## Fertilization and acidity in a cultivated tropical alfisol Fertilisation et acidité dans un alfisol tropical cultivé

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The new concepts (Van Breemen 1983) and methods (Heylar & Porter 1989, Poss et al. 1995) for acidification analysis were adapted to a set of data from a low-acid sandy clay alfisol from the western Venezuelan savanna. A simplified evaluation of the acidification processes induced by the different treatments was obtained.

The studied soil was used to grow corn as a single crop for twenty years using urea fertilization. Successive samplings were performed over the last two years (1993-1994) during crop growth in the upper two soil layers (0-20 cm and 20-40 cm) in a control plot and plots fertilized only with urea (132 kgN.ha-1) or with NPK fertilizer (100 P, 100K, 132N), with or without liming (1Mg CaCO<sub>3</sub>). Two companion treatments under permanent pasture and a laboratory column experiment were used to improve data interpretation. Five measurements of pH, buffering capacity and hydrosoluble (NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>) or exchangeable (NH<sub>4</sub><sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, Al<sup>+++</sup>) elements were done before and during the cultivations and leaching experiments.

The different treatments induced variations in the ratio of aluminium to pH in water or in KCl which could be related to climatic sequences, liming and nitrogen fertilization. The statistical analysis of the 210 samples of top-soil (0-10 cm), middle soil (10-20 cm) and sub-soil (20-40 cm) demonstrated that:

- the first ten centimeters of soil always had significatively lower Al than the middle soil and sub soil layers, but showed no significant difference for pH

- under permanent pasture, the three soil levels were progressively more acidic and aluminic with depth and the effect of urea was null.

- under maize, urea induced a decrease in pH and an increase in aluminium concentration when used alone, while it only induced a decrease in pH with no increase in aluminium when used along with superphosphate and potassium chloride,

- pH and aluminium are sensitive indicators of the actual processes occuring in the soil but are cannot be used for estimating Acid Neutralization Capacity (ANC). ANC depends mainly on exchangeable  $Ca^{++}$  and was stable when urea was broadcast alone over maize. All the other treatments induced an increase in ANC.

Key Words: Acidity, Aluminium, Buffer Capacity, CEC, Urea, Maize Mots clés: Acidité, Aluminium, Pouvoir tampon, CEC, Urée, Maïs

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#### Introduction

Some of the alfisols in the Venezuelan llanos are interesting for use in acidification studies as they represent some of the best arable acid soils in the Latin American savannas (Sarmiento, 1984). Their low natural fertility induces constant use of urea, practice which is thought to increase bases leaching, acidify the soil and lead aluminum or manganese toxicity (Bouman et al 1995). The new procedures of Aluminium speciation had also introduced considerable changes in the evaluation of aluminium toxicity (1994 Fallavier, 1995). These changes have made it necessary to revize the interpretation of previous results of aluminium extractions using KCl, which have been the standard for testing aluminium toxicity in the soil for the past decades (Dahlgren 1994; Li 1994). In the last fifteen years, the study of the acidification processes has been redirected to the examination of protons balance by various authors (Ven Breemen 1983 Heylar & Porter 1989, Poss et al. 1995)

The first goal of the present work was to look for a possible acidification effect of urea on the acid sandy clay alfisol of Barinas serie and if it could induce aluminium toxicity.

The second goal was to use the set of field and laboratory data obtained over two years to generate a general simplified method to evaluate acidification processes caused by urea or any other other product. This method applies Van Breemen's concept of Acid Neutralizing Capacity (ANC) but based on the « historic » approach of comparing successive samples rather than on his « actualistic » approach of proton budgets.

The third goal was to analyse  $Ca^{++}$ ,  $Mg^{++}$  and  $K^{+}$  leaching which is considered as the main factor involved in ANC variations. This analyse was performed using three percolations of urea and  $Ca(NO_3)_2$  solutions through soil columns in the laboratory.

#### **Materials and Methods**

#### Study site, climate, soil, cultivations, sampling and analysis.

The study was performed in the Botanical Garden of the Experimental University of Llanos, Unellez at Barinas (8°37'N, 70°12'W, altitude: 180m). The climate was typical of seasonal savannas (Sarmiento, 1984).

The soil on which the corn was grown was an acidic alfisol (Kandic Paleustalf with a wellbalanced texture). The mineral reserves consisted primarily of potassium  $(24 \text{ cmol kg}^{-1})$  and magnesium (8 cmol kg<sup>-1</sup>) associated with primary minerals, meanwhile calcium is rather low (3 cmol kg<sup>-1</sup>) 10 to 20% of it being found in its exchangeable form.

Maize cultivations had been continously grown as a single crop for eighteen years using urea fertilization (about 100 kg N a year) before the present work. After soil preparation including P, K, inputs the first year (100 units P and K by hectare as Potassium chloride and Calcium Superphosphate) maize was sowed by hand to obtain, after thinning, a density of 55 000 plants ha<sup>-1</sup>. Three weeks after sowing,, urea was uniformly spread on the surface between rows spaced 0.9 m apart.

Ten successive samplings were performed over the two years during maize growth in the upper two soil layers (0-20 cm and 20-40 cm) in a control plot, where the fertilization was interrupted, and plots fertilized only with urea (132 kgN.ha<sup>-1</sup>) or with NPK fertilizer (100 P, 100K, 132N) with or without liming (1Mg CaCO<sub>3</sub>). Two companion treatments under permanent pasture (Digitaria decumbens) with and without the same dosis of urea, were also organized in the same site to observe by difference the influence of tilling on nitrification and leaching.

For both years and cultivations, the first samples, PO, were taken at sowing, P1: 30 days later, i.e. 8 days after urea application, P2: one month afterwards (60 days after planting (« DAP »), P3: 101 DAP and P4: at final harvest, i.e. approximately 130 DAP.Three soil samples were taken using an auger in each of the plots, representing a total of approximately 5 kg fresh soil, which was mixed and sieved to form a representative composite sample of the plot.

The samples were stored at 4°C until analysis, 8 days later. Three sub-samples representing 10 g of dry soil were used to measure pH and to extract nitrogen and other mineral elements in water (NO3<sup>-</sup>, K<sup>+</sup>) and 1M KCl (NH4<sup>+</sup>, Ca<sup>++</sup>, Mg<sup>++</sup>, Al<sup>+++</sup>) based on McLean (1982) and Bremner, (1965). The buffering capacity, CEC and AEC of the reference sample was measured according to the Gilman's method (1991)

The results are expressed as charge units to make it possible comparisons between all elements either in  $\text{cmol}_c \text{ kg}^{-1}$  or in  $\text{kmol}_c \text{ ha}^{-1}$  using a conversion factor of 26 in the 0-20 cm soil layer (bulk density 1.3) or 30 in the 20-40 cm (B.D. 1.5).

Nine columns (250g 25cm high bd =1,3) of mixed top and middle soil previously humidified with the N solution (0N control 5mgN as urea or calcium nitrate) were repeatdly leached with 100ml of distilled water, ten hours a day during six weeks. The recycled solution was changed weekly and sub-sampled, filtred and frozen for further analysis.

#### **Results and discussion**

Spatial variability for pH and mineral nitrogen was measured before treatment using twelve samples taken the same day from plots used for related experiments (C.V. about 5% for pH, CEC,18%20% for N-NH<sub>4</sub><sup>+</sup> and 30% for N-NO<sub>3</sub><sup>-</sup> for concentrations above 5 mg kg<sup>-1</sup>). The field spatial variability was larger for Mg<sup>++</sup> and Al<sup>+++</sup> (C.V. = about 25%) than for Ca<sup>++</sup> (C.V.about 20%).

#### pH and Aluminium Relationships

The concentration of toxic forms of aluminium in the soil solution was calculated for the more acidic samples (under maize fertilized by urea alone) by Geochem software (P.Fallavier comm.pers.) None of the samples showed more than 1  $\mu$ mol Al<sup>+++</sup> activity while the accepted threshold for aluminium toxicity is 10  $\mu$ mol Al<sup>+++</sup>.

The statistic analysis of the 210 samples of top-soil (0-10 cm) middle soil (10-20 cm) and sub-soil (20-40 cm) first demonstrated that the repartition of the whole population

of samples follow the classical linear relationship between pH (water) and aluminium (KCl) with a correlation coefficient ( $r^2 = 0.45$ ) (Fig 1). The equations of the representative rights had quite the same slope but the correlation was, for both years, better for the top soil ( $r^2 = 0.51$ ) than for the middle ( $r^2 = 0.27$ ) and suboil ( $r^2 = 0.16$ ) probably due to the presence of diversified forms of aluminium in the lower layers.

Only pH was affected by the climatic difference between the two years (Fig 1 a and b). Liming only affect pH values in the top soil during the first year and middle and subsoil the second as a result of tillage and leaching.During the second drier year, pH values were slightly higher in the three layers, but aluminium values looked identical. (Fig 1b).

Under pasture, the correlation Al-pH only existed if all samples from the three layers were considered as a whole. Within each soil layer none correlation appeared (Fig 1c). Middle and subsoil samples under maize form a single population with the highest aluminium content. This fact was considered as a secondary effect of nitrification and subsequent leaching (Fig 1d).

The main conclusion which can be drawn form these results is that pH and aluminium cannot detect aluminium toxicity but were sensitive to the processes occuring in the soil under maize according to the different treatments (horizon, year, culture, fertilization, liming).

#### **ANC evolution versus Treatments during the two years** Fig 2

The following graphs are based on the differences (+ or -) in concentrations of each element between two successive samplings. The decrease in ANC based on a "no leaching" hypothesis imply that all the nitric nitrogen which disappeared between two sampling dates was absorbed by the plants. The magnitude of this ANC underestimation was negligible compared with exchageable calcium which was the main variation factor.

The only treatment under which ANC did not increase during the two studied years, was maize fertilized by urea alone. This effect of urea input on maize was attributed to leaching which is always relatively high below maize and null below pasture. Liming had a different effect with or without NPK fertilizing but the final ANC increase were similar.

Nevertheless, the observed variations were primarily due to the behavior of calcium and magnesium, rather than to nitrogen, whose acidifying and alkalinizing effects balance each other out when no strong leaching occurs. This type of graph based on results commonly available in any laboratory can easily be improved by adding more data and by an analysis of the behavior of each soil layer. It thus offers a simple way of estimating acidifcation defined as a decrease in ANC.

#### **Experimental leaching Fig 3**

Leaching was nearly zero (N 0,03  $\text{cmol}_c \text{kg}^{-1}$  almost nitric and 0,35  $\text{cmol}_c \text{kg}^{-1}$  cations as a whole) below the control columns after four weeks.

The presence of urea increase nitrogen leaching ten times (N 0,3 cmol<sub>c</sub> kg<sup>-1</sup>, 0,12 of them being ammonium) and almost twice the leached cations (0,53 cmol<sub>c</sub> kg<sup>-1</sup>). The first cation to be leached was K<sup>+</sup> (0,16) followed by Mg<sup>++</sup>, Mn<sup>++</sup> Ca<sup>++</sup> (0,08) and Al<sup>+++</sup>. The cationic charges were not balanced by nitric ones. Other anions has to be taken in account to understand leaching mechanisms.

Adding calcium nitrate induce three times more nitrogen losses (0,9 cmol<sub>c</sub> kg<sup>-1</sup> mainly nitric) and five times more cations (2,4 cmol<sub>c</sub> kg<sup>-1</sup> 0,7 Mg<sup>++</sup> and Mn<sup>++</sup> only 0,8 Ca<sup>++</sup>).

In all treatments the sum of Mg<sup>++</sup> and Mn<sup>++</sup> was always higher than that of leached calcium. This result is probably very important for further studies. But before taking in account

Aluminium and Manganese in ANC calculations more theoretical and experimental work needs to be performed to determine how these elements contribute to the buffer power.

#### Conclusion

Aluminium toxicity should not be easily reached in the alfisols of Barinas serie. However, the diversity and the mobility of aluminium polymers is related with pH and may be used for better understanding of soil evolution of cultivated acid soils.

An estimate of the acidification process may be obtained by analyzing the evolution of acid neutralization capacity, ANC whose accuracy has to be improved increasing the number of elements taken included in the analysis.

Apparently Aluminium, Magnesium and Manganese are equally or more important than Calcium in the experimental leachates. If this result was confirmed in field studies these elements have to be taken in account in further studies of ANC evolution in cultivated soils

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