Maize for acid soils
First scientific report -2001

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Abstract :

The objectives for the first year of the work package 10 were to write and calibrate a model of Al and P dynamics in the rhizosphere. The Rhizodyn model, developed within the preceding European program "*Fitting maize for acid soil*", was supplemented (i) for its use on Windows 2000/NT environment, (ii) with a module of adsorption for the anions (phosphate and organic anions), and (iii) with a thermodynamic data base including the constants of formation of the complexes between anions and Al and Fe. In parallel, the model was calibrated for the P adsorption in using isothermal and kinetic studies highlighting the effect of the pH on the fixing of P. An experimental study was done with a soil of Colombia using a special culture device, making possible to conveniently analyse the rhizosphere soil. This work allowed a detailed study of the interactions between H, Al and P in the rhizosphere. It will allow later the validation of the model and the study of sensitivity of the parameters.

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The objectives for the first year of the work package 10 were to write and calibrate a model of Al and P dynamics in the rhizosphere. A part of this work has been done in the framework of a thesis (PhD) supported in september 2001 (Firdaus, 2001).

Writing of the model

The Rhizodyn model was developed to some extent during preceding program INCO1 *Fitting maize for acids soils* (Calba et al., 1999). This model represented the dynamics of the cations H, Al and Ca in the acid soils. It mainly consisted in the writing, the calibration and the validation of an ionic module of exchange using 3 sites (model of associative Donnan including a site with variable charge for organic matter, a site with fixed charges for clays, and a third site with fixed charges for numerical adjustment), coupled to a module of Al and P speciation in solution. The program had been developed under DOS (Microsoft, USA) using the software Turbo Pascal 7 (Borland, France).

Work carried out this first year consisted of 3 points:

1. <u>the adaptation and harmonization of the whole of the calculation and peripheral programs with the new Windows environment</u>. All the programs were upgraded in object programming using the software DELPHI 3 (Borland, France), and were adapted to WINDOWS 2000/NT (Microsoft, USA) environment, transfer of the data in 32 bits, follow-up of calculations in windows supported by WINDOWS, etc…. This stage was a precondition to the developments projected within the framework of this new contract.

2. <u>the writing of a module of anion (phosphate or organic anion) adsorption on the soils surfaces</u>. The concentrations C_f of adsorbed anions are supposed to be relied to the total concentrations C_s of anions in solution by empirical formalisms of Freundlich ($C_f = a\ K_d\ C_s^b$) or Langmuir ($C_f = a\ K_d\ C_s^b / [1 + a\ K_d\ C_s^b]$), optionally. Moreover, adsorbing surfaces can be regarded as in equilibrium with the solution, or without equilibrium, optionally again. When adsorbing surfaces are in equilibrium with the solution, the chemical module of speciation integrates the fixed anions as new species: the mass conservation within the system is then imposed by the relation : $[C_t] = [C_s] + [C_f]$ where C_t is the total concentration within the system. When adsorbing surfaces are not in equilibium, the concentrations of anion in solution and fixed on the adsorbing surfaces are relied by a kinetic law as: $(dC/dt) = L_f\ (C_{f,\ actuel} - C_{f,\ équilibre})$ where L_f is a kinetic constant characteristic of the couples anion/surface.

3. <u>the identification of significant complexation reactions and bibliographical research of the values of thermodynamical constants for phosphate and organic anions (citrate, oxalate, malate, succinate) with H, Fe and Al</u>. A data base has been compiled and written. Its use need a modification of the program inputs, projected for the end of 2001.

Parameters of the model with P : Kinetics – isotherms – pH effect

Adsorption isotherms with P^{32}

We used two oxisols, one of Cameroon the other of Colombia. The use of P^{32} makes it possible to plot adsorption isotherms of P on the soil for very weak amounts of P, corresponding to 1, 10, 20, 30, 60 and 100 mg kg^{-1} of P [Ca(H$_2$PO$_4$)2H$_2$O], by adapting the method of Bingham et al. (1978) (fig. 1). For the concentration 100 mg kg^{-1}, known quantities of HCl and NaOH were added in order to equilibrate the soils with different pH (fig. 2). The soils were put in contact and were stirred 24h with the solutions of P labelled with P^{32}, then centrifuged, filtered and analysed using a liquid scintillation counter (model 1209 RACKBETA).

results

Figure 1 shows the relations between the quantities of P fixed to the soils and the concentrations of P in solution coming from P^{31} marked by P^{32} and measured with the pH of the soil.
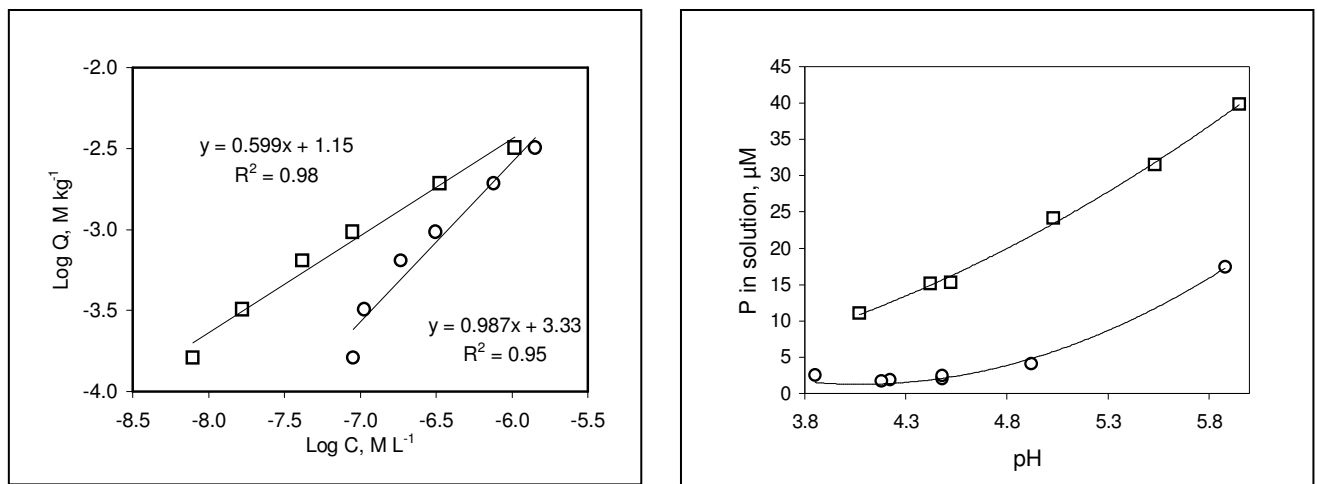

Figure 1: P adsorbed (log Q$_f$) on Columbia (O) and Cameroon (⊡) soils as a function of P concentration in solution (log C$_s$).

Figure 2: P in solution in Columbia (O) and Cameroon (⊡) soils treated with 100 mg kg^{-1} P as a function of soil pH.

It appears that the soil of Cameroon fixes more P for the weak quantities of P added because of this more acid pH. The function of adjustment (fig. 1) is a function power of the Freundlich type, usually used in the formalisms of representation of the adsorption isotherms, in particular for P adsorption : **Q$_f$ = a C$_s$^{b}** or in a linear form: log **Q$_f$ = log a + b log C$_s$**
where **Q$_f$** is the quantity of adsorbed P (mol kg^{-1}), C$_s$ is the P concentration in solution with equilibrium, **a** and **b** are coefficients of adjustment.

Freundlich function was retained to describe in the model the relations between P in solution and P fixed for the weak concentrations of P in solution. Figure 2 shows the concentrations of P in solution after addition of 100 mg kg^{-1} of P and for different pH. It appears that for a same pH Colombia soil fixes more P than Cameroon soil because of its content of Al hydroxide. In

both cases, the P concentration in solution decreased with the pH. These variations will be taken into account in the model.

Table 3.1.2.2 Coefficients of adjustment a and b according to the function of Freundlich for the adsorption isotherms of P carried out with pH 4.0, 5.3 and 6.0 with the soils of Colombia and Cameroon.

Columbia	Function of adsorption (in mole), adjustment according to Freundlich		
	$Q_f = \log a + b * \log C_s$	$Q_f = aC_s^b$	r^2
pH	Coef. a	Coef. b	
5.3	349	0.858	0.99
Cameroon	Function of adsorption (in mole), adjustment according to Freundlich		
	$Q_f = \log a + b * \log C_s$	$Q_f = aC_s^b$	
PH	Coef. a	Coef. b	r^2
4.6	14	0.599	0.98

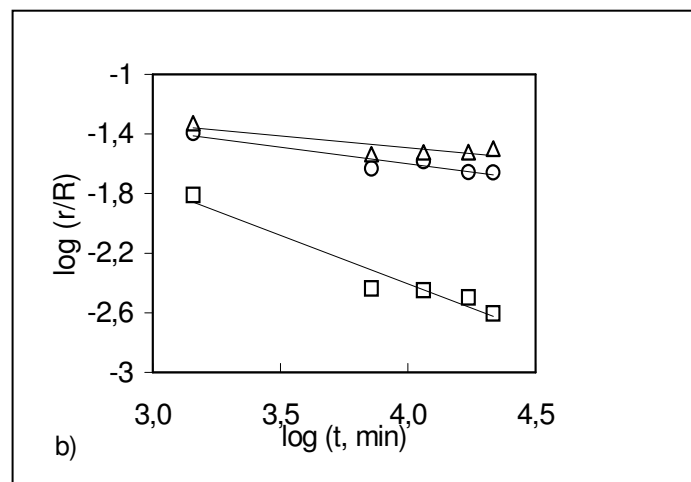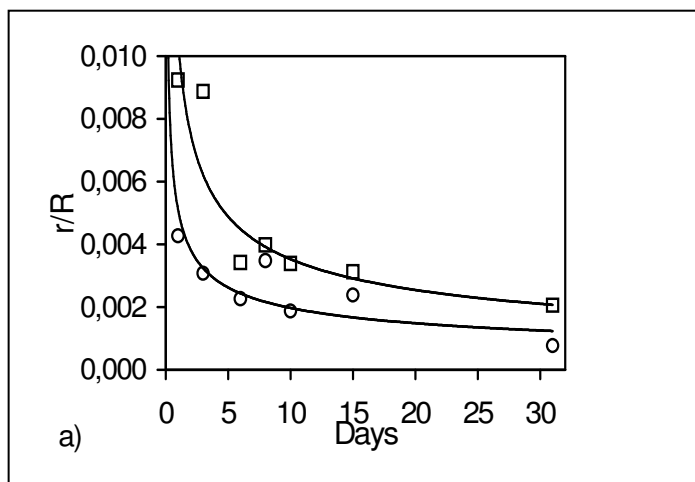## Adsorption kinetics with P^{32}

Figure 3 : isotopic ratio, measured P^{32} activity in solution (r) vs P^{32} activity in the soil at t=0(R), as a function of incubation length of time in Columbia (O) and Cameroon (9) soils.

Figure 4 : log of isotopic ratio (r/R) as a function of incubation length of time in Columbia soils for three levels of pH, pH 5.35 (O), pH 4.0 (9), pH 6.0 (Δ) r/R=1 at t=0.

The phosphate nutrition is a kinetic process. The removal of P by the roots decreases the P concentration in the soil solution and generates a P remove starting from the solid phase, phenomenon dependent on the time and the physicochemical composition of the soil (Morel and Hinsinger, 1999). The method of the isotopic kinetics of exchange allows to estimate the potentialities of release of P ions by a soil. If X an unknown quantity of P in a complex pool of a mixture in which X cannot be given directly by extraction.

When a quantity of R of radioactivity and mass X of P known, is added in a soil-water mixture and for a perfect mixture: $rt / R = qt / X-qt$, or rt and qt is respectively the radioactivity and the quantity of P in solution at the moment t.

Figure 3 shows the evolution of the isotopic ratio r/R according to time. It appears that the fraction of P remaining in solution after 24 hours of contact is lower than 1% of P added in the soil-water system. The adsorption kinetics of P is faster in the case of the Colombia soil. For the modelling of the data we considered that a preliminary incubation of phosphorus and soil during 48 hours can avoid introducing into the model a kinetic function of P adsorption, at least for the duration of culture used (14 days).

The rate of isotopic dilution of P in the soil of Colombia is faster when the soil pH becomes more acid (fig. 4). However, one observes that the rate of isotopic dilution decreases very slowly after several hours of incubation. For the adjustment of the model, only the effect of the pH will be considered.

Studying the effect of P supply (phosphate rock) on P, Al and H dynamics in the rhizosphere.

Materials and methods

Soil and phosphate rock : Studied soil was oxisol from Columbia 0-20cm: The phosphate rock (PR) used was a finely ground (<160µm) of Gafsa phosphate rock from Tunisia. Its P content was 29.51% P_2O_5, then 0.129 g P per g and 4.16 mmol P per g of rock. Its reactivity is classified as high for agronomic effectiveness according to the reactivity classification

Soil incubation : Effect of PR was studied in mixing 0, 0.2 and 2.0 mg PR g^{-1} of soil, then 0.8 and 8.3 µmol P per g^1 of soil. Experiments were conducted according to the closed incubation systems. Soil was mixed with 2 µg PR g^{-1} of soil, then placed in plastic pots and moistened to 2/3 of the soil water capacity. The mixture was then incubated at 25°C for 2 days. Its water content was maintained constant by daily addition of water based on pot weight variation. At the end of experiments, pH, soluble and exchangeable Al and Ca, soluble and extractable P were determined.

Culture device, preparation of plant material and conditions of culture : The culture device was adapted from Hinsinger et al. (1992). It consisted of two pots separated by a 0.2 µm polyamide mesh. The upper pot contained the plants cultivated: it was a PVC cylinder of 5.5 cm internal diameter with a 30 µm polyamide mesh as bottom to prevent the root growth outside. The lower pot contained the soil sample: it was a PVC cylinders 3 mm depth with a 6.8 cm internal diameter, filled with the mineral substrate and covered with the 0.2 µm polyamide mesh. The 0.2 µm mesh separated physically the roots and the soil samples. It prevented the rootlets and root hairs to grow into the mineral substrate and the mineral particles to pollute the plant roots, and thus made it possible to collect and analyse them directly. The water supply was assured by a filter paper placed under the soil sample and immersed in nutrient solution. The entire culture device consisted of the two plant and soil pots placed one onto the other one, above a becker containing 5 L of nutrient solution.

The plant material was an Al tolerant cultivar of maize (*Zea mays* L. cv ATP Yellow) originated from Cameroon. Seeds were surface sterilized for 15 min in 0.3% sodium

hypochlorite solution, then washed thoroughly in distilled water. Ten seeds were placed in each culture pot, then germinated in incubator at 25°C for 60 h on 200 µM $CaCl_2$ solution. After germinating, 6 healthy seedlings were retained per pot and grown for 14 days in solution containing macroelements (µM): 200 $Ca(NO_3)_2$ $4H_2O$, 200 KNO_3, 100 K_2SO_4, 100 $MgSO_4$ $7H_2O$, 200 NH_4Cl, 5 NaH_2PO_4, and microelements (µM): 15 $MnSO_4$ H_2O, 0.38 $ZnSO_4$ $7H_2O$, 0.16 $CuSO_4$ $5H_2O$, 0.058 H_3BO_3, 16 $(NH_4)_6Mo_7O_{24}$ $4H_2O$, 10 FeEDTA. The plantlets were grown in a chamber regulated to a temperature of 25/20°C and relative humidity 75/80. At the end of pregrowth period, the roots covered all the mesh surface and the plant pots were placed onto the soil pots for experiment.

Determination of effect of phosphate rock and N-fertilizing on the rhizosphere dynamic after 14 days of culture : The ability of maize to acidify its rhizosphere was affected by supplying the plants with different concentrations and sources of K and N: 250µM NO_3^- and 250µM K^+, 250µM NH_4^+ and 250µM K^+, 500µM NH_4^+ and 500µM K^+, 750µM NH_4^+ and 750µM K^+. Maize was cultivated for 14 day on the soil mixture. At the end of the experiments, the roots and the soil mixture were collected for analysis. pH, soluble and exchangeable Al and Ca, soluble and extractable P were determined in the soil. Exchangeable Al was measured in the roots. Each measurement included 2 replications.

Analysis of roots and soils : The root samples were dried at 60°C during several days until constant weight, weighed, cut into small pieces and ashed at 500°C for 2 h. The ashes were digested with 2 ml HCl 6M, then filtrated. The concentrations in Ca and Al of the solution were determined by inductively coupled plasma spectrophotometry.
The soil solutions were extracted by water at a 1:1.5 soil:solution ratio. The suspensions were shaken during 24 h and centrifuged. pH was measured using a glass electrode. Al and Ca concentrations were determined by ICP. P concentration was measured by colorimetry using the phosphomolybdate method.
The exchangeable ions were extracted by 3.7 mM cobaltihexamine solution. The suspensions were shaken during 24 h and centrifuged. The pH was measured in the supernatant.. The concentrations in Ca and Al The of the supernatant were determined by ICP.
The P fixed in the soil samples was extracted according to Olsen-Dabin method, i.e. 0.5M $NaHCO_3$ and 0.5M NH_4F at pH 8.5. The suspension was filtered and P in solution was determined by spectrometry using the phosphomolybdate method.

Results

Effect of P supply on rhizosphere properties

The effect of P supply on the rhizosphere properties was analysed after 14 days of culture of maize fed with different NH_4^+/NO_3^- ratios to induce different rates of H^+ release by roots. Figure 5 shows that maize decreased pH in rhizosphere. However, the pH decrease was reduced by the PR supply. The pH changes were in order of one pH unit when PR supply was low, and less than 0.6 pH units when PR supply was high. This H^+ buffer effect of PR was however weak in this soil, i.e. as H^+ buffer capacity of soil was initially high.
Figure 5 shows moreover that extractable P increased with PR supply. For supplies of 0.8 and 8.3 µmol P g^1 of soil, the extracted P were in average 0.56 and 2.66 µmol g^1. The mean P extracted without P supply being 0.29 µmol g^1, the P recovery ratio was thus 34% of P supply. In the same time, P concentration in solution were as much high as the final pH in rhizosphere was low and as the PR supply was high (Figure 6). The high fixing capacity for P

of the Columbia soil increased the solubilization of PR by sink effect, but restricted the concentration of P in solution.

The analysis of exchange complex of soils shows that, in general pattern, exchangeable Al increased and exchangeable Ca decreased when pH decreased in the rhizosphere (Figure 7). Low PR supply did not modify significantly exchangeable Al and Ca. However, high PR supply increased the exchangeable Ca which reached 2.0 $cmol_+$ kg^1, and reduced slightly but significantly the exchangeable Al in the rhizosphere. So the PR supply reduced the exchangeable Al in the rhizosphere in the same time by increasing the available Ca in the rhizosphere, and by buffering the pH decrease induced by root H^+ release.
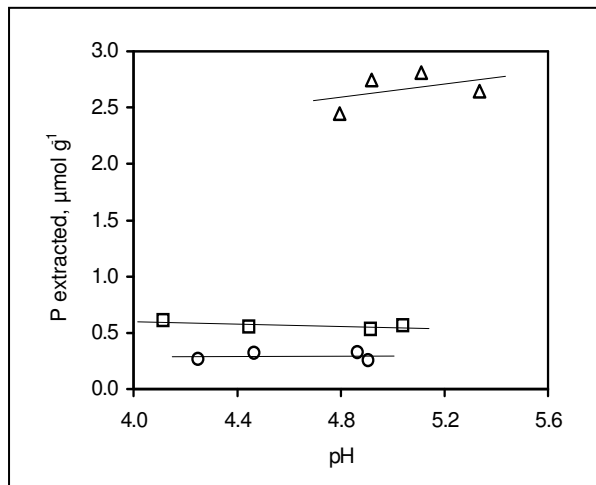

Figure 5 : P extracted by modified Olsen method as a function of soil pH for three levels of RP, 0 (O), 0.2 (9), and 2.0 (Δ) g kg^{-1}
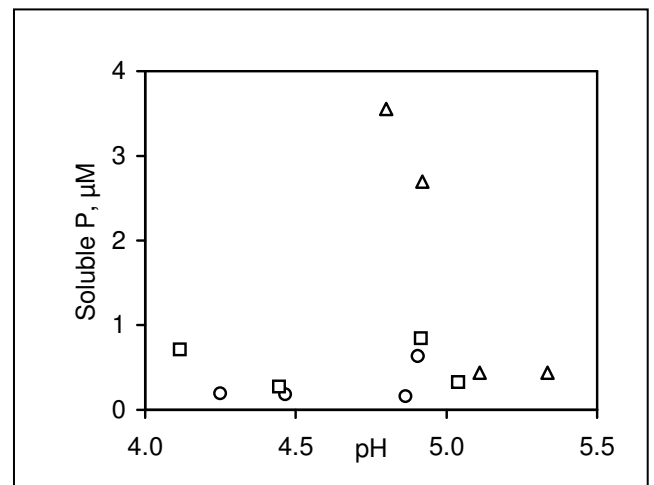
Figure 6 : Soluble P as a function of soil pH for three levels of RP, 0 (O), 0.2 (9), and 2.0 (Δ) g kg^{-1}

The analysis of the composition of the final solutions in the rhizosphere (Figure 8) shows that for a given PR supply, Ca in solution increased when pH decreased. For a given pH, Ca in solution increased when PR supply increased. For all PR supplies, Al in solution increased when the final pH in the rhizosphere decreased. PR supply had therefore an effect on Ca concentration in solution, but not on Al concentration in solution which only depend on the final pH in the rhizosphere. The behaviour of Al and Ca in solution is different of P in solution of which the concentration remained low, lower than 6 µM for all RP supplies.
Al content in roots increased when the final pH in rhizosphere decreased (Figure 9). PR supply modify slightly the Al root content.

Discussion

The soil incubation with PR in closed system show that the rate of PR dissolution was great in soils with high P and Ca fixing capacities. Moreover, PR dissolution had a liming effect and increased the soil pH. However, the pH increase was low in soil with high H^+ buffering capacity, which were often soils with high P and Ca fixing capacities. This result is in good agreement with other workers (Dodor et al., 1999; Loganathan et al., 1995).
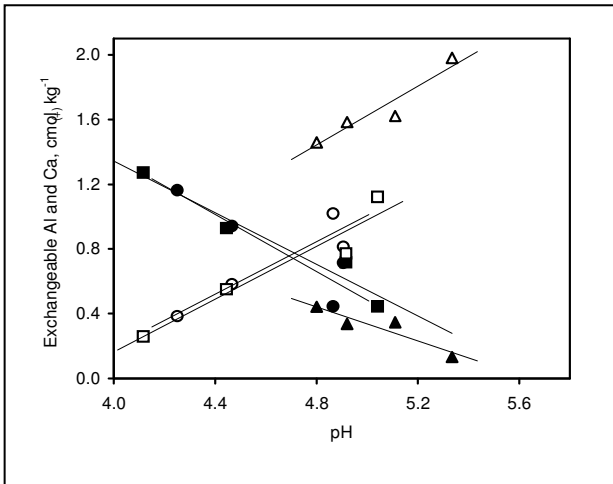
Figure 7 : Exchangeable Al (black) and Ca (white) as a function of soil pH for three levels of RP, 0 (O), 0.2 (9), and 2.0 (Δ) g kg^{-1}
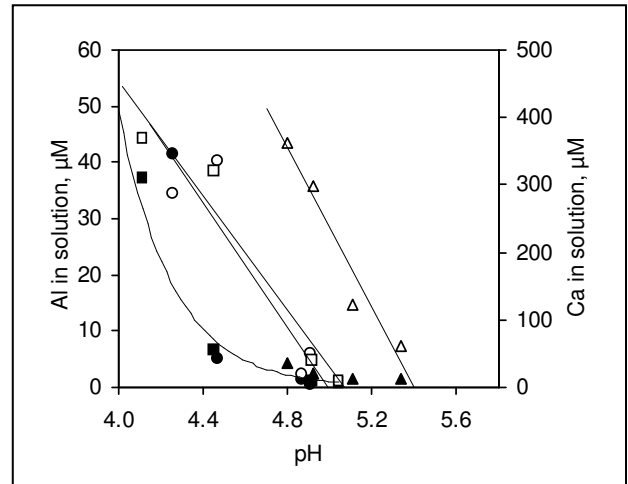
Figure 8 : Soluble Al (black) and Ca (white) as a function of soil pH for three levels of RP, 0 (O), 0.2 (9), and 2.0 (Δ) g kg^{-1}
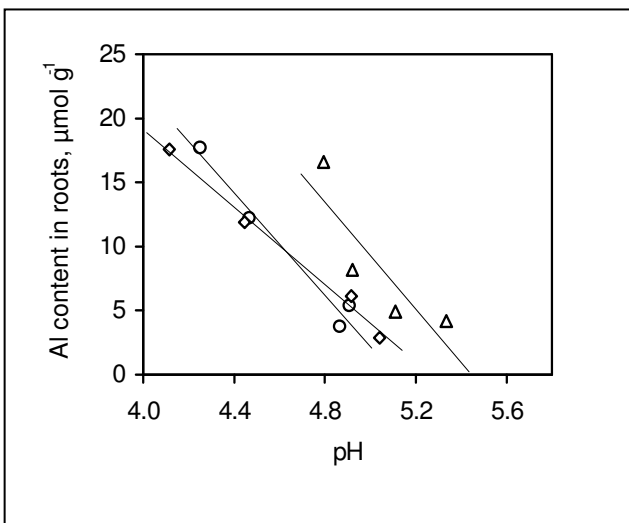

Figure 9 : Al content in roots as a function of soil pH for three levels of RP, 0 (O), 0.2 (9), and 2.0 (Δ) g kg^{-1}
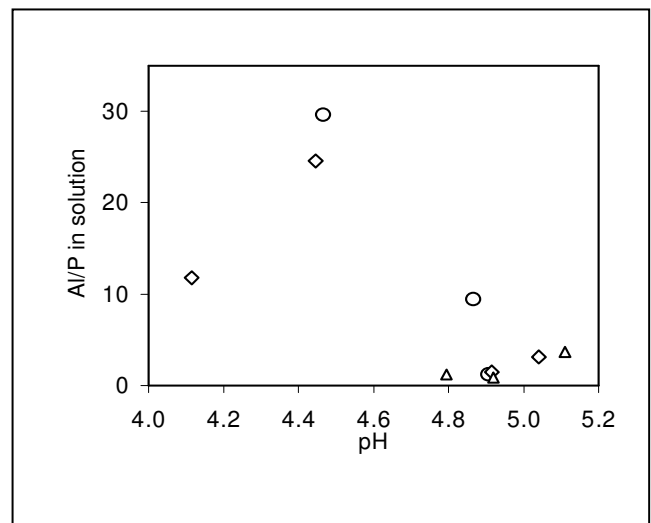
Figure 10 : Al/P in solution as a function of soil pH for three levels of RP, 0 (O), 0.2 (9), and 2.0 (Δ) g kg^{-1}

The study of the evolution of rhizosphere properties of maize cultivated without PR show that (i) pH, exchangeable Al and Ca are in close relation in acid soils, (ii) the plant modify the chemical properties in the rhizosphere mainly by releasing H$^+$. Proton released by roots mobilised likely amorphous Al in the soil, which is then fixed by exchange complex by removing exchangeable Ca. The Al root uptake, and then the risk of Al toxicity, increases with available Al in the rhizosphere. As several authors have shown (Keltjens 1988; Haynes 1990), a way for reducing Al toxicity in acid soils is to limit rhizosphere acidification.

The study of maize rhizosphere cultivated with different rates of PR supply show that PR had three main effect: (i) a H^+ buffering of soil, which restrict the pH decrease induced by roots in the rhizosphere, (ii) the increasing of exchangeable Ca, which decreases exchangeable Al and thus the available Al for roots, (iii) the increasing of adsorbed P in soil, and eventually the available P for plants. The intensity of the effects was in relation to the PR supply and the P and Ca fixing capacities of soil.

Plants take up mineral ions in solution. The effect of PR supply on plant growth depend therefore on the changes in solution composition induced by RP and root activity. Our results show that, in an oxisol with high fixing capacity, P concentration in solution remain low and Al in solution depended only on the pH in the rhizosphere. Studying the Al/P/Ca system in nutrient solution, Alva et al. (1986) showed that the Al toxicity was related to Al/P ratio which modify the activity of monomeric form of Al in solution. The figure 10 presents the relation between final Al and P concentrations in rhizosphere solution. It shows that the Al/P ratio was near the unit when the final pH in the rhizosphere was higher than 4.8. According to Alva et al. (1986), the activity of monomeric Al was in these conditions five times lower than the total Al concentration. It is likely that Al in solution was mainly complexed by P. When pH was lower than 4.8, i.e. when insoluble Al forms of soil can be massively dissolved, the Al/P ratio increased extensively because P concentration remained low. It is likely that Al species in solution is then mainly monomeric toxic form Al^{3+}. So, the Al root content increased in accordance with decreasing pH.

The question arise to specify the nature of interactions between Al and P in solution and the becoming of such Al-P complexes in the root cell walls. Some authors (Galsomies et al., 1992) have indeed observed Al-P precipitates in vacuole of roots of maize.

Conclusion

The results show that PR supply results in closed, complex and dynamic interactions between H, Al, Ca and P in the rhizosphere. These interactions depend strongly from chemical properties of soil, especially its proton buffering and ion fixing capacities, and from the plant ability to modify chemical conditions of its rhizosphere, especially its pH. The analyse of the dynamic of the plant-soil interactions at the rhizosphere scale should make it possible to optimise the use of direct application of phosphate rock in acid soils. Our results suggest for instance that it would be interesting to maintain the rhizosphere pH between 4.8 and 5.5 to optimise in the same time the mineral nutrition of plant and the PR dissolution in soil. That might be done taking into account the plant ability to modify rhizosphere pH.

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