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A mechanistic model for understanding pH effect on phosphorus availability in rhizosphere and bulk soil

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Introduction

Phosphorus (P) is the least mobile major nutrient in many soils and is frequently the prime limiting factor for plant growth in terrestrial and aquatic ecosystems. Many studies have tried to model P bioavailability, i.e. the actual flux of P taken up by the plant. Barber (1995) showed that the concentration of P in soil solution which is made available for plant, reference here as P available, was the second variable controlling P bioavailability, after root elongation rate. However those models systematically underestimate P uptake by plants under conditions of low P supply (Mollier et al., 2008). This failure to predict P bioavailability may be cause to the use of the P availability obtained for bulk soil chemistry in such models, with little account of rhizosphere chemistry. Roots and microorganisms are however well known to induce dramatic chemical changes in the rhizosphere, which ultimately determine P uptake. For inorganic P, a number of chemical properties of soils, such as pH, concentrations of inorganic ligands, redox potential, and ionic strength can indeed alter P availability in the rhizosphere (e.g. Hinsinger, 2001). Many studies have measured changes of some of those chemical parameters in the rhizosphere and attempted to relate them to P bioavailability. Amongst them, a major chemical change observed in the rhizosphere is a pH variation which can reach up to several units as measured by Solaiman et al (2007) for wheat plants in response of low P supply. Even the few models which considered root-induced chemical changes failed at adequately predicting P uptake by plants (Kirk, 2002). This failure may be due to the simplistic, non mechanistic, simulation of the concentration of P in soil solution, used here as indicator of P availability. Adsorption isotherms and derived constant such as Kd which are commonly used to simulate P availability in those models cannot account for the effects of all of the above-mentioned chemical changes induced in the rhizosphere. In spite of an abundant literature on soil P availability, it is still difficult to understand to what extent and even in what direction (decrease or increase) P availability would change in response to a variation of soil pH (Hinsinger, 2001). In our study, we used a mechanistic model to unravel the mechanisms controlling soil P availability. Such kind of models have mostly been used to predict P availability in simple systems, made of a single mineral or a mixture of two minerals. To the best of our knowledge, only one of those former studies has been devoted to P availability in complex system such as a soil (Gustafsson, 2001) and none has been yet applied to the rhizosphere.

The objectives of this study were (i) to use a mechanistic, geochemical model in an attempt to simulate the variations of available P as a function of soil pH, both in the bulk soil and rhizosphere and (ii) to relate the difference of P availability between the rhizosphere and bulk soil to the amount of P taken up by plant (P bioavailability) and to the other chemical changes induced in the rhizosphere. The P availability was determined by using $CaCl_2$ and water as extractions media.

Material and method

Soil properties

We studied a topsoil (0-20 cm depth) classified as a Chromic Cambisol (FAO-UNESCO, 1989), with a silty clay texture. The total adsorbed P concentration was estimated by an ammonium oxalate extraction. The cation exchange capacity and the concentrations of the cations adsorbed by the soil material were estimated by extraction with cobalthexamine chloride. The mineralogy of the soil was determined using XRD analysis and standard chemical extractions. In addition to the primary minerals (quartz and K-feldspar), XRD

analysis showed the presence of illite, kaolinite and Fe-oxides. In order to assess the concentrations of kaolinite and illite in the soil material, we assigned the total concentrations of Si, Al, Fe and K measured in the clay-size fraction to the chemical composition of kaolinite and illite, according to the following formulas: $[Si_4O_{10}]$ $[Al_4(OH)_8]$ and $[(Si_{6.7}Al_{1.3})O_{20}]$ $[(Al_{1.95}Fe^{3+}_{1.95})$ $(Fe^{2+}_{0.05}Mg_{0.05})$ $(OH)_4]K_{1.3,}$ respectively. The nature (cristallinity) and concentrations of Al and Fe-oxides were estimated by extractions with ammonium oxalate and citrate-dithionite-bicarbonate.

Experimental data

To assess the effect of pH on P availability in the rhizosphere and bulk soil, P availability was measured along a wide range of soil pH values obtained by adding 5 to 200 mmol of acid or alkali. For rhizosphere studies, rhizosphere was obtained after growth of durum wheat on 64g of soil (*Triticum turgidum durum* var. Acalou) during 21 days as described by Li (2008). Extractions of inorganic P was performed with $CaCl_2$ (0.01M) and water according to the procedure proposed by Houba (1990). The concentration of P in the extracts was measured with the malachite green method. The soil pH was measured both in $CaCl_2$ and water supernatants using a Metrohm-744 pH meter.

Model description

We used the additive approach to simulate P availability in the bulk soil and rhizosphere samples over a wide range of pH values. This approach considers that the properties of the overall soil can be described as the sum of the individual properties of its constituents (Gustafsson, 2001). We tested both the stability of the major Ca-phosphate minerals and the adsorption behaviour of inorganic P for the different soil constituents. We used the thermodynamic equilibrium of the most likely phosphate minerals formed during the course of our experiment. As a potential secondary phase, the most common forms were considered as: hydroxyapatite ($Ca_5(PO_4)_3OH$), octacalcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4.5H_2O$) and dicalcium phosphate dihydrate ($CaHPO_4.2H_2O$).

In order to simulate the adsorption behaviour of the soil constituents, we used two adsorption models: (i) the 1-pK Triple Plane Model (TPM) for the adsorption of cations and anions by minerals (Hiemstra and Van Riemsdijk, 1998), and (ii) NICA-Donnan for the adsorption of cations by the soil organic matter. The specific surface area, point-of-zero charge and site density of the five secondary minerals considered in our study are based on the literature. The thermodynamic equilibrium used to simulate surface complexes formed between P and minerals during adsorption reactions were also obtained from the literature or are have been calibrated from literature data.

We used the chemical equilibrium software Visual MINTEQ (Gustafsson, http://amov.ce.kth.se/people/gustafjp/vminteq.htm) for the speciation calculations, as both the 1-pK TPM and NICA-Donnan models are available for the simulation of the adsorption processes. Thermodynamic data for aqueous species were those of the MINTEQA2 version 4.0 database (US Environmental Protection Agency, 1999).

The total concentration of P used in the model corresponds to the sum of dissolved and adsorbed P. In our modelling, this value was set to P concentration measured in the ammonium oxalate extract. Total Ca concentration used in the modelling was set to the sum of exchangeable Ca (measured by cobalthexamine method) and Ca supplied by $CaCl_2$ when used as an extractant (0.01 M). For the total Cl concentration, we similarly used Cl supplied by $CaCl_2$.

Results and Discussion

Figure 1 shows the concentration of P extracted with $CaCl_2$ and water from the rhizosphere and bulk soils over a range of pH values. In the bulk soil, the different amounts of acid and alkali induced pH variations from 4 to 9. The pH change due to the add of acid or alkali in the rhizosphere was slightly altered, as a consequence of pH change induced by root activities. Water always extracted more P than $CaCl_2$. We also observed from Figure 1 an increase in P availability in both the rhizosphere and the bulk soil above pH = 7.5, irrespective of the nature of the extractant. The greater change in P availability driven by pH variations reached a factor of 6.3, in water extracts of the rhizosphere. The effect of pH was smaller in the bulk soil (3.7 fold). The influence of pH on P availability was also more sensitive for water than $CaCl_2$ extracts. For the same pH increase, P availability increased by a factor of 4.5 in the water extract whereas it was less than 2 in the $CaCl_2$ extract. Modelling results first showed that the composition of water and $CaCl_2$ extracts were undersaturated with respect to P minerals. Accordingly, the influence of pH on P availability as measured through the two extraction methods was satisfactory reproduced by account only for the adsorption process (RMSE = 5.6 µg.kg^{-1}). Modelling also showed that the difference of P concentrations obtained with the two extraction methods is related to the adsorption of Ca. This divalent cation seems to facilitate P adsorption (and thus decrease extracted P) through the addition of positive charges at mineral surfaces, leading to an enhancement of the adsorption of negatively charge phosphate species onto soil minerals.

Variations of P availability in the rhizosphere showed contrasting results for the two extractants. For $CaCl_2$ extraction, P availability was always lower in the rhizosphere than in the bulk soil, in average 12 µg.kg^{-1} lower. For water extraction, P availability was also smaller in the rhizosphere than in the bulk soil for pH lower than pH = 6, while above pH = 6, P availability was greater in the rhizosphere than in the bulk soil. The difference between the two extraction methods was greater in the rhizosphere than in the bulk soil.

In the rhizosphere, the decrease in P availability which was observed for $CaCl_2$ extractions may be related to a depletion of the pool of soil P which could replenish the soil solution. The calculated amount of adsorbed P depleted to induce the observed decrease of $CaCl_2$ available P in the rhizosphere was equal to 6 mg.kg^{-1} (RMSE = 5.2 µg.kg^{-1}). This amount of depleted P is close to the amount of P taken up by durum wheat during the 21 days of growth, i.e. 6.2 mg.kg^{-1}. These results also suggest that most of the P taken up by wheat, i.e. bioavailable P, was originating in the pool of inorganic P adsorbed on soil minerals. Finally, when assessing P availability with $CaCl_2$ extraction, it occurs that no other process than pH change and plant uptake should be accounted for modelling changes of P availability in the rhizosphere of durum wheat.

In contrast, when assessing P availability with water extraction, plant uptake can hardly explain the observed increase which occurred in the rhizosphere relative to bulk soil at neutral to alkaline pH values. Even for pH lower than 6, plant uptake *per se* could not explain the observed decrease in P availability in the rhizosphere as this was higher than the quantity of P taken up. Our model indicated that the main process which could explain such a change of P availability in the rhizosphere with water extraction media was the Ca uptake by durum wheat (RMSE = 20 µg.kg^{-1}). Indeed, a decrease of 3.8 mg.kg^{-1} of Ca concentration introduced in the model was necessary to find a good agreement between P availability modelled and measured in the rhizsophere. This Ca concentration was rather close to the concentration of Ca taken up by durum wheat during 21 days, i.e. 4 mg.kg^{-1}. The decrease of Ca concentration in the soil impacted both (i) the positive charge brought on mineral surfaces which facilitates P adsorption and (ii) the ionic strength of the soil solution. The decrease in ionic strength affected P availability mainly in acid conditions, whereas P availability was prominently

affected by the charge effect under alkaline conditions. This influence of Ca uptake on P availability was masked in the case of CaCl$_2$ extractions. To sum up, the uptake of P and Ca were important to take into account for properly simulating P availability as assessed by water extraction.

For both rhizosphere and bulk soil, change of P availability in response to soil pH can be accurately predicted by means of adsorption process simulated with our mechanistic model. In rhizosphere of durum wheat, the modelling concentrations of P availability after remove P as well as Ca concentrations taken up by durum wheat seem indicated that pH change is the main driver which control P availability. The mechanistic description of P availability provided by our model shows up the need to account for a number of interacting processes in the rhizosphere, such as the uptake of other ions by plants, Ca uptake in the present case. Such interaction between P and Ca ions is likely to play a significant role in many soils as Ca is often a major cation in soil solutions. The agreement between P available measured and modelled in response to soil pH in rhizosphere and bulk soil seems indicated that such surface complexation model could be introduced in plant nutrition model as suggest by Nowack (2006) to better understand crops nutrition.

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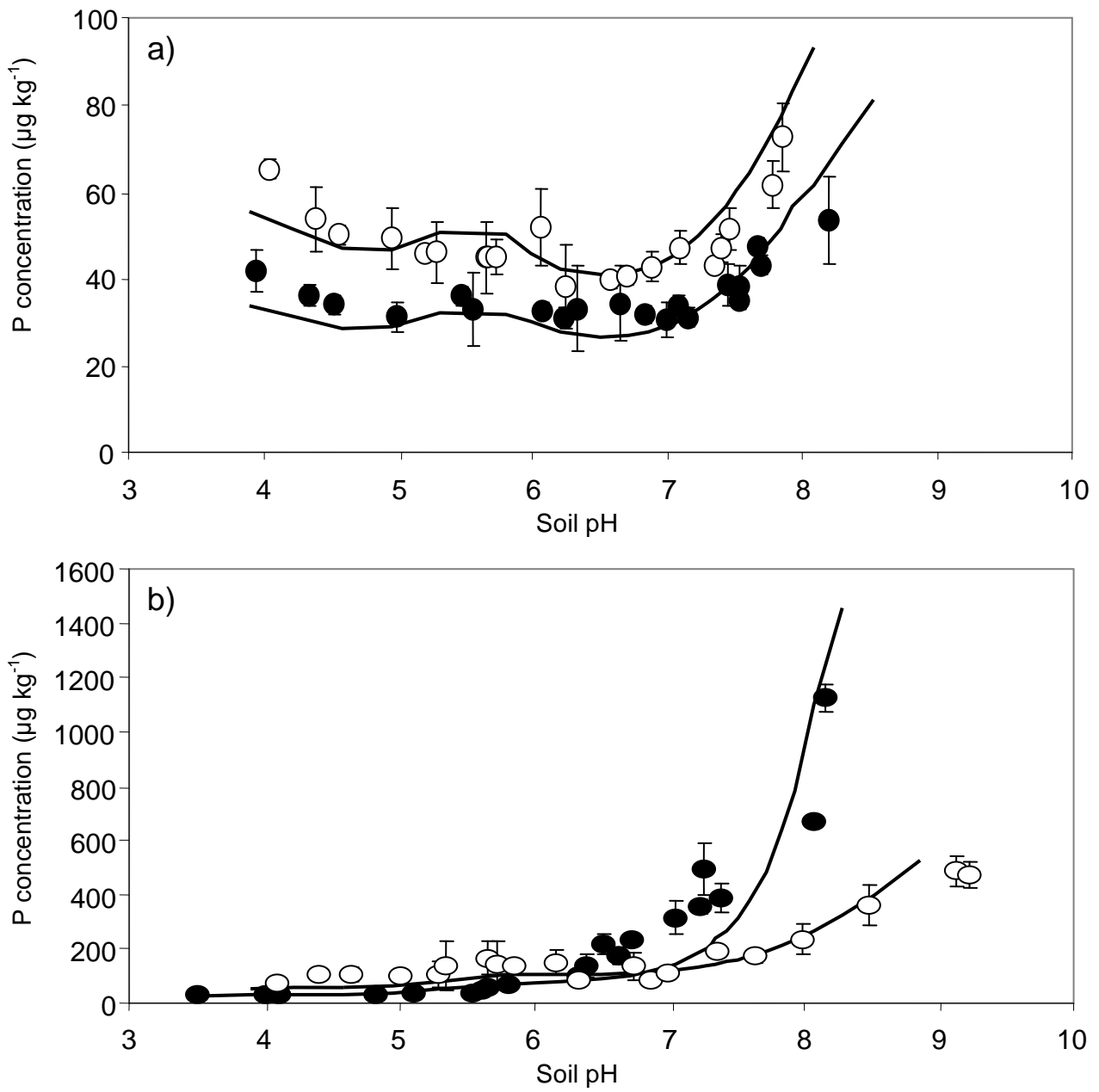
Fig 1. Relationship between soil pH and concentration of phosphorus extracted with (a) $CaCl_2$ (0.01M) and (b) with water for the bulk soil (open circle) and the rhizosphere (filled circle).