Maize for acid soils
Third scientific report -2003

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Abstract

The objectives for the third year of the Work Package 10 were the validation of the model for Al-H-P interactions in acid soils, while putting the emphasis on the interactions between H, Al, P and organic anions released by roots. The development of the model has been purchased in the direction of interactions between phosphate and organic anions adsorbed. The model was validated at the laboratory in relation to the associates (7.8) who have provides the numerical parameters acquired in the experiments with the field and necessary to this validation, i.e. biomass and mineral mass, growth of the roots. The final objective was a substantial contribution to the comprehension of the functioning of the rhizosphere in the acid soils and the interactions between Al-H-P. The model highlighted the particular characteristics of the soils in relation with the rate of Al dissolution, the fixation and the dissolution of P and its interaction with an organic acid excreted by the roots of maize, the citrate. The influence of the excretion of citrate on the dynamics of P is shown. However, the simulated citrate concentrations remain weak. So the incidence of the increase in the solubility of P on the mineral nutrition of this element by maize remains to be quantified.

In prospect, it is necessary to note the need for studying the dynamics of slow fixing of P on the soil as well as the influence of the conditions of medium on the excretion of citrate and other organic acids. The study of citrate fixed on the soil during the cultivation must also be the object of a methodological investment related on the extraction and the analysis of the fixed element.

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The objectives for the third year of the Work Package 10 of INCO programme *Maize for sustainable cropping systems on tropical acid soil* were the validation of the model for Al-H-P interactions in acid soils, while putting the emphasis on the interactions between H, Al, P and organic anions released by roots. The validation of the Rhizodyn model for the dynamics of H-Al-Ca-P has yet been presented in the last report (see Calba et al., 2003). However, the development of the model has been purchased in the direction of interactions between phosphate and organic anions adsorbed, of which the previous developments did not give satisfaction. The model was validated at the laboratory in relation to the associates (7.8) who have provides the numerical parameters acquired in the experiments with the field and necessary to this validation, i.e. biomass and mineral mass, growth of the roots. The final objective was a substantial contribution to the comprehension of the functioning of the rhizosphere in the acid soils and the interactions between Al-H-P

1- Agronomic data for modelling

Table 1: yield, production of biomass and removal[*] of the nutritive elements by maize in the soils of Colombia and of Cameroon.

Reference		Columbia (2002)		Cameroon (2001)	
Density of sowing		70000 ha^{-1}		50000 ha^{-1}	
Yield		Control	+ lime	Control	+ lime
Grain	Ton ha^{-1}	2.3	6	1.3	5.4
Aerial part (anthesis)	Ton ha^{-1} DM	13.2	28	5.7	16.7
Root (inco 1 report)	Ton ha^{-1} DM	0.6	1.6		
*Budget of the elements removed by the whole maize plant at flowering		Aerial part at anthesis (stem + leave) and roots			
		Control	+ lime	Control	+ lime
N	Kg ha^{-1}	355	614	176	510
P	Kg ha^{-1}	38	73	17	57
K	Kg ha^{-1}	204	530	113	441
Ca	Kg ha^{-1}	78	92	16	19
Mg	Kg ha^{-1}	8	37	12	120

*The evaluation of the mineral removals was carried out by multiplying the results obtained on a plant (stem+leaves+roots) at the flowering stage by the density of sowing.

Agronomic data used for the validation of the model and simulations of situations consisted of the compilation of results, yield, biomasses and mineral content of leaves, stems and roots, from the experiments carried out by the partners (7,8), Colombia and Cameroon (Table 1). Plant analyses were carried out at the flowering stage by the CORPOICA (Colombia) on the treatments, lime, P, chicken manure and cowpea and by the CIRAD on samples taken in Cameroon in 2001 on the treatments ATP and Tuxpeno, control, lime, chicken manure.

2. Experimental data of laboratory and parameters of the model

The Rhizodyn model makes it possible to study the dynamics of the ions (Al, Ca, H, P) in the rhizosphere. It requires to define parameters of calibration like the exchange constants between the elements in solution and the sites of fixation, present in the rhizosphere on the surface of the soil and the walls of the roots. These parameters were published (Calba et al. 1999, 2003). The model also requires the establishment of the equilibrium constants and the kinetics constants of dissolution of minerals tested, gibbsite and apatite. The constants were defined starting from experiments in laboratory described in the two preceding scientific reports of the program. The experiments consisted of the study of the root effect of maize cultivated during 14 days on a fine plate of soil (3mm thickness). The various experimental protocols used aimed at highlighting, the dynamics of the elements H, Al, Ca, and P with or without acidification of the rhizosphere. The results made it possible to validate the model in three principal situations, i) acidification of the soils controls of the experimental sites under the effect of a nutritive solution containing NH_4^+ as source of nitrogen, ii) same experiment with addition of rock phosphate, iii) removal of P brought in a soluble form by different cultivars with a nutrient solution containing NH_4^+ (acidifying) or NO_3^- (non-acidifying). Simulations were carried out by supposing that the plant removed in the solution of the soil, with constant rate throughout the culture, the mineral elements which it needs. The rates of removals of Ca and Mg were calculated on the basis of measured variation of their concentration on exchange complex of the soil between the beginning and the end of the culture, in the case of the experiments without rock phosphate. The rate of Al removal was calculated on the basis of measured accumulation of Al in the roots at the end of the culture. The rates of removal of the univalent ions, K^+ or NO_3^- according to needs, were adjusted so as to control the acidification of the rhizosphere: they were calculated so as to find the pH value measured at the end of the culture in the rhizosphere. The constants of rate $L_{Al(OH)_3}$ and $L_{apatite}$ of dissolution of the Al hydroxides and rock phosphate were adjusted so as to find the value of Al concentration and Al adsorbed on exchange complex measured at the end of the culture for the measured pH in the rhizosphere. Simulations presented are thus, by construction, those which reproduce best the initial and final states measured in the rhizosphere of maize cultivated during 14 days, for H, Al, Ca and Mg. Their interest thus resides mainly in the values of the static and kinetic parameters used to produce them, and in the variations observed between simulated curves and experimental data.

The whole of the parameters of simulation in acidifying condition is reported in table 2.

3 Modelling

3.1. Influence of phosphate on H, Al and Ca dynamics

The effect of a rock phosphate added in the soil was described in the scientific report 1 (2000-2001). It consisted of the study of the Al dynamics, Ca, H and P in a soil enriched with rock phosphate under the acidifying effect of the maize roots. The model of cation exchange was used to explain for buffer effect of phosphate on the acidification of the rhizosphere and the dynamics of the elements between the soil and the plant.

Table 2 : Kinetic plant and soil parameters (expressed in mol L^{-1} s^{-1}) used to model the dynamics of H, Al, Ca and Mg in the rhizosphere of maize growing for 14 days on Columbia, Cameroon soils with different treatments: range of constant rate of Ca, Mg and Al uptake by maize, and kinetic constant for Al-hydroxide dissolution. The data have been calculated from the measured variations of elemental concentrations in soils (Ca and Mg uptake, $L_{Al(OH)_3}$) or

roots (Al uptake) between final and initial states. They were moreover assumed constant all along the dynamics.

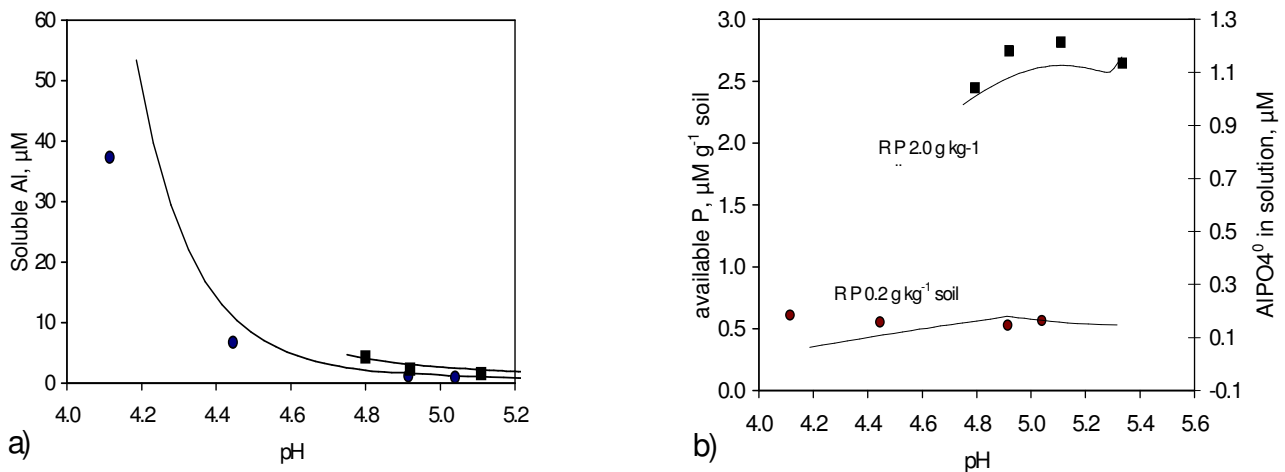| Soil	Columbia	Cameroon
Ca uptake, $\text{mol L}^{-1} \text{s}^{-1}$	$20 - 33\ 10^{-10}$	$10 - 50\ 10^{-10}$
Mg uptake, $\text{mol L}^{-1} \text{s}^{-1}$	$0.5 - 1.9\ 10^{-10}$	$3 - 9\ 10^{-10}$
Al uptake, $\text{mol L}^{-1} \text{s}^{-1}$	$8 - 12.10\ 10^{-10}$	$6 - 10\ 10^{-10}$
$L_{Al(OH)_3}$, $\text{mol L}^{-1} \text{s}^{-1}$	$5.0\ 10^{-9}$	$3.5\ 10^{-9}$

Figure 1 : Soluble Al (a), available P extracted by Olsen method in solution (b) in the soil of Columbia after 14 days of maize cultivation as a function of the rhizospheric pH. Points represent experimental data for different level of rock phosphate 0.2 g Kg^{-1} (round), 2.0 g Kg^{-1} (square). Lines represent simulated soluble Al (Fig. 1.a) and soluble $AlPO_4^0$ (Fig. 1.b)

The results show the adjustment of the experimental data using the model (fig. 1.a). The influence of the effect of the rock phosphate amounts on the rhizospheric pH is translated perfectly by simulation. For P, this model with only cation exchangers does not make it possible to take into account the modification of the anion exchange (P fixation) when the pH of the rhizosphere changes. Simulations obtained in the figure 1.b were fitted by using the correction parameters of the pH effect on the P fixation defined beforehand (see scientific report 2001). This figure shows the simulation of the evolution of $AlPO_4^0$ in solution, which is the principal form of P in solution in this range of pH. This simulate values of P are in close relation with available phosphorus measured by the Olsen method. It results from these observations that the modelling of the dynamics of the cations (Al, Ca, Mg, H) in the presence of rock phosphate is workable with a cation exchanger as presented in the preceding research program INCO. The figure also shows that the concentration of the $AlPO_4^0$ form does not increase when the pH decreases whereas the Al concentration in solution increases. This

shows the importance of the P fixation on the soil according to the pH. Thus, the fixation of P on anion exchange complex requires the taking into account of the variation of the exchange capacity of this complex according to the pH. This evolution can be simulated using isotherms of P fixation according to the pH or by the use of an anion exchanger with variable charge.

3.2. Influence of added soluble P marked with P^{32}

The kinetics of P removals by the plant as well as the effect of the pH on P in solution were presented in the preceding scientific report 2001-2002. It came out from these experiments that the rate of P removal by maize in the culture device decreased quickly in the case of the soil of Cameroon cultivated with an amount of P of 200 mg kg $^{-1}$, this rate was constant in the case of the soil of Colombia. In the two soils, the removal of P was minimum when the concentration of P in solution was close to 1μM. With amount 100 Mg kg $^{-1}$ of P, the removal of P by the plant was weak, 3% of P added, because of the high fixation capacity of these soils. The concentration of P in solution was lower than 0.6μM. The concentration of P in solution is the resultant of the P fixation according to the state of the soil. According to Fardeau (1993), for the isotopic exchange ranging between 30s and 4 months, the simplified relation representative of the transfer of the phosphate ions since the solution towards the solid phase is form: $rt / R = (r1 / R) t^{-n}$. The relation between: $\log(rt / R)$ and $\log (t)$ are linear. The analysis of the experiments carried out on the two levels of P supply showed: i) the flux of P removal by the plant in the soil receiving 200 Mg kg $^{-1}$ of P tended towards a constant value when $\log(rt / R)$ was lower than –3.0 for the soil from Cameroon and –3.5 for that of Colombia, ii) the $\log(rt / R)$ for a P supply of 100 Mg kg $^{-1}$ was lower than this value, respectively of –3.3 and –3.5 at the beginning of experiment (t = 48h) for the two soils, iii) the amount of P removed by the plant decreased with the pH of the rhizosphere.

## 3.3. Simulation using a model with anion and cation exchanger

The development of the model has been purchased in the direction of interactions between phosphate and organic anions adsorbed, because of the previous developments did not give entire satisfaction. Mineral and organic anions are likely adsorbed onto the same sites of soil surfaces, what makes it possible to remove a given anion by adding another one (phosphate by citrate for instance). The experimental data show that P and citrate sorption were in good agreement with Freundlich equation : $C_f = a\ K_d\ C_s^b$. To represent the interactions between anions, we have so first tested a Freundlich formalism. The use of this formalism showed that, for each anion *A,* the values of affinity constants K_d must also vary according to the adsorption ratio of anions. Moreover, the model neglected the charges of anions and consequently rise up a problem of charge balance in the soil solution induced by the adsorption of anions. In conclusion, Freundlich equation is a global formalism, badly adapted to represent fine interactions between anions onto the soil surfaces. We have consequently look for another formalism.

We chose a representation similar to that of adsorption of the cations, by defining a potential of charge related to the presence of functional groups positively charged and likely to accept proton during the soil acidification. The isotherms of exchange between P and the citrate showed that beyond the concentration of citrate 1mM added to the soil the quantity of P in solution remained constant and was a function of the time of contact between P and the soil. This quantity of P extracted by citrate decreased quickly in the first hours of contact then more slowly after 48 hours. The model in its current design takes into account the process of adsorption without considering the slow fixation of P in materials of the soil. The fast adsorption of P on the soil is followed of a slower process. Many authors (Barrow, 1987; Strauss, 1997) proposed the hypothesis of one diffusion in a solid state in materials which fix

P. The kinetics of P dissolution is adjusted overall with the general constant of exchange of the anions on the positive charge of the soil. An exchange capacity of P on the soil is defined on the basis of experimental result of exchange with citrate. It was shown the combined effect of sulphate and the pH on the bio availability of P by the plant (Geelhoed, 1997). The model also takes into account the adsorption of sulphate on the soil and their removal by the plant.

3.3.1 Theory

Adsorption of anions onto soil surfaces result from electrostatic and chemical-sorbing processes. In the first part of this work, we have written a multi-cation exchange model that was in good agreement with experimental data. We have consequently started again the research from this basis. The basic equation became then:

$$A^n + nS^+ \Leftrightarrow S_nA \qquad\qquad \text{or: } 1/n \ A^n + S^+ \Leftrightarrow SA_{1/n}$$
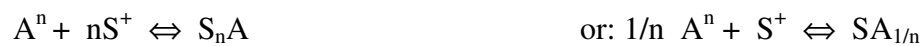
with : $\qquad [S_nA] = K_{SA} [S^+]^n [A^n] \qquad\qquad$ or : $[SA_{1/n}] = K'_{SA} [S^+] [A_{1/n}{}^n]^{1/n}$

where n is the charge of the anion A, and S^+ is a positive reactive surface site. K_{SA} (or K'_{SA}) is the association constant between surface and anion and the formation constant of S_nA. Note that this relation is near to a Freundlich equation ($C_f = aK_d C_s{}^b$) with $aK_d = K_{SA} [S^+]^n$ and $b = 1$.

The model can be extended to the non-charged molecule (n=0) A^0 as :

$$A^0 \Leftrightarrow S_0A$$

with : $\qquad [S_0A] = K_{SA} [A^0]$

where S_0A corresponds to the adsorbed form of A^0 onto surface but not bound ($S_{x=0}A$) to reactive surface site. The relation is then near to a Freundlich equation ($C_f = aK_d C_s{}^b$) with $b = 1$.

We must finally define the concentration of total adsorbing sites S_t as :

$$S_t = [S^+] + \Sigma n [S_nA] = \text{Anion Exchange Capacity (AEC)}$$

Two kinetic processes are moreover taken into account:
(i) the kinetic of sorption: as for cation exchange model, we suppose that the positive surface charge define a Donnan space around the surface, that exchange ions with soil solution according to a kinetic rule;
(ii) second, the kinetic of irreversible immobilisation: as Morel (2002), we suppose that adsorbed anions such as P can diffuse irreversibly inside the solid and then get out the chemical system studied. This process is represented as:

$$\partial A/\partial t = A_{\text{total adsorbed, t}} \ t^{-p} \qquad\qquad \text{and } \partial S_t/\partial t = 0$$

This new model appears very general:

(i) it makes it possible to represent conveniently interactions between many mineral and organic anions such as hydroxyl, sulphate, phosphate, citrate or oxalate;
(ii) it makes it possible to represent chemical-sorption of neutral molecules onto soil surface;
(iii) it respects the charge balance between soil solution and surface and the electro-neutrality of the different compartments (solution, Donnan space, surface);
(iv) it makes it possible to take into account kinetic processes.

The first calibration essays show it is also numerically impressive.

3.3.1 Fitting of the experimental values using the model

The fitting was carried out by using the experimental values obtained using the culture device (figure 2). Three varieties of maize Al-tolerant, P-efficient, P inefficient were cultivated 14 days on the soils of Cameroon and Colombia. The fitting of the P level in solution using the model was carried out for various rates of P removal according to the mineral nutrition, acidifying or alkalising. The citrate concentration in solution of 1µM did not vary during simulation.
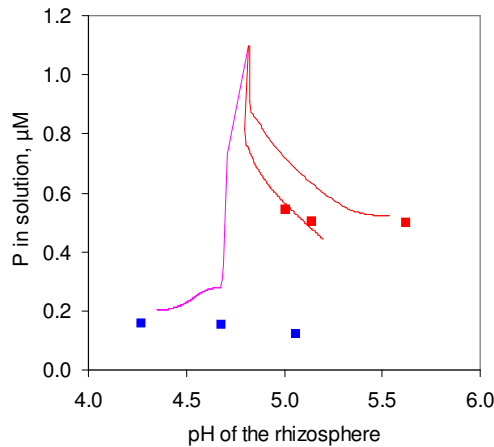

Figure 2: simulation of the evolution of the soluble P concentration in the soil of Cameroon (line) according to the pH with a level of acidification (blue) and 2 levels of alkalisation (red). The experimental data (points) were obtained with three maize cultivars acidifying or alkalising the rhizosphere more or less.

3.3.2. Effect of citrate adsorption on Al and P in soil solution

With equilibrium, the activities of Al and P in solution are a function of the solubility products of Al hydroxides and the activities of different Al ligands (P, citrate). Figure 3 shows the influence of various citrate concentrations in solution on the concentrations of $AlPO_4^0$ and $AlCitr^0$ estimated by the model. The distribution of the various species in solution was checked and validated using soilchem (Sposito & Coves 1988). The citrate competes with P in solution. The increase in the citrate concentration strongly decreases the quantity of Al phosphate in solution and increases the concentration of the form Al-Citrate. The total concentration of soluble Al simulated with pH 4.7 in the presence of citrate 1µM is equal to 4.5µM. It is equal to 10.8µM if the citrate concentration in solution is fixed at 8µM.
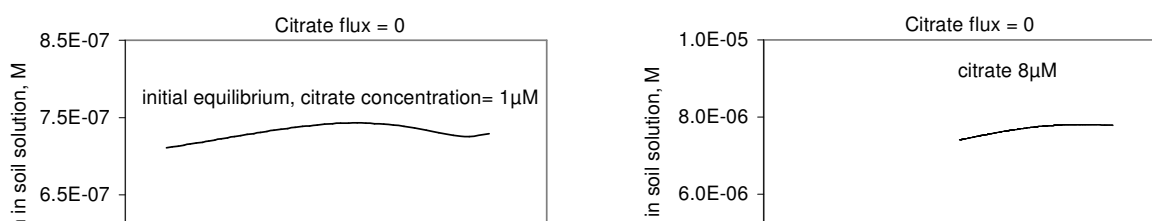
Figure 3: evolution of the simulated concentration of $AlPO_4^0$ and $AlCitr^0$ (Al-citrate) at equilibrium in the solution of the Cameroon soil as a function of pH and for three citrate concentration in solution, 1, 4, 8 µM.

3.3.3. Simulation of a citrate flux in the rhizosphere

The citrate released by the plant competes first with P linked with Al in the soil solution in contact with the root then for the sites of fixation of the soil constituted by positive charges on Al and Fe oxohydroxydes.
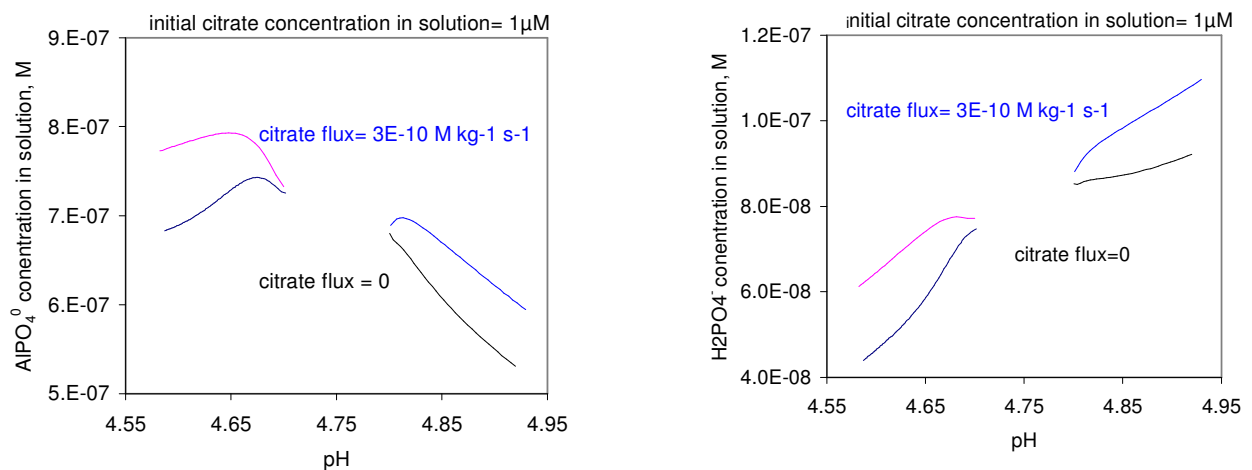

Figure 4: evolution of the simulated concentration of $AlPO_4^0$ and $H_2PO_4^-$ in the soil solution of the Cameroon soil as a function of pH and for two citrate flux, 0 and $3*10^{-10}$ M kg^{-1} s^{-1}.

The effect of the citrate release by the plant is simulated for a constant rate of P removal in culture systems acidifying and alkalising. The citrate flux used is fixed at 3.10^{-10} mol kg soil^{-1} s^{-1} or 9 picomoles per gram of dry root and a second. This flux corresponds in our experiments to 0.9 picomoles per gram of fresh root and a second.

Figure 4 shows that contrary to the preceding results the increase in the quantity of citrate released to the soil causes an increase of the concentration of the $AlPO_4^0$ and $H_2PO_4^-$ forms.

The model simulates the fixation of citrate on exchange complex, which has as a consequence a displacement of P adsorbed. With pH 4.6, increase in concentration in solution of the $AlPO_4^0$ form reached 0.1µM for a citrate flux of about size of that measured for a root of maize in the presence of Al.

Discussion

The agronomic data made it possible to locate the values of fluxes of element mainly Ca and Mg obtained using the culture device in laboratory, by considering the percentages of Ca and Mg removals on the soils: 1) with and without Ca added, 2) with and without acidification of the soil by the root. With Ca addition with pH close to 5.0, the maize takes 50% of exchangeable Ca in the soil. Without Ca with pH close to 4.5, 70% and 80% of exchangeable Ca and Mg are taken respectively in the soils of Colombia and Cameroon. While transposing these results to the fields experiments for 90 days of cultivation, average calculated Ca and Mg fluxes are respectively, $3 \ 10^{-10}$ and $3.6 \ 10^{-11}$ mol kg soil^{-1} s^{-1} for the soil of Cameroon, $6.1 \ 10^{-10}$ and $3.0 \ 10^{-11}$ mol kg soil^{-1} s^{-1} for the soil of Colombia. These values are lower than those indicated in table 2 in acidifying condition for the laboratory experiments, mainly for Mg. They are close to the values used for the simulation of the results obtained at the laboratory in alkalising condition. These results do not have anything of surprising if it is considered that the culture device allows a more intense action of the roots on the soil. Moreover, the fact of integrating the removal of the elements over 90 days of maize cultivation can decrease the values of calculated fluxes. The conditions of simulations also diverge compared with the agronomic data owing to the fact that the experiments with alkalisation had been obtained by modifying the source of nitrogen NH_4^+ for the acidification and NO_3^- for alkalisation in the place of the lime used in the field. Fluxes of Ca and Mg removal can be thus modified. Moreover, ratio NO_3^- / total N measured in situ in Cameroon in the soil control was equal to 66%, that is to say conditions less acidifying than those tested at the laboratory.

Simulations were carried out with a citrate addition of 0.9 picomole per gram of fresh s^{-1}, corresponding to the secretion of a root of maize. Jones (1998) gives flux variations of citrate excretion for maize cultivated in nutritive solution from 0.1 to 38 picomoles per gram fresh root s^{-1}. Simulations using the model show that in the soil of Cameroon, with pH 4.58, the citrate concentration reached 5µM when the Al concentration simulated is equal to 10.5 for an experimental measured concentration of 12.3 µM. According to Jones (1998) the concentration of the organic acids in the solution of the soil range between 1 and 50µM. Under our conditions of simulation, the increase in soluble P resulting from the citrate flux is about 0.1µM and the flux of P removed by plant increases by 20%. It is possible that the citrate concentrations increase with the interface between the root or the root hairs and the soil, increasing by this fact the displacement of P of exchange complex and its removal by the plant. It would be necessary to then admit a simultaneous and a significant increase in the Al concentration in solution. An increase of Al concentration was measured with both P-effecent and P-inefficient cultivar at pH close to 5.0 in our experiments using a fine layer of soil.
In our experiments, the conditions of P removal become limiting for the plant when the concentration out of P is lower than 0.5µM, the increase in the concentration of P simulated by the citrate addition (0.1µM) is of the order of Cmin of the maize plant.

Conclusion

The model used made it possible to analyse the dynamics of the elements H, Al, Ca and P in the rhizosphere of the soils of Cameroon and Colombia and to highlight the particular

characteristics of these soils in relation with the rate of Al dissolution, the fixation and the dissolution of P and its interaction with an organic acid excreted by the roots of maize, the citrate. It also made it possible to simulate variations of coherent conditions of medium with the agronomic observations carried out on the two studied sites.

The role of citrate as a ligand of Al in solution is well highlighted. The influence of the excretion of citrate on the dynamics of P is shown. However, the simulated citrate concentrations starting from data of fluxes taken in the literature and adjusted with the experimental data and thermodynamic equilibrium remain weak. So the incidence of the increase in the solubility of P on the mineral nutrition of this element by maize remains to be quantified.

In prospect, it is necessary to note the need for studying the dynamics of slow fixing of P on the soil as well as the influence of the conditions of medium on the excretion of citrate and other organic acids. The study of citrate fixed on the soil during the cultivation must also be the object of a methodological investment related on the extraction and the analysis of the fixed element.

References :

Barrow, N. J. 1987. "Reactions with variable-charge soils." Martinus Nijhoff pub, Kluwer acad. Dordrecht: 191p.

Calba, H., P. Cazevielle, B. Jaillard 1999. "Modelling of the dynamics of Al and protons in the rhizosphere of maize cultivated in acid substrate." Plant and Soil **209**: 57-69.

Calba H, Firdaus, Cazevieille P, Thé C, Poss R, Jaillard B 2003 The Dynamics of Protons, Aluminium, and Calcium in the Rhizosphere of Maize Cultivated in Tropical Acid Soils : Experimental Study and Modelling. *Plant and Soil, in press.*

Fardeau, J. 1993. "Le phosphore assimilable des sols: sa représentation par un modèle fonctionnel à plusieurs compartiments." agronomie **13**: 317-331.

Geelhoed, J., W. H. Van Riemsdijk, et al. 1997. "Effects of sulfate and pH on the plant-availability of phosphate adsorbed on goethite." Plant and Soil **197**: 241-249.

Jaillard B, Calba H 2002 Dynamics of H, Al and Ca in the rhizosphere : Interest and major limitations of modelling the chemical functioning of the rhizosphère. Influence of phosphate rock on aluminium dynamics in the rhizosphere of maize grown in acid soils. *2nd Meeting of COST 631 Understanding and Modelling Plant-Soil Interaction in the Rhizosphere, Vienna, Austria, 11̄13 October 2002.*

Jones D L 1998. Organic acids in the rhizosphere – a critical review. Plant and Soil 205 : 25-44.

Morel JL 2002 Caractérisation de la phytodisponibilité du phosphore du sol par la modélisation du transfert des ions phosphates entre le sol et la solution. *Mémoire d'Habilitation à Diriger des Thèses, Nancy.*

Sposito, G. and J. Coves 1988. " Soilchem: A computer program for the calculation of chemichal speciation." Univ. of California Riverside and berkeley, the Kearney Foundation of Soil Sciences Univ. of California.

Strauss, R., G. Brümer, et al. 1997. "Effects of crystallinity of goethite: II. Rates of sorption and desorption of phosphate." European Journal of Soil Science **48**: 101-114.