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

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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

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, myo-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, myo-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 desorbed. On Fe and Al oxides, G6P and GLY were more desorbed than myo-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

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 myo-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, myo-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 myo-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 myo-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 myo-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 myo-IHP-goethite complexes. Similar results by Lagos et al., (2016) showed limited desorption of myo-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

77 investigated. To our knowledge, no study has evaluated and compared P desorption from the main OP
78 compounds (IHP, GLY, and G6P) that were adsorbed onto the main soil minerals (Fe and Al oxides,
79 and clay minerals). There is a need to bridge this gap of knowledge to identify the properties that govern
80 OP adsorption and desorption processes and gaining insight into the behavior of OP compounds at the
81 surface of soil minerals.

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

94 ## 2. Materials and methods

95 ### 2.1. Organic P forms and individual soil minerals

96 Three organic P (OP) compounds, myo-IHP, GLY, G6P and one IP (KH_2PO_4) (Fig.1) were selected
97 based on their predominance in organic wastes and soils and their contrasted properties (type of P bonds,
98 different molecular sizes). The individual soil minerals were selected to be representative of the
99 predominant soil minerals involved in P adsorption in soils. Four individual soil minerals were used.
100 Goethite [FeO(OH)] and gibbsite [Al $(OH)_3$] were chosen as representative of Fe and Al oxides;
101 kaolinite and montmorillonite were selected as clay minerals, particularly 1:1 phyllosilicate and 2:1
102 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 m^2 g^{-1}), gibbsite (120-364 m^2 g^{-1}), kaolinite (19 m^2 g^{-1}) and K-montmorillonite (83 m^2 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 (Table S1**)** for mineral references)

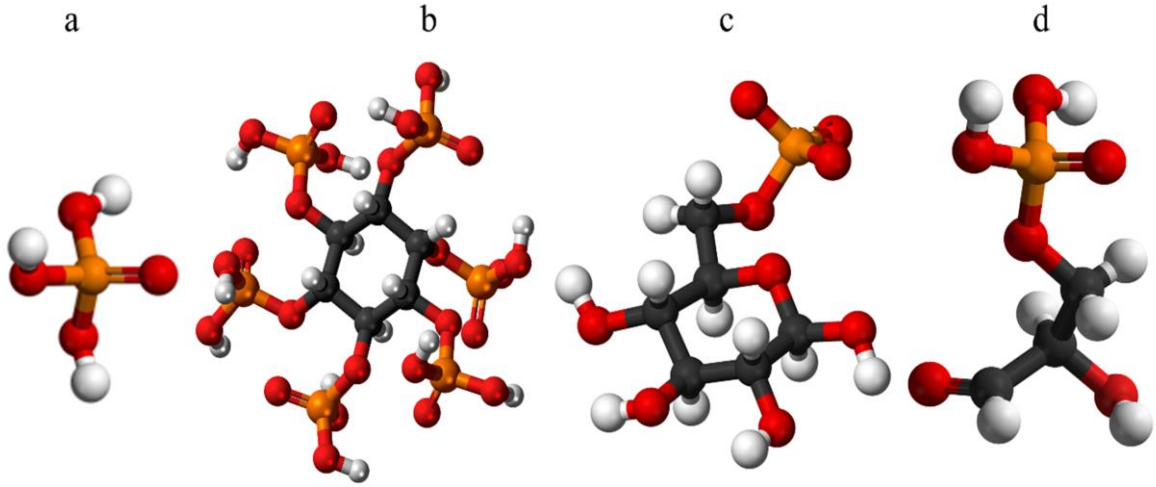


Fig.1. Chemical structure of potassium dihydrogen phosphate, IP (a), myo-inositol hexakisphosphate, IHP (b), β-D-Glucopyranose-6-phosphate, G6P (c) and Glycerol phosphate, GLY(d).

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-µm 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):

$$Q_{ads} = Qm\ K_L\ [Ce/\ (1+ K_L\ Ce)] \quad (1)\ ;$$

where Ce 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 Qm is the P adsorption maxima (µg g^{-1}). The ability of soil minerals to resist a change in solution P concentration was measured as the maximum adsorption buffer capacity: MBC = $K_L \times (Qm)$; where K_L and Qm are the binding-energy related constant and maximum adsorption, respectively, in the Langmuir equation.

$$Q_{ads} = K_F\ Ce^{1/nF} \quad (2);$$

where Q_{ads} (µg g^{-1}) is the total amount of P adsorbed, Ce is the adsorbate equilibrium concentration in solution, K_F (µmol L^{-1}) is adsorption capacity, and nF (mmol L^{-1}) is Freundlich exponent.

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.

147 Then, 200 ml of 0.1 *M* KCl were added and the bottles were shaken for 24 hours at 25°C to sufficiently
148 hydrate the adsorption sites on the minerals. The pH was maintained at 5.5 ± 0.05 by adding 0.1 *M* HCl
149 or NaOH solution. To start the complex formations, each of the 1L bottles containing the soil minerals
150 was filled with 800 ml of P solutions. This was done in order to obtain all the mineral-P complexes, for
151 example for goethite we will have: goethite-IP, goethite-IHP, goethite-G6P and goethite-GLY and
152 similarly for the other minerals. In each 1L bottles containing both the soil minerals and P compounds,
153 some drops of hexanol were added to suppress microbial activities. The final samples containing in the
154 bottles were shaken on a mechanical shaker for 24 hours at 25°C and then centrifuged (3000 g for 15
155 minutes). The 1L bottles were distributed into several small 250-mL bottles, centrifuged, and the
156 supernatants were collected. Centrifugation was repeated until the maximum volume of supernatants
157 was removed. The produced P-loaded minerals was agitated in deionized water and frozen at -20◦C. The
158 amounts of adsorbed P were determined using the same procedure as described in Section 2.2. The
159 amounts of adsorbed P (µgP g^{-1}) were similar to the Qm values (Table 1) of the adsorption data
160 (Section 2.2) that were predicted by the Langmuir model.
161 Desorption kinetics experiments were initiated by adding 40 ml of 0.1 *M* KCl adjusted to pH
162 5.5 to 0.5g of the different minerals-P complex. Samples were shaken on a mechanical shaker at 25°C
163 at regular intervals (24h, 48h, 72h, 96h). After the first cycle (24h), the entire suspension was removed
164 and immediately filtered through a 0.22-µm membrane filter. A fresh 40 ml solution of 0.1 *M* KCl was
165 added to start the second cycle (48h). The same process was applied for the remaining cycles. The P
166 concentration in the supernatant was determined as described above. Desorption maxima and rate were
167 determined by fitting data to the non-linear form of the Elovich kinetic model (Bulut et al., 2008) (3):

168 $Q = A + B * Lnt$ (3);

169 where q is the amount of P desorbed at time t, and A and B are the constants with $A = \frac{1}{\beta}$ and $B =$
170 $\frac{1}{\beta} Ln\alpha\beta$ (α and β are the constants in the original formula of Elovich equation). The A value (mgP kg^{-1})
171 in the Elovich equation is the amount of P desorbed in the first day of desorption (q = A +B*ln t, A = q
172 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 (Dm) was calculated as total amount P desorbed.

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.

3. Results

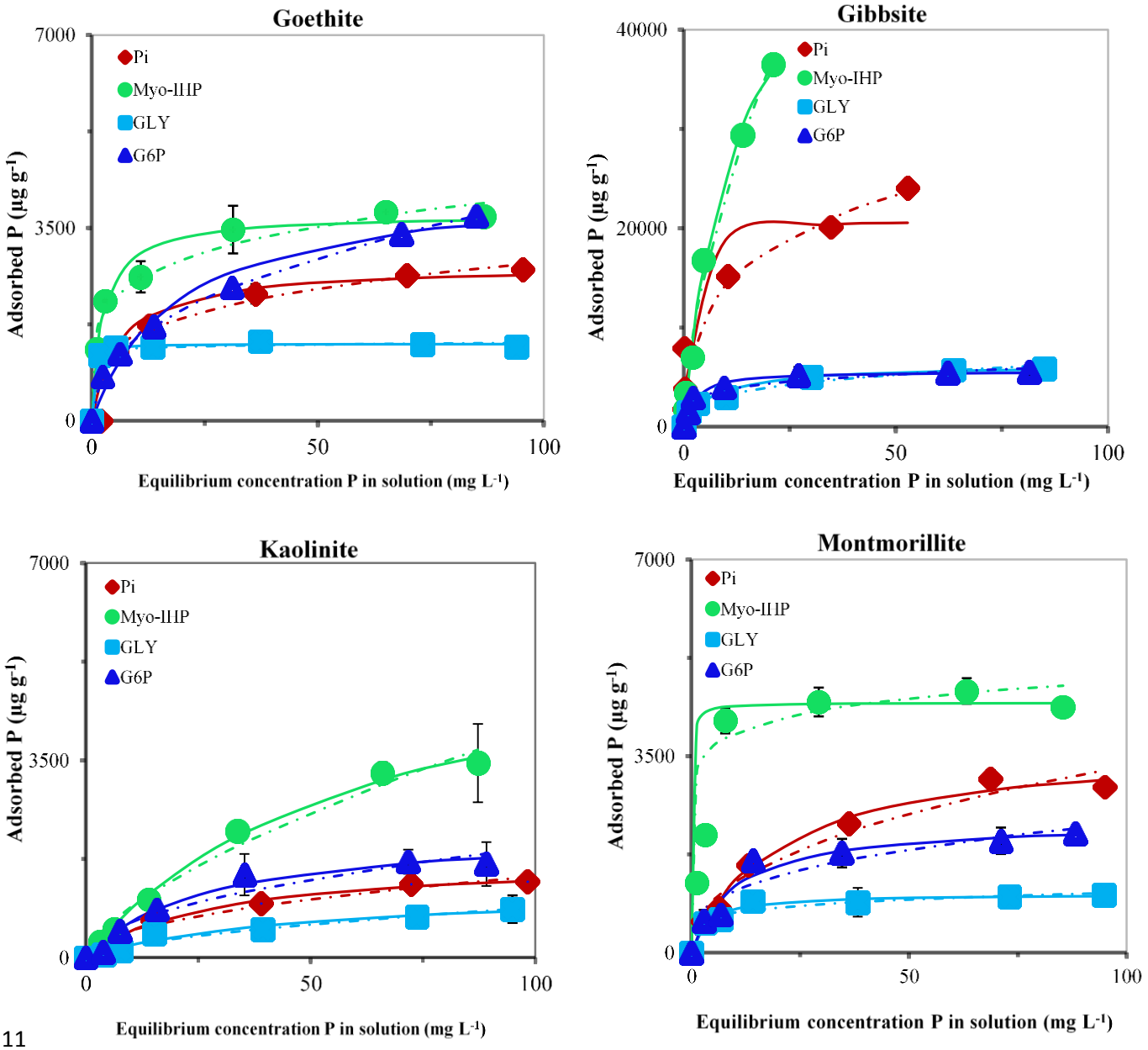
3.1. Dynamics of Organic Phosphorus Adsorption

3.1.1. Effect of OP forms on adsorption dynamics

Organic P adsorption differed for each specific OP compounds (Table 1). The strongest differences in OP adsorbed among the different isotherms occurred with the greatest initial OP concentrations (Fig. 2). In addition, the magnitude of OP adsorption increased rapidly when the initial OP concentration was low (< 25 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 Qm, i.e. maximum OP adsorption capacity from the Langmuir equation (Table 1) ranged from 1045 µg g^{-1} to 56697µg g^{-1},

197 indicating marked variations in the amount of OP adsorbed. Among the OP compounds, myo-IHP was
198 the most adsorbed form (3742-56697 μg g^{-1}) followed by G6P and then GLY (1045-6237 μg g^{-1}) (Fig.
199 2 and Table 1). The adsorption maxima of OP increased with increasing molar mass in this order: GLY
200 (172 g mol^{-1}) < G6P (260 g mol^{-1}) < myo-IHP (660 g mol^{-1}), which showed that the size of the molecule
201 would have favored the adsorption of OP compounds.

202 Compared to IP, a contrasted adsorption behavior of OP compounds was observed. The
203 adsorption dynamics followed the trend myo-IHP > IP > G6P > GLY, showing that myo-IHP was more
204 adsorbed than IP, which in turn was more adsorbed than the G6P and GLY forms (Fig. 2 and Table 1).
205 The K_L value, i.e. the binding energy between OP and minerals surfaces were highly variable. With the
206 exception of montmorillonite, GLY or G6P showed higher or equal binding strength compared myo-
207 IHP (Table 1). Our results showed that the adsorption dynamics of OP was strongly controlled by their
208 biogeochemical properties in the soil. The myo-IHP, GLY and G6P form showed a different adsorption
209 process from each other as well as from the IP form. In general, myo-IHP was found to be the most
210 adsorbed P form and GLY the least adsorbed form.



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213 Fig. 2. Adsorption isotherms of OP forms by different soil minerals in 0.1 *M* KCl at pH 5.5: Symbols
214 are data points, solid lines are Langmuir isotherms, and dashed lines are Freundlich isotherms. Gibbsite
215 was different from other minerals because of the large difference in the maximum adsorption amount.
216 Values of adsorbed quantities (Qads) and error bars (Se) are also provided as supplementary data (Table
217 S2).

218 Table 1. Isotherm parameters of the Langmuir and Freundlich models for P adsorption.

Soil components	P Forms	Langmuir equation				Freundlich equation		
		Qm (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

Qm: maximum adsorption capacity, K_L: binding-energy related constant, R^2: model fitting degree, MBC: maximum buffer capacity (ability of soil minerals to resist a change in solution P concentration).

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221 3.1.2. Adsorption dynamics as affected by soil minerals

222 Isotherms of OP adsorption for the four tested minerals demonstrated that OP adsorption patterns of the
223 Fe and Al oxides (goethite and gibbsite, respectively) were very similar but quite different from that of
224 clays minerals (montmorillonite and kaolinite) (Fig. 1). Fe and Al oxides rapidly adsorbed OP and their
225 adsorption maximum was reached at a lower initial concentration than for clays. All tested minerals
226 fitted the Langmuir and Freundlich equation (Table 1). Adsorption capacity (K_F) of OP by soil minerals
227 followed the trend kaolinite < montmorillonite < goethite << Gibbsite (Table 1), showing a marked
228 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 myo-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 << Fe and Al oxides (Table 1). 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 1). 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. Fig. 6 illustrates a conceptual framework showing the relationship between soil mineral properties (PZC, SSA) and Langmuir model adsorption parameters (K_L and Qm). 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).

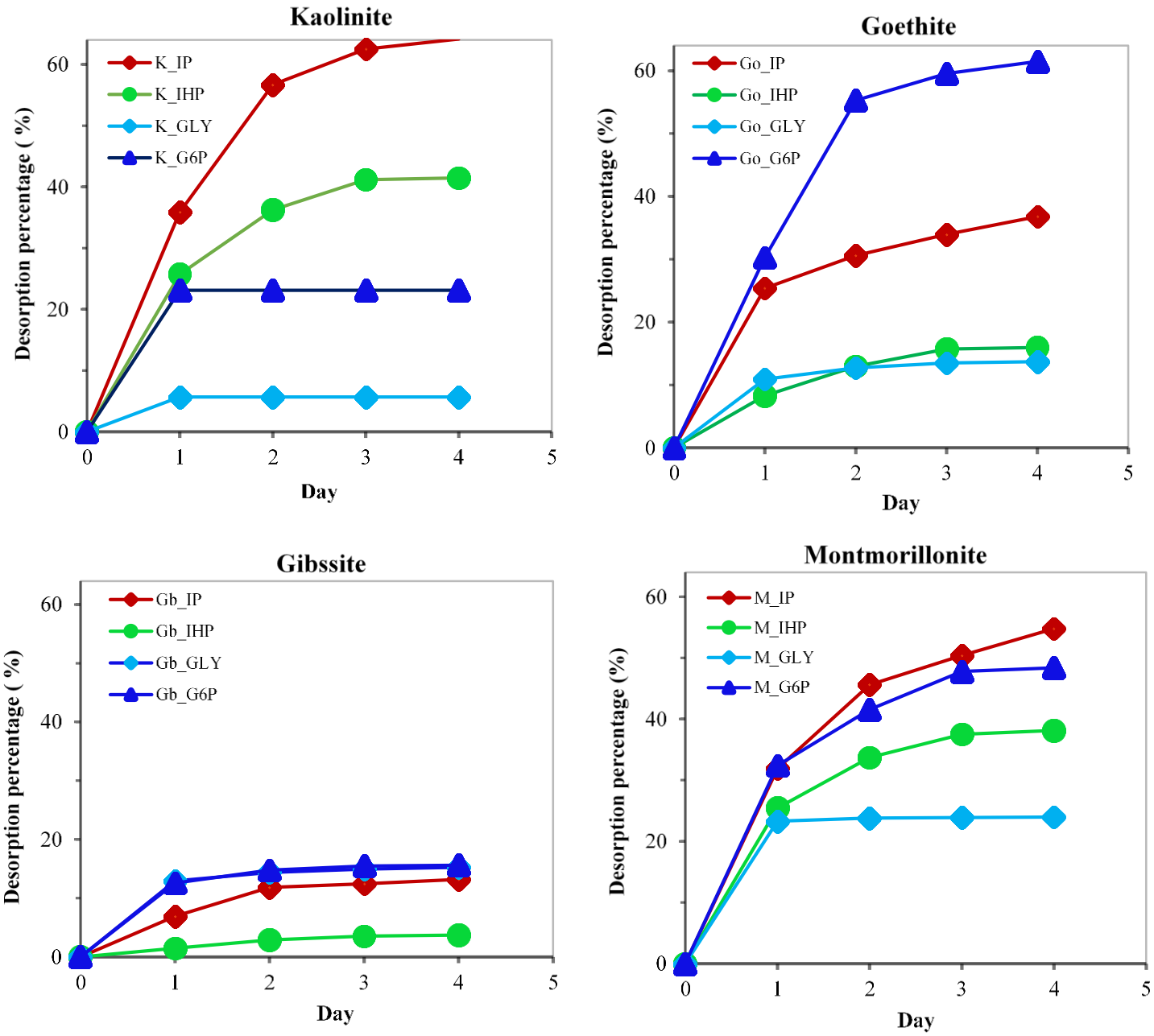
3.2. Dynamics of Organic Phosphorus Desorption

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 2). 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 (Fig. 3 and Table 2) 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 (Fig. 3 and Table 2).

The Dm values refer to the predicted maximum desorption capacity of OP obtained from the Elovich model (Table 2). Organic P compounds showed different Dm trends by mineral type. Both G6P and GLY showed higher Dm values (13%-56%) than myo-IHP (3%-14.44%) on Fe and Al oxides. On clay minerals, the pattern was rather opposite, with myo-IHP desorption being higher than other OP forms (Table 2). The desorption maxima of all of the OP compounds were 4%-56%, lower than those of IP which were between 13 % to 70% (Table 2 and Fig. 3), 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 Fig. 6 showed negative correlations between Dm 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 2). 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 (Fig. 4): 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 myo-IHP and G6P from montmorillonite and high desorption rate complexes (20% > per day) which include only G6P from goethite (Fig. 3).



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275 Fig. 3. Desorption kinetics of myo-IHP, GLY and G6P by 0.1 M KCl at pH 5.5 and at 25˚C.

276 Table 2. 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 ($q = A + B * Lnt$, $B = q$ when $t = 1$), R^2: model fitting degree.

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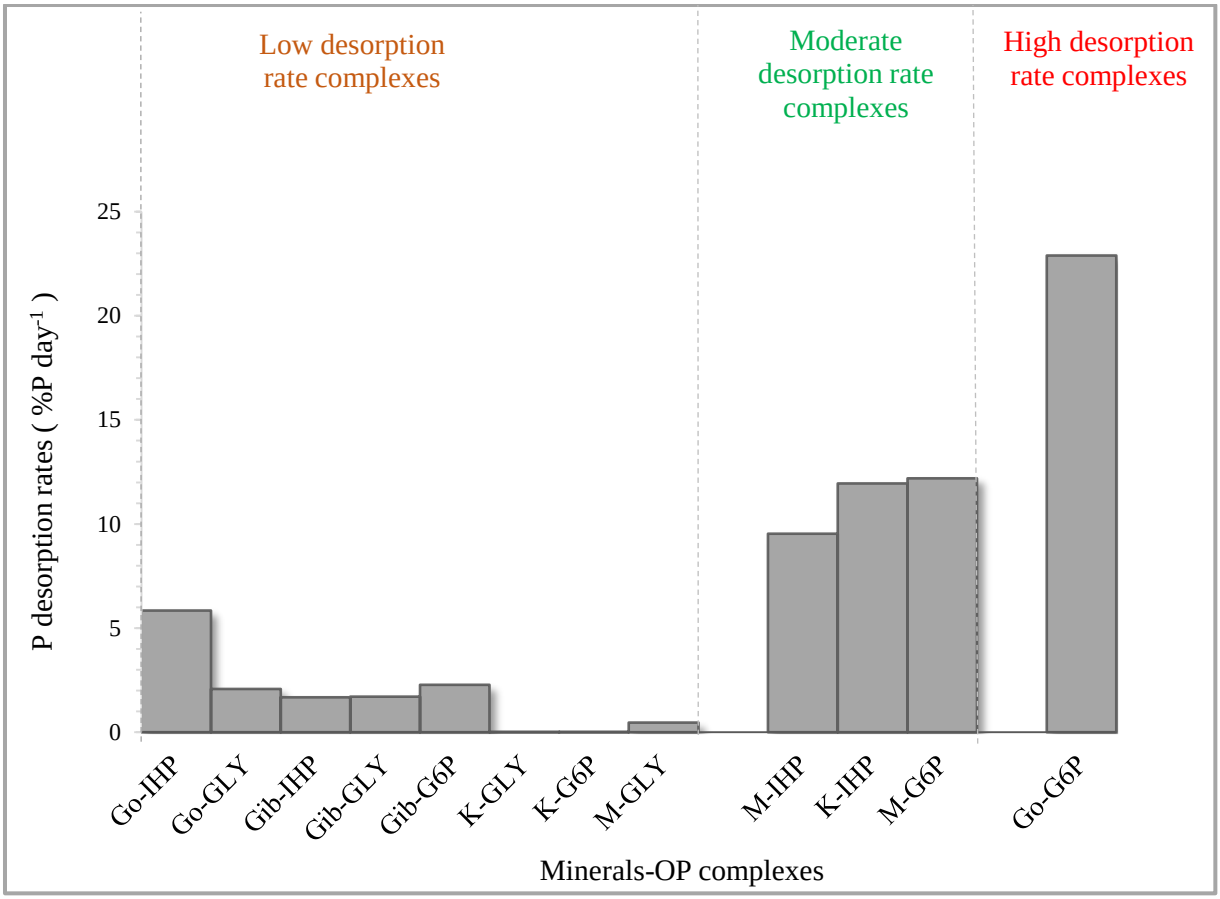
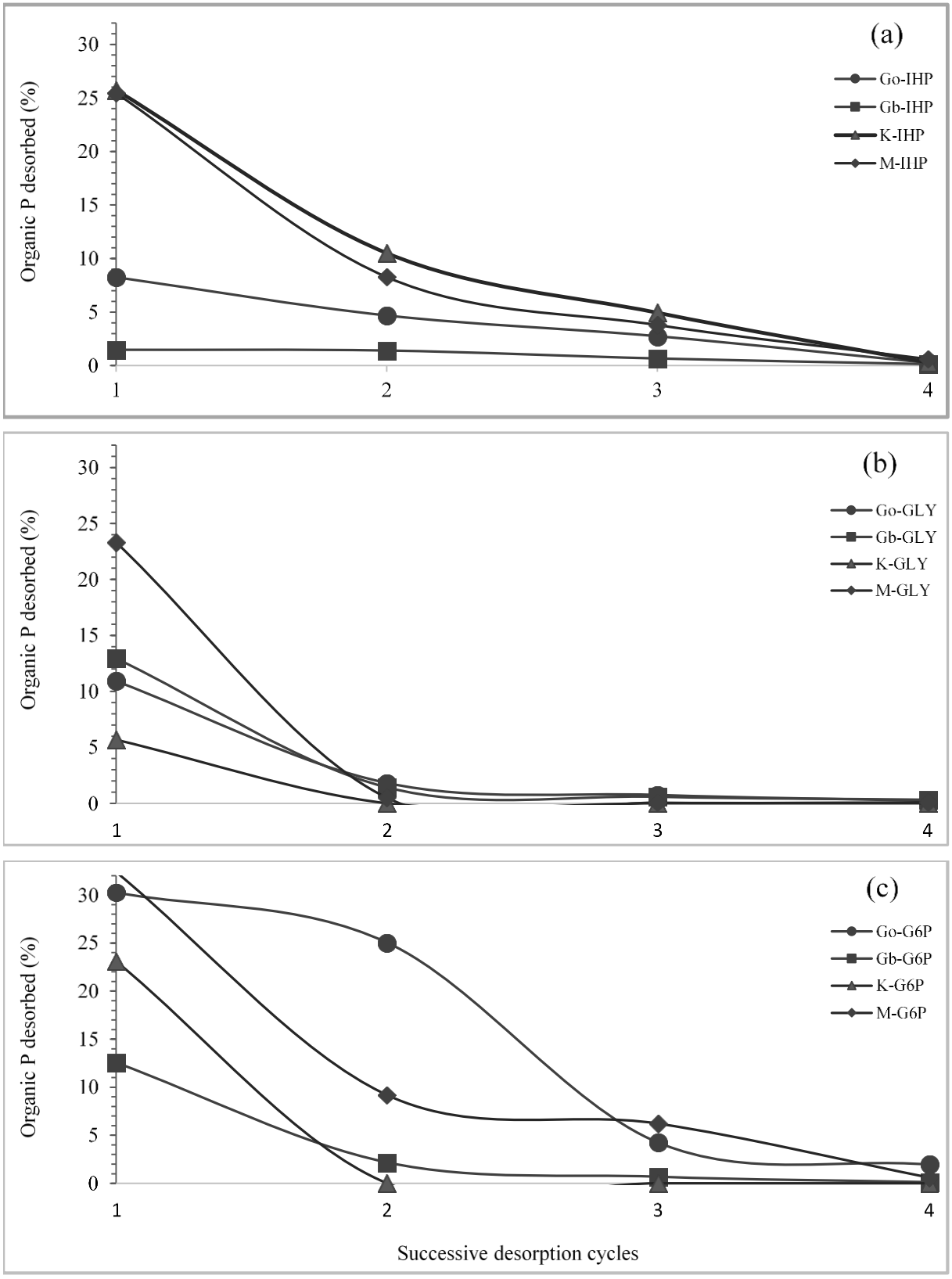


Fig. 4. Variation in P desorption rates of mineral-OP complexes.

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 Fig. 3). 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, Fig. 3). 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 (Fig. 6).

292 Successive desorption (Fig. 5) using KCl showed that more than 25% of the adsorbed OP (myo-
293 IHP, G6P, GLY) on montmorillonite was desorbed in the first cycle and there was no desorption after 4
294 cycles. Compared to the clays-myo-IHP complex, P desorbed from Fe, A1 oxide- myo-IHP was lower
295 but declined more slowly with increasing number of cycles (Fig. 5). The same trends were observed
296 with the Fe andA1 oxide-GLY complexes. For instance, at the first cycle, more myo-IHP and GLY was
297 desorbed from the clay minerals than from the Fe and A1 oxides, but from the second cycle, Fe and Al
298 oxides had desorbed almost as much myo-IHP and GLY as the clays. At the fourth cycle, the amount of
299 myo-IHP and GLY desorbed from the clay minerals was lower or equal to that from Fe and A1 oxides.
300 This suggests that the clays-myo-IHP and GLY complex supplied P rapidly but over a short period
301 whereas the Fe and A1 oxide-IHP and GLY complex supplied P slowly but over a long period. With
302 slight differences, the soil mineral-G6P complexes appeared to show the same trend as mineral-IHP or
303 GLY. As mentioned above for the results of the adsorption mechanisms of montmorillonite, the
304 desorption properties (kinetics, amount and rate of desorption) are also only valid for K-saturated
305 montmorillonite.



306

307 Fig. 5. Successive desorption of (a) IHP, (b) GLY and (c) G6P from OP-mineral complexes by KCl.

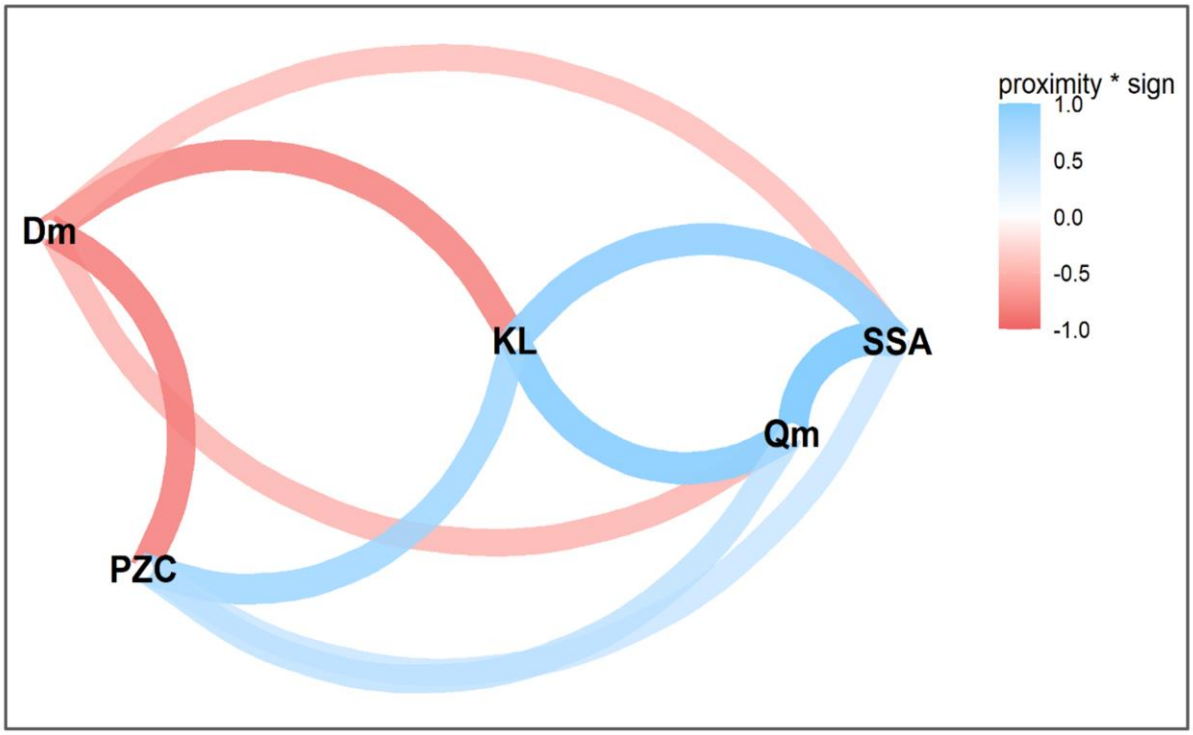


Fig. 6. Conceptual framework showing the linkage among soil minerals properties (PZC, SSA) and adsorption/desorption parameters (bonding strength, K_L; adsorption capacity, Qm, and desorption capacity, Dm). *The linkage is based on the relationships between different variables. The color of each line refers to the degree of relationship between the variables.* $R^2 > 0.5$

4. Discussion

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, myo-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-Al_2O_3) increased with decreasing molecular massas 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 myo-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 myo-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 myo-IHP for the same active sites on soil minerals, the binding energy of GLY or G6P would be higher than that of myo-IHP. Therefore, one

could expect easier desorption of myo-IHP from soil compared to GLY and G6P even though this would be highly dependent on soil minerals.

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 (120-364 m^2 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 << 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 Po. 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. 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 A1 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 contrasts, 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

405 (Prietzel et al., 2016; Ruttenberg and Sulak, 2011; Prietzel and Klysubun, 2018). As an outlook, we
406 strongly suggest studies to better understand the involvement of a wide range of iron oxides in the
407 dynamics of OP forms. More generally, though our results provide a mechanistic understanding of the
408 sorption processes of various OP forms on selected soil minerals, the role of other soil minerals alone
409 or in combination needs still to be investigated to generate a better overview of OP dynamics in real
410 complex soil systems. In addition, it is also important to point out that our results regarding the
411 comparison between the P (de)sorption properties of montmorillonite and other soil minerals are only
412 valid for the K-saturated montmorillonite used here. For Al- or Ca-saturated montmorillonite, a much
413 stronger P sorption or less pronounced P desorption would be expected compared to K-saturated
414 montmorillonite. Furthermore, in agroecosystems, with the exception of periods immediately following
415 heavy K fertilization, K-saturated montmorillonite, which was used here as the montmorillonite type, is
416 rare in most soils. Thus, the results must be considered in light of the type of clay used (K-saturated
417 montmorillonite in this study).

418 4.3. Adsorption and desorption dynamics of OP relative to IP

419 Compared to IP, myo-IHP was generally more strongly adsorbed whereas the opposite was observed
420 for G6P and GLY. This result showed that specific forms of OP, depending on their characteristics, had
421 contrasting adsorption dynamics with respect to IP. Therefore, the weaker retention of OP compared to
422 IP which is generally suggested in the literature (Anderson et al., 1974; Condron et al., 2015, 2005) did
423 not apply to all organic P compounds as higher inositol phosphate esters can be strongly retained in soil.
424 Berg and Joern, (2006) found that soils pretreated with myo-IHP or having combinations of myo-IHP
425 and IP in solution had reduced IP adsorption by successfully competing for binding sites, indicating that
426 there was a preference in the adsorption of myo-IHP over IP. This preference may either lead to the
427 release of already adsorbed IP or prevent further adsorption of IP, leading to an increase in both available
428 IP for plants and soluble IP for runoff (Leytem et al., 2002). Furthermore, in the presence of different
429 OP forms in soils, the preferential adsorption of myo-IHP or IP over both G6P and GLY may increase
430 G6P and GLY availability and promote their mineralization. Thus, this contrasting adsorption dynamics
431 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.

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 myo-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 myo-IHP and the other organic P forms (G6P and GLY) relative to IP form, with myo-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 myo-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

459 forms. Fe and Al oxides showed very different OP adsorption mechanisms compared to clays regarding
460 their binding energy and adsorption amount, which were related to different in properties (SSA and
461 PZC). The Fe and especially Al oxides (gibbsite) exhibited the highest maximum adsorption capacity
462 for all OP forms.

463 The desorption dynamics of the adsorbed OP was markedly affected by both OP and soil
464 minerals characteristics. Montmorillonite showed the highest desorption for OP suggesting higher OP
465 release when organic inputs are applied soils dominated by 2:1 phyllosilicate. However, the results are
466 very dependent on the specific type of montmorillonite used in this study. In fact, the results related to
467 the comparison between the P (de)sorption properties of montmorillonite and other soil minerals are
468 only valid for the K-saturated montmorillonite used here. If Al- or Ca-saturated montmorillonite, which
469 are the most common types of montmorillonite in soils, had been used, much higher P sorption and
470 lower P desorption would be expected compared to K-saturated montmorillonite. Finally, despite their
471 overall high adsorption, the higher desorption of G6P or GLY relative to IP from Fe and Al oxides
472 indicated that G6P and GLY release would be less affected than IP by such soil compounds, which are
473 especially abundant in highly weathered soils. However, since the P concentration used in our study
474 may be higher than that of real soil systems, it would be interesting to investigate the effect of P
475 concentration on adsorption processes by performing sorption experiments at different (and lower) P
476 concentrations.

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

481 **Declaration of Competing Interest**

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

484 **Acknowledgements**

Acknowledgments: The authors thank the Institut Polytechnique UniLaSalle Beauvais and Pro-gramme Opérationnel FEDER/FSE Picardie 2014–2020 for their support for the start of the global research project in agriculture focusing on sustainable management of soil fertility and ecoeffi-ciency of phosphorus management in farming systems. We also thank Adaline Adam, Céline Roisin, Aurore Coutelier, Nicolas HONVAULT, Philippe Jacolot, Hamza MOHIEDDINNE for their technical assistance.

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