0,72±	18,75±	6,368±	0,12±	0,23±	0,13±	0,08±
		5,344	0,49	15,68	0,03	0,043	0,168	1,599	0,03	0,14	0,02	0,00
	GLY	34,39±	3,12±	84,39±	0,80±	-0,34±	18,65±	6,056±	0,11±	0,09±	0,15±	0,08±
		5,702	0,27	32,00	0,03	0,170	0,086	1,679	0,06	0,14	0,06	0,01
<i>p-value</i>		<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	0.0001	0.01	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	
C3 : Intermediate												
<i>Lens culinaris</i>	IP	31,47±	1,59±	24,13±	0,63±	-0,31±	18,40±	33,14±	0,11±	0,48±	0,18±	0,20±
		13,14	0,61	7,599	0,01	0,010	0,010	28,15	0,10	0,60	0,10	0,03

	IHP	38,75±	1,94±	40,19±	0,60±	-0,22±	18,50±	60,97±	0,07±	0,05±	0,13±	0,14±
		11,97	0,53	18,64	0,08	0,004	0,208	24,02	0,04	0,00	0,03	0,02
	GLY	33,02±	1,74±	33,29±	0,62±	-0,26±	18,45±	40,08±	0,04±	0,43±	0,13±	0,14±
		8,719	0,39	12,57	0,08	0,043	0,065	2,513	0,02	0,13	0,01	0,04
	<i>p</i> -value	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	0,001	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	0,04
C4: Morphological												
<i>Lolium perenne</i>	IP	8,264±	0,65±	102,3±	0,83±	-0,25±	18,80±	26,53±	0,03±	0,98±	0,04±	0,014±
		5,021	0,32	48,20	0,04	0,008	0,177	8,880	0,01	0,70	0,01	0,00
	IHP	5,689±	0,45±	185,7±	0,86±	-0,27±	18,82±	74,56±	0,01±	0,05±	0,02±	0,005±
		4,339	0,23	100,8	0,09	0,041	0,081	40,45	0,00	0,98	0,00	0,00
	GLY	8,277±	0,75±	182,7±	0,85±	-0,24±	18,85±	34,15±	0,01±	0,45±	0,02±	0,008±
		4,338	0,37	78,13	0,05	0,035	0,088	3,475	0,00	0,21	0,00	0,00
<i>p</i> -value	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	0,01	0,01	<i>Ns</i>	0,01	0,001	
<i>Phacelia tanacetifolia</i>	IP	1,625±	0,11±	84,38±	0,50±	-0,28±	18,41±	42,43±	0,07±	0,17±	0,07±	0,01±
		1,301	0,11	79,29	0,16	0,009	0,032	7,501	0,02	0,08	0,02	0,00
	IHP	0,943±	0,08±	60,98±	0,79±	-0,32±	18,57±	225,0±	0,05±	0,22±	0,05±	0,00±
		0,459	0,03	25,88	0,12	0,050	0,169	222,1	0,03	0,15	0,03	0,00
	GLY	1,455±	0,11±	85,23±	0,73±	-0,32±	18,69±	100,9±	0,05±	0,63±	0,05±	0,00±
		0,770	0,07	56,59	0,05	0,020	0,208	70,13	0,03	0,42	0,03	0,00
<i>p</i> -value	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	0,03	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	
<i>Trifolium alexandrinum</i>	IP	10,98±	0,88±	108,7±	0,80±	-0,28±	19,11±	50,17±	0,05±	0,32±	0,06±	0,03±
		4,528	0,37	111,4	0,04	0,026	0,128	16,90	0,02	0,14	0,02	0,01
	IHP	8,417±	0,65±	148,1±	0,76±	-0,23±	19,10±	54,77±	0,06±	0,29±	0,07±	0,01±
		4,595	0,33	53,07	0,07	0,035	0,080	38,31	0,02	0,15	0,02	0,00
	GLY	8,796±	0,62±	92,33±	0,76±	-0,19±	18,78±	56,87±	0,05±	0,09±	0,07±	0,03±
		4,200	0,22	27,93	0,08	0	0,114	23,29	0,02	0,11	0,03	0,01
<i>p</i> -value	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	0,001	0,001	<i>Ns</i>	<i>Ns</i>	0,04	<i>Ns</i>	0,01	

Table 26: Mean values ± standard error and P-acquisition strategies by species among different P forms on kaolinite.

FR Fine root percentage (<0.5 mm diameter), Leaf [P] Leaf phosphorus concentration (mg P g⁻¹), PME Phosphomonoesterase activity (µg nitrophenol g⁻¹ hour⁻¹), RLD Root length density (cm cm⁻³), SRL Specific root length (m g⁻¹), TCE Total carboxylate release rate (µmol g root⁻¹ hour⁻¹), ΔpH Change in rhizosheath pH, P uptake (mgPpot⁻¹), P available (mgPpot⁻¹) and biomass (g).

Species/Clusters	P forms	RSA	RLD	SRL	FR	ΔpH	PME	TCE	Leaf [P]	Available P	P uptake	Biomass
C1: Physiological/exudation												
<i>Lupinus albus</i>	IP	71,86±	2,63±	25,73±	0,32±	-0,03±	19,08±	446,8±	0,03±	0,05±	0,15±	0,58±
		11,44	0,43	7,884	0,06	0,005	0,076	205,4	0,00	0,02	0,08	0,06

<i>Pisum sativum</i>	IHP	74,66±	2,85±	19,04±	0,38±	-0,02±	19,03±	143,3±	0,03±	0,04±	0,18±	0,65±
		5,597	0,26	2,518	0,03	0,004	0,155	185,2	0,00	0,00	0,02	0,04
	GLY	61,03±	2,60±	43,13±	0,43±	-0,07±	19,07±	693,4±	0,06±	0,03±	0,22±	0,53±
		12,31	0,38	8,131	0,05	0,040	0,105	237,6	0,04	0,02	0,04	0,08
	p-value	Ns	Ns	0.001	0.02	0.01	Ns	0.01	Ns	Ns	Ns	0.03
<i>Pisum sativum</i>	IP	83,95±	3,29±	20,98±	0,58±	-0,30±	18,86±	110,9±	0,04±	0,19±	0,17±	0,37±
		8,633	0,49	3,961	0,04	0,017	0,209	30,65	0,03	0,05	0,12	0,17
	IHP	62,43±	1,85±	18,46±	0,51±	-0,23±	18,80±	97,55±	0,03±	0,13±	0,19±	0,38±
		31,58	0,55	7,455	0,03	0,041	0,064	25,00	0,00	0,13	0,09	0,04
	GLY	75,86±	2,54±	11,72±	0,53±	-0,26±	18,86±	88,00±	0,03±	0,20±	0,27±	0,56±
		7,307	0,32	4,682	0,03	0,031	0,144	38,69	0,00	0,09	0,04	0,11
p-value	Ns	0.01	Ns	Ns	0.01	Ns	Ns	Ns	Ns	Ns	Ns	
<i>Vicia faba</i>	IP	85,22±	2,35±	6,320±	0,17±	-0,39±	18,65±	86,10±	0,04±	0,09±	0,05±	1,14±
		18,79	0,34	1,475	0,06	0,125	0,309	43,42	0,03	0,02	0,03	0,21
	IHP	68,28±	2,25±	8,267±	0,26±	-0,31±	18,87±	80,17±	0,02±	0,23±	0,19±	0,67±
		14,04	0,44	1,688	0,03	0,046	0,144	37,20	0,00	0,02	0,06	0,07
	GLY	75,05±	2,72±	17,17±	0,36±	-0,22±	19,12±	179,0±	0,03±	0,75±	0,21±	0,50±
		27,32	1,07	6,048	0,12	0,026	0,051	120,7	0,00	0,31	0,15	0,27
p-value	Ns	Ns	0.001	0.01	0.01	0.01	Ns	Ns	0.0001	0.05	0.001	
C2 : intermediate / morphological												
<i>Hordeum vulgare</i>	IP	32,31±	3,04±	79,17±	0,83±	-0,21±	19,29±	5,648±	0,19±	0,07±	0,21±	0,08±
		4,568	0,42	18,32	0,01	0,058	0,848	1,274	0,05	0,03	0,05	0,00
	IHP	35,04±	3,11±	87,10±	0,80±	-0,19±	18,78±	8,774±	0,10±	0,23±	0,13±	0,08±
		4,681	0,54	19,26	0,01	0,005	0,560	1,372	0,01	0,04	0,01	0,00
	GLY	28,55±	2,54±	66,06±	0,79±	-0,19±	18,92±	3,049±	0,18±	0,08±	0,21±	0,18±
		3,954	0,30	38,87	0,03	0,013	0,042	2,698	0,04	0,11	0,04	0,14
p-value	Ns	Ns	Ns	Ns	Ns	Ns	0.001	0.01	0.01	0.01	0.01	
C3 : Intermediate												
<i>Lens culinaris</i>	IP	31,64±	1,63±	60,23±	0,62±	-0,25±	18,44±	44,82±	0,12±	0,17±	0,16±	0,12±
		9,680	0,48	61,21	0,10	0,034	0,014	7,812	0,12	0,15	0,10	0,06
	IHP	27,51±	1,39±	46,72±	0,61±	-0,19±	18,82±	53,57±	0,11±	0,35±	0,17±	0,13±
		12,57	0,47	21,44	0,06	0,008	0,229	7,099	0,02	0,20	0,03	0,07
	GLY	16,38±	0,91±	25,55±	0,64±	-0,27±	18,69±	23,19±	0,09±	0,17±	0,21±	0,10±
		8,730	0,57	16,80	0,13	0,056	0,285	18,41	0,08	0,18	0,03	0,04
p-value	Ns	Ns	Ns	Ns	0.01	0.04	0.01	Ns	Ns	Ns	Ns	
C4: Morphological												
<i>Lolium perenne</i>	IP	8,613±	0,65±	122,2±	0,80±	-0,32±	18,62±	49,97±	0,02±	0,36±	0,03±	0,01±
		2,900	0,23	125,6	0,05	0,028	0,247	19,95	0,00	0,25	0,00	0,00

	IHP	6,815±	0,59±	89,13±	0,84±	-0,37±	18,57±	25,37±	0,02±	0,08±	0,03±	0,01±	
		4,960	0,35	44,95	0,05	0,101	0,174	12,25	0,00	0,08	0,00	0,00	
	GLY	9,676±	0,91±	146,5±	0,86±	-0,38±	18,69±	34,89±	0,03±	0,79±	0,04±	0,02±	
		3,520	0,32	93,90	0,02	0,031	0,186	37,52	0,03	0,50	0,03	0,04	
	<i>p-value</i>		<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>0.01</i>	<i>Ns</i>	<i>Ns</i>
<i>Phacelia tanacetifolia</i>	IP	1,482±	0,12±	91,67±	0,77±	-0,26±	18,70±	111,4±	0,02±	0,21±	0,02±	0,005±	
		0,592	0,03	28,10	0,08	0,060	0,294	114,8	0,00	0,16	0,00	0,00	
	IHP	1,586±	0,10±	78,00±	0,46±	-0,17±	18,57±	412,3±	0,05±	0,26±	0,05±	0,009±	
		0,876	0,08	58,20	0,14	0,025	0,260	36,02	0,00	0,13	0,00	0,00	
	GLY	1,185±	0,09±	68,11±	0,83±	-0,24±	18,63±	39,38±	0,02±	0,73±	0,02±	0,008±	
		0	0	9,536	0	0,011	0,345	46,61	0	0,71	0	0	
<i>p-value</i>		<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>0.01</i>	<i>Ns</i>	<i>Ns</i>	<i>0.001</i>	<i>0.001</i>	<i>Ns</i>	<i>0.0001</i>	<i>0.001</i>	
<i>Trifolium alexandrinum</i>	IP	5,545±	0,39±	64,27±	0,76±	-0,23±	18,96±	27,33±	0,07±	0,14±	0,09±	0,02±	
		0,775	0,05	15,17	0,03	0,008	0,007	13,04	0,02	0,09	0,02	0,00	
	IHP	8,193±	0,60±	165,1±	0,73±	-0,13±	18,58±	69,54±	0,05±	0,13±	0,06±	0,02±	
		1,885	0,12	68,92	0,10	0,034	0,155	25,67	0,03	0,05	0,03	0,00	
	GLY	6,144±	0,48±	97,19±	0,81±	-0,26±	18,76±	67,64±	0,04±	0,24±	0,06±	0,02±	
		0,977	0,06	26,57	0,02	0,210	0,262	19,06	0,01	0,15	0,01	0,00	
<i>p-value</i>		<i>0.02</i>	<i>0.01</i>	<i>0.01</i>	<i>Ns</i>	<i>Ns</i>	<i>0.01</i>	<i>0.01</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	<i>Ns</i>	

7.3.5 Modeling the relationships between leaf and root traits combination on P acquisition from OP

The overall relationships between P uptake and factors involved in group formation were investigated with GLM (Table 27). The best-fitting models have a lower AICc and a Δ AICc closer to zero. PLS was used to highlight the combinations of traits and the type of P acquisition strategies that best predict P uptake (Figure 30). Because the best selected models were similar for both mineral types, we presented the results by P forms (Table 27 and Figure 30).

For species expressing physiological traits, the best model fit on the IP form was achieved with total carboxylate release alone. On the IHP form, the best fit was with a combination of carboxylate release and PME activity and on the GLY form with a combination of carboxylate release and rhizosheath acidification. For species with intermediate traits, SRL, fine root percent, PME activity and leaf [P] was the best predictor of P uptake on the IP form. RSA, RLD and leaf [P] combination provided the best fit on the IHP form while on the GLY form it was RLD, PME activity and leaf [P] that provided the most suitable fit. For morphologically trait-using species, RLD and percent fine roots gave the best model fit for P acquisition on the IP form. The addition of SRL to the previous combination was also a better predictor, but performed worse than models incorporating both RLD and fine root percentage.

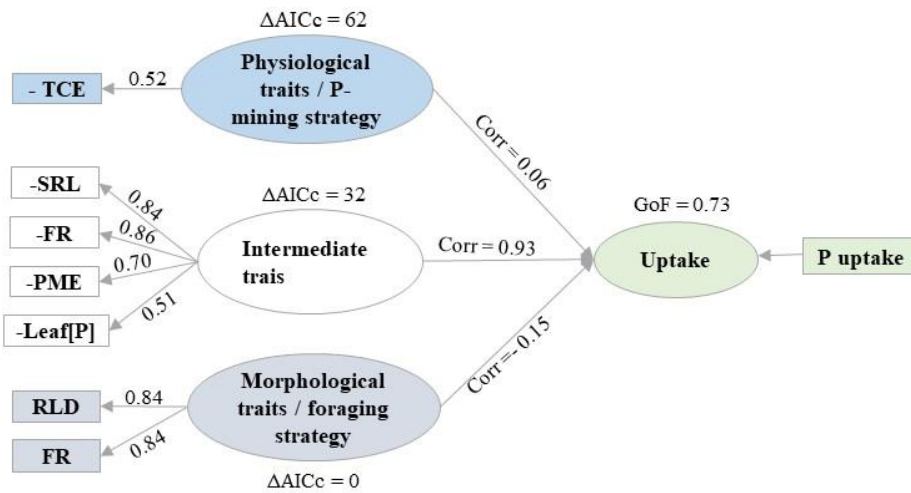
The model incorporating RLD was the best predictor on the IHP form, whereas on the GLY form, the best predictor was SRL. The combination of RLD and RSA was also a good predictor on the IHP form, but performed poorly compared with the model incorporating only RLD. Similarly, for GLY form, the RSA and SRL combination was also a good predictor, but with poor fit compared with the model with only SRL. The PLS approach gave similar results to the GLM model. On the IP form ($GoF_{PLS} = 0.73$), total carboxylate release was the best single predictor of the physiological components. Fine root percentage topped the intermediate component contributors, followed by SRL, PME activity, and leaf [P]. SRL contributed as much as fine root percentage to the morphological components. In this form of IP, it was found that the intermediate component had the highest predictive weight ($corr = 0.93$), followed far behind by the morphological component ($corr = 0.15$). The physiological component was found to have very negligible predictive capacity ($corr = 0.06$). On the IHP form, PLS analysis ($GoF = 0.72$) highlighted the importance of the intermediate component ($corr = 0.81$), as well as the physiological component ($corr = 0.17$), whereas the morphological parameter showed poor predictive performance. PME activity and total carboxylate release were found to be the most significant contributors for the physiological component, respectively. For the intermediate component, it was leaf [P], RLD, and RSA, respectively. The RLD was the unique contributor for the morphological component. On GLY form, and as for other forms of P, the greatest weight was associated with the intermediate component ($corr = 0.58$, $AICc = 51$) followed by the morphological component ($corr = 0.22$, $AICc = 0$); for this form, the lowest predictive ability was from the morphological component. RLD and PME activity had the greatest impact on the intermediate component, followed by leaf [P]. SRL was the only contributor to the morphological component. In summary, the PLS analysis revealed that the intermediate component had the highest predictive ability on all forms of P. The physiological component was the second most important contributor on IHP while on GLY it was the morphological component.

Table 27: Selected models fitted to phosphorus uptake sorted from best fit to worst by strategies

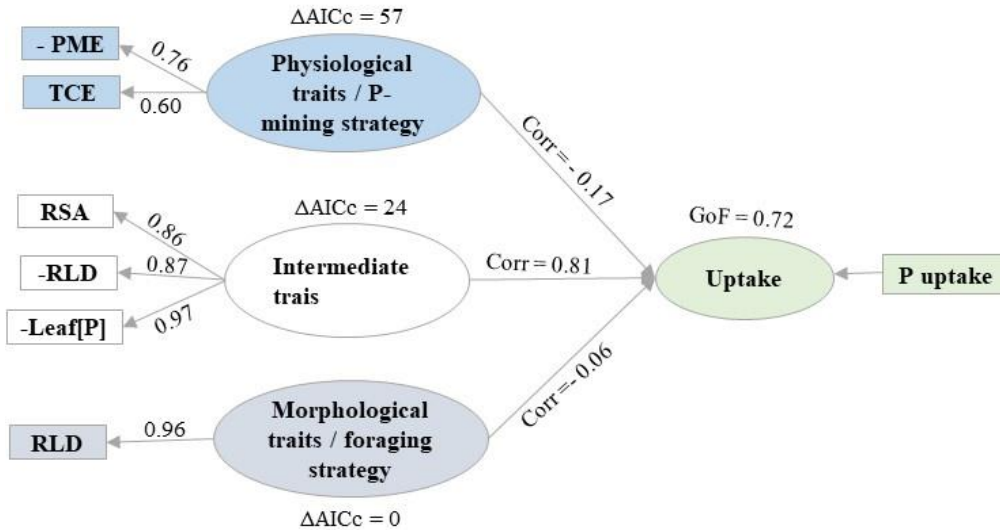
The process of selecting the combinations of traits that give the best model fits for predicting P uptake was performed under R software with the `stepAIC()` and `bestglm()` functions that are based on the stepwise and best subset approaches. $AICc$ second order Aikake's information, FR Fine root percentage ($<0.5 \text{ mm } \varnothing$), PME Phosphomonoesterase activity, RSA Root surface area, ΔpH change in rhizosheath pH.

P forms	Strategies	Models	AICc	Δ AICc
IP	Physiological traits	~ TCE	-57.55	0.00
		~ DpH + PME	-57.08	0.47
		~ DpH + PME + TCE	-54.82	2.73
	Intermediate traits	~ SRL + FR + PME + Shoot_P	-89.85	0.00
		~ SRL + FR + PME + TCE + Shoot_P	-87.68	2.17
	Morphological traits	~ RLD + FR	-121.18	0.00
		~ RLD + SRL + FR	-119.17	2.01
		~ RSA + RLD + SRL + FR	-115.94	5.24
	IHP	Physiological traits	~ PME + TCE	-74.47
~ DpH + PME + TCE			-68.91	5.56
Intermediate traits		~ RSA + RLD + Shoot_P	-104.23	0.00
		~ RSA + RLD + DpH + Shoot_P	-101.73	2.50
		~ RSA + RLD + SRL + DpH + Shoot_P	-97.42	6.81
Morphological traits		~ RLD	-128.33	0.00
		~ RSA + RLD	-125.94	2.36
		~ RSA + RLD + FR	-123.69	4.64
GLY		Physiological traits	~ DpH + TCE	-45.00
	~ DpH + PME + TCE		-43.37	2.37
	Intermediate traits	~ RLD + PME + Shoot_P	-63.84	0.00
		~ RLD + FR + PME + Shoot_P	-60.66	3.18
	Morphological traits	~ SRL	-114.73	0.00
		~ RSA + SRL	-113.97	0.76
		~ RLD + FR + DpH + PME + Shoot_P	-55.92	7.92

IP form



IHP form



GLY form

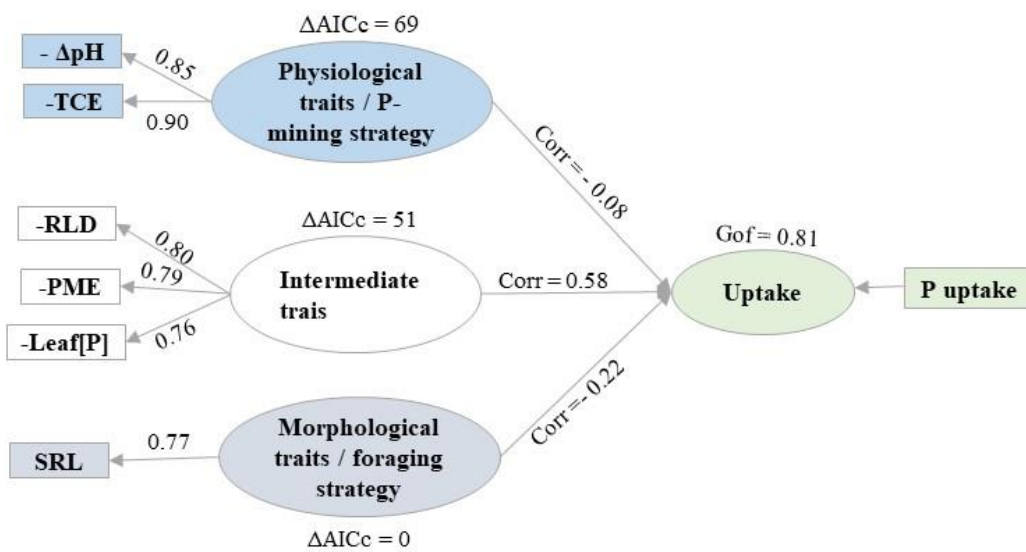


Figure 30 : Partial least square-path models predicting phosphorus uptake. Based on three latent variables, namely root physiological traits, root morphological traits and intermediate in tree IP and organic P (IHP and GLY)

Corr is the correlation effect. Variables negatively transformed indicated by -(variable). GoF = Goodness of Fit of the model. ΔpH: change in rhizosphere pH; FR: percentage roots with diameters less than 0.5 mm; PME: acid phosphomonoesterase activity; RLD: root length density; RSA: root surface area

7.4 Discussion

7.4.1 Impact of P forms on P acquisition strategies

Phosphorus acquisition strategies of crop species may depend on P forms and thus the nature of the applied P fertilizer. Previous work has suggested that plant species have different P acquisition traits, leading to preferential sources for P acquisition (Ceulemans et al., 2017; Nobile et al., 2019). Compared to IP, the response of P acquisition strategies to OP compounds has received much less attention (Amadou et al., 2021; Turner, 2008). Crop species traits could be used to recycle more P in soils amended with organic amendments, but this requires a better understanding of the response of P acquisition strategies to P sources, and their effect on P mobilization and acquisition from soil minerals (Feng et al., 2019; Sulieman and Mühling, 2021). The results of the GLM model showed that two of the physiological traits (carboxylates and pH variation), one of the morphological traits (fine root percentage) and leaf [P] were significantly affected by P forms and their interaction with species and minerals. This suggests differential expression of P acquisition traits among the P forms examined and supports our hypothesis that P acquisition strategies (i.e., *foraging* and *mining*) differ among P sources (Wang and Lambers, 2020). However, this does not apply to all traits, as some traits showed no variation among P forms. Organic P forms impacted P acquisition traits in a species-specific manner. In *Lolium perenne* (C4) and *Phacelia tanacetifolia* (C4), carboxylate release and percent fine roots were significantly enhanced by OP application compared to IP form. PME activity and other traits were also higher under OP forms but were not significant. Between OP forms, P acquisition traits of both species were significantly higher in the IHP form than in the GLY form. These results show that P-acquisition traits of *Lolium perenne* and *Phacelia tanacetifolia* mainly carboxylate release, PME activity and percent fine roots responded more to OP forms and that IHP form most impacted P-acquisition traits compared to GLY. Shahzad et al. (2017) showed that organic amendments increased the amount of carboxylate in the rhizosphere of maize compared to inorganic fertilization. Other studies have shown an increase in soil phosphatase activity in either incubation or field experiments (Criquet et al., 2007; Hamdi et al., 2019; Houben et al., 2019). Chickpea, for example, appears to produce both phosphomonoesterases and diesterases following the input of organic fertilizers into the soil (Darch et al., 2018; Pang et al., 2010). Our observations are also consistent with other results showing that some species express higher levels of carboxylate and fine root to access more OP in the soil (Haling et al., 2018; Wen et al., 2019). The higher expression of the traits found on the IHP form compared to GLY,

may be due to its greater affinity with soil, and its resistance to enzymatic hydrolysis that would stimulate the expression of traits in the species. This emphasizes that the chemical nature of specific OP forms affects plant P acquisition strategies in soil. In contrast to the previous species, *Pisum sativum* (C1) and *Hordeum vulgare* (C2) P-acquisition traits (rhizosphere pH, total carboxylate release as well as SRL and fine root percentage) were higher under the IP form when compared to the OP form, indicating that these species were less affected by OP forms. Furthermore, we found that the P acquisition traits of *Lupinus albus* (C1), *Vicia faba* (C1), *Lens culinaris* (C3), and *Trifolium alexandrinum* responded to both forms of P. Change in rhizosphere pH of these species was significantly enhanced under the IP form, whereas under the OP forms (IHP and GLY), it was mainly the total carboxylate release, PME activity, and some morphological traits (SRL, percentage of fine roots) that were significantly important. This indicates that these species respond to both IP and OP forms by expressing different P acquisition traits. Thus, on IP forms, rhizosphere pH was more important and this was likely to promote P acquisition and on OP forms, carboxylate release, PME activity, and certain morphological traits were more important that were likely to access, solubilize, and mineralize OP forms (Damon et al., 2014; Neumann et al., 1999). These results are also evidence that the response of P acquisition traits to specific forms of OP is also species dependent (Lambers et al., 2008; Wang and Lambers, 2020). For example, *Lens culinaris* and *Trifolium alexandrinum* showed a greater response to the specific form IHP and *Lupinus albus* and *Vicia faba* to the GLY form.

In conclusion, the P acquisition traits of the species studied changed between the application of the OP forms and the application of the IP form, a difference in trait expression was also observed between the specific OP forms, i.e. IHP and GLY. Furthermore, trait expression was highly species dependent, with some species expressing more traits exclusively on the IP or OP form while others had different important traits expressed based on the P forms. The contrasting physicochemical nature of the P forms as well as the nature of the different species may explain the varied responses of P acquisition strategies to the P forms.

7.4.2 Role of P acquisition strategies on OP availability and P acquisition

Various P mobilization and acquisition strategies in crop species and cultivars have been demonstrated, but their efficacy in acquiring P from different forms of OP remains poorly studied (Robles-Aguilar et al., 2019; Simpson et al., 2011). For example, the availability of different forms of OP (IHP, GLY, DNA, and RNA) as a direct effect of P acquisition strategies (*P mining* and *foraging*) remains unclear (Amadou et al., 2021). Here, P acquisition strategies (i.e., *foraging* and *mining*) were found to differ among P sources, and further GLM analysis showed that P availability and uptake were also significantly different among species, their interaction with P forms, and the overall interaction of factors (Species x Minerals x P Forms). Hence, we infer that the different response of P acquisition strategies to P forms (IP and OP) led to varied P acquisition by species. We found P acquisition strategies of *Vicia faba* (C1) and

Pisum sativum (C1) showed higher P availability and uptake from OP forms compared to IP forms across both soil minerals. Similarly, the P acquisition strategies of *Phacelia tanacetifolia* (C4) and *Lupinus albus* (C1) led to significantly high P acquisition from OP forms, but only in kaolinite. This improvement in P acquisition from OPs supports our overall hypothesis that P acquisition strategies would differ in their responses to P sources, which would promote greater OP availability and acquisition. Indeed, *Vicia faba* (C1), *Pisum sativum* (C1), and *Lupinus albus* (C1) comprised the "physiological/exudation" group C1 that exhibited the greatest exudation of carboxylic acids, an important activity of PME in the rhizosphere. In addition, trait response analysis to P forms showed that these species had greater total carboxylate release, PME activity, and some morphological traits (SRL, percentage of fine roots) on OP forms than on the IP form. All of these may collectively explain their ability to promote P availability and uptake from OPs forms (García-López et al., 2020; Li et al., 2004). Thus, in agreement with our second hypothesis, the P acquisition strategies of these species, i.e., pH modification, carboxylate and phosphatase release, would have increased the turnover of OP forms sorbed on goethite and kaolinite via desorption, solubilization and mineralization processes; thus, resulting in increased P availability and acquisition (Guppy et al., 2005; Weisskopf et al., 2006). Indeed, similar to the above species, many plant species belonging to the Fabaceae family have already been classified as efficient solubilizers of OP (Schneider et al., 2019). A wide range of biochemical, physiological, and molecular mechanisms may give *Fabaceae* a superior dynamic capacity to utilize soil OP more efficiently. Simultaneously, most legumes have a high potential capacity to establish a dual symbiosis with AMF and rhizobia (Sulieman and Mühling, 2021). This tripartite symbiosis may provide an additional potential benefit that could aid in OP mobilization. Similarly, *Phacelia tanacetifolia* (C4), which belonged more to the morphological group C4, had a high percentage of fine roots and the highest SRL, as well as carboxylates that were all higher on the OP form than on the IP forms. These traits, which would be involved in P foraging, would induce a diffusion gradient which, in turn, would favor the desorption process of the different adsorbed OP forms and thus the availability of P in the soil confirming our first hypothesis (Haling et al., 2018; Rubio et al., 2003; White and Hammond, 2008). These observations are consistent with other results reporting that plant species with finer roots may be more efficient in mobilizing OP from the soil (Haling et al., 2018; Wen et al., 2019) because of their ability to promote the exploration and contact of a larger volume of soil per unit root area (Hammond et al., 2009).

Numerous studies have demonstrated that plants have a limited ability to access P in the form of IHP (the major form of OP) due to its low availability in the soil solution and the low level of extracellular phosphatase or phytase (George et al., 2008; Richardson et al., 2009). It has also been shown that wheat and many other species are able to utilize P from GLY, and phosphodiester (DNA and RNA) due to their *mining* ability, but are limited to acquiring P directly from IHP, although it is abundant in many soils (George, 2007). However here we found that P acquisition of species (*Vicia faba* *Pisum sativum* *Phacelia tanacetifolia* *Lupinus albus*) was higher from IHP forms than on GLY forms

with some variation depending on the mineral. This result contradicts the extensive literature that revealed the low availability of IHP to crops as compared to other forms of P in soils (Findenegg and Nelemans, 1993; Gerke, 2015; Xu et al., 2019). However, this indicates that the P acquisition strategies of the above species were effective in mobilizing IHP on the different soil mineral types. Thus, we suggest that despite the higher accumulation of IHP reported in most soils (Amadou et al., 2022; Vincent et al., 2013), its desorption and hydrolysis may be more facilitated by species with high physiological and morphological traits potential. However, although this is at odds with recent results (Amadou et al., 2022; Garcia-Lopez et al., 2015) it responds to Gerke (2015) who suggests that P acquisition from IHP and its mobilization from the surface of soil components could be effective by root exudates of cover crop species, primarily di- and tricarboxylic acids, which can increase the solubility of IHP. In contrast, compared to the previous species, *Lentil culinaris* (C3), *Hordeum vulgare* (C2), and *Trifolium alexandrinum* (4) showed broadly equivalent P uptake between P forms. It is thought that this non-difference in P uptake is due to the fact that these species, with the exception of *Trifolium alexandrinum* (4), had "intermediate" traits that varied very slightly, and their main characteristic was P concentration in the leaf. Finally, *Lolium perenne* (4) was more efficient in acquiring the IP form than the OP forms. Indeed, *Lolium perenne* had P acquisition traits that generally did not differ between P forms. The inability of these species to mobilize OP is intensely demonstrated in the literature (Amadou et al., in press; Chen et al., 2002, 2002). Our hypothesis that P acquisition from OPs will be greater in strategies involving P *mining* than in those involving P *foraging*, because OPs will be hydrolyzed by the strong PME activities, was confirmed in this study (George, 2007; Richardson, 2005). The main result supporting the hypothesis was that species from the physiological trait group (*Vicia faba*, *Pisum sativum*, *Phacelia tanacetifolia*, *Lupinus albus*) were able to take up more P from the OP than those from the morphological and intermediate group species. However, our last hypothesis that regardless of the strategy, P acquisition from OPs will be lower than that from IPs due to their strong sorption on minerals was not confirmed, as the P acquisition strategies of the species studied led to higher or equal P uptake from OPs (except *Lolium perenne*). This exception with *Lolium perenne* is thought to be due to the fact that *Lolium perenne* has no P mobilization capacity and thus can only utilize readily available P. According to our previous results (Amadou et al., in press), *Lolium perenne* was able to utilize 2-3 times more P in the IP form than in the OP form, because IP was less sorbed and was more available.

7.4.3 Soil minerals affect P acquisition strategy on OP availability and P acquisition

Soil minerals and especially their interactions with species significantly affected the response of traits towards OPs because of their contrasting physicochemical properties. Global comparison of traits response to P forms revealed a greater expression of traits on goethite, although *Phacelia tanacetifolia* and *Vicia faba* had more traits on kaolinite. Nevertheless, the resulting P acquisition from OPs was

generally more important on Kaolinite. Soil minerals such as Fe, Al oxides and clay minerals are known to significantly reduce the efficiency of crop species to utilize P from applied organic amendments (Amadou et al., 2022; Ganta et al., 2021; Giaveno et al., 2010). To date, there are relatively few studies that explore the effect of major soil minerals on P acquisition strategies of crop species and how these strategies influence OP mobilization. It is assumed that OP adsorbed on Fe and Al oxides is protected from being affected by plant P acquisition strategies, leading to its accumulation in the soil (Stutter et al., 2015). Yet, in this study, we showed that P acquisition strategies of individual species promoted P acquisition from OPs across all soil minerals. The greater expression of traits on goethite is thought to be due to its high P adsorption capacity and high-energy binding to OP, which renders the medium more P-deficient and thus leads to a stimulation of trait expression by the species (Faucon et al., 2015; Simpson et al., 2011). This corroborates the literature that most plants develop more P acquisition traits in high P-deficient soils to specifically access different forms of OP and increase soil P acquisition (Richardson et al., 2009; Simpson et al., 2011). However, although the P acquisition traits were more strongly expressed on goethite, we found that P acquisition from OPs was lower on this mineral but higher on kaolinite. This suggests that mineral-OP interaction properties affect plant P acquisition strategies. Indeed, OP is known to desorb more from clay minerals (montmorillonite and kaolinite) than from Fe and Al oxides (Amadou et al., 2022; Fang et al., 2017). Since clays have also been shown to have a lower P binding capacity, it can be expected that P acquisition strategies on this mineral will result in greater OP availability (Bortoluzzi et al., 2015; He et al., 1994). Overall, our results highlighted the central role of soil minerals and their interactions with P forms and species on the response of P acquisition traits and how this can promote P availability from OPs. A better understanding of these interactions is an important challenge for modeling OP dynamics and predicting P release depending on crop and soil type (Raven et al., 2018; Wen et al., 2019).

7.4.4 Highlight main traits involved in OP *mining* and *foraging* and the contribution on P availability and acquisition

Overall, the P *mining* and *foraging* strategies highlighted in this study positively affected P utilization from OP forms. However, it remains unclear which key traits of these strategies directly or indirectly contribute to P availability and acquisition, as the process differs depending on the nature of the P forms (Lambers et al., 2006). The results of GLM and PLS modeling of phosphorus uptake showed that RLD and SRL were the most important traits involved in OP *foraging* (for the specific forms IHP and GLY respectively). In the case of OP *mining*, it was rather a combination of TCE and PME or TCE and DpH. PME activity was the most important contributor for the IHP form and TCE for GLY. These findings suggested that among the plant architectural traits, root length density, would best enable plants to improve their *foraging* capacity for the specific form IHP and within the morphological traits, specific root length would contribute the most to GLY availability (Haling et al., 2018; Ma et al., 2018; Pang et

al., 2010). Various individual effects of SRL, RLD or PME on P dynamics and its contribution to P uptake have been reported in several species (Wang and Lambers, 2020; Zhu et al., 2005). Higher RLD in the upper soil layers was found to be the most important root trait of wheat for P mobilization in response to organic fertilizer application (Lamont, 2003). In maize genotypes, the effects of varying RLD and root hair length led to a 100% increase in total P mobilized from organic amendments (Zhu et al., 2005). However, the very few studies on the forms of OP do not adequately quantify their potential contribution to P availability in the organic fertilizer-soil-plant system (Amadou et al., 2021; Klotzbücher et al., 2020; Sulieman and Mühlhling, 2021). The main features involved in P *mining* and *foraging* highlighted in this study and their strong contribution to the prediction of P acquisition, offer opportunities to improve P cycling in multi-species systems, including exploiting the inherited P pool. Furthermore, the results of the PLS analysis show that phosphorus uptake is best predicted by root morphological traits ($\Delta AICc = 0$), followed generally by intermediate traits. Although several correlations between a single trait and P uptake have been observed previously (Pearse et al. 2006; Lambers et al. 2006; Rose et al. 2010; Wen et al. 2017), our results add to our incomplete knowledge on the variation and contribution of individual traits to the acquisition of specific forms of soil organic P (Lyu et al. 2016). In sum, our results highlighted the specific traits of OP acquisition strategies that best predict P acquisition. Crop models to estimate total soil P reserves and at least its specific forms (IHP, G6P, GLY, etc.) in a multispecies cropping system can be developed based on the plant traits highlighted in this study, including inter- and intraspecific variability in traits and soil properties. This approach to trait-based OP mobilization modeling can be potentially useful in different climates.

7.5 Conclusion

Crop species traits could be used to improve OP cycling and availability in cropping systems, thereby helping to rethink P fertilization, but this requires a better understanding of the response of P acquisition strategies to OP sources, and their effect on OP mobilization and acquisition from soil minerals. Morphological and physiological traits include various P acquisition strategies that differ depending on the nature of the IP or OP forms and the physicochemical properties of the soil.

Our results showed a differential P acquisition trait response to P forms and a strong dependence of trait expression on species type. We found that species P acquisition traits changed between the application of OP forms and the application of the IP form. In addition, a difference in trait expression was also observed between the specific OP forms, i.e., IHP and GLY. There was strong species dependence in the expression of traits, some species expressed more traits exclusively on the IP or OP form while others had different important traits expressed on both types of P. The contrasting physicochemical nature of P forms as well as the characteristics of different species may help explain the varied responses of P acquisition strategies to P forms. The improvement in P acquisition of most species from OPs demonstrated that the positive response of P acquisition strategies (i.e., *foraging* and

mining) to OP sources has resulted in greater availability and acquisition of P from OPs. Regardless of strategy, the higher P acquisition from OPs compared to IPs showed that, despite stronger sorption of OPs to the soil, limiting their availability, both plant P *foraging* and *mining* strategies were able to improve the cycling and availability of OPs compared to IP forms. Nevertheless, our results highlighted that soil minerals have a central role on the response of P acquisition traits and P availability from OPs is driven by soil mineral properties. The greater P acquisition from OPs in strategies involving P *mining* than in those involving P *foraging* emphasizes the importance of plant physiological traits in recycling OPs in the soil. Finally, the identification by modeling of the major traits involved in P *mining* and *foraging* and their ability to better predict P acquisition, offer opportunities to design crop species compositions and more specifically functional structure of cultivated plant communities (e.g. intercropping, cover crops...) to estimate total soil OP reserves and at least its specific forms (IHP, G6P, GLY, etc.) in a multi-species cropping system. We found some species and strategies specific to certain P forms, highlighting specialized ecological niches. In addition, some species and strategies with high plasticity show a wide ecological niche and a strong potential to improve P availability, P recycling from the diversity of P forms in soils or bio-based fertilizers.

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DISCUSSION

8 DISCUSSION

Facing the depletion of rock phosphate resources, instability of fertilizer prices, and the adverse environmental effects of over-fertilization, practices, and technologies proposing to increase P cycling efficiency in agroecosystems are gaining interest (Menezes-Blackburn et al., 2018; Richardson et al., 2011) and are increasingly adopted (Sulieman and Mühling, 2021). In this way, P from organic input is increasingly considered as a complement to P fertilizers produced from phosphate rocks (Bennett and Schipanski, 2013). Organic input use represents a shift from linear utilization of a finite resource to a circular economy as it promotes the reduction of fossil fuel use and greenhouse gas emissions (McCormick and Kautto, 2013) while contributing to the development of new green markets (Zulkifli et al., 2019). The use of OPs to improve P cycling efficiency in cropping systems, however, requires a better understanding of the forms and biochemical properties of various OP interactions with soil minerals and the mechanisms governing their mobilization/acquisition for crop plants. The objectives of this thesis were to understand better the role of OP forms, soil minerals, N, and crop functional traits and their interactions on P availability and acquisition by plants to optimize organic fertilizer management in agroecosystems. Based on a biogeochemical approach, the dynamics of adsorption and desorption of several forms of OP on several representative soil minerals and their influence on OP uptake by plants in ecosystems were elucidated (**Chapters 1 and 2**). Importantly, the study of interactions between N and OP (**Chapter 3**) has improved our understanding of ecosystem P cycling under N addition and the biogeochemical properties involved, which is necessary for ecosystem models to accurately predict plant N-P limitation and its impacts. The functional approach adopted here provides valuable information on plant traits and strategies that are very useful for designing cropping systems (the multispecific cover crops, and the succession of cash crops) to increase P availability (**Chapter 4**). Furthermore, the references produced and the new knowledge acquired on the influence of plant P acquisition strategy on the P cycle in agroecosystems could contribute to the improvement of existing models and their integration into decision support systems. These systems would in turn allow us to assess the overall effects of organic input-soil-plant interactions on P availability and to support farmers' management decisions such as adapted P fertilization.

8.1 Effect of OP forms and soil minerals on OP dynamics and P availability to plants

With the increasing use of organic inputs to replace mineral P fertilizers and the need to recover P from the soil, it is essential to understand better the interactions between various forms of OP and soil minerals and their consequences on P availability (Amadou et al., 2021). A large body of research has evaluated the adsorption of various individual sources of organic and inorganic P to soils or to soil

minerals. However, no study has evaluated and compared the P desorption of major OP compounds that have been adsorbed to major soil minerals and their consequence on plant nutrition (Amadou et al., 2022a, 2022b). To help fill this knowledge gap, **Chapters 1 and 2** elucidated the dynamics of adsorption and desorption of several forms of OP on several representative soil minerals and the implications for P uptake. Factors related to soil mineral properties and molecular characteristics of OPs directly affected the reactions of OPs and their release into the soil (**Chapter 1**). Similarly, these factors affected P availability in the rhizosphere and its uptake by the plant (**Chapter 2**). All OP forms studied (IHP, GLY, and G6P) showed contrasting and significantly different adsorption processes from each other, as well as from the IP form used for comparison (**Chapter 1**). Desorption experiments revealed that approximately 30% could be readily desorbed (**Chapter 1**) and this desorbed P was available for plant use (**Chapter 2**), indicating that adsorbed OPs can act as a source of P for plants (Amadou et al., 2022b). The trend in OP availability (GLY >> G6P > IHP) highlighted in **Chapter 2** was potentially explained by their distinct desorption dynamics (**Chapter 1**), as the lowest desorption was found for IHP-P, followed by G6P-P and then GLY-P (chapter 2). The trend could also be related to their various degrees of hydrolysis by enzyme activity (Annaheim et al., 2010), as phosphatase activity was the highest in the presence of GLY and the lowest in the presence of IHP (**Chapter 2**).

The positive relationship between the adsorption dynamics of OPs and the number of phosphate groups in the organic molecule (**Chapter 1**) was consistent with the literature and shows that the adsorption capacity of each OP compound is determined by the number of orthophosphate groups associated with the C moiety (Bai et al., 2021). IHP, which has six orthophosphates per C moiety, was adsorbed in greater amounts than the other orthophosphate monoesters (G6P and GLY), reinforcing previous explanations of its low desorption (**Chapters 1 and 2**) and limited utilization by plants (**Chapter 2**). The generally lower or equal binding strength of IHP to minerals compared to GLY or G6P (**Chapter 1**), albeit at odds with recent results (Ganta et al., 2019; Kubicki et al., 2012) suggested that the higher adsorption of the IHP compared to other OP compounds (**Chapter 1**) does not necessarily imply that its binding capacity and/or energy is always strong and stable under all environmental conditions. Thus, it is conceivable that under organic input supply conditions, if GLY and G6P species compete with IHP for the same active sites on soil minerals, the difference in binding energy could facilitate the desorption of IHP from the soil more effectively than GLY and G6P (Amadou et al., 2022a). Correlation analysis performed on different extraction data showed that the availability of adsorbed OPs to plants does not depend on their binding strength to soil minerals (**Chapters 1 and 2**) but rather on their degree of hydrolysis by soil and root enzymes (**Chapter 2**). We also pointed out that the general idea of higher adsorption of OPs relative to IP suggested by the literature does not apply to all OP compounds since, although IHP was more strongly retained relative to IP, G6P and GLY were more weakly retained (Figure 31).

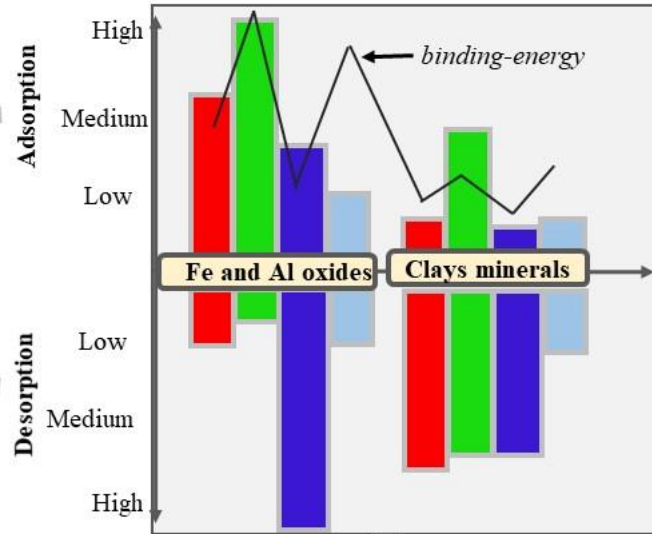
The high OP desorption (**Chapter 1**) and acquisition (**Chapter 2**) from montmorillonite relative to other minerals (**Chapter 2**) indicated that soils rich in 2:1 phyllosilicate may have greater P availability

than soils rich in Fe and Al oxyhydroxides or 1:1 mineral (Figure 31). Nevertheless, the observed higher desorption of GLY from Al oxyhydroxides (**Chapters 1 and 2**), which are known to limit P availability in highly weathered soils in tropical regions, emphasized the high potential for using GLY as a P source in these regions (Zhang et al., 2017). The low P uptake from kaolinite-OP complexes (**Chapter 2**) is consistent with previous observations showing that kaolinite-P is a bidentate, inner-sphere surface complex below pH 6 (Hu et al., 2020; Ruyter-Hooley et al., 2015), and that P adsorbed on kaolinite is difficult to desorb (Kafkafi et al., 1988; Xiong et al., 2022). This, therefore, emphasizes that Fe and Al oxyhydroxides were less responsible for limiting OP availability than kaolinite, despite their generally higher adsorption capacity in soil (**Chapter 1**). However, since the P concentration used in our study may be higher than that of real soil systems, it would be interesting as a prospect to investigate the effect of P concentration on adsorption processes by performing sorption experiments at different (and lower) P concentrations.



Chapter 1

Adsorption and desorption dynamics of OP forms.
Simulation via Langmuir and Freundlich isothermal models.



Environmental OP losses

Chapter 2

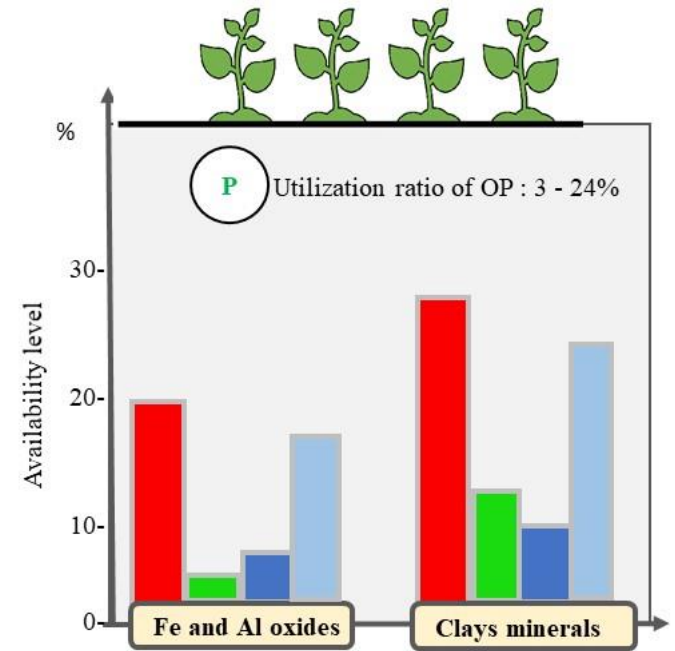


Figure 31: Illustration summarizing the effects of OPs and soil mineral interactions properties on OP dynamics and plant P availability.

OP: Organic P, IHP: Myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate, and IP: Inorganic P; Fe and Al oxides included goethite and gibbsite and clay minerals included kaolinite and montmorillonite

8.2 Evidence of important OP mobilization by plants as a result of N-OP interactions and plant trait responses

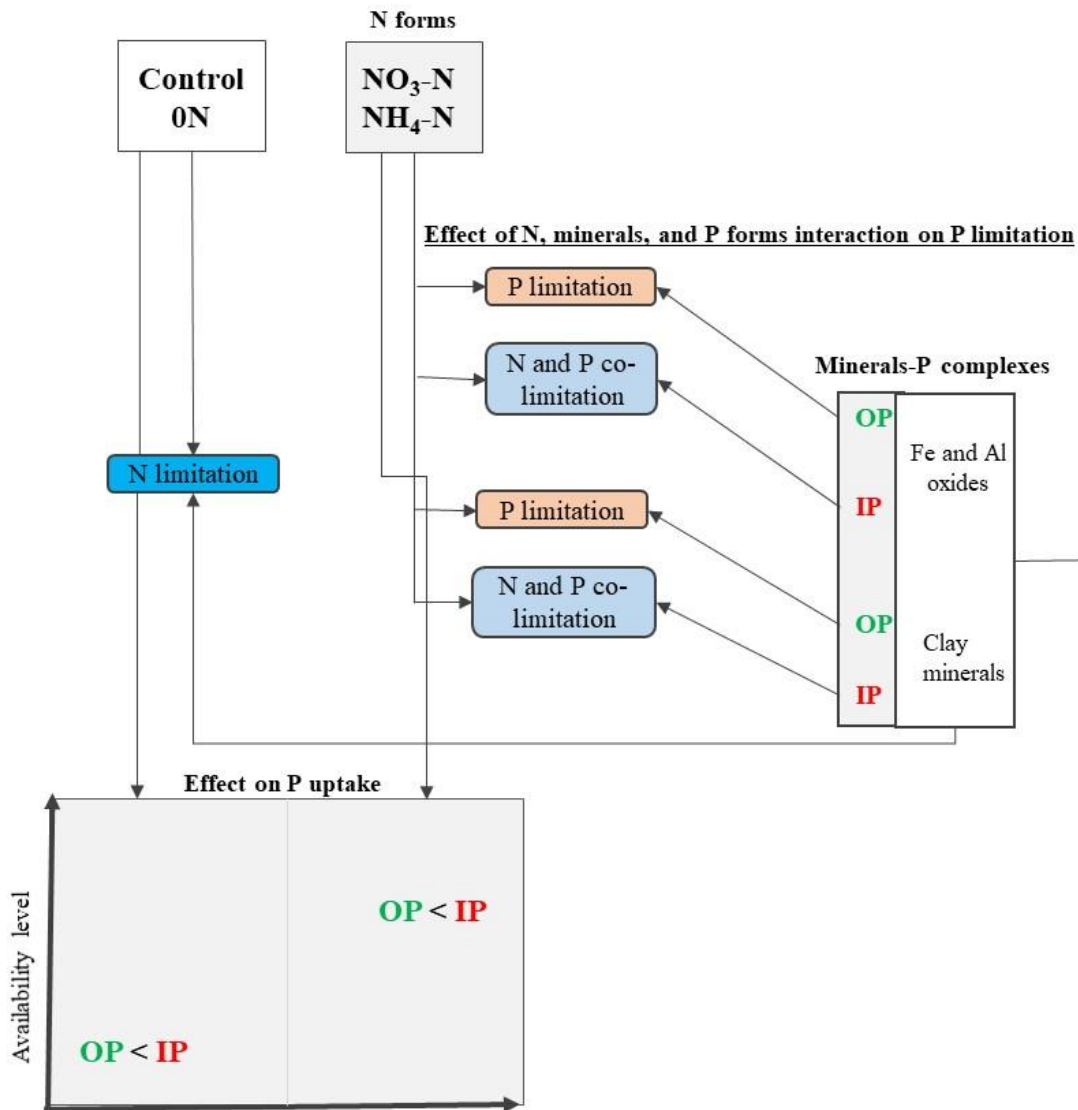
The N characteristics in organic fertilizers added to enhance P use can affect the availability of OP in the soil-plant system. The literature showed that the addition of N can increase plant P demand, which in turn promotes soil P mobilization (Schleuss et al., 2020; Zhang et al., 2017). This highlights the ecological importance of the beneficial effect of N on plant P use efficiency (Vitousek et al., 2010). Overall, it has been stated that plants could trade N for P by adjusting N and P acquisition rates from the soil, potentially explaining synergistic growth responses to N and P addition (Long et al., 2016; Peng et al., 2019). Furthermore, different OP mobilization and acquisition strategies in crop species and cultivars have been demonstrated, but their efficacy in acquiring P from the different OP and IP forms remains understudied (Lambers et al., 2011). These strategies involve morphological, architectural (Lynch, 2011) and physiological traits (Richardson et al., 2009), microorganisms, or a combination of both to effectively contribute to the ability of plants to access different reservoirs of poorly available OP in soils (Wang et al., 2022; Wang and Lambers, 2020). To date, it remains unclear how the chemical forms of N, plant P acquisition strategies, and their interactions with OP and minerals influence OP availability, acquisition, and limitation by plants in ecosystems.

The beneficial effect of N addition and further positive consequences of the responses of P acquisition strategies by the plant on OP availability was highlighted in the characterization of N-OP-mineral interactions (**Chapter 3**) and the effect of root traits-OP-mineral interaction (**Chapter 4**). Compared to no N addition (**Chapters 1 and 2**), the increase of P uptake by plants with N addition, especially with NO₃-N forms (**Chapter 3**), highlighted the synergistic effects of N and OP and their interactions with minerals on P dynamics, i.e. its availability and limitation (Figure 32). Within specific forms of OPs, results in **Chapter 3** suggested that the addition of N would promote the mobilization of IHP (major forms of OPs in soil and organic amendments) and make it less limiting to plants compared to other forms of OPs, i.e., GLY or G6P, highlighting the central role of the interaction between N, OP, and minerals on the OP cycle (Hou et al., 2021, 2020). In addition, these results highlight a new mechanism by which interactions of N forms with OP pools could accelerate OP cycling, including increasing the availability of IHP, which is the important form of OP and also the most adsorbed and least available form (**Chapters 1 and 2**), and thus delay the onset of P limitation of this form for plant growth (**Chapter 3**). High phosphatase activity and P availability in the rhizosphere with the addition of N (**Chapter 3**) likely contributed to plant P uptake (Long et al., 2016). Correlations indicated that total P uptake was positively related to available P and phosphatase activity (**Chapter 3**). Most likely, the addition of N allowed plants to synthesize N-costly phosphatases (Schleuss et al., 2020), which then made OP available for plant uptake (Helfenstein et al., 2018). Thus, it seems likely that with the addition of N, OP is recycled more intensively from OP pools irrespective of soil minerals (Widdig et al., 2019). The interaction of N with IP forms led to greater P uptake and markedly reduced P limitation compared

to the interaction of N with OP forms, presumably because of the high adsorption and low availability of OP, as shown in **Chapters 1 and 2**. Thus, it can be deduced that in agroecosystems where P is very strongly sorbed (such as OP forms), N additions can indeed lead to a rapid depletion of available P and thus to a very strong limitation of P, but in systems where P is relatively more available (such as IP forms), N additions do not lead to a systematic limitation of P but rather to a colimitation of N and P. With the addition of N, more OP was recycled from the clay minerals (kaolinite) and thus delaying P limitation compared to iron and aluminum oxides (goethite) which highlights the importance of considering the soil mineral in the design of cropping systems to mobilize OP. Thus, **Chapter 3** strongly suggests that despite the higher adsorption of OP forms (**Chapter 1**), N additions can indeed lead to OP use efficiency in the soil-plant system.

To further explore effective mechanisms for OP mobilization in the soil, the response of P acquisition strategies to various forms of OP interacting with soil minerals and their consequences for OP availability and acquisition were examined in eight major plant species (**Chapter 4**). The differential expression of P acquisition traits among the OP forms supports our hypothesis that P acquisition strategies (i.e., *foraging* and *mining*) are affected by the type of OP sources and their biogeochemical properties (Wang and Lambers, 2020). Similar to the effect of N-OP interactions (**Chapter 3**), the positive response of P acquisition strategies to OP sources (**Chapter 4**) resulted in greater P availability and acquisition from OPs (Figure 32). Irrespective of plant strategies, the higher P acquisition from OPs relative to IPs (**Chapter 4**) showed that, despite the higher sorption of OPs in the soil (**Chapters 1 and 2**), plant P *foraging* and *mining* strategies were able to improve the cycling and availability of OPs relative to IP forms. Taken together, the findings of **Chapters 3 and 4** suggest that the various forms of N contained in organic inputs and the P acquisition strategies of crop species can be exploited to enhance the mobilization of OPs in the organic fertilizer-soil-plant system (Figure 32). The agronomic application of this result is particularly important for limiting the use of chemical fertilizers.

Chapter 3



Chapter 4

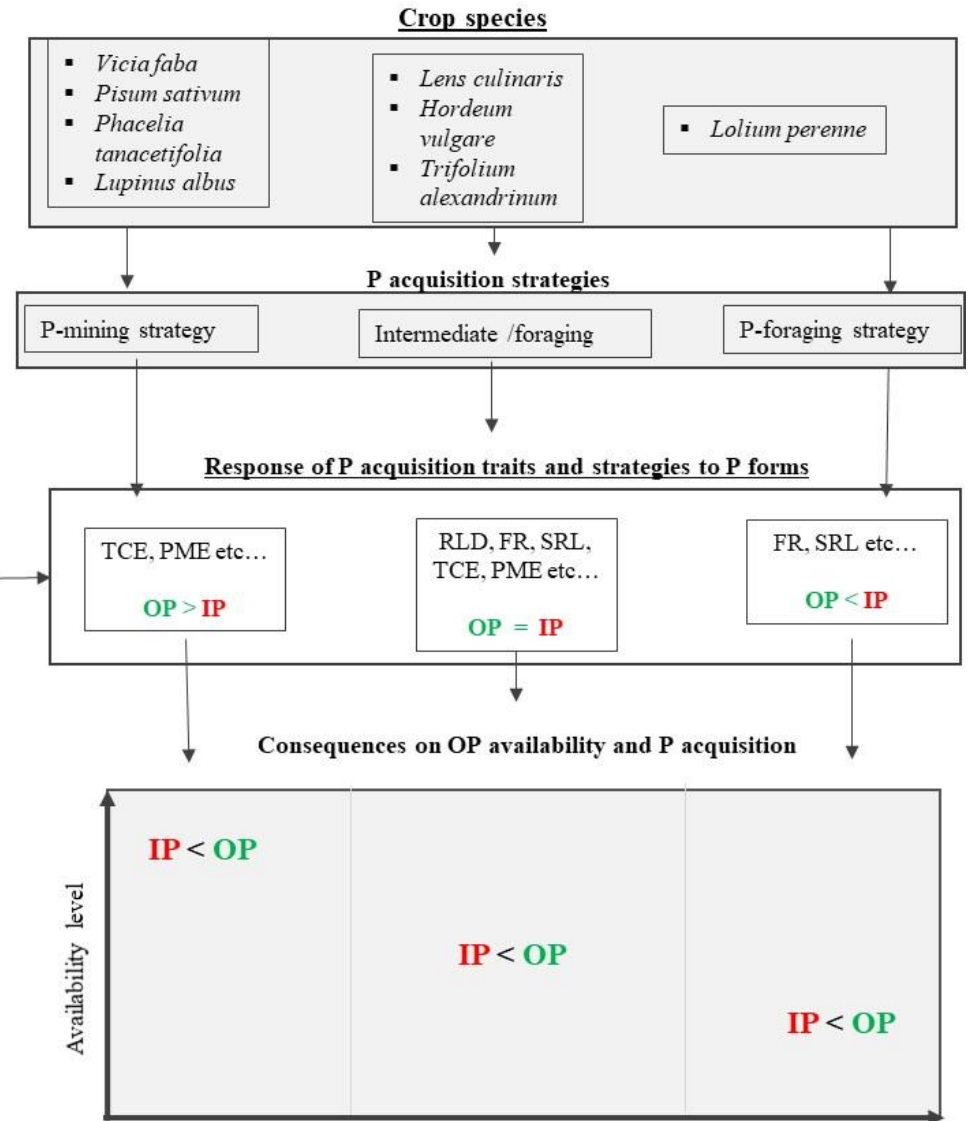


Figure 32 : Synthesis of the effect of N-OP interactions and plant trait responses on OP mobilization by plants.

OP (in green): Organic P includes the speciated forms that are: Myo-inositol hexakisphosphate, IHP , Glycerophosphate, GLY, glucose-6-phosphate, G6P . IP (in red): Inorganic P.

8.3 Designing functionally optimal crops with high OP mobilization capacity: insights into species selection, phosphorus acquisition strategies, and N forms

Designing for improved P availability in agroecosystems via management of organic amendment N content and plant P acquisition traits can therefore help address major challenges such as increasing recycled fertilizer use (Faucon et al., 2015). However, this suggests careful consideration when designing crop composition and amendment supply (Hallama et al., 2019). A major implication of this thesis is the potential to manage N forms in organic inputs while adapting crop composition to improve OP availability in agroecosystems through the advantageous effect of N-OP interactions (**Chapter 3**) but also through the positive response and effect of plant strategies and functional traits (**Chapter 4**). In general, N-OP interactions resulted in the much greater mobilization of OPs (**Chapter 3**), furthermore, the effects of the P acquisition strategies of the different species discussed in **Chapter 4** were found to favor greater P acquisition from OPs than from IPs. All of these observations indicate that despite the stronger sorption of OPs to soil demonstrated in **Chapter 1**, which limited their availability for plants in **Chapter 2**, plant P *mining* and *foraging* strategies were successful in improving the cycling and availability of OPs over IP forms (**Chapter 4**). Taken together, these results can help guide the selection of efficient cropping systems and the formulation of N in organic fertilizers for better mobilization of OP forms. Species groups consisting of *Vicia faba*, *Pisum sativum*, and *Lupinus albus* that produced greater carboxylic acid exudation, and significant PME activity in the rhizosphere than other species in response to OP forms (Nobile et al., 2019), may benefit from fertilization with organic inputs (Figure 32). These species, which are all belonging to the Fabaceae family and whose strategies involve P *mining*, have promoted greater mobilization/acquisition of OPs than IPs. Consequently, in a rotational system, this could improve P availability that would then benefit subsequent crops, which are generally non-mobilizing (Haling et al., 2018). In practice, since organic inputs slowly increase soil P availability to plants after incorporation into the soil (Gerke, 2015), these Fabaceae species could be the first choice in a crop rotation or in a cover crop to improve crop P content from soil OP forms. The species *Lens culinaris*, *Hordeum vulgare*, and *Trifolium alexandrinum* that respond to OP forms with a high percentage of fine roots and specific root length and intermediate expression of P *mining* traits, may be more effective in releasing the various forms of OPs adsorbed and/or precipitated on soil constituents, such as IHP which is very strongly adsorbed on the soil (Figure 32). From an agronomic standpoint, a system that combines N-rich organic fertilizer in the form of NO₃-N and the establishment of *Fabaceae* species may be effective in utilizing OPs and specifically IHP, which is the major form of OP in the soil.

8.4 From theory to practice: Incorporate all mechanisms/processes into models and decision support tools to estimate soil P availability and manage P fertility from organic inputs

Agricultural systems modeling can be used to improve our understanding of the complex interactions between soil, plants, and the environment and thus support decision making (Jones et al., 2003). However, modeling changes in the cycling of OP forms with respect to their availability and contribution to plant growth is a challenging task (Honvault et al., 2020). The challenge of simulating complex chemical reactions related to OP is related to the fact that key processes can be very different across soil types, organic fertilizer types, application strategies, and environmental conditions. An effective soil-crop mineral OP model could serve as a tool to improve P fertilizer management for different soil types, climate, and farming practices (Li et al., 2019). However, while many attempts have been made to simulate P behavior in agricultural systems, most of them have focused on field and watershed scales and have been specifically designed to predict P losses and transport to groundwater and surface water (Achat et al., 2016), rather than to predict P dynamics in soil-plant systems (Table 28). Those that do are generally based on simplified OP cycles that seek to predict P transformations and soil P availability (Table 28), with an emphasis on the interaction between the available P pool and crop demand that determines crop P uptake (Achat et al., 2016). It is therefore unclear whether current modeling platforms are able to accurately account for the dynamics of OPs in different soil types, their interactions with N forms, and the plant acquisition strategies that determine their fate. The interaction with environmental factors such as soil water content, which affect both root activity/distribution and crop P acquisition, is also not well understood. To effectively simulate the dynamics of OP in an organic fertilizer-soil-crop system, an effective model must include four of the key components (Figure 33, Table 28): (i) a component that thoroughly simulates the intrinsic properties that govern mineral-OP interaction, i.e., modeling the adsorption and desorption dynamics of several major forms of OP on several representative soil minerals; (ii) a component capable of accurately reflecting the demand for and uptake of P from OP forms by plants, as well as the effects of P on crop growth, and one related to the cycling and transformations of soil OP that determine the amount of soil P available for uptake by plants; (iii) a component that evaluates and simulates the irrespective and interactive effects of N and P forms and their interaction with soil minerals on P limitation and P uptake in plants and finally (vi) a component on the role of P acquisition strategies on the mobilization and acquisition of specific forms of OP. The four components must of course accurately represent the key processes, but in order to effectively simulate the dynamics of OP or more generally P in a cropping system, the interactions between these components are also essential, particularly the responses of crop growth to changes in OP availability (Daroub et al., 2003).

8.4.1 The need to incorporate the parameters of adsorption and desorption of OPs to develop a model to predict the release of OPs in agroecosystems

The first P model that attempted to integrate P pools, soil, and plant components was the P module developed in the 1980s for the Erosion-Productivity Impact Calculator (EPIC) model and reported by Jones et al. (1984). This EPIC model was constructed from regression analyses of 78 different soils from the United States and Puerto Rico (Sharpley et al., 1984), with the soils then divided into three categories: calcareous, slightly weathered, and heavily weathered. These three soil categories are then used to guide the initialization of the "labile P" pool by combining soil P pools with an equation related to soil type. On the other hand, the DSSAT model proposed by Daroub et al. (2003) sets the P pool size based on the sequential P fractionation results of Hedley et al. (1982) and the transfer equations between P pools are linked to specific soil properties ("low pH weathered soils" and "high pH calcareous soils"). Some soil P models have also distinguished between IP and OP pools, allowing simulation of inorganic and organic P fertilization. However, these models are overall focused on a very simplified simulation of soil P dynamics and hardly any agricultural models have tested and integrated the dynamics of OP despite its importance in predicting plant productivity. The surface movement of dissolved P, for example, is considered in the ANIMO and GLEAMS models, but not the processes of P adsorption and desorption, nor those of OP in the soil, even though some very simplified equations are included in the GLEAMS model (Raymond et al., 2021). The widely used APSIM and DAYCENT model considers only sorbed IP in equilibrium with soil labile P from which leaching occurs, and includes representation of P loss through soil erosion. Furthermore, none of these models consider the important desorption process of IP, with the exception of the MACRO model, which incorporates it in a very simplified manner without linking it to the forms of OP (Yang et al., 2014). A major implication of deciphering the interactions between soil minerals and the predominant forms of OP in soils and organic fertilizers (**Chapter 1**) and of studying P availability to plants from several mineral-OP complexes (**Chapter 2**) is the incorporation of these product parameters into modeling approaches or to improve existing models (Figure 33). Adsorption parameters, determined by fitting data to the nonlinear form of Langmuir and Freundlich isotherm models (**Chapter 1**; Amadou et al., 2022a), provide several equations that could be incorporated as predictive mechanisms for OP immobilization in existing models such as EPIC, DSSAT or MACRO. In addition, desorption-related parameters calculated by fitting data to the nonlinear form of the Elovich kinetic model (Bulut et al., 2008) also emerge as important parameters to strengthen existing models to predict OP release to soils while reducing OP losses to the environment. Current models do not consider properties related to specific forms of OPs such as IHP and other important OP pools such as GLY or G6P (Raymond et al., 2021; Yang et al., 2014), which, together with IHP, nevertheless account for a significant portion of total P in soil (Darch et al., 2014). Furthermore, the influence of physicochemical properties of the main specific soil minerals, which are

major determinants of the ability of soil minerals to interact with P, is not considered. Through the study of the mechanisms controlling the dynamics of various OP compounds (IHP, GLY and, G6P) into and from several soil minerals, including Fe and Al oxides (goethite and gibbsite, respectively) and clay minerals (kaolinite and montmorillonite), we argue that factors related to soil properties and OP molecular traits directly affect OP reactions and release in soil. Therefore, the integration of these information is necessary to improve the accuracy of the prediction models (Table 28). In addition, the consequences of interactions between minerals and OP forms on plant P nutrition elucidated in **Chapter 2**, provide important information for the development of a specific model for predicting OP release to the soil (Figure 33).

Table 28: Biogeochemical and crop model characteristics and roadmap for improving coupled biogeochemical and ecosystem C-N-P cycle models based on this study

Models	Main gaps	Priority	Modelers' roadmap	Empiricists' roadmap
APSIM CLM-CNP GLEAMS MACRO ECOSYS DAYCENT ANIMO	<u>OP cycle:</u> Dynamics of organic P	Very high	A detailed description of the biogeochemical and molecular properties of specific forms of OPs such as IHP, GLY, G6P, and others.	Need to consider parameters related to the properties of OP forms (Amadou et al., 2022a).
EPIC CREAMS	Release of OP through weathering of soil minerals	High	Improvement of functions; but lack of data	Need for dedicated study of environment-weathering interactions for different OP forms and soils
CASA-CNP JSBACH-CNP WATBAL	<u>IP cycles:</u> Dynamics of inorganic P	Moderate	A better description of the effects of soil properties and root traits	Need for general relationships between soil properties and inorganic P dynamics (i.e. Achat et al., 2016; Gérard, 2016)
N14CP APSIM CLM-CNP SWATRE	<u>Soil minerals and OP cycles:</u> Poor insight into mineral-OP interactions	High	Simultaneously analyzing the interactions between various OP forms and various soil mineral	Need to establish and model general relationships between properties of multiple soil types and OP dynamics (Amadou et al., 2021)

JSBACH-CNP	<u>N and OP cycles and</u>			
CASA-CNP	<u>minerals:</u>			
DSSAT				
APSIM	Biogeochemical	Very High	Investigate and generate data on the	Need for data to enable ecosystem
ECOSYS	processes of N-OP-soil minerals.		irrespective and interactive effects of N and OP forms and their interaction with soil minerals on P limitation.	models to accurately predict plant N-P limitation and its impacts, but also to develop robust ecosystem models with fully coupled N-P interactions.
APSIM	<u>Interactions</u>			
CLM-CNP	<u>between</u>			
JSBACH-CNP	<u>C, N, and OP</u>			
N14CP	<u>Cycles:</u>			
CASA-CNP				
DSSAT	Plant adjustments	High	Implementation using existing data; need for	Model-experiment interactions to
ECOSYS	inducing changes inOP		a more reliable approach to predicting	evaluate model assumptions
SWATRE	use efficiency		stoichiometric flexibility (Zaehle et al. 2014); selection of the most accurate mode of representation of N and OP growth limitation by multiple resources (Rastetter 2011)	Zaehle et al. (2014) and to improve the understanding of global change impacts (e.g. effects of increased N and P limitations)
			Mineralization fluxes currently	
	Plant growth response	High	based on C:N:P stoichiometry	Need for in-depth studies on
	to multiple		assumption; but lack of	poorly understood processes
	limitations due to		experimental evidences on OP sources	(e.g. N and OP limitations ; Ellsworth et al. (2015))
	OP or other resources			
	scarcity			
APSIM	<u>OP and Crops P</u>			
CLM-CNP	<u>acquisitions strategies:</u>			
JSBACH-CNP				
N14CP	Plant P <i>foraging</i> and			
CASA-CNP	<i>mining</i> strategies	High	Characterizing the key traits involved in	Need for highlighting the major traits
DSSAT	affecting OP dynamics		<i>mining</i> and <i>foraging</i> OPs and their ability to better predict P acquisition	involved in OP-based <i>mining</i> and <i>foraging</i> and their contribution to P availability and acquisition.
	Tradeoffs between P			
	acquisition traits	High	Design of crop species composition and more specifically the functional structure of crop communities (e.g. intercrops, cover crops...) to estimate total soil OP reserves and at least its specific forms (IHP, G6P, GLY, etc.) in a multi-species cropping	Need for a combined field and experimental approach with different crop species and different forms of Organic fertilizers; Coupled model- experiment study

8.4.2 Improving functioning ecosystem modeling by incorporating biogeochemical N-OP interaction and their impacts on plant N-P limitation

Ecosystem N and P cycles consist of multiple biogeochemical pools and processes that are linked and interdependent, jointly controlling soil P availability, plant P uptake and plant P limitation (Vitousek et al., 2010). Recently, P modules have been integrated into ecosystem models such as CASA-CNP (Wang et al., 2010), JSBACH-CNP (Goll et al., 2012), CLM-CNP (Yang et al., 2014), and N-COM (Zhu et al., 2016) to study nutrient limitations on carbon cycling and C-N-P interactions. In these models, P is typically stored in several pools, including plant biomass, litter, available soil P forms (Vitousek et al., 2010). P dynamics are often coupled to C and/or N cycling through the stoichiometric relationship of C, N, and P in plant tissues and soils (Goll et al., 2012; Wang et al., 2010). With the ANIMO and DAYCENT models (Achat et al., 2016), soil N is represented as NO_3N and NH_4N . They consider the movement of N from applied fertilizer or manure. Although efforts have been made recently to add interactions between N-IP pools in some models, the influence of N forms, OP chemical forms, and their interactions with soil minerals are poorly represented or simplified in C-N-P models, which could have consequences for model predictions (table 28). More importantly, this limits the ability of ecosystem models to analyze the effects of potential future climate change on overall ecosystem productivity (Deng et al., 2017; Goll et al., 2012). We found that irrespective of soil minerals, when N is added, the plant becomes co-limited in N and P in the presence of IP, whereas the plant systematically shifts to P limitation in the presence of OP forms (**Chapter 3**). The pattern of available P and P limitation after N addition ($\text{IP} > \text{IHP} > \text{GLY}$, **Chapter 1**), reinforces the assumptions that the type and biochemical nature of OP sources determine the degree of nutrient limitation in plants (Amadou et al., 2022b). Therefore, the biochemical properties of OP forms and the properties of soil minerals are both required in C-N-P models to account for the N-P interaction in the soil-plant system (Figure 33). The influences of N additions on OP pools and processes revealed in this study could help for understanding the roles that N and P play in controlling plant growth and internal nutrient accumulation and to accurately parameterize the C-N-P models (Achat et al., 2016). The degree of P limitation varies considerably between mineral types and forms of P (**Chapter 3**) due to the contrasting physicochemical properties of the minerals used (**Chapter 1**, Bai et al., 2021; Yang et al., 2014) and the biochemical nature of P sources (Anderson, 1980; Condron et al., 2005). Thus, incorporating physicochemical properties of specific key soil minerals that drive N-OP interactions into ecosystem models is necessary to specifically

simulate the effects of N on ecosystem productivity and carbon accumulation potential by mitigating N and/or P limitations (Elser and Bennett, 2011). The data generated on the effects of specific interactions of several forms of OP, N interacting with different soil minerals (**Chapter 3**) in combination with the properties deciphered in **Chapter 1** could potentially be specified in the CASA-CNP and CLM-CNP models for optimization. The integration of the data and parameters generated from **Chapters 1, 2** and **3** into the C-N-P models is necessary for more comprehensive studies of ecosystem processes, feedback, and responses to environmental change. In particular, because tropical ecosystems have a significant effect on the global carbon cycle, future C-N-P models will need to be able to account for the heterogeneity of N versus P limitation in these ecosystems (Figure 33).

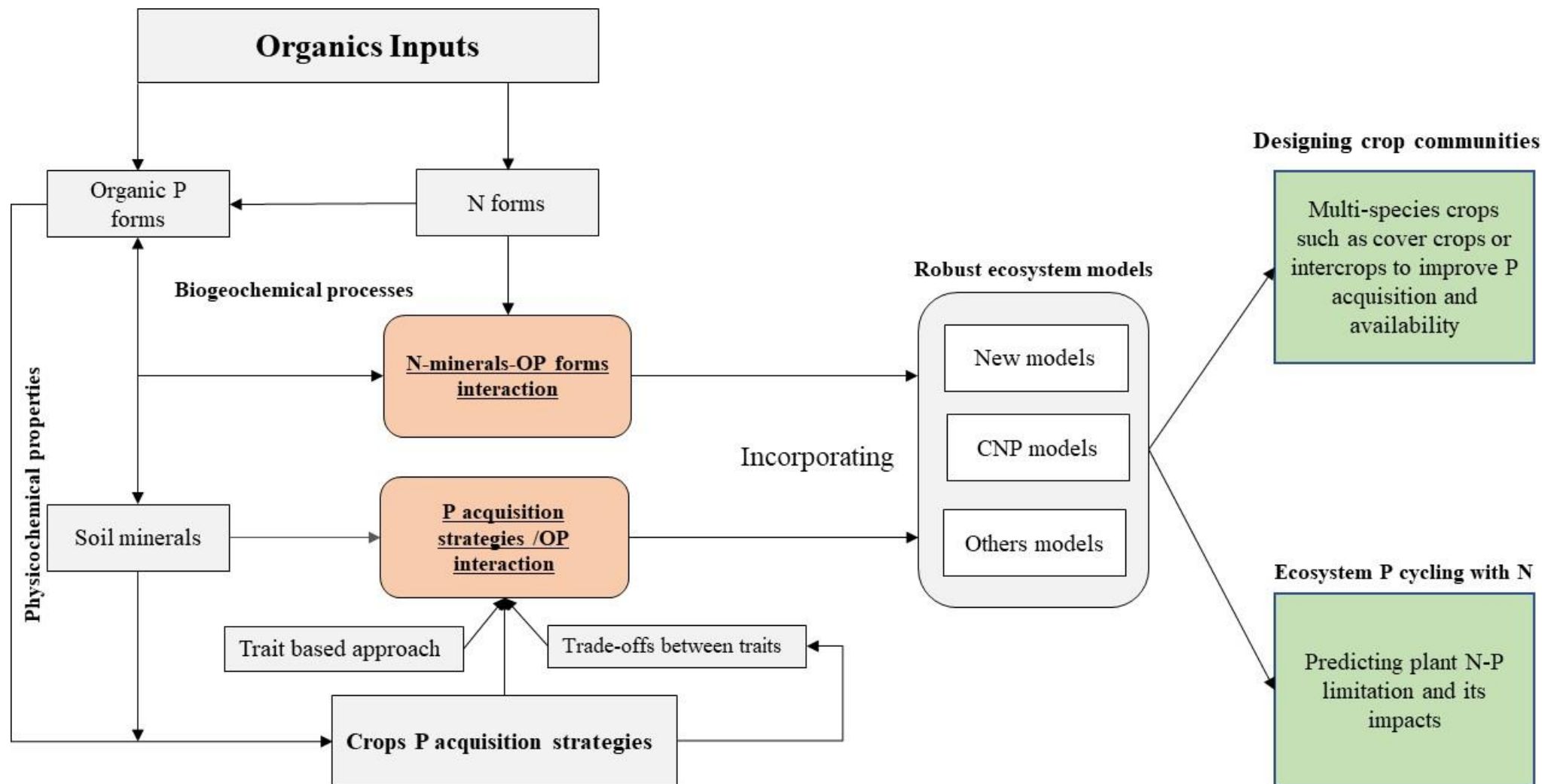


Figure 33 : Challenges and processes that need to be included in the models based on these studies.

The arrows represent the different interactions and influences between N forms, organic P forms, and soil minerals and plant P acquisition strategies in the organic fertilizer-soil-plant system. Considering these processes is expected to allow ecosystem models to accurately predict plant N-P limitation and its impacts, but also to develop robust ecosystem models with fully coupled N-P or C-N-P interactions. At the agricultural level, this would allow the design of crop communities (i.e., multi-species crops), such as cover crops or intercroops, to enhance P

8.4.3 The importance of incorporating the role of P acquisition strategies in OP availability into models and decision support systems for optimal crop and organic fertilizer management

A major implication of examining the response of P acquisition strategies to various forms of inorganic and organic P (**Chapter 4**) and their consequences for OP availability and P acquisition is the incorporation of this knowledge into modeling approaches. Modeling the role and impact of plant P acquisition strategies, which are related to multiple morphological and physiological traits and interactions among them, allows for the assessment and quantification of the potential benefits and effectiveness of cropping strategies on OP availability and uptake from soil minerals and its potential availability to subsequent crops. Attempts to model these processes, even partially, could provide a basis for incorporating the effects of P acquisition strategies on P availability into decision support systems, allowing farmers to optimize their crop design and management and tailor their OP-rich fertilization (Damon et al., 2014). While the contribution of cover crop P mobilization to subsequent crop P uptake is highlighted in a recent study that suggests incorporating it into models (Hallama et al., 2019; Zhu et al., 2016), as is the contribution of positive microbial feedbacks (Hallama et al., 2019), no model contains a module developed to specifically assess the impact of P acquisition strategies on plant mobilization of different forms of OP. Several models have demonstrated the ability to incorporate P release from crop residues and manures into crop growth and yield projections, including the modeling frameworks The Agricultural Production Systems Simulation (APSIM) (Keating et al., 2003), Century (Parton et al., 1988) and CERES-Wheat (Daroub et al., 2003; Nain and Kersebaum, 2007). However, these models require specific and detailed information about the biogeochemical processes that govern the dynamics of OPs, and simple tools that can be used by a layman (Table 28). The implication of soil types, N and OP composition of amendments, and crop strategies is not widely recognized, and there is currently no decision support system that can predict it from a set of simple and readily available variables (Table 28). Thus, optimization of current models requires detailed information that is not readily available at the farm level (Damon et al., 2014). For instance, several species in this study (**Chapter 4**) were efficient in utilizing OPs without the assistance of the rhizosphere microbiome. Several other crop species with different root traits are similarly known to access and mobilize more OP in low P soil (Bates and Lynch, 2000). Thus, the knowledge generated here (**Chapter 3 and 4**) could be formulated into simple, readily available, and easy-to-use variables, which is advantageous for implementing models as part of a larger decision support system accessible to farmers. Modeling the relationships between the combination of leaf and root traits on P acquisition from OP (**Chapter 4**) allowed us to reinforce observations of changes in the direct contribution of P acquisition strategies (*mining* and *foraging*) on different forms of OP (IHP, G6P, GLY, DNA and RNA) sorbed to different soil mineral conditions, but they also had the benefit of highlighting remaining knowledge gaps to be filled in evaluating the effects of different crop design systems on OP availability. Selection by PLS

modeling (**Chapter 4**) of plant-specific traits involved in the dynamics of species of different forms of OP (IHP, GLY) under different soil mineral types can be considered in future models (Figure 33). Targeted elucidation of these plant P acquisition strategies in a range of contexts and at the field level could provide more accurate estimates of crop effects on P availability via P release from OP forms. However, as noted in **Chapter 4**, the relative contribution of a specific process to the effects of P acquisition strategies (*mining* and *foraging*) on P availability is likely to be highly dependent on species, biochemical nature of P forms, and soil conditions, and in particular P availability. Plant P *mining* and *foraging* strategies have been successful in improving the cycling and availability of OPs relative to IP forms (**Chapter 4**), despite the stronger sorption of OPs to soil demonstrated in **Chapter 1**, which limited their availability to plants (**Chapter 2**). A better understanding of these processes should contribute to the development of more accurate and comprehensive models for agroecological intensification.

8.5 A proposed global model design to improve the efficiency of OP utilization on a global scale

Significant advances have been made in recent years in ecosystem models, incorporating formulations of P-specific processes and C-N-P interactions (Achat et al., 2016). However, there is considerable room for further improvement, especially in processes related to soil mineralogy, the OP forms of organic fertilizers, and their interactions with C and N forms and concentrations that are known to control plant response to climate change and nutrient limitation (Table 28). At the global scale, results related to soil minerals, P forms and to some extent plant P acquisition strategies as well as pH and climatic data are highly relevant for P availability and dynamics (i. e. different OP and IP forms). Based on the results of simulations and modeling of processes related to N-OP-mineral interactions and related crop traits, we suggest to modelers and empiricists the following building blocks complement the current C-N-P model processes and thus improve soil OP mobilization (Figure 34).

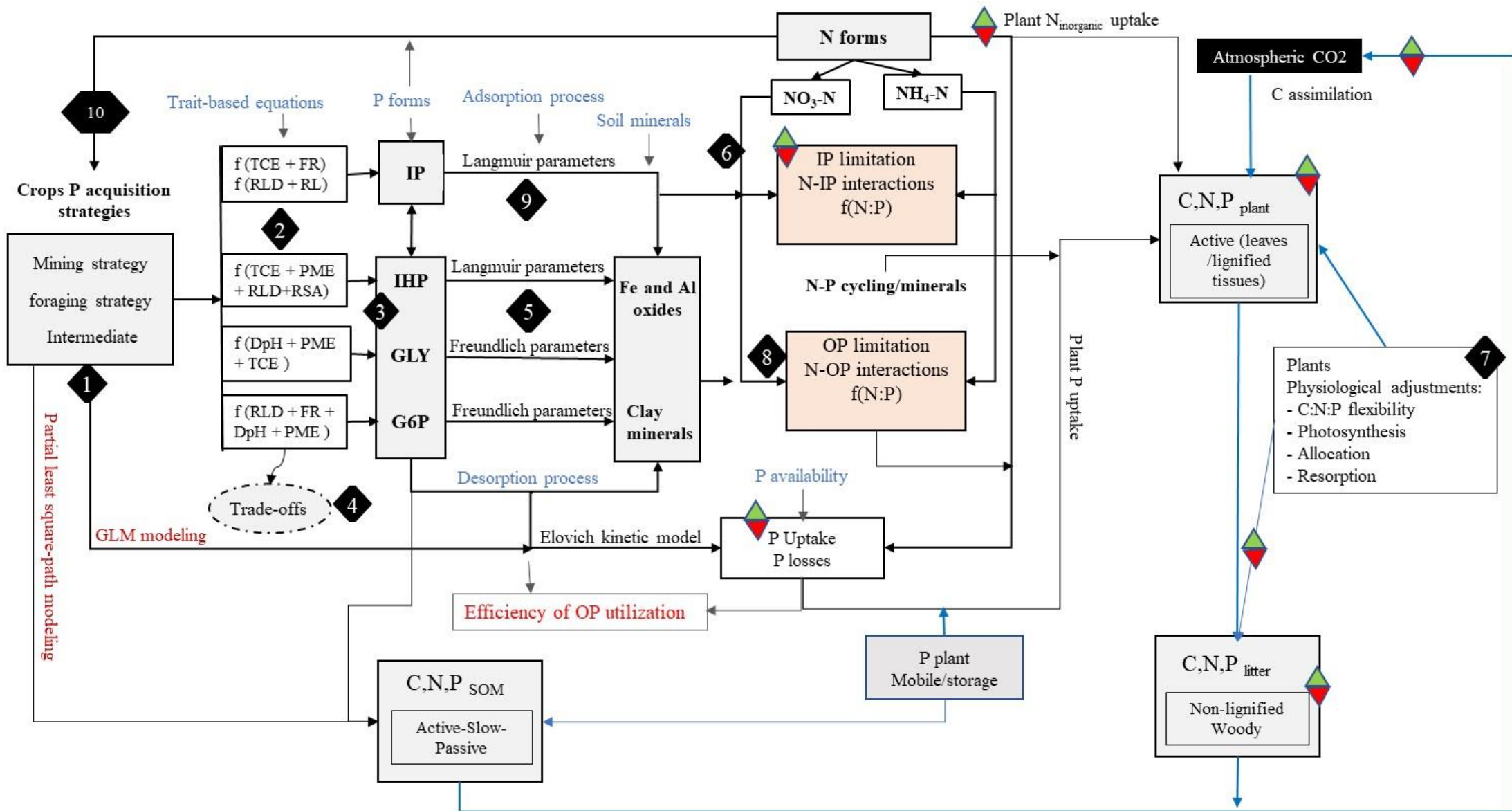


Figure 34: Proposed process for a C-N-P model to improve the efficiency of OP use and measure its impact on P limitation.

The basic processes existing in C-N-P models have been simplified (processes that include the blue arrows). Black arrows connect the processes proposed in our study (globally non-considered in C-N-P models) and blue arrows represent the simplified processes of C-N-P models from previous studies. The red-green icons show the C-N-P interactions that are generally considered. The

main gaps in C-N-P interactions that were proposed in this study (black box numbers) are: (1) response and effect of *foraging* and P-plant *mining* strategies on OP dynamics; (2) modeling of specific root traits involved in the mobilization efficiency of the OPs used; (3) a detailed description of the biogeochemical and molecular properties of specific forms of OPs such as IHP, GLY, G6P, and others; (4) trade-offs between root P acquisition traits of crop species for OP mobilization; (5) modeling OP dynamics from various soil minerals; (6) interactive effects of N and OP forms and their interaction with soil minerals on P limitation; (7) mechanistic approach to model C:N:P flexibility and other plant adjustments; (8) modeling the impact of N-OP-mineral interaction on P uptake and P limitation; (9) inorganic P dynamics: effects of soil properties, consistency between time to reach equilibrium between P pools and model time steps; (10) mechanistic representation of root traits, i.e., PME, TCE production, controlled by N and P (other exudates and fungal infection are generally not considered in the models).

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APPENDICES

9 APPENDICES

APPENDIX A– SUPPLEMENTARY INFORMATION FIRST CHAPTER

APPENDIX A– SUPPLEMENTARY INFORMATION SECOND CHAPTER

APPENDIX B– LIST OF PUBLICATIONS AND COMMUNICATIONS

9.1 APPENDIX A – Supplementary information first chapter

Table S1: References of minerals

Goethite (sigma):
 Ref: 71063
 CAS No.: 20344-49-4
 EC No.: 243-746-4

Gibbsite (sigma):
 Ref: 239186
 CAS No.: 21645-51-2
 EC No.: 244-492-7

Kaolinite (sigma):
 Référence de produit : 03584
 Numéro CAS : 1318-74-7

Montmorillonite (VWR) :
 Référence de produit : L15160.30
 Numéro MDL : MFCD00132796
 Numéro CAS : 1318-93-0

Table S2: Amount of adsorbed P (Qads) and associated standard error (Se). Ci : initial P concentrations (C0 = 0, C1= 4, C2= 8, C3= 16, C4= 32, C5= 75, C6= 100 mgg⁻¹)

Minerals	P forms	Ci (mgL ⁻¹)	Qads (µg g ⁻¹)	Se	
Goethite	IP	C0	0	± 0	
		C1	652.12	±51.47	
		C2	1320.19	±54.49	
		C3	1889.86	±42.54	
		C4	2401.37	±177.44	
		C5	2581.69	±15.72	
		C6	2639.41	±55.45	
	IHP	C0	0	±0	
		C1	1173.94	±47.48	
		C2	2049.98	±18.99	
		C3	3041.44	±283.56	
		C4	3465.61	±432.52	
		C5	3604.08	±118.56	
	GLY	C0	0	±0	
		C1	1196.23	±34.71	
		C2	1322.32	±92.77	
		C3	1366.78	±31.57	
		C4	1386.3	±109.8	
			C5	1391.8	±30.92

		C6	1393.07	±13.39
	G6P	C0	0	±0.62
		C1	477.7	±21.34
		C2	1063.39	±26.06
		C3	1826.11	±143.4
		C4	2695.29	±12.22
		C5	3400.51	±348.3
		C6	3549.65	±905.97
Gibbsite	IP	C0	0	±0
		C1	3786.76	±1.32
		C2	4176.71	±1.84
		C3	4044.4	±2.86
		C4	19087.85	±181.93
		C5	20353.51	±401.35
		C6	20553.76	±425.39
	IHP	C0	0	±0
		C1	1191.95	±4.55
		C2	2334.82	±9.1
		C3	8312.38	±36.39
		C4	15660.78	±53.51
		C5	30263.72	±160.54
		C6	36017.74	±170.16
	GLY	C0	0	±0
		C1	920.96	±5.17
		C2	1976.18	±28.16
		C3	3655.18	±232.31
		C4	5049.36	±38.48
		C5	5613.24	±290.24
		C6	5757.88	±109.6
	G6P	C0	0	±0
		C1	1569	±27.33
		C2	2608.53	±125.59
		C3	4433.58	±2.04
		C4	5118.91	±829.85
		C5	5373.9	±465.71
		C6	5422.82	±371.52
Kaolinite	IP	C0	0	±0
		C1	189.38	±69.48
		C2	366.07	±160.83
		C3	608.51	±126.23
		C4	1018.9	±79.97
		C5	1259.62	±68.06
		C6	1357.61	±90.75
	IHP	C0	0	±0

		C1	298.92	±46.53
		C2	570.49	±97.98
		C3	1127.46	±17.12
		C4	2152.24	±54.83
		C5	3148.88	±195.33
		C6	3566.47	±693.4
	GLY	C0	0	±0
		C1	98.64	±2.45
		C2	174.59	±2.83
		C3	302.89	±30
		C4	560.54	±49.47
		C5	750.07	±108.59
		C6	821.24	±243.52
	G6P	C0	0	±2.94
		C1	286.46	±40.72
		C2	502.73	±171.83
		C3	850.57	±28.5
		C4	1306.37	±366.46
		C5	1672.42	±213.77
		C6	1765.95	±387
Montmorillonite	IP	C0	0	±0
		C1	444.46	±12.57
		C2	916.56	±171.05
		C3	1484.75	±74.51
		C4	2412.39	±130.14
		C5	2890.91	±149.94
		C6	3078.23	±137.43
	IHP	C0	0	±0
		C1	1401.83	±35.95
		C2	2477.21	±68.48
		C3	3491.83	±224.4
		C4	4399.07	±256.06
		C5	4633.78	±226.87
		C6	4689.44	±150.78
	GLY	C0	0	±0
		C1	489.81	±12.35
		C2	686.71	±60.02
		C3	835.58	±17.56
		C4	956.52	±257.07
		C5	996.78	±10.31
		C6	1007.43	±48.28
	G6P	C0	0	±1.36
		C1	512.69	±198.69
		C2	940.61	±128.54

C3	1369.95	±44.67
C4	1814.2	±252.49
C5	2049.91	±235.07
C6	2099.92	±470.13

9.2 APPENDIX B – Supplementary information second chapter

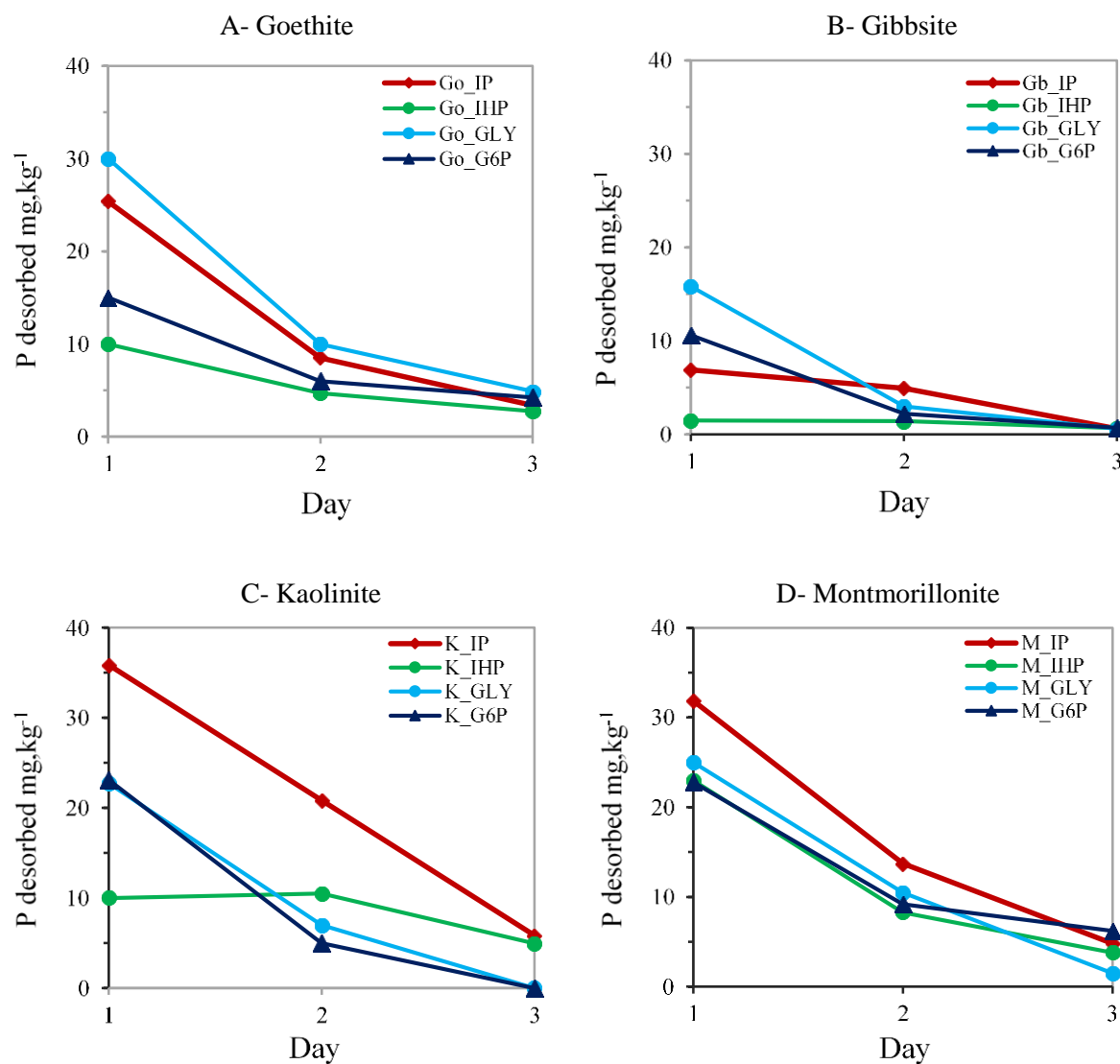


Fig S1 Desorption dynamics of P from P-mineral complexes. Desorption were initiated by adding 40 ml of 0.1 M KCl adjusted to pH 5.5 to 0.5g of the different minerals-P complex. Samples were shaken on a mechanical shaker at 25 °C at regular intervals (24h, 48h, 72h). Soils minerals (Go: goethite, Gib: gibbsite, K: kaolinite and M: montmorillonite); Phosphorus compounds (IHP: myo-inositol hexakisphosphate, GLY: glycerophosphate, G6P: glucose-6-phosphate and IP: KH_2PO_4); The dashes (-) identify the mineral-phosphorus complexes produced by the adsorption of P forms onto soil minerals. Example Go-IHP refers to goethite and myo-inositol hexakisphosphate complexes.

9.3 APPENDIX C– list of publications and communications

Articles published in international peer-reviewed journals

Amadou, I., Houben, D., & Faucon, M. P. (2021). Unravelling the role of rhizosphere microbiome and root traits in organic phosphorus mobilization for sustainable phosphorus fertilization. A review. *Agronomy*, 11(11), 2267. <https://www.mdpi.com/2073-4395/11/11/2267>

Amadou, I., Faucon, M.-P., Houben, D., 2022a. New insights into sorption and desorption of organic phosphorus on goethite, gibbsite, kaolinite and montmorillonite. *Appl. Geochem.* 143, 105378. <https://doi.org/10.1016/j.apgeochem.2022.105378>

Amadou, I., Faucon, M.-P., Houben, D., 2022b. Role of soil minerals on organic phosphorus availability and phosphorus uptake by plants. *Geoderma* 428, 116125. <https://doi.org/10.1016/j.geoderma.2022.116125>

Oral communications in national and international congresses

Amadou I, Faucon MP, Houben D. Adsorption and desorption of organic forms of phosphorus by Fe/Al oxyhydroxides, clay minerals and humic substances. Journées d'étude des sols (JES) 2021: June 21-25 Montpellier

Amadou I, Faucon MP, Houben D. Adsorption and desorption of organic Phosphorus forms by Fe/Al oxyhydroxides, clay minerals and humic substances. 22nd world congress of soil science: 31 July - 5 August 2022 in Glasgow.

Amadou I, Faucon MP, Houben D. Role of soil minerals on organic phosphorus availability and phosphorus uptake by plants. Sustainable Phosphorus Alliance organized by Arizona State University (ASU) November 1-4.

RESUME ETENDU

RESUME ETENDU

Rôle des formes de phosphore organique, des minéraux du sol, de l'azote et des traits fonctionnels des plantes sur la disponibilité et l'acquisition du phosphore par les plantes pour une gestion optimale des engrais organiques dans les agrosystèmes

Issifou AMADOU

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Introduction

Enjeux agroécologiques de la mobilisation du phosphore organique pour une fertilisation phosphorée durable

Le phosphore (P) est un nutriment limitant pour la productivité des agroécosystèmes. Ceci est dû à sa faible disponibilité dans le sol qui résulte de sa faible solubilité et de sa forte affinité pour les surfaces minérales. La fertilisation phosphorée est donc nécessaire pour obtenir des rendements élevés. La plupart du P actuellement utilisé dans les engrais chimiques provient des roches phosphatées. Ces ressources sont inégalement réparties à la surface de la Terre et, dans l'Union européenne (UE), la production alimentaire dépend des importations de P primaire. Étant donné que les réserves ne se trouvent qu'à quelques endroits sur la Terre, et qu'elles sont donc contrôlées par quelques pays, l'approvisionnement en P de l'UE est vulnérable aux questions géopolitiques, avec des problèmes possibles d'accessibilité et de prix des engrais P à moyen terme. De plus, le phosphate naturel est une ressource stratégique dont l'exploitation peut entraîner des occupations et des conflits armés. Dans l'optique d'une gestion plus durable du P dans les systèmes de culture, les amendements organiques renouvelables et riches en nutriments sont de plus en plus considérés comme un complément aux engrais P produits à partir de roches phosphatées, non seulement par les scientifiques mais aussi par les politiciens et les parties prenantes. L'utilisation d'intrants organiques représente le passage d'une utilisation linéaire d'une ressource limitée à une économie circulaire, car elle favorise la réduction de l'utilisation des combustibles fossiles et des émissions de gaz à effet de serre, tout en contribuant au développement de nouveaux marchés verts et d'emplois en favorisant la conversion des déchets en produits à valeur ajoutée. L'utilisation d'intrants biologiques privilégie la transition vers une agriculture durable, en mettant l'accent sur la prévention des impacts environnementaux, grâce à l'adoption de systèmes technologiques innovants. L'avantage en termes de durabilité de l'utilisation de P organique renouvelable dépend des systèmes agricoles associés à de faibles émissions de carbone provenant du trafic de P renouvelable, tels que les systèmes d'élevage qui utilisent des effluents ou des digestats, ou d'autres systèmes agricoles qui utilisent des coproduits de l'agro-industrie à l'échelle du territoire, et les systèmes d'agriculture urbaine et périurbaine qui valorisent les boues. L'utilisation d'intrants organiques comme ressource durable et renouvelable est une nécessité pour répondre aux questions socio-économiques et scientifiques qui ont été récemment soulevées concernant les approches de gestion durable du P. Par exemple, en France, 78 % et 62 % du P et du N, respectivement, utilisés en agriculture proviennent d'intrants organiques. En 2007, on estime qu'un total de 10 millions de tonnes de boues d'épuration ont été produites dans l'UE. Ce chiffre devrait dépasser 13 millions de tonnes en 2020 et continuer à augmenter en raison de la mise en œuvre de la directive sur le traitement des eaux urbaines résiduaires (directive 91/271/CE). Cependant, contrairement aux engrais P conventionnels, tels que le superphosphate triple, le P est présent dans les intrants organiques sous diverses formes inorganiques et

organiques qui varient dans leur disponibilité pour les plantes. La plupart des recherches sur le devenir du P appliqué au sol se sont concentrées sur la dynamique du P inorganique (IP). En revanche, le devenir des formes de OP, qui peuvent représenter jusqu'à 80 % du P total du sol, a été négligé jusqu'à présent, et il reste un manque de connaissances sur la contribution de ces formes à la nutrition des plantes. Des études ont montré que le P provenant d'apports organiques pouvait être plus disponible que le P provenant d'engrais chimiques. Cependant, cette disponibilité était affectée par les minéraux du sol, les niveaux et formes de l'azote (N) et les traits d'acquisition du P des racines des plantes cultivées. Par conséquent, une meilleure compréhension des interactions entre les formes de OP, les minéraux du sol, les caractéristiques des racines et les microbiomes de la rhizosphère, peut aider à mieux gérer la fertilisation en P organique.

Rôle des minéraux du sol dans la dynamique du phosphore organique

Les minéraux du sol tels que les oxyhydroxydes de fer (Fe) et d'aluminium (Al) (par exemple, la goéthite et la gibbsite, respectivement) et les minéraux argileux (par exemple, la kaolinite, la montmorillonite) sont des composants majeurs du sol. Ils ont fait l'objet d'une attention considérable en raison de leur forte capacité d'adsorption du P qui peut conduire à une utilisation inefficace des OP dans les sols (de 5 à 10 %). Cela conduit à une piètre utilisation des sources d'OP dans les agroécosystèmes. En effet, des formes spécifiques d'OP telles que l'inositol hexakisphosphate (IHP), le glycérophosphate (GLY) et le glucose-6-phosphate (G6P), sont généralement considérées comme des formes majeures dans les engrais organiques. Chaque forme diffère des autres par sa teneur en P et sa taille moléculaire. Ces composés organiques de P adsorbés sur les minéraux se sont avérés être les formes les plus stables de P dans différents types de sol. Cela est dû à leur mécanisme de liaison spécifique. En effet, il a été constaté que le nombre de groupes phosphate dans un certain composé OP détermine la stabilité de son complexe avec la surface minérale. Par exemple, l'IHP, avec ses six groupes phosphates, présente généralement une forte liaison et une grande stabilité par rapport à d'autres composés OP ou IP qui ont un plus petit nombre de groupes phosphates. Jusqu'à quatre groupes phosphates de l'IHP interagissent avec la surface de la goéthite, ce qui entraîne la formation de complexes de sphère interne entre les groupes phosphates de l'IHP et la surface de la goéthite. Un mécanisme similaire a été suggéré pour d'autres complexes OP-minéraux. La désorption du P des surfaces minérales serait plus limitée pour les composés OP que pour les IP. Cependant, la mesure dans laquelle les composés OP adsorbés aux minéraux du sol peuvent se désorber reste mal comprise et leur disponibilité pour les plantes est encore débattue. Il a été suggéré que les complexes minéraux-OP ne sont pas disponibles pour les plantes parce que ces complexes sont formés pendant la phase de réaction lente avec les minéraux du sol. Ce processus a été supposé être une cause majeure de la limitation de la croissance des plantes. Ainsi, il a été suggéré que la disponibilité de l'OP est principalement limitée par sa solubilité et non par l'activité enzymatique. Quoi qu'il en soit, l'affinité des composés OP pour les minéraux du sol est plus grande que celle des composés IP, ce qui

indique la formation d'un complexe très stable d'OP avec les surfaces minérales. Par conséquent, on peut s'attendre à ce que la désorption et la disponibilité pour les plantes des complexes minéraux-OP soient plus faibles que celles des composés IP. Cependant, les très rares études sur les OP ne permettent pas de quantifier correctement leur contribution potentielle à la disponibilité du P dans le système engrais organique-sol-plante. À ce jour, on ne sait pas comment les formes chimiques des OP, et leurs interactions avec les minéraux du sol, influencent l'absorption du P à partir des OP par les plantes dans les écosystèmes. La rareté des recherches sur le processus limite considérablement notre capacité à comprendre la dynamique globale du cycle du P dans les écosystèmes et à optimiser l'utilisation des engrais P renouvelables qui contiennent souvent diverses formes d'OP.

Processus biogéochimiques impliqués dans la disponibilité et la limitation des OP : influence des formes de N et d'OP et de leur interaction avec les minéraux du sol sur la disponibilité et l'absorption de P par les plantes

Les intrants organiques, en plus des différentes formes d'OP qu'ils contiennent, diffèrent également en termes de concentration en N. Les interactions N-OP jouent un rôle majeur dans la dynamique des OP, créant des effets de Co-limitation ou de synergie selon leurs concentrations. Les interactions N-OP jouent un rôle majeur dans la dynamique des OP, créant des effets de Co-limitation ou de synergie en fonction de leurs concentrations, ce qui explique que la fertilisation organique soit gérée conjointement dans le système de culture. Ces interactions déterminent si les plantes sont limitées par le P, ou à la fois par le N et le P, ce qui influence la productivité et le fonctionnement des écosystèmes. L'ajout d'azote affecte l'absorption de P par les plantes directement en favorisant la croissance des plantes et la production de protéines, mais aussi indirectement en interagissant avec les pools de OP du sol. En particulier, il est bien connu que selon sa forme inorganique dans la solution du sol (c'est-à-dire $\text{NH}_4\text{-N}$ ou $\text{NO}_3\text{-N}$), l'azote peut augmenter ou diminuer la solubilité de l'OP, ce qui entraîne des changements dans la limitation et la disponibilité du P. Globalement, il a été déclaré que les plantes pourraient échanger N contre P en ajustant les taux d'acquisition de N et de P du sol, expliquant potentiellement les réponses synergiques de la croissance à l'ajout de N et de P. En outre, selon la disponibilité du P, l'effet de l'azote peut être plus ou moins prononcé, ce qui entraîne une limitation du P différenciée entre les formes IP et OP. Les avantages de l'ajout de N sur le cycle du P dépendent aussi fortement des propriétés des minéraux impliqués. Cela suggère que l'interaction entre les formes d'azote et les minéraux du sol est également cruciale dans le processus de mobilisation des formes de P. Le cycle de N et du OP dans l'écosystème consiste en de multiples bassins biogéochimiques et processus qui sont liés et interdépendants, contrôlant conjointement la disponibilité du P dans le sol, l'absorption du P par les plantes et la limitation du P. À ce jour, la manière dont les formes de N, les formes chimiques de OP et leurs interactions avec les minéraux du sol influencent à la fois la limitation du P et l'absorption par les plantes dans les écosystèmes n'est toujours pas claire. La rareté des recherches sur l'effet de ces

importants processus biogéochimiques (N-OP-minéraux du sol) limite considérablement notre capacité à comprendre les processus écologiques qui sous-tendent l'altération du cycle du OP dans les écosystèmes avec les ajouts d'azote. Plus important encore, cela limite notre capacité à comprendre le cycle du P dans l'écosystème. Une meilleure compréhension du cycle du P de l'écosystème en cas d'ajouts de N et des propriétés biogéochimiques impliquées est nécessaire non seulement pour permettre aux modèles d'écosystème de prédire avec précision la limitation de N-P des plantes et ses impacts, mais aussi pour développer des modèles d'écosystème robustes avec des interactions N-P ou C-N-P entièrement couplées.

Rôle des plantes et leurs traits dans la dynamique du P organique

Plusieurs approches directes et innovantes ont été identifiées pour améliorer la mobilisation et l'acquisition des formes OP par les plantes. Il s'agit notamment de l'identification et de la sélection d'espèces/génotypes cultivés sur la base de leurs traits fonctionnels. Cette approche utilise des traits morphologiques, architecturaux et physiologiques, des micro-organismes ou une combinaison des deux pour accéder à des formes de OP peu disponibles. En général, ces caractéristiques pourraient être classées en trois types de stratégies d'acquisition du P : La stratégie de " *foraging* ", la stratégie de " *mining* " et une stratégie combinant les deux. La stratégie de " *foraging* " de P des plantes est l'acquisition de P dans la solution du sol par des traits morphologiques et architecturaux en maximisant l'exploration du sol. Grâce à ces stratégies, les plantes peuvent induire un gradient de diffusion qui, à son tour, favoriserait le processus de désorption des différentes formes de OP adsorbées (Fang et al., 2017 ; White et Hammond, 2008). La stratégie de " *foraging* " implique des traits morphologiques tels que la longueur spécifique des racines, le pourcentage de racines fines et la surface des racines, et des traits architecturaux incluant la densité de la longueur des racines, la biomasse racinaire et la formation de racines groupées ou de symbioses mycorhiziennes à arbuscules qui permettent aux plantes d'augmenter leur capacité de butinage. La la stratégie de " *mining* " du P par les plantes, est l'acquisition du P dans la solution du sol par des traits physiologiques qui sont libérés dans le sol par les racines, y compris les glucides, les acides organiques et aminés, les composés phénoliques, les protéines, les acides gras, les stérols, les enzymes, les polysaccharides et les phospholipides. La stratégie collective fait référence à l'investissement de ressources par les plantes pour interagir avec la communauté microbienne afin d'accéder aux OP du sol. Plusieurs espèces végétales sont supposées être relativement efficaces dans l'utilisation des OP sans l'aide du microbiome de la rhizosphère. Les défis de la mobilisation et de l'acquisition des OP sont de comprendre la réponse des traits fonctionnels des plantes en fonction des formes d'OP et des propriétés du sol pour améliorer l'acquisition et la mobilisation du P des espèces cultivées. Globalement, les traits d'acquisition du P des plantes sont connus et leurs effets indirects et parfois même directs sur l'acquisition/mobilisation du P ont été démontrés. Les processus diffèrent en fonction de la nature des formes IP ou OP (phosphate mono ou diester) et des propriétés physico-

chimiques du sol. Ainsi, la disponibilité des différentes formes OP (IHP, G6P, GLY, ADN et ARN) en tant qu'effet direct des stratégies d'acquisition du P (*P-foraging, mining*) reste peu claire probablement en raison de sa forte liaison au sol. Ainsi, il a été suggéré que les stratégies des plantes peuvent être exploitées en utilisant des combinaisons d'espèces avec des stratégies contrastées ou en utilisant une seule espèce pour mieux comprendre leurs effets réels sur la mobilisation et l'acquisition des OP dans les agroécosystèmes. En bref, une meilleure compréhension de l'impact des stratégies d'acquisition du P sur la mobilisation et l'acquisition des OP par les plantes, qui sont liées aux multiples traits morphologiques et physiologiques et aux interactions entre eux, est essentielle pour la gestion de la disponibilité des OP. Par rapport à la IP, la réponse des stratégies d'acquisition du P aux composés OP et leur impact sur l'acquisition du P dans les sols amendés avec diverses formes d'OP ont reçu beaucoup moins d'attention. Les caractéristiques des espèces cultivées pourraient être utilisées pour augmenter la mobilisation des OP, ce qui aiderait à repenser la fertilisation en P, à maintenir la production et à recycler davantage d'OP dans les sols amendés avec des amendements organiques.

Objectifs

Ce projet de doctorat vise à mieux comprendre le rôle des formes de P organique, des minéraux du sol, de l'azote et des traits fonctionnels des cultures et leurs interactions sur la disponibilité et l'acquisition du P par les plantes pour optimiser la gestion des fertilisants organiques dans les agrosystèmes. Pour répondre à cet objectif général, quatre chapitres ont été produits pour examiner les questions centrales et toujours en suspens.

Le **chapitre 1** a examiné la dynamique de sorption et la désorption des formes majeure du P organique sur la goethite, la gibbsite, la kaolinite et la montmorillonite avec pour objectif de d'élucider la dynamique de l'adsorption et de la désorption de plusieurs formes d'OP sur plusieurs minéraux du sol représentatifs des différents types de sol. Plus spécifiquement, il s'agissait de déterminer les facteurs déterminants de l'adsorption et de la désorption des OP sur les minéraux du sol.

Le **chapitre 2** a ensuite examiné le rôle des minéraux du sol sur la disponibilité du OP et l'absorption du P par les plantes avec pour objectif d'élucider dans quelle mesure l'OP lié aux oxyhydroxydes de Fe et d'Al et aux complexes de minéraux argileux contribue à l'acquisition de P par les plantes. Plus précisément, nous avons déterminé la disponibilité du P pour les plantes à partir de plusieurs complexes de IHP, G6P et GLY qui ont été adsorbés sur des oxyhydroxydes de Fe et d'Al (goethite et gibbsite) et des minéraux argileux (kaolinite et montmorillonite). Les trois principales hypothèses suivantes ont été abordées : (1) le P des composés OP adsorbés est disponible pour le ray-grass et varie avec les propriétés minérales du sol ; (2) l'absorption relative du P des différents complexes OP-minéraux dépend de leur force de liaison et (3) les composés OP adsorbés sont moins disponibles que l'IP adsorbé car il se désorbe moins et nécessite non seulement une désorption mais aussi un clivage enzymatique avant d'être absorbé par le ray-grass.

Le **chapitre 3** vise à mieux comprendre comment l'azote et la minéralogie du sol déterminent la limitation du P et l'absorption du P par les plantes à partir de formes inorganiques et organiques de P. Les objectifs étaient d'évaluer les effets indépendants et interactifs des formes de N et de P et de leur interaction avec les minéraux du sol sur la limitation du P chez les plantes, d'élucider les processus biogéochimiques impliqués dans la limitation du P en caractérisant le rôle des formes de N et de P et leur interaction avec les minéraux du sol dans la disponibilité et l'absorption du P par les plantes. Les hypothèses étaient que (1) l'ajout de N sous diverses formes spécifiques augmenterait la limitation en P dans des conditions de faible disponibilité en P, c'est-à-dire avec des formes OP et des minéraux du sol, (2) le passage de la limitation en N à la limitation en P serait dû à l'effet bénéfique de l'ajout de N sur les processus de la rhizosphère impliqués dans la mobilisation/acquisition de P par les plantes, et (3) le degré de limitation en P et l'absorption totale de P par les plantes varieraient de manière significative selon le type de minéraux et les formes de P en raison des propriétés physico-chimiques contrastées des minéraux utilisés et de la nature biochimique des sources de P.

Enfin, le **chapitre 4** a pour objectif d'examiner la réponse des stratégies d'acquisition de P envers les formes de P (IP et OP) en interaction avec les minéraux du sol et leurs conséquences sur la disponibilité et l'acquisition de OP. Nous avons émis l'hypothèse que les stratégies d'acquisition de P (c'est-à-dire la recherche de nourriture et l'exploitation minière) diffèrent dans leurs réponses aux sources de P, ce qui favoriserait une plus grande disponibilité des OP et l'acquisition de P à partir des minéraux du sol.

Approche méthodologique

Quatre approches complémentaires ont été utilisées afin d'atteindre notre objectif global. Tout d'abord, les dynamiques d'adsorption et de désorption des formes OP sur plusieurs minéraux du sol ont été examinées et modélisées. Puis, dans un deuxième temps, les résultats des expériences de sorption et de désorption ont été validés en analysant l'absorption de P par les plantes en réponse à l'application de diverses formes d'OP sorbées sur divers minéraux du sol. Puisque les engrais P renouvelables diffèrent en termes de concentration en azote (N), ce qui peut avoir un impact sur les propriétés physico-chimiques et biologiques du sol et donc sur la dynamique des OP, la troisième étape a consisté à caractériser le rôle des formes N et P et leur interaction avec les minéraux du sol dans la disponibilité et l'absorption des OP par les plantes. Les trois premières étapes ont été réalisées en utilisant des composés organiques de P et un composé inorganique de P, et le ray-grass a été utilisé comme plante test. La dernière étape consistait à examiner la réponse des stratégies d'acquisition du P aux formes d'OP interagissant avec les minéraux du sol et leurs conséquences sur la disponibilité et l'acquisition du P organique, avant de modéliser les impacts attendus sur la disponibilité du P. Dans cette étape, des plantes avec diverses caractéristiques de mobilisation/acquisition de P ont été testées seules (traitement d'une seule espèce).

(Figure 7)

Chapitre 1 : Nouvelles perspectives sur la sorption et la désorption du phosphore organique sur la goethite, la gibbsite, la kaolinite et la montmorillonite

Face à l'utilisation croissante de ressources organiques pour la fertilisation en P, la dynamique d'adsorption et de désorption de diverses formes de P organique (OP) reste une lacune importante à combler afin d'améliorer la disponibilité du P. Cette étude a examiné les dynamiques d'adsorption et de désorption de divers composés OP (myo-inositol hexakisphosphate, IHP ; glycérophosphate, GLY ; et glucose-6-phosphate, G6P) sur et à partir de plusieurs minéraux du sol, y compris les oxydes de Fe et d'Al (goethite et gibbsite, respectivement) et les minéraux argileux (kaolinite et montmorillonite). Dans l'ensemble, le IHP était la forme la plus adsorbée, suivie par le G6P puis le GLY, ce qui montre que l'adsorption des OP augmente en fonction du nombre de groupes phosphates et/ou de la taille de la molécule organique. Les oxydes de Fe et d'Al ont montré une plus grande capacité d'adsorption des OP que les argiles, l'adsorption suivant la tendance kaolinite < montmorillonite < goethite <<<< gibbsite. Les expériences de désorption ont révélé que l'adsorption n'était pas entièrement réversible, car seulement 30 % pouvaient être facilement désorbés. Sur les oxydes de Fe et d'Al, le G6P et le GLY ont été plus désorbés que le IHP alors que la tendance inverse a été trouvée sur les minéraux argileux. De plus, la désorption des OP des minéraux du sol a suivi la tendance gibbsite < goethite < kaolinite < < montmorillonite. Le complexe argile-OP a libéré le P rapidement mais sur une courte période de temps, tandis que le complexe Fe- et Al-OP a libéré le P lentement mais sur une plus longue période de temps. La comparaison entre les propriétés d'adsorption et de désorption du P de la montmorillonite et d'autres minéraux du sol n'est valable que pour la montmorillonite saturée en K utilisée ici. Les résultats pourraient être différents si la montmorillonite était saturée en Al ou en Ca. En déchiffrant les interactions entre les minéraux du sol et les formes prédominantes de P dans les sols et les engrais organiques, nos résultats fournissent de nouvelles perspectives pour la gestion durable du P dans les agroécosystèmes.

Chapitre 2 : Rôle des minéraux du sol sur la disponibilité du phosphore organique et l'absorption du phosphore par les plantes

Le P organique (OP) représente une fraction significative du pool total de P dans les sols. Avec l'utilisation croissante de ressources organiques pour remplacer les engrais minéraux P et la nécessité de récupérer le P du sol, il est essentiel de mieux comprendre les interactions entre les différentes formes de OP et les minéraux du sol et leurs conséquences sur la disponibilité du P. Nous avons cherché à élucider dans quelle mesure les composés OP adsorbés sur les principaux minéraux du sol peuvent être disponibles pour les plantes. Ici, nous cherchons à élucider la mesure dans laquelle les composés OP adsorbés sur les principaux minéraux du sol peuvent être disponibles pour les plantes. Des plantes de ray-grass (*Lolium multiflorum*) ont été cultivées dans des dispositifs RHIZOtest en présence d'OP comprenant de l'hexakisphosphate de myo-inositol (IHP), du glycérophosphate (GLY), et du glucose-

6-phosphate (G6P) et de composés de P inorganique (IP) qui ont été préalablement adsorbés sur des oxyhydroxydes de Fe et d'Al (goethite et gibbsite, respectivement) et des minéraux argileux (montmorillonite et kaolinite). La disponibilité du P et l'absorption de P ont ensuite été déterminées par la caractérisation de la rhizosphère et des plantes. Indépendamment du type de minéral, le ray-grass a été capable d'absorber environ 3-18% des composés OP adsorbés. L'ampleur de la disponibilité et de l'absorption dépendait des composés OP et du type de minéraux du sol. La disponibilité potentielle des OP adsorbés par différents minéraux a été fortement médiée par les types et les propriétés de l'interaction minéral-OP. L'absorption de P a augmenté dans l'ordre suivant : kaolinite-OP << gibbsite-OP ≤ goethite OP << montmorillonite-OP. L'absorption de P à partir des composés OP adsorbés a montré des tendances contrastées par rapport à l'IP adsorbé et dépendait davantage de la concentration de P disponible dans la rhizosphère plutôt que de la force de liaison des OP à la surface minérale.

Chapitre 3 : L'azote et la minéralogie du sol déterminent la limitation du phosphore et l'absorption de P par les plantes à partir de formes inorganiques et organiques de P

Les cycles de l'azote et du phosphore dans les écosystèmes sont composés de multiples formes et processus biogéochimiques qui contrôlent conjointement l'absorption et la limitation du P par les plantes. À ce jour, la manière dont les formes chimiques de l'azote, le P organique (OP) et leurs interactions avec les minéraux du sol influencent à la fois la limitation du P et son absorption par les plantes dans les écosystèmes n'est toujours pas claire. La rareté des recherches sur l'effet de ces importants processus biogéochimiques (N-P-minéraux du sol) limite considérablement notre capacité à comprendre les processus écologiques qui sous-tendent l'altération du cycle du P dans les écosystèmes avec des ajouts d'azote. Les objectifs de cette étude étaient d'évaluer les effets indépendants et interactifs des formes de N et P et leur interaction avec les minéraux du sol sur l'absorption et la limitation du P chez les plantes. Nous avons caractérisé le rapport N:P, l'absorption de P et les propriétés de la rhizosphère du ray-grass cultivé sous plusieurs complexes d'IP et d'OP (IHP et GLY) adsorbés sur des oxyhydroxydes de Fe (goethite) et des minéraux argileux (kaolinite) avec et sans ajout de N. Nous avons émis l'hypothèse que l'ajout de N sous diverses formes spécifiques augmenterait la limitation de P dans des conditions de faible disponibilité de P, c'est-à-dire, avec les formes d'OP et les minéraux du sol, et que le passage des plantes d'une limitation de N à une limitation de P serait dû à l'effet bénéfique de l'ajout d'azote. Nous avons constaté que les interactions entre les formes de N, les formes de P et les minéraux du sol modifiaient fortement la dynamique du P, par rapport aux effets individuels. Ces interactions ont augmenté la limitation en P des plantes et l'absorption de P via la modification de la chimie de la rhizosphère. Le degré de limitation du P dépendait fortement du degré de disponibilité des sources de P, nous avons donc constaté que l'interaction entre les formes de P et les minéraux du sol était un déterminant majeur de la limitation du P. Par conséquent, nous avons constaté que l'interaction de l'azote avec les formes IP a conduit à une plus grande absorption du P et à une réduction marquée de

la limitation du P par rapport à l'interaction de l'azote avec les formes OP. Ainsi, nous avons déduit qu'en plus du degré de disponibilité du P, les caractéristiques et la nature biochimique des sources de P déterminent le degré de limitation en P des plantes. En outre, nous avons constaté qu'avec l'ajout de N, davantage de P était recyclé à partir des minéraux argileux et que la limitation du P était retardée par rapport aux oxydes de fer. Cette étude fournit donc des informations importantes sur le cycle du P dans l'écosystème en cas d'ajout de N et sur les propriétés biogéochimiques impliquées, ce qui permettra aux modèles d'écosystème de prédire avec précision la limitation N-P des plantes et ses impacts, et aidera également à construire des modèles d'écosystème robustes avec des interactions N-P ou C-N-P entièrement couplées.

Chapitre 4 : Rôle des stratégies d'acquisition du phosphore sur la mobilisation et l'acquisition du P organique

Les stratégies d'acquisition du P par les plantes (c'est-à-dire la recherche de nourriture et l'exploitation minière) sont généralement considérées comme ayant accès aux réservoirs de P hérités dans le sol. Cependant, comparé au P inorganique, l'impact de ces stratégies dans un sol amendé avec diverses formes de P organique (OP) a reçu beaucoup moins d'attention. Le but de cette étude était d'examiner la réponse des stratégies d'acquisition du P envers les formes de P (IP et OP) dans les interactions avec les minéraux du sol et leurs conséquences sur la disponibilité de l'OP et l'acquisition du P. Nous avons caractérisé les stratégies d'acquisition du P chez huit espèces végétales de diverses lignées phylogénétiques connues avec des traits contrastés d'acquisition du P qui ont été cultivées sous plusieurs complexes de IP et OP (IHP, et GLY) adsorbés sur des oxyhydroxydes de Fe (goethite) et des minéraux argileux (kaolinite). Les résultats ont montré une plasticité importante des caractéristiques des racines en réponse aux formes d'IP et d'OP. Les traits d'acquisition de P des espèces ont changé entre l'application des formes OP et l'application de la forme IP. Une différence dans les réponses des traits a également été observée entre les formes OP spécifiques, c'est-à-dire IHP et GLY. Les traits d'acquisition du P étaient généralement plus importants sur les formes OP que sur la forme IP. La réponse positive des stratégies d'acquisition du P aux sources OP a entraîné une plus grande disponibilité et acquisition du P à partir des OP. On a constaté que les espèces avaient des réponses contrastées entre les formes de P. *Vicia faba* et *Pisum sativum* ont eu une acquisition de P significativement plus élevée à partir des formes OP, tandis que *Lolium perenne* a eu une absorption globale de P plus élevée sur la forme IP. D'autre part, *Lens culinaris*, *Hordeum vulgare* et *Trifolium alexandrinum* ont eu une acquisition de P globalement équivalente entre les formes P. Comparativement aux stratégies impliquant la recherche de P, celles impliquant l'extraction de P ont entraîné une plus grande acquisition de P à partir des OP. Les cultures employant des stratégies intermédiaires (impliquant les deux stratégies d'acquisition de P) ont également montré une importante acquisition de P. Néanmoins, les résultats de la modélisation ont montré que l'absorption du P était mieux prédite par les traits morphologiques des racines que par les

traits physiologiques des racines. Cette étude a montré que la réponse positive des stratégies d'acquisition de P aux formes de OP a conduit à l'acquisition de P à partir de OP, améliorant ainsi potentiellement l'utilisation des ressources renouvelables de OP par l'optimisation des combinaisons de cultures et du type d'engrais P appliqué

Discussion générale et perspectives

Effet des formes d'OP et des minéraux du sol sur la dynamique des OP et la disponibilité du P pour les plantes

Avec l'utilisation croissante d'intrants organiques pour remplacer les engrais minéraux P et la nécessité de récupérer le P du sol, il est essentiel de mieux comprendre les interactions entre les différentes formes d'OP et les minéraux du sol et leurs conséquences sur la disponibilité du P (Amadou et al., 2021). Un grand nombre de recherches ont évalué l'adsorption de diverses sources individuelles de P organique et inorganique sur les sols ou sur les minéraux du sol. Cependant, aucune étude n'a évalué et comparé la désorption du P des principaux composés OP qui ont été adsorbés aux principaux minéraux du sol et leurs conséquences sur la nutrition des plantes (Amadou et al., 2022a, 2022b). Pour aider à combler ce manque de connaissances, les chapitres 1 et 2 ont élucidé la dynamique de l'adsorption et de la désorption de plusieurs formes d'OP sur plusieurs minéraux du sol représentatifs et les conséquences sur l'absorption du P. Les facteurs liés aux propriétés minérales du sol et aux caractéristiques moléculaires des OP ont directement affecté les réactions des OP et leur libération dans le sol (**chapitre 1**). De même, ces facteurs ont affecté la disponibilité du P dans la rhizosphère et son absorption par la plante (**chapitre 2**). Toutes les formes OP étudiées (IHP, GLY, et G6P) ont montré des processus d'adsorption contrastés et significativement différents les uns des autres, ainsi que de la forme IP utilisée pour la comparaison (**Chapitre 1**). Les expériences de désorption ont révélé qu'environ 30% pouvaient être facilement désorbés (**Chapitre 1**) et que ce P désorbé était disponible pour une utilisation par les plantes (**Chapitre 2**), indiquant que les OP adsorbés peuvent agir comme une source de P pour les plantes (Amadou et al., 2022b). La tendance de la disponibilité des OP (GLY >> G6P > IHP) mise en évidence dans le **chapitre 2** a été potentiellement expliquée par leur dynamique de désorption distincte (**chapitre 1**), car la désorption la plus faible a été trouvée pour IHP-P, suivie par G6P-P et ensuite GLY-P (**chapitre 2**). Cette tendance pourrait également être liée à leurs différents degrés d'hydrolyse par l'activité enzymatique (Annaheim et al., 2010), puisque l'activité phosphatase était la plus élevée en présence de GLY et la plus faible en présence de IHP (**chapitre 2**).

La relation positive entre la dynamique d'adsorption des OP et le nombre de groupes phosphates dans la molécule organique (**chapitre 1**) était cohérente avec la littérature et montre que la capacité d'adsorption de chaque composé OP est déterminée par le nombre de groupes orthophosphates associés à la fraction C (Bai et al., 2021). Le IHP, qui possède six orthophosphates par fragment C, a été adsorbé en plus

grande quantité que les autres monoesters d'orthophosphate (G6P et GLY), ce qui renforce les explications précédentes concernant sa faible désorption (chapitres 1 et 2) et son utilisation limitée par les plantes (**chapitre 2**). La force de liaison généralement plus faible ou égale du myo-HP aux minéraux par rapport au GLY ou au G6P (**chapitre 1**), bien qu'en désaccord avec des résultats récents (Ganta et al., 2019 ; Kubicki et al., 2012) a suggéré que l'adsorption plus élevée du IHP par rapport aux autres composés OP (**chapitre 1**) n'implique pas nécessairement que sa capacité et/ou son énergie de liaison soit toujours forte et stable dans toutes les conditions environnementales. Ainsi, il est concevable que dans des conditions d'approvisionnement en intrants organiques, si les espèces GLY et G6P entrent en compétition avec le IHP pour les mêmes sites actifs sur les minéraux du sol, la différence d'énergie de liaison pourrait faciliter la désorption du IHP du sol plus efficacement que celle du GLY et du G6P (Amadou et al., 2022a). L'analyse de corrélation effectuée sur différentes données d'extraction a montré que la disponibilité des OP adsorbés pour les plantes ne dépend pas de leur force de liaison aux minéraux du sol (**chapitres 1 et 2**) mais plutôt de leur degré d'hydrolyse par les enzymes du sol et des racines (chapitre 2). Nous avons également souligné que l'idée générale d'une adsorption plus élevée des OP par rapport à la IP suggérée par la littérature ne s'applique pas à tous les composés OP puisque, bien que le IHP ait été plus fortement retenu par rapport à la IP, le G6P et le GLY l'ont été plus faiblement.

La désorption (**chapitre 1**) et l'acquisition (**chapitre 2**) élevées d'OP à partir de la montmorillonite par rapport aux autres minéraux (**chapitre 2**) ont indiqué que les sols riches en phyllosilicate 2:1 peuvent avoir une plus grande disponibilité de P que les sols riches en oxyhydroxydes de Fe et Al ou en minéraux 1:1. Néanmoins, la désorption plus élevée observée du GLY à partir des oxyhydroxydes d'Al (chapitres 1 et 2), qui sont connus pour limiter la disponibilité du P dans les sols très altérés des régions tropicales, a souligné le fort potentiel d'utilisation du GLY comme source de P dans ces régions (Zhang et al., 2017). La faible absorption de P par les complexes kaolinite-OP (**chapitre 2**) est cohérente avec les observations précédentes montrant que la kaolinite-P est un complexe de surface bidenté, à sphère interne, en dessous de pH 6 (Hu et al., 2020 ; Ruyter-Hooley et al., 2015), et que le P adsorbé sur la kaolinite est difficile à désorber (Kafkafi et al., 1988 ; Xiong et al., 2022). Cela souligne donc que les oxyhydroxydes de Fe et d'Al étaient moins responsables de la limitation de la disponibilité des OP que la kaolinite, malgré leur capacité d'adsorption généralement plus élevée dans le sol (**chapitre 1**). Cependant, étant donné que la concentration en P utilisée dans notre étude peut être plus élevée que celle des systèmes de sol réels, il serait intéressant comme perspective d'étudier l'effet de la concentration en P sur les processus d'adsorption en réalisant des expériences de sorption à des concentrations en P différentes (et plus faibles).

Preuve d'une mobilisation importante des OP par les plantes en raison des interactions N-OP et des réponses des traits des plantes

Les caractéristiques de l'azote dans les engrais organiques ajoutés pour améliorer l'utilisation du P peuvent affecter la disponibilité des OP dans le système sol-plante. La littérature a montré que l'ajout de N peut augmenter la demande en P des plantes, ce qui favorise la mobilisation du P du sol (Schleuss et al., 2020 ; Zhang et al., 2017). Cela souligne l'importance écologique de l'effet bénéfique de l'azote sur l'efficacité d'utilisation du P par les plantes (Vitousek et al., 2010). Dans l'ensemble, il a été déclaré que les plantes pourraient échanger N contre P en ajustant les taux d'acquisition de N et de P à partir du sol, expliquant potentiellement les réponses synergiques de croissance à l'ajout de N et de P (Long et al., 2016 ; Peng et al., 2019). En outre, différentes stratégies de mobilisation et d'acquisition des OP dans les espèces et cultivars de cultures ont été démontrées, mais leur efficacité dans l'acquisition de P à partir des différentes formes d'OP et d'IP reste peu étudiée (Lambers et al., 2011). Ces stratégies impliquent des traits morphologiques, architecturaux (Lynch, 2011) et physiologiques (Richardson et al., 2009), des micro-organismes, ou une combinaison des deux, pour contribuer efficacement à la capacité des plantes à accéder à différents réservoirs d'OP faiblement disponibles dans les sols (Wang et al., 2022 ; Wang et Lambers, 2020). À ce jour, on ne sait toujours pas comment les formes chimiques de l'azote, les stratégies d'acquisition du P par les plantes et leurs interactions avec l'OP et les minéraux influencent la disponibilité, l'acquisition et la limitation de l'OP par les plantes dans les écosystèmes.

L'effet bénéfique de l'ajout de N et les autres conséquences positives des réponses des stratégies d'acquisition de P par la plante sur la disponibilité de l'OP ont été mis en évidence dans la caractérisation des interactions N-OP-minéraux (**chapitre 3**) et l'effet des traits racinaires-OP-minéraux (**chapitre 4**). Par rapport à l'absence d'ajout de N (**chapitres 1 et 2**), l'augmentation de l'absorption de P par les plantes avec l'ajout de N, en particulier avec les formes $\text{NO}_3\text{-N}$ (**chapitre 3**), a mis en évidence les effets synergiques de N et OP et leurs interactions avec les minéraux sur la dynamique du P, c'est-à-dire sa disponibilité et sa limitation. Au sein de formes spécifiques d'OP, les résultats du **chapitre 3** ont suggéré que l'ajout de N favoriserait la mobilisation de l'IHP (formes majeures d'OP dans le sol et les amendements organiques) et le rendrait moins limitant pour les plantes par rapport à d'autres formes d'OP, c'est-à-dire GLY ou G6P, soulignant le rôle central de l'interaction entre N, OP et minéraux sur le cycle des OP (Hou et al., 2021, 2020). En outre, ces résultats mettent en évidence un nouveau mécanisme par lequel les interactions des formes d'azote avec les pools d'OP pourraient accélérer le cycle de l'OP, notamment en augmentant la disponibilité de l'IHP, qui est la forme importante de l'OP et également la forme la plus adsorbée et la moins disponible (**chapitres 1 et 2**), et ainsi retarder le début de la limitation en P de cette forme pour la croissance des plantes (**chapitre 3**). L'activité élevée des phosphatases et la disponibilité du P dans la rhizosphère avec l'ajout de N (**chapitre 3**) ont probablement contribué à l'absorption du P par les plantes (Long et al., 2016). Les corrélations ont indiqué que l'absorption totale de P était positivement liée au P disponible et à l'activité phosphatase (**chapitre 3**). Très probablement, l'ajout de N a permis aux plantes de synthétiser des phosphatases coûteuses en N (Schleuss et al., 2020), ce qui a ensuite rendu l'OP disponible pour l'absorption par les plantes (Helfenstein et al., 2018). Ainsi,

il semble probable qu'avec l'ajout de N, l'OP soit recyclée plus intensivement à partir des pools d'OP, indépendamment des minéraux du sol (Widdig et al., 2019). L'interaction de N avec les formes IP a conduit à une plus grande absorption de P et à une limitation de P nettement réduite par rapport à l'interaction de N avec les formes OP, probablement en raison de la forte adsorption et de la faible disponibilité de l'OP, comme le montrent les chapitres 1 et 2. Ainsi, on peut déduire que dans les agro-écosystèmes où le P est très fortement sorbé (comme les formes OP), les ajouts de N peuvent en effet conduire à un épuisement rapide du P disponible et donc à une très forte limitation du P, mais dans les systèmes où le P est relativement plus disponible (comme les formes IP), les ajouts de N ne conduisent pas à une limitation systématique du P mais plutôt à une colimitation de N et P. Avec l'ajout de N, plus d'OP a été recyclé à partir de minéraux argileux (kaolinite) et a ainsi retardé la limitation de P par rapport aux oxydes de fer et d'aluminium (goethite), ce qui souligne l'importance de considérer le minéral du sol dans la conception des systèmes de culture pour mobiliser l'OP. Ainsi, le **chapitre 3** suggère fortement que malgré l'adsorption plus élevée des formes d'OP (**chapitre 1**), les ajouts de N peuvent effectivement conduire à une efficacité d'utilisation des OP dans le système sol-plante.

Pour explorer davantage les mécanismes efficaces de mobilisation de l'OP dans le sol, la réponse des stratégies d'acquisition du P à diverses formes d'OP interagissant avec les minéraux du sol et leurs conséquences sur la disponibilité et l'acquisition de l'OP ont été examinées chez huit espèces végétales majeures (**chapitre 4**). L'expression différentielle des traits d'acquisition du P parmi les formes d'OP soutient notre hypothèse selon laquelle les stratégies d'acquisition du P (c'est-à-dire la recherche de nourriture et l'extraction) sont affectées par le type de sources d'OP et leurs propriétés biogéochimiques (Wang et Lambers, 2020). Comme pour l'effet des interactions N-OP (**chapitre 3**), la réponse positive des stratégies d'acquisition du P aux sources d'OP (**chapitre 4**) a entraîné une plus grande disponibilité du P et son acquisition à partir des OP (figure 32). Indépendamment des stratégies des plantes, l'acquisition plus élevée de P à partir des OP par rapport aux IP (**chapitre 4**) a montré que, malgré la sorption plus élevée des OP dans le sol (chapitres 1 et 32), les stratégies de recherche et d'extraction de P des plantes ont été capables d'améliorer le cycle et la disponibilité des OP par rapport aux formes IP. Pris ensemble, les résultats des chapitres 3 et 4 suggèrent que les diverses formes de N contenues dans les intrants organiques et les stratégies d'acquisition de P des espèces cultivées peuvent être exploitées pour améliorer la mobilisation des OP dans le système engrais organique-sol-plante (figure 32). L'application agronomique de ce résultat est particulièrement importante pour limiter l'utilisation d'engrais chimiques.

Conception de cultures fonctionnellement optimales à forte capacité de mobilisation de l'OP : aperçu de la sélection des espèces, des stratégies d'acquisition du phosphore et des formes d'azote.

La conception d'une meilleure disponibilité du P dans les agroécosystèmes via la gestion de la teneur en N des amendements organiques et des traits d'acquisition du P par les plantes peut donc contribuer à relever des défis majeurs tels que l'augmentation de l'utilisation d'engrais recyclés (Faucon et al., 2015). Cependant, cela suggère une réflexion approfondie lors de la conception de la composition des cultures et de l'approvisionnement en amendements (Hallama et al., 2019). Une implication majeure de cette thèse est le potentiel de gérer les formes d'azote dans les intrants organiques tout en adaptant la composition des cultures pour améliorer la disponibilité des OP dans les agroécosystèmes grâce à l'effet avantageux des interactions N-OP (**chapitre 3**) mais aussi grâce à la réponse positive et à l'effet des stratégies et des traits fonctionnels des plantes (**chapitre 4**). En général, les interactions N-OP ont entraîné une mobilisation beaucoup plus importante des OP (**chapitre 3**), de plus, les effets des stratégies d'acquisition du P des différentes espèces discutées dans le **chapitre 4** ont été trouvés pour favoriser une plus grande acquisition du P à partir des OP que des IP. Toutes ces observations indiquent que malgré la sorption plus forte des OP au sol démontrée au **chapitre 1**, qui a limité leur disponibilité pour les plantes au **chapitre 2**, les stratégies d'extraction et de recherche de P des plantes ont réussi à améliorer le cycle et la disponibilité des OP par rapport aux formes IP (**chapitre 4**). Pris ensemble, ces résultats peuvent aider à guider la sélection de systèmes de culture efficaces et la formulation de l'azote dans les engrais organiques pour une meilleure mobilisation des formes OP. Les groupes d'espèces composés de *Vicia faba*, *Pisum sativum* et *Lupinus albus* qui ont produit une plus grande exsudation d'acide carboxylique et une activité PME significative dans la rhizosphère que les autres espèces en réponse aux formes OP (Nobile et al., 2019), peuvent bénéficier d'une fertilisation avec des intrants organiques (Figure 32). Ces espèces, qui appartiennent toutes à la famille des Fabaceae et dont les stratégies impliquent l'exploitation du P, ont favorisé une plus grande mobilisation/acquisition des OP que des IP. Par conséquent, dans un système de rotation, cela pourrait améliorer la disponibilité du P qui profiterait alors aux cultures suivantes, qui sont généralement non mobilisatrices (Haling et al., 2018). En pratique, étant donné que les apports organiques augmentent lentement la disponibilité du P du sol pour les plantes après incorporation dans le sol (Gerke, 2015), ces espèces de Fabaceae pourraient être le premier choix dans une rotation de cultures ou dans une culture de couverture pour améliorer la teneur en P des cultures à partir des formes OP du sol. Les espèces *Lens culinaris*, *Hordeum vulgare*, et *Trifolium alexandrinum* qui répondent aux formes d'OP avec un pourcentage élevé de racines fines et de longueur spécifique de racine et une expression intermédiaire des traits de minage du P, peuvent être plus efficaces pour libérer les différentes formes d'OP adsorbées et/ou précipitées sur les constituants du sol, comme l'IHP qui est très fortement adsorbé sur le sol (Figure 32). D'un point de vue agronomique, un système qui combine un engrais organique riche en N sous forme de $\text{NO}_3\text{-N}$ et l'établissement d'espèces de Fabaceae peut être efficace pour utiliser les OP et spécifiquement l'IHP, qui est la principale forme d'OP dans le sol.

Role of organic phosphorus forms, soil minerals, nitrogen, and plant functional traits on phosphorus availability and acquisition by plants for optimal organic fertilizer management in agroecosystems

Phosphorus (P) deficiency in soils limits the productivity of many agroecosystems. Modern agricultural practices rely heavily on mineral fertilizers derived from mined phosphate rock, a limited and constantly diminishing resource. In an effort to manage P nutrition in agroecosystems more sustainably, organic phosphorus (OP) from organic and soil inputs is increasingly considered as a complement to mineral P fertilizers. However, the dynamics of P supply through organic fertilizer are not always well understood. We have shown that factors related to soil mineral properties and molecular characteristics of OPs directly affected the reactions of OPs and their release into the soil. Similarly, these factors affected the availability of OPs in the rhizosphere and their uptake by the plant. By characterizing N-OP-mineral interactions we provided important information on ecosystem P cycling under N addition and the biogeochemical properties involved, which will allow ecosystem models to accurately predict plant N-P limitation and its impacts and will also help build robust ecosystem models with fully coupled N-P or C-N-P interactions. The positive response of P acquisition strategies to OP sources has resulted in greater P availability and acquisition from OPs. Finally, the identification through modeling of major traits involved in P acquisition strategies and their ability to better predict P acquisition offers opportunities to design crop species compositions and more specifically the functional structure of crop plant communities. These systems would in turn allow the assessment of the overall effects of organic input, soil, and plant interactions on P availability and support farmers' management decisions, such as appropriate P fertilization.

Keywords: agroecology; biogeochemistry; organic inputs; organic phosphorus; plant traits; Adsorption; desorption; organic phosphorus; phosphorus availability; soil fertility; N and P (co)-limitation; P acquisition strategies; P-foraging; P-mining; ecological niches

Rôle des formes de phosphore organique, des minéraux du sol, de l'azote et des traits fonctionnels des plantes sur la disponibilité et l'acquisition du phosphore par les plantes pour une gestion optimale des engrais organiques dans les agroécosystèmes

La carence en phosphore (P) des sols limite la productivité de nombreux agroécosystèmes. Les pratiques agricoles modernes sont fortement tributaires des engrais minéraux dérivés de la roche phosphatée extraite, une ressource limitée et en constante diminution. Dans l'optique d'une gestion plus durable de la nutrition en P dans les agroécosystèmes, le phosphore organique (OP) provenant d'intrants organiques et du sol est de plus en plus considéré comme un complément aux engrais minéraux P. Cependant, la dynamique de l'apport de P par le biais de l'engrais organique n'est pas toujours bien comprise. Nous avons montré que les facteurs liés aux propriétés minérales du sol et aux caractéristiques moléculaires des OP affectaient directement les réactions des OP et leur libération dans le sol. De même, ces facteurs ont affecté la disponibilité des OP dans la rhizosphère et leur absorption par la plante. En caractérisant les interactions N-OP-minéraux nous avons fourni des informations importantes sur le cycle du P dans les écosystèmes en cas d'ajout de N et sur les propriétés biogéochimiques impliquées, ce qui permettra aux modèles d'écosystèmes de prédire avec précision la limitation N-P des plantes et ses impacts, et aidera également à construire des modèles d'écosystèmes robustes avec des interactions N-P ou C-N-P entièrement couplées. La réponse positive des stratégies d'acquisition de P aux sources d'OP a entraîné une plus grande disponibilité et acquisition de P à partir des OP. Enfin, l'identification par modélisation des traits majeurs impliqués dans les stratégies d'acquisition du P et leur capacité à mieux prédire l'acquisition du P, offre des opportunités pour concevoir des compositions d'espèces cultivées et plus spécifiquement la structure fonctionnelle des communautés végétales cultivées. Ces systèmes permettraient à leur tour d'évaluer les effets globaux des interactions entre les intrants organiques, le sol et les plantes sur la disponibilité du P et de soutenir les décisions de gestion des agriculteurs, telles qu'une fertilisation P adaptée.

Mots clés : agroécologie ; biogéochimie ; apports organiques ; phosphore organique ; traits végétaux ; adsorption ; désorption ; phosphore organique ; disponibilité du phosphore ; fertilité des sols ; (co)-limitation de l'azote et du phosphore ; stratégies d'acquisition du phosphore ; fourrage du phosphore ; extraction du phosphore ; niches écologiques.