



Influence of phosphorus on Cu sorption kinetics: Stirred flow chamber experiments

C. Pérez-Novo, D. Fernández-Calviño*, A. Bermúdez-Couso, J.E. López-Periago, M. Arias-Estévez

Área de Edafología e Química Agrícola, Departamento de Biología Vegetal e Ciencia do Solo, Universidade de Vigo, Facultade de Ciencias, 32004 Ourense, Spain

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ABSTRACT

A stirred flow reactor was used to study the influence of phosphorus on the adsorption and desorption kinetics of copper in two acid soils on granite and amphibolite. The presence of P was found to significantly increase Cu adsorption in both soils, albeit at different types of sites (mainly in slow adsorption sites in the soil on granite, and both in fast and slow adsorption sites in that on amphibolite). The increased Cu sorption at fast sites in the amphibolite soil was due to its high content in Fe oxyhydroxides, which bound P and released OH⁻ as a result, thereby raising the pH and leading to a higher sorption capacity during fast reactions. On the other hand, the increased Cu sorption at slow adsorption sites was due to Cu²⁺ acting as a bridging element between P and organic matter.

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1. Introduction

Copper is an essential element that can damage plants by both deficiency and excess. Cu deficiencies can result in a slow plant growth, stunted, distorted leaves and death of growing point. The excess of Cu can promote iron deficiency, slow growth and root stunted [1]. The natural background concentrations of metal normally found in soils are between 22 and 55 mg kg⁻¹, depending on the nature of the parent material [2]. As an average, Cu content in plants is 6 mg kg⁻¹ in plant dry matter. The application of copper-based fungicides [3], whether as organic or inorganic fertilizers [4], or animal manure containing Cu from additives in feed [5], can raise Cu levels in soil. Cu is scarcely mobile in soils, and hence it tends to accumulate in surface horizons [6]. Accumulation of Cu in soil can lead to phytotoxic levels of the metal and cause environmental problems [7]. However, the potential toxicity of copper is due to its presence in solution rather than to its total concentration. In fact, adsorption–desorption processes have a strong influence on the concentration of Cu in the soil solution, and hence on its mobility and potential toxicity in soil. Adsorption–desorption processes are governed by some soil properties (particularly pH and the amount and type of colloids present [8]). Studies on Cu sorption–desorption in acid soils are very important inasmuch as the metal is more readily dissolved in them than it is in neutral or alkaline soils [2]. The copper sorption capacity of soil can be altered by the presence of

anions or other metals. In fact, metals added simultaneously with copper to soil have been found to compete for adsorption sites [9–11]. The effect of anions on metal sorption has received less attention despite its potentially high relevance [12–15]. Phosphate is one of the most frequently used anions in agriculture, particularly as a fertilizer for acid soils intended to fulfill their macro element requirements for appropriate crop growth. Soils with a low soil pH require increased amounts of P in order to offset its easy retention by Fe and Al oxyhydroxides. Soil organic matter in acid soils can immobilize large amounts of additional P [16]. A high concentration of P in soil can have a significant effect on Cu adsorption–desorption. Thus, non-kinetic batch tests have shown that Cu adsorption can be increased by the addition of P to acid soils [15], and also that phosphate rocks can immobilize metals such as Pb, Cu or Zn [17,18]. The processes by which Cu is adsorbed by, and released from, soil are not instantaneous. Although this makes appropriate kinetic studies essential with a view to understanding the metal dynamics in soil [19], no kinetic study on the effect of P addition to soil on Cu sorption kinetics has seemingly been reported to date. Sorption–desorption kinetics can be examined in batch or soil column experiments; however, batch experiments are hampered by the long time needed for equilibrium to be reached, and soil column experiments by the risk of sorption–desorption effects being confused with those of film diffusion. These shortcomings are efficiently circumvented by the stirred flow technique [20]. Because the sorbate is continuously stirred and circulated through a stirred flow chamber, any potential interference due to diffusion through the soil matrix is avoided; also, sorption is accelerated by effect of the sorbate concentration in the liquid

* Corresponding author.

E-mail address: davidfc@uvigo.es (D. Fernández-Calviño).

Table 1
General properties of the soil samples.

Soil	P.M.	Sand	Silt	Clay	Texture	C	pH	eCEC	Al _n	Fe _d
1	G	74	16	10	Sandy loam	3.0	4.4	4.4	2.0	1.8
2	A	55	28	17	Sandy loam	3.2	5.2	4.1	6.3	34.4

P.M., parent material; G, granite; A, amphibolite; C, organic carbon (%); eCEC, effective cation exchange capacity (cmol_c kg⁻¹); Al_n, sodium hydroxide-extractable Al (mg g⁻¹); Fe_d, dithionite–citrate-extractable Fe (mg g⁻¹).

phase being kept constant and desorption by removal of desorbed metal.

In this work, we used the stirred flow chamber technique to examine the effect of P on Cu sorption and desorption in acid soils differing in their contents in iron oxyhydroxides. To this end, we determined the Cu sorption capacity of the soils in the presence and absence of P, and explored the potential rate-determining mechanisms for Cu sorption and desorption.

2. Materials and methods

2.1. Soil samples

Experiments were conducted on 2 surface horizons (0–20 cm) in maize-cropped soils on granite and amphibolite, respectively. Once in the laboratory, the soil samples were air-dried, sieved through 2 mm and stored in polyethylene bottles until analysis. The proportions of sand (2–0.05 mm), silt (0.05–0.002 mm) and clay (<0.002 mm) of the soils were determined by wet sieving for the size fractions larger than 0.05 mm and with the international pipette method for all others [21]. The pH in water (pH_w) was measured at a soil/water ratio of 1:2.5 [21], and the total carbon content determined on a ThermoFinnigan 1112 Series NC elemental analyser. The cation exchange capacity at soil pH (eCEC) was estimated as the combination of exchangeable base cations (K, Na, Ca, and Mg) extracted with 0.2 M NH₄Cl [22] and Al extracted with 1 M KCl [23]. Al oxyhydroxides were determined by selective extraction with 0.5 M NaOH [24] and Fe oxyhydroxides by dithionite–citrate extraction [25]. The concentrations of Ca, Mg, Al and Fe were determined by flame atomic absorption spectrometry, and those of Na and K by flame atomic emission spectrometry. All experiments were carried out in triplicate.

Table 1 summarizes the properties of the soil samples. As can be seen, the sand fraction (0.05–2 mm) was the most abundant as regards particle size in both soils. The samples were acid (pH 4.7 for the granite soil and 5.2 for the amphibolite soil) and sandy loam in texture. The cation exchange capacity was low and very similar for both soils (4.4 for the granite soil and 4.1 for the amphibolite soil). The total content in organic carbon was also very similar (3.0% and 3.2%, respectively). The content in Al oxyhydroxides was 3.2 times higher in the amphibolite soil than in the granite soil. The main difference between the two soils was in the amount of Fe oxyhydroxides, which was 1.8 g kg⁻¹ on granite and 34.4 g kg⁻¹ on amphibolite (i.e. 18.7 times higher in the latter).

2.2. Stirred flow chamber experiments

The 1.5 cm³ polypropylene stirred flow reactor used (Fig. 1) was a slightly modified version of that reported by López-Periágo [26], with a side inlet at the bottom and an outlet in the lid both of which were connected to a Gilson Minipuls 3 peristaltic pump (Gilson S.A.S., Villiers Le Bel, France) by 0.5 mm polytetrafluoroethylene (PTFE) tubing, and both covered with 0.45 μm PTFE filters 10 mm in diameter to retain soil in the reactor. Stirring was provided by a PTFE-coated magnetic bar spun at 400 rpm, and output solution

fractions were collected in 2 mL polypropylene Eppendorf vials by using a Gilson FC 203G automatic fraction collector at a rate of one vial every 2.5 min. Tests were performed in a cabinet thermostatted at 25.0 ± 0.1 °C. The flow rate was monitored throughout and found to vary by less than ±3%. The experimental procedure was as follows: after the reactor was loaded with approximately 0.2 g of soil sample, a solution containing 75 μM Cu(NO₃)₂ and 7.5 mM NaNO₃ (pH 4.75) was passed for 200 min. In the Cu sorption tests involving the presence of P, a solution containing 75 μM Cu(NO₃)₂, 75 μM H₂NaPO₄ and 7.5 mM Na(NO₃)₂ (pH 4.75) was passed for 200 min. Adsorption runs were immediately followed by passage of a 7.5 mM Na(NO₃)₂ solution for a further 200 min in order to evaluate Cu desorption. The use of NaNO₃ as background electrolyte is required to keep a constant ionic strength throughout the experiment. A flow rate $J_w = 0.60 \text{ mL min}^{-1}$ was used throughout in all tests, and blank runs with no soil in the reactor were performed to allow the amount of metal sorbed to be calculated as described below. The concentrations of Cu in the output solutions were determined by FAAS $q(i)$, which denotes the metal content of the soil sample at time $i \Delta t$ (where Δt is the time taken to collect each output solution sample), was calculated from Eq. (1) [27]

$$q(i) = \left\{ \sum_{j=1}^i \left[\frac{(C_1(j) - C_2(j)) \Delta t J_w}{V_e} \right] + [C_1(i+1) - C_2(i+1)] \right\} \frac{V_e}{m} \quad (1)$$

where $C_1(i)$ and $C_2(i)$ are the concentrations of metal in the i -th output solution sample in the absence and presence of soil, respectively; V_e is the effective volume of solution in the reactor; and m the mass of the soil sample. All experiments were carried out in duplicate.

A stopped flow run was carried out with granite soil prior to the experiments in order to check whether the kinetics of Cu sorption was not “instantaneous”, but rather controlled by sorption, on the time window afforded by the experimental set-up [28]. Halting the flow of Cu(NO₃)₂ for 30 min caused the Cu concentration in the output solution to be reduced by 29%, which indicates that Cu sorption was not instantaneous, and hence, that kinetic experiments could be done.

2.3. Data evaluation

2.3.1. Sorption modeling

Different models can be used to describe non-equilibrium metal adsorption and desorption kinetics. In many cases, the reaction kinetics can be described equally well by different models [29], and the rate coefficient obtained using these equations is usually an apparent coefficient that changes with flow rate and the initial solute concentration [27]. The simplest equations are the one-site kinetic equations. However, in some cases, the one-site kinetic models provide a high deviation of experimental data. Therefore, the use of models with two classes of sites is recommendable in those cases [29].

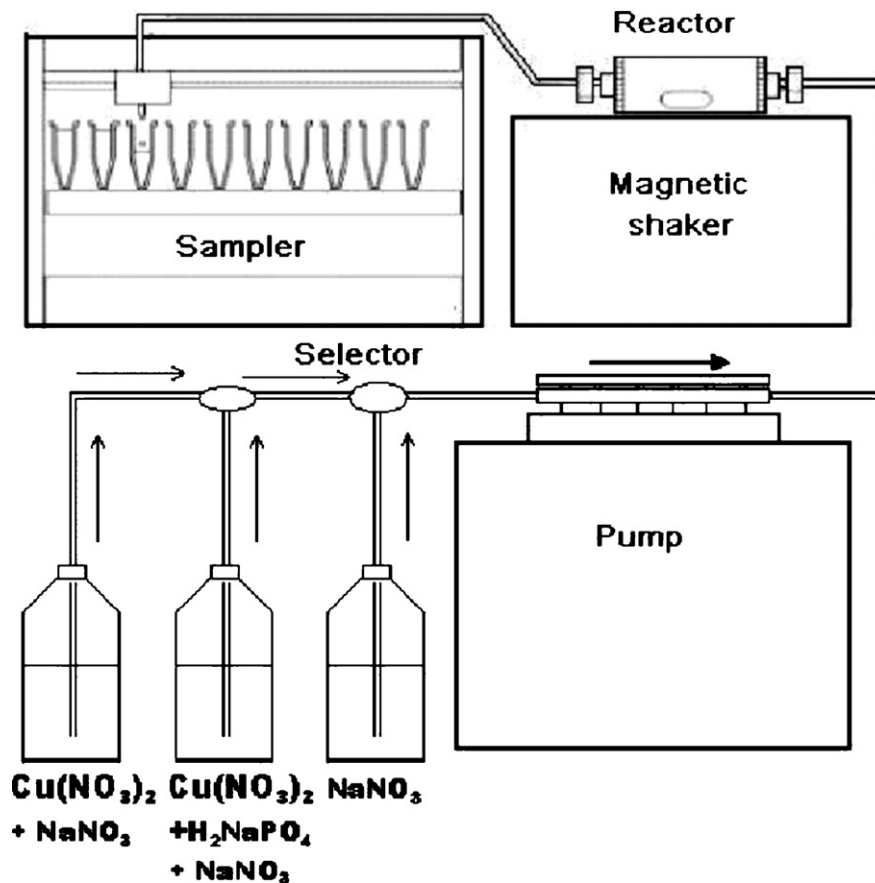


Fig. 1. Schematic description of the stirred flow reactor.

The *pseudo* first-order equation [30] with two sorption sites can be expressed as follows:

$$\begin{aligned} \frac{dq_x}{dt} &= k_{x1}(Fq_{x\max} - q_x) \quad \text{for } qx < qF \\ \frac{dq_x}{dt} &= k_{x2}((1 - F)q_{x\max} - q_x) \quad \text{for } qx \geq qF \end{aligned} \quad (2)$$

where dq_x/dt ($\text{mmol kg}^{-1} \text{min}^{-1}$) is the copper adsorption or desorption rate, k_{x1} the adsorption or desorption rate constant for fast sites (min^{-1}), k_{x2} that for slow sites (min^{-1}), F the fraction of fast sites, $q_{x\max}$ (mmol kg^{-1}) the maximum adsorption or desorption capacity of the soil under the experimental conditions used, q_x the amount of Cu adsorbed or desorbed by the soil, and q_F is the retained or released Cu in the transition from fast to slow sites. F values were determined using an iterative method by finding successive approximations to the solution. When F is equal to 1, the model became the *pseudo* first-order equation with one sorption site.

To apply the equation, it is necessary a linear relationship between dq_x/dt and q_x , or a composite curve with two lines. If there is no linear relationship between dq_x/dt and q_x a second-order equation should be used:

$$\frac{dq_x}{dt} = k_{x1}C + k_{x2}(q_{x\max} - q_x) \quad (3)$$

where dq_x/dt ($\text{mmol kg}^{-1} \text{min}^{-1}$) is the metal adsorption or desorption rate, k_{x1} ($\text{L kg}^{-1} \text{min}^{-1}$) a adsorption or desorption constant, C (mmol L^{-1}) the Cu concentration in the chamber, k_{x2} the adsorption or desorption rate constant (min^{-1}), $q_{x\max}$ (mmol kg^{-1}) the maximum amount of Cu that could be retained or released under our experimental conditions, and q_x (mmol kg^{-1}) the amount of Cu retained or released from the soil.

In both equations ((2) and (3)), x can be s (in the adsorption experiments) or d (in the desorption experiments).

2.3.2. Speciation

Calculations of Cu–P species were performed using the MINTQA2 computer speciation program [31].

3. Results and discussion

3.1. Influence of phosphorus on copper sorption

Fig. 2 shows the amount of Cu adsorbed (q_s) by the two soils as a function of time (t). Copper retention in both soils was higher in the presence of added P than in its absence. The increase in Cu sorption in the granite soil (Fig. 2A) was smaller than that in the amphibolite soil (Fig. 2B). Initially (first 75 min in the granite soil and first 40 in the amphibolite soil), Cu sorption was similar in the presence and absence of P. The absence of early changes may have resulted from that of interactions of Cu and P at a low coverage or to a limited copper inflow. Fig. 3 shows the variation of the Cu sorption rate as a function of the amount of Cu adsorbed. As can be seen, the Cu sorption rate was initially constant (phase 1). During this phase, Cu sorption is faster than Cu inflow, and hence, Cu sorption is limited by the input of Cu in the reactor. Then, the rate decreased very rapidly (phase 2) and, finally, more slowly towards the end of the test (phase 3). During the adsorption process, Cu in solution decreased quickly due to the fast adsorption. As the reaction time increases, the solution Cu concentration changed little due the slow reactions [32]. This is reflected in Fig. 3, which shows that during the phase 2, the adsorption rate decreases faster than in phase 3. Therefore, the first and second phase of the process involved fast

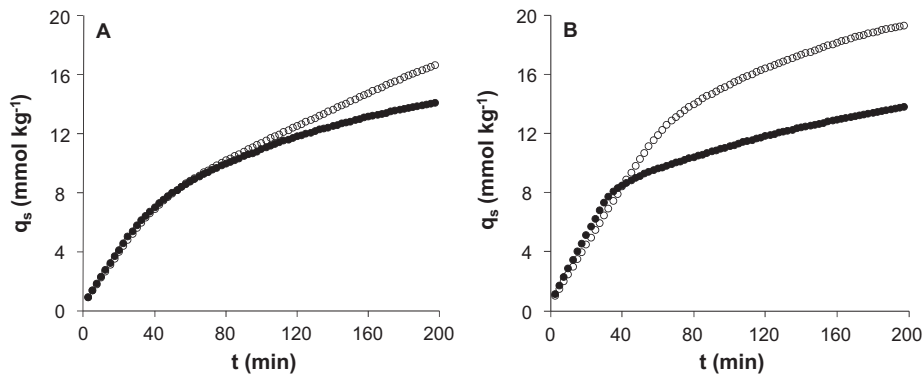


Fig. 2. Cu cumulative sorption (q_s) in the absence of P (black circles) and its presence (white circles) in the granite soil (A) and amphibolite soil (B).

sorption sites and the third slow sorption sites. No points from the first retention phase were used to fit the equations.

The Cu sorption kinetics at fast sorption sites in the granite soil (Fig. 3A) was very similar in the presence and absence of P; on the other hand, the presence of P reduced the Cu sorption rate fall at slow adsorption sites in the same soil (Fig. 3A). By contrast, P had an appreciable effect on Cu adsorption at both types of sites in the amphibolite soil (Fig. 3B).

In the absence of P, the fitted values of $q_{s\text{max}}$ were very similar in the granite and amphibolite soil (Table 2). This may have been a result of the similar organic carbon content of both soils (Table 1), since Cu sorption is known to be affected by organic matter. In acid soils, Cu is bound mainly by organic matter [33], and also, to a much lesser extent, by metal oxides, silicates, phosphates and carbonates [34]. In previous work, Arias-Estévez [35] found more than 80% of Cu to bind to organic matter within 24 h of incubation; also, Pérez-Novo [36] showed removal of organic matter from soil to considerably reduce Cu sorption. Although the Cu binding capacity of organic matter is highly dependent on pH [37], our results as regards outflow pH (4.4) were very similar at the end of all tests.

$q_{s\text{max}}$ was significantly higher (66% in the granite soil and 47% in the amphibolite soil) in the presence of P than in its absence (Table 2). In the granite soil, the increase in Cu sorption was mainly provided by slow sites; in the amphibolite soil, it was due to both fast and slow sites (see F in Table 2). The differences between the two soils during the fast sorption phase (Fig. 3) can be ascribed to a difference in pH changes between the soils in this phase (Fig. 4). In the granite soil, the pH of outflow in the first 80 min was the same in the presence and absence of P (paired $t = 1.2$, $p = 0.229$); in the amphibolite soil, however, the pH of the outflow was significantly higher (paired $t = 3.1$, $p = 0.004$) in the presence of P than in its absence. This was probably a result of the large amount of Fe

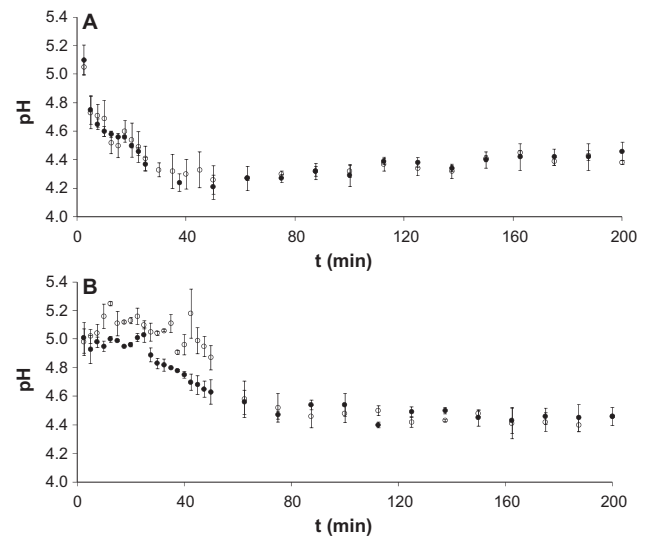


Fig. 4. Variation of pH in the chamber during Cu sorption in the absence of P (black circles) and its presence (white circles) in the granite soil (A) and amphibolite soil (B).

oxyhydroxides present in the amphibolite soil relative to the granite soil (Table 1). Phosphorous can be adsorbed by Fe oxyhydroxides through partially reversible reactions resulting in the formation of hydroxy-ferric phosphates and OH⁻ release—which can help maintain a high pH in the presence of Cu and hence increase the Cu binding capacity of organic matter during this phase.

As can be seen from Table 2, the greatest differences in fitted parameters between the two soil types in the absence of P were

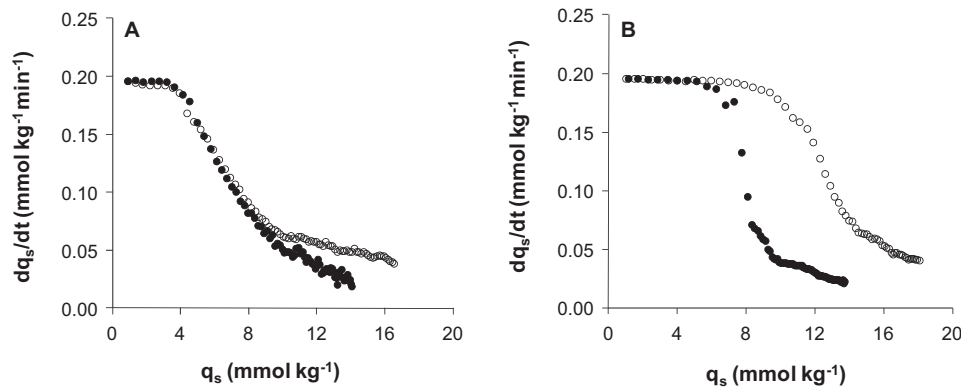


Fig. 3. Cu sorption rate against Cu cumulative sorption in the absence of P (black circles) and its presence (white circles) in the granite soil (A) and amphibolite soil (B).

Table 2
Cu sorption fitted parameters.

Soil		q_f	F	q_{\max}	k_{s1}	k_{s2}	R_1^2	R_2^2
1	Copper	8.88	0.53	16.71	0.025	0.008	0.990	0.928
	Copper and phosphorous	9.20	0.33	27.72	0.021	0.004	0.995	0.961
2	Copper	8.93	0.52	17.15	0.064	0.006	0.926	0.922
	Copper and phosphorous	14.28	0.56	25.14	0.025	0.007	0.976	0.964

q_f , Cu retained in the soil in the transition from fast to slow sites (mmol kg^{-1}); F , fraction of fast sites; q_{\max} , maximum retention capacity of the soil under the experimental conditions (mmol kg^{-1}); k_{s1} , retention rate constant for fast sites (min^{-1}); k_{s2} , retention rate constant for slow sites (min^{-1}).

those in k_{s1} , which was 2.6 times higher in the amphibolite soil than in the granite soil; by contrast, k_{s2} was 1.3 times smaller in the former.

Judging by the similarity of the sorption rate curves obtained during the fast sorption phase (Fig. 3), the changes in k_{s1} caused by presence of P in the granite soil were small (Table 2). The kinetic constant (k_{s2}) was 50% less in the presence of P than in its absence (Table 2). The kinetic parameters in the amphibolite soil changed in the opposite direction to that in the granite soil; thus, k_{s1} was 61% less in the presence of P, whereas k_{s2} was similar in its presence and absence (Table 2). Therefore, the presence of P in the granite and amphibolite soil primarily affected the Cu adsorption kinetics in slow and fast sites, respectively. Although both soils have a similar pH and organic matter content, the amount of Fe oxyhydroxides and Al oxyhydroxides are 19.1 and 3.2 times higher in the amphibolite soil than in the granite soil. This difference could explain the different Cu sorption rate behavior among both soils.

The reactions occurring at fast sites are most likely adsorption via electrostatic attraction, and/or inner-sphere complexation with functional groups present in the soil components [38]. Copper is known to be bound by organic matter mainly via bidentate inner-sphere complexes [34], so this should be the principal adsorption mechanism for its sorption at fast sites.

The sorption mechanism for the slow reaction phase is poorly understood [39]; however, it is believed to involve intraparticle diffusion, precipitation and/or sorption at sites with a higher activation energy than that for fast sorption sites [38]. In our case, simulations with MINTEQA2 excluded precipitation at the outflow pH during slow reactions, which ranged from 4.3 to 4.5. The other two processes (viz. slow intraparticle diffusion and sorption at sites with a higher activation energy than the fast sorption sites) could not be discarded, however.

As regards the increase in Cu adsorption at slow sites in the presence of P, 99% of all copper at the experimental pH (4.3–4.5) was Cu^{2+} , Cu–P species accounting for only a very small fraction of copper (less than 0.2%). Therefore, the formation of readily sorbed Cu–P species in solution can be discarded as a potential mechanism for slow reactions in acid soils. The pH during the slow sorption phase in the granite and amphibolite soils (after the first 80 min, Fig. 4) was identical in the presence and absence of P. Therefore, an effect of pH on the increase in Cu sorption at slow sites in the presence of P can also be discarded. Our hypothesis is that, in the presence

of P, Cu^{2+} (like Fe^{3+} or Al^{3+} [40]) may act as a bridging element between P and organic matter since, like the previous two cations, Cu^{2+} is a Lewis acid [41]. Although Cu^{2+} ion is softer than Al^{3+} and Fe^{3+} [41] – and its bonds weaker as a result – the Cu concentration in our solution was much higher than those of Fe and Al, so the formation of Cu bridges between organic matter and P was highly likely.

3.2. Influence of phosphorus on copper desorption

Fig. 5 shows the Cu desorption curves for the granite and amphibolite soil as a plot of desorbed Cu (q_d) versus time (t). The amount of Cu desorbed was greater in the presence of P than in its absence in both soils. Initially (first 7.5 min in the granite soil and 17.5 min in the amphibolite soil), however, the amount of Cu released in the presence and absence of P was similar in both soils. Based on Fig. 6, the desorption kinetics observed could not be described by the first-order equation for one or two sites as these led to non-linear curves.

Table 3 shows the fitted desorption parameters. The fitted values of $q_{d\max}$ were low in the desorption tests in the absence of P ($2.56 \text{ mmol kg}^{-1}$ in the granite soil and $1.97 \text{ mmol kg}^{-1}$ in the amphibolite soil, which amount to 15% and 11%, respectively, of $q_{s\max}$). $q_{d\max}$ was higher in the presence of P than in its absence ($6.34 \text{ mmol kg}^{-1}$ in the granite soil and $9.01 \text{ mmol kg}^{-1}$ in the amphibolite soil, which amount to 23% and 36%, respectively, of $q_{s\max}$).

In the desorption experiments, Cu adsorption in the absence of P reflected in similar values for k_{d1} in both soils, with a k_{d1} -granite/ k_{d1} -amphibolite ratio of 1.1. However, k_{d2} was 2.2 times higher in the amphibolite soil than in the granite soil. This indicates that the desorption rate was lower for the granite soil than for the amphibolite soil. In the presence of P, k_{d1} was higher than in its absence in both the granite soil and the amphibolite soil (Table 3); on the other hand, k_{d2} was lower in the presence of P (Table 3). The difference may be due to a greater effect of intraparticle diffusion on desorption in the presence of P than in its absence. In order to check this hypothesis, we plotted $q_d/q_{d\max}$ against $t^{1/2}$. If the Cu release process were controlled by intraparticle diffusion, then the plot should exhibit the typical linear variation of diffusion-controlled processes [42]. As can be seen from Fig. 7, linearity in Cu release after Cu sorption in the presence of P was better than in its

Table 3
Cu desorption fitted parameters.

Soil		$q_{d\max}$	k_{d1}	k_{d2}	R^2
1	Copper	2.56	0.934	0.006	0.983
	Copper and phosphorus	6.34	1.395	0.002	0.979
2	Copper	1.97	0.865	0.013	0.981
	Copper and phosphorus	9.01	1.793	0.001	0.996

$q_{d\max}$, maximum amount of Cu that could be released under the experimental conditions (mmol kg^{-1}); k_{d1} , Cu release constant ($\text{L kg}^{-1} \text{ min}^{-1}$); k_{d2} , desorption rate constant (min^{-1}).

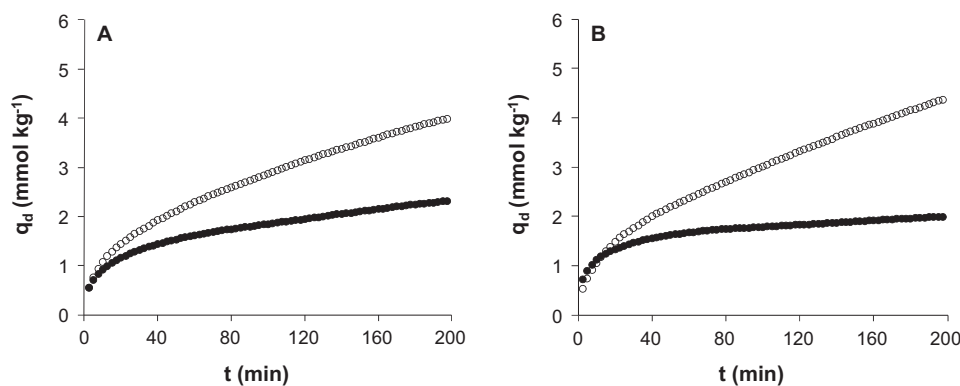


Fig. 5. Cu cumulative desorption (q_d) after Cu sorption in the absence of P (black circles) and its presence (white circles) in the granite soil (A) and amphibolite soil (B).

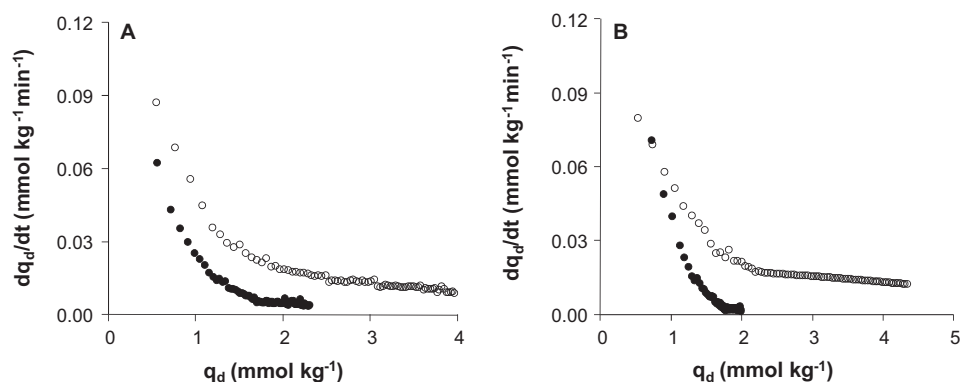


Fig. 6. Cu desorption rate against Cu cumulative desorption after Cu sorption in the absence of P (black circles) and its presence (white circles) in the granite soil (A) and amphibolite soil (B).

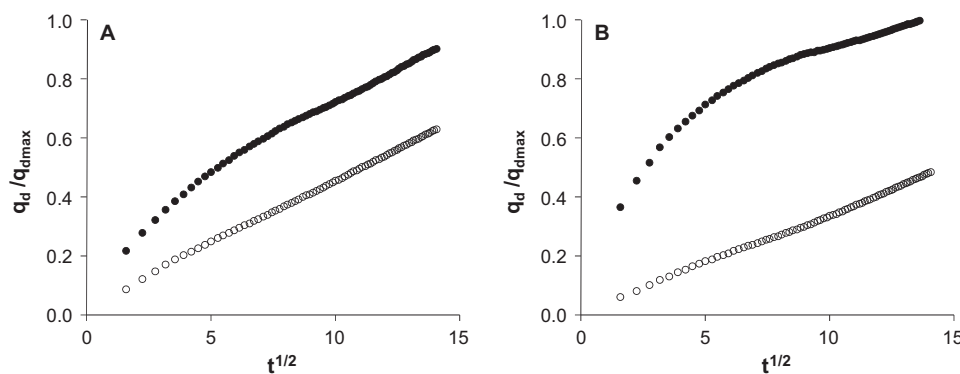


Fig. 7. Fractional cumulative desorption (q_d/q_{dmax}) against $t^{1/2}$ after Cu sorption in the absence of P (black circles) and its presence (white circles) in the granite soil (A) and amphibolite soil (B).

absence in both types of soil. That is, in the presence of P is more evident than in the absence of P, that the amount of Cu desorbed is greater than the rate of intraparticle diffusion. This result, and the higher proportion of Cu desorbed in the presence of P, indicate that a significant portion of Cu adsorbed in the presence of P was more weakly bound to the soil than in its absence. It is well known that Cu has a very high affinity for humic acids when is added to organic matter in absence of P ions [43,44]. Moreover, other studies have found that copper is adsorbed almost irreversibly by humic acids in absence of P [45,46]. This high affinity for humic acids was attributed to inner-sphere complexes [34]. Desorption experiments in the present work suggest a weaker bound when Cu act as a bridging element between P and organic matter than when Cu bounds directly to organic matter. In this sense, Guardado et al. [47] show that the stability of phosphate–metal–humic complexes is inversely related to the stability of the metal–humic interac-

tion. Further investigations are needed in order to clarify binding capacity and strength of P–Cu–organic matter complexes related to Cu–organic matter complexes.

4. Conclusions

The results presented in the present work show that Cu retention is higher in the presence of added P than in its absence. Moreover, results show changes in the Cu sorption rates behavior in the presence of P related to Cu sorption in absence of P. In the soil with a low amount of Fe and Al oxyhydroxides the Cu sorption rate behavior at fast sorption sites was very similar in the presence and absence of P. However, the presence of P increased the Cu sorption during the slow adsorption sites. In the soil with a high amount of Fe and Al oxyhydroxides, P had an appreciable effect on Cu adsorption at both types of sites. This could be justified a high pH in the

presence of P during the fast sorption reactions, and hence, a higher Cu binding capacity of soil. The results also suggest that, in the presence of P, Cu act as a bridging element between P and organic matter during slow sorption reactions, and that this bounding mechanism is weaker than the Cu–organic matter complexes.

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