ACIDIFICATION EVIDENCES OF NO-TILLED SOILS OF THE CENTRAL REGION OF ARGENTINA

LAURA ANTONELA ITURRI[1,*]; DANIEL EDUARDO BUSCHIAZZO[2] & MARTÍN DÍAZ-ZORITA[3]

1 CONICET (Instituto de Ciencias de la Tierra y Ambientales de La Pampa, INCITAP, CONICET-UNLPam) y Facultad de Agronomía de la Universidad Nacional de La Pampa.
2 INTA Anguil, Facultad de Agronomía de la Universidad Nacional de La Pampa y CONICET (Instituto de Ciencias de la Tierra y Ambientales de La Pampa, INCITAP, CONICET-UNLPam).
3 CONICET, Facultad de Agronomía de la Universidad de Buenos Aires y Merck Crop Bioscience Argentina S.A.
* Autor para correspondencia: antonelaiturri@conicet.gov.ar

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ABSTRACT

Empiric evidences indicate that agricultural soils of Argentina tend to acidify. The objective of this study was to determine the pH values of no-tilled and urea-fertilized-agricultural soils of Argentina during several years. Results indicated that both the actual pH (pH_A) and the potential pH (pH_P) values were lower in humid than in dry environments. The ratio between «mean annual precipitation:mean annual temperature» of the sites explained between 60 and 80% of the variability in pH values. This suggests that climatic conditions were responsible for current soil pH values. The pH_A was 1.14 points higher tan pH_P in all studied sites ($p<0.01$), indicating that a generalized natural acidification process existed. In soils of drier environments, differences between both pH_A and pH_P were, on average, higher than 1.21, indicating a more intense acidification process. However, pH values were not low enough to affect the normal growth of crops and soil organisms. In soils of humid environments, differences between pH_A and pH_P were higher than 1.10, being pH_A values (6.17 and 5.80) acidic enough to affect the microbial activity and the development of pH sensitive crops. Fertilization with urea decreased pH_A between 0.18 and 0.32 points compared to non-fertilized treatments ($p<0.05$), indicating that fertilization contributed to a decrease in pH values in the studied soils. In conclusion, fertilization with urea slightly increased the natural tendency to soil acidification in most of the studied soils.

Keywords. Soil acidification, Nitrogen fertilizers, Soil degradation.

EVIDENCIAS DE ACIDIFICACIÓN DE SUELOS DE LA REGIÓN CENTRAL DE LA ARGENTINA BAJO SIEMBRA DIRECTA

RESUMEN

Evidencias empíricas indican que los suelos agrícolas de la Argentina tienden a la acidificación. El objetivo de este estudio fue determinar valores de pH de suelos agrícolas de la Argentina bajo siembra directa de larga duración y fertilización con urea. Los resultados indican que tanto los valores de pH actual (pH_A) como de pH potencial (pH_P) fueron más bajos en ambientes húmedos que en los más secos. El cociente entre «precipitación media anual : temperatura media anual» de los sitios explicó entre un 60 y un 80% de la variabilidad de los valores de pH. Esto sugiere que las condiciones climáticas fueron responsables de los valores de pH presentes en estos suelos. El pH_A fue 1,14 puntos mayor que el pH_P en todos los sitios estudiados ($p < 0,01$) indicando que existió un proceso natural generalizado de acidificación. En suelos de ambientes más secos, las diferencias entre el pH_A y el pH_P fueron, en promedio, mayores a 1,21. Esto indicaría una acidificación más intensa. Sin embargo, los valores de pH no fueron lo suficientemente bajos como para afectar el normal crecimiento de cultivos y de organismos del suelo. En suelos de ambientes húmedos, las diferencias entre el pH_A y el pH_P fueron superiores a 1,10, siendo los valores de pH_A (6,17 and 5,80) lo suficientemente ácidos como para afectar la actividad microbiana y el desarrollo de cultivos sensibles a bajos pHs del suelo. La fertilización con urea disminuyó el pH_A entre 0,18 y 0,32 puntos en relación a los tratamientos no fertilizados ($p < 0,05$), indicando que la fertilización contribuyó al descenso de los valores de pH en los suelos estudiados. Se concluye que la fertilización con urea incrementa levemente la tendencia natural de los suelos a la acidificación en la mayoría de los sitios estudiados.

Palabras clave. Acidificación de suelos, Fertilizantes nitrogenados, Degradación de suelos.

INTRODUCTION

Acidification is a frequent chemical degradation process of many soils (Mayer, 1998; Borùvka *et al.*, 2007). The main natural cause of this process is the leaching of exchangeable bases by infiltration water (Dubiková *et al.*, 2002) while the use of fertilizers (Haynes & Mokolobate, 2001), the extraction of bases by crops (Zhang *et al.*, 2009) and acid rain (Kelly & Stricklan, 1986; Lee *et al.*, 2006; Ward, 2009) are the main anthropogenic causes.

Acidification affects soil properties and plant growth (Malhi *et al.*, 1998). Acid soils are deficient in exchangeable bases for crop development (Darusman *et al.*, 1991; Dubiková *et al.*, 2002) and have higher concentrations of phytotoxic substances in the soil solution, mainly active compounds of aluminum (Al) (Borùvka *et al.*, 2005; Drábek *et al.*, 2005), iron (Fe) (Hell & Stephan, 2003; Rust Neves *et al.*, 2009), and manganese (Mn) (Watmough *et al.*, 2007).

The use of fertilizers in agricultural systems, mainly under no-till (NT) farming, has drastically increased in Argentina in the last years (Montoya *et al.*, 1999; Díaz-Zorita, 2005). The effect of nitrogenous fertilizers, especially urea, on soil acidification has been scarcely analyzed in this country. Vazquez (2005) demonstrated that ammonium fertilizers acidify the soil. Also, Fabrizzi *et al.* (1998) found that urea fertilization reduced the pH of a Typic Argiudoll by 0.39 units. Urricarriet *et al.* (1999) observed that after seven years of urea fertilization, pH values of a Typic Argiudoll from Argentina decreased from 6.40 to 5.60. Other authors found that liming increased crop production in soils with pH under 5.00 in the Humid Pampas (Gambaudo, 1998; García *et al.*, 2002). This practice can improve some physical soil properties.

No-till farming is used for crop production along a broad climatic and edaphic gradient in Argentina. Climatic conditions vary from subtropical to temperate; agricultural soils are composed by different Subgroups (US Soil Taxonomy) of Haplustolls, Hapludolls and Argiudolls (Moscatelli, 1990). Considering this variability, it can be assumed that the more developed soils, with higher organic matter, clay contents, cation exchange capacity and base saturation will present a lower acidity than the less developed soils. The objective of this study was to test this assumption by analyzing the pH values of no-tilled agricultural soils, with and without urea fertilization history in the central region of Argentina.

MATERIALS AND METHODS

Soils of six sites of Argentina under varying climatic and intrinsic properties were sampled from field plots of a 5 year long no-till experiments. Three soil samples were taken randomly from the topsoil (0-20 cm) of every 100 m^2 area of fertilized (urea) and non-fertilized plots at each site. Table 1 shows the main characteristics of soils and management history at each site.

Soil samples were air-dried, ground and sieved through a 2 mm mesh to determine actual pH (pH$_A$, soil:water 1:2.5) and potential pH (pH$_p$, soil:KCl 1 eq dm^{-3} 1:2.5) (Vazquez, 2005). Exchangeable cations were extracted with ammonium acetate 1 eq dm^{-3} buffered at pH 7, and subsequently determined by atomic absorption spectrometry (Page *et al.*, 1982). Soil cation exchange capacity (CEC) and the percent of base saturation (BS) were then calculated. Soil organic matter content was determined by the Walkey & Black method (1934). Soil particle size distribution was determined by the Robinson's pipette method (Klute, 1982).

Soil pH values were correlated by simple linear regression analysis with the Lang's climatic index (Lang, 1920), expressed by the ratio between the mean annual precipitation (mm) and the

Table 1. Main characteristics of the studied soils (F = Fertilized and NF = Non- Fertilized soils).
Tabla 1. Principales características de los suelos estudiados (F = Fertilizados y NF = No Fertilizados).

Site	Las Breñas (Chaco) (A)		Obispo Colombres (Tucuman) (B)		Rosario (Santa Fe) (C)		Gral. Baldissera (Cordoba) (D)		San Jorge (Santa Fe) (E)		Armstrong (Santa Fe) (F)	
	NF	F	NF	F	NF	F	NF	F	NF	F	NF	F
Location	27º05‘ S 61º06‘ W		26º49‘ S 64º51‘ W		32º43‘ S 60º60‘ W		33º30‘ S 62º38‘ W		32º10‘ S 61º49‘ W		32º38‘ S 61º20‘ W	
Soil	Oxic Haplustoll		Typic Haplustoll		Typic Argiudoll		Typic Hapludoll		Typic Argiudoll		Aquic Argiudoll	
P/T (mm ºC^{-1})	45,7		51,8		53,3		53,9		56,7		56,8	
Years of no-till	5		20		4		6		12		20	
Crops sequence	S-Sg-Ct-C		nd		C-W/S		C-W/S		C-W/S		C-W/S	
Years of fertilization	0	5	0	20	0	9	0	9	0	9	0	8
Annual rate of urea fertilization	0	52	0	100	0	171	0	171	0	171	0	171
Organic matter (%)	2.9	2.7	1.9	2.1	2.5	2.8	2.2	2.6	3.3	3.3	2.3	2.7
CEC (cmol kg^{-1} soil)	24.3	24.9	24.6	22.2	15.7	17.7	24.0	26.7	24.5	23.4	27.8	22.9
Base saturation (%)	73.7	72.7	56.2	67.2	64.3	63.4	56.3	54.8	58.1	61.4	55.4	69.9
Texture	Sandy clay loam		Silty loam		Loamy clay		Loam		Silty clay loam		Silty loam	

nd: no data, Ct: Cotton , S: Soybean, Sg: Sorghum, M: Corn, W: Wheat, P: Medium annual precipitation, T: Medium annual temperature, CEC: Cation exchange capacity.

mean annual temperature (ºC) (P/T) at each site, in order to evaluate the effect of climatic conditions.

The Fisher test was used to compare variances of pH values and the Student t-test to compare mean values. A covariance analysis was performed to compare regression lines. A principal component analysis (PCA) was performed to analyze the association between variables. All statistical and mathematical analyses were done with the Microsoft Excel and the InfoStat/ Professional version 1.1. (Di Rienzo *et al.*, 2002) programs.

RESULTS AND DISCUSSION

Soil pH_A values ranged from 5.62 to 7.07 and soil pH_P ranged from 4.64 to 6.01 (Table 2). Both pH_A and pH_P values were highly correlated (linearly and negatively) with the P/T ratio of each site in both fertilization treatments (Fig. 1). This ratio explained between 60 and 80% of pH variances. These results indicate that pH values are highly dependent on climatic conditions, as a probable result of higher losses of exchangeable bases by leaching (Dubiková *et al.*, 2002) in more humid environments, as well as the higher exchangeable base extraction by more productive crops (Vázquez *et al.*, 2000; Gelati & Vázquez, 2008; Zhang *et al.*, 2009).

Linear regression slope was significantly ($p < 0.01$) higher in the pH_A - P/T than in the pH_P - P/T relationship, for both fertilization treatments. These results show that differences between pH_A and pH_P were higher in dry than in humid environments. In environments with a P/T quotient between 45 and 52, differences between actual and potential pH values averaged 1.21 points, while in environments with P/T quotient between 53 and 57, the differences averaged 1.10. This would mean that, even though absolute pH values were lower in humid environments, the acidification magnitude in the driest envi-

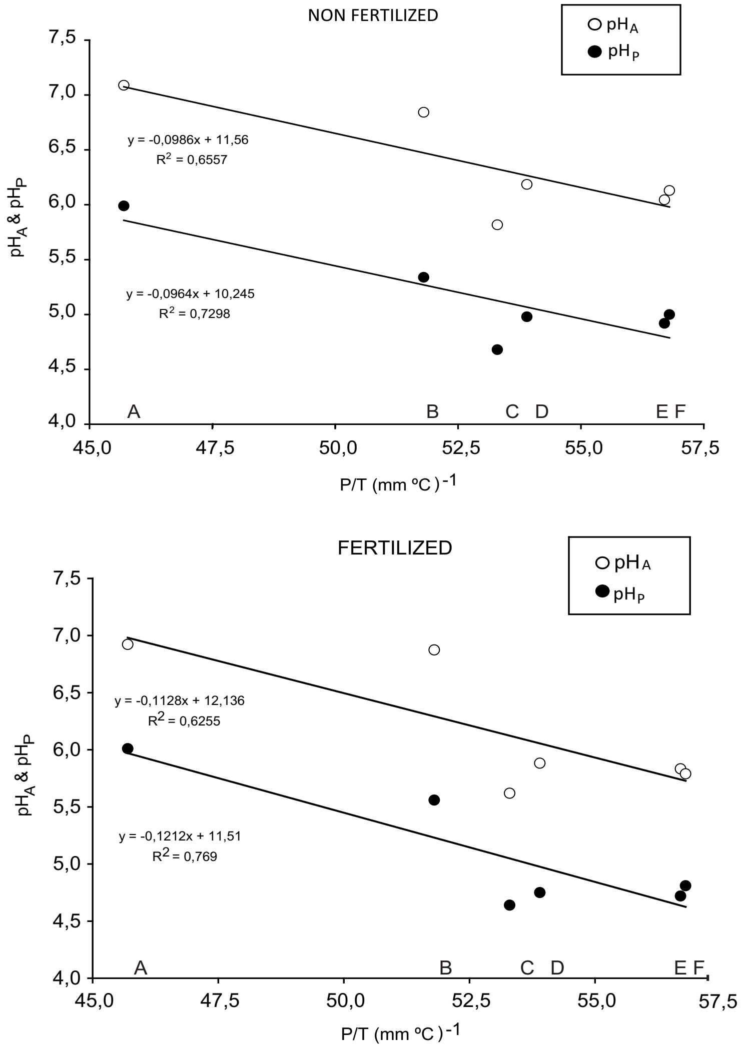

Figure 1. Values of pH_A and pH_p as a function of the ratio «mean annual precipitation: mean annual temperature» (P/T) of a) non-fertilized and b) urea-fertilized soils.

Figura 1. Valores de pH_A y pH_p en función del cociente «precipitación media anual: temperatura media anual» (P/T) de a) suelos no fertilizados y b) suelos fertilizados con urea.

ronments is higher. On the other hand, such results can be also be affected by measurement methods, as mentioned by Thomas (1996).

Values of soil pH_A were significantly ($p < 0.01$) higher than those of soil pH_P in all studied sites (Table 2). Soil pH_A values averaged 6.33 for the non-fertilized treatments and 6.15 for the fertilized ones, whereas pH_P values averaged 5.13 and 5.08, respectively. The mean pH_A - pH_P difference was 1.20 and 1.08 in non-fertilized and fertilized treatments, respectively. A difference between pH_A and pH_P higher than 1.00 indicates that soil acidification existed, as this pH difference would potentially produce an increase of H^+ by 10 times in the soil solution if the dissociation of all adsorbed H^+ occurred.

Both, pH_A and pH_p values were lower in fertilized than in non-fertilized soils (Table 2). The non-fertilized soil of the site with the lowest P/T ratio (site A from Chaco province) had an average pH_A value of 7.07 and an average pH_P of 5.97; the difference was 1.10. In turn, the soil of the site with the highest P/T ratio (site F from Santa Fe province) had a pH_A of 6.11 and a pHp of 4.98, with a difference of 1.30. The fertilized soils of site A presented a pH_A of 6.92 and a pH_P of 6.01; with a difference of 0.91. The soil of site F presented a pH_A of 5.79 and a pHp of 4.81, being their difference 0.98. These results indicate that the observed pH decreases are due to an acidification of environmental origin rather than being anthropogenic (Cnossen *et al.*, 2008; Noyes *et al.*, 2009). Urea fertilization increased this general acidification trend linked to a medium to low base saturation (72.7 for site A and 69.9 for site F) and to low organic matter contents (2.7 in both sites).

Urea fertilization caused significant decreases in soil pH_A($p < 0.05$). The decreases were greater in the more humid sites (C, E, F and D) than in the drier sites (A and B). In site A (Chaco province), pH_A and pH_P values varied between 6.00 and 7.00 across all fertilization treatments. Such values should not cause detrimental effects on pH sensitive crops and soil organisms (Borùvka *et al.*, 2005; Drábek *et al.*, 2005; Watmough *et al.*, 2007; Rust Neves *et al.*, 2009). However, pH_P was significantly lower than pH_A ($p < 0.05$) in both fertilization treatments (differences between 1.10 and 0.91, respectively), suggesting that a weak acidification process is in progress. Such process is probably not linked to fertilization, as the fertilization rate of urea was low in this site (Table 1).

The soil of site B (Tucumán province) showed no evidences of acidification due to fertilization, even though the fertilization rate was twofold and the fertilization events quadruplicated that of site A. In site B, soil pH_A was 1.50 points higher than pH_P in the non-fertilized soil and 1.31 points in the fertilized one. This indicates that acidification was not produced by the use of fertilizers but by another process. In site B, the intense industrial activity may be the source of protons added to the soil. Even though acidification is evident in this site, pH_A values are within the optimum range for the growth of most crops (Porta *et al.*, 1999; Drábek *et al.*, 2005; Stevens *et al.*, 2009). However, soil pH_P values are below 5.56, which can be considered critical for the growth of most crops. The acidification sources in this region must be detected in order to avoid future adverse effects on soils and crops.

Both soil pH_A and pH_P values were significantly ($p < 0.05$) lower in fertilized soils than in non-fertilized soils of more humid environments (sites C, D and F) (Table 2). Differences between pH_A and pH_P were 0.97 and 1.15 in average, respectively. In the C, D and F sites, pH_A values ranged from 6.25 to 5.70 in the non-fertilized soils, and 5.90 to 5.77 in the fertilized soils. The corresponding pH_P values ranged from 4.90 to 4.64 in the non-fertilized soils and 4.91 to 4.62 in the fertilized soils. These pH values indicate that, despite of their higher buffer capacity linked

Table 2. Actual (pH_A) and potential pH (pH_p) of no-tilled soils, fertilized (F) and non-fertilized (NF) with urea.

Tabla 2. pH actual (pH_A) y potencial (pH_p) de suelos bajo siembra directa, fertilizados (F) y no fertilizados (NF) con urea.

Site	pH_A		pH_p	
	NF	F	NF	F
A	7.07 a, A	6.92 a, A	5.97 a, B	6.01 a, B
B	6.82 a, A	6.87 a, A	5.32 a, B	5.56 a, B
C	6.03 a, A	5.83 b, A	4.66 a, B	4.64 b, B
D	6.17 a, A	5.88 b, A	4.96 a, B	4.75 a, B
E	5.80 a, A	5.62 b, A	4.90 a, B	4.72 b, B
F	6.11 a, A	5.79 b, A	4.98 a, B	4.81 b, B

Lowercase letters indicate significant differences between fertilization treatments within each site and pH type ($\alpha = 0.05$). Different capital letters indicate significant differences between pH types within each site and fertilization treatment ($\alpha = 0.05$).

to their higher organic matter contents and CECs (Table 1), the application of urea was responsible for the decreased pH values of these soils. All these values were low enough to produce Ca and Mg deficiencies (Dubiková *et al.*, 2002), reduction of the microbial activity (Porta *et al.*, 1999; Drábek *et al.*, 2005; Stevens *et al.*, 2009) and the solubilization of Fe, Mn or Al (Drábek *et al.*, 2005; Watmough *et al.*, 2007 y Rust Neves *et al.*, 2009).

A principal component analysis (PCA) was applied as a data reduction or structure detection method (Fig. 3). The average values of the studied variables are represented in the center of the *biplot*. At that point, non-fertilized and fertilized treatments presented the following values: pH_A 6.33 and 6.15, pH_P 5.13 and 5.08, CEC 23.48 and 23.00 cmol kg^{-1}, percent of base saturation 60.68 and 64.94% and OM 2.51 and 2.70%. Both pH values were negatively correlated with OM contents ($r = -0.35$ and -0.18, $p < 0.05$), and positively with CEC ($r = 0.34$ and $r = 0.32$, $p < 0.05$) and BS ($r = 0.41$ and 0.59, $p < 0.05$), as reflected by both the flat and acute angles between variables in the *biplot* (Fig. 2).

This PCA confirmed the results from the simple regression analysis, which determined three soil populations (Fig. 2): a) soils of sites A and B characterized by their pH values near neutrality, medium to high exchangeable base saturation and medium to high CEC values and OM contents; b) soils of sites D, E and F, with pH lower than the average of all the studied sites, medium to high BS and medium to low CEC and OM content; and c) soils of site C with the lowest pH values, high BS, and low CEC and OM contents of all analyzed sites (Table 1).

CONCLUSIONS

Differences between pH_A and pH_P higher than 1.00 were observed in all studied soils, indicating a generalized acidification process. Nevertheless, less developed soils showed higher pH differences than the more developed ones. The existence of higher acidification in less developed soils must be further analyzed.

The pH values of the less developed soils were always above the critical threshold for crop and microorganism growth.

Soil acidification was slightly promoted by urea fertilization in most of the studied sites.

The «mean annual precipitation: mean annual temperature» ratio was negatively related to both the actual and the potential pH, and explained 60- 80% of the variability.

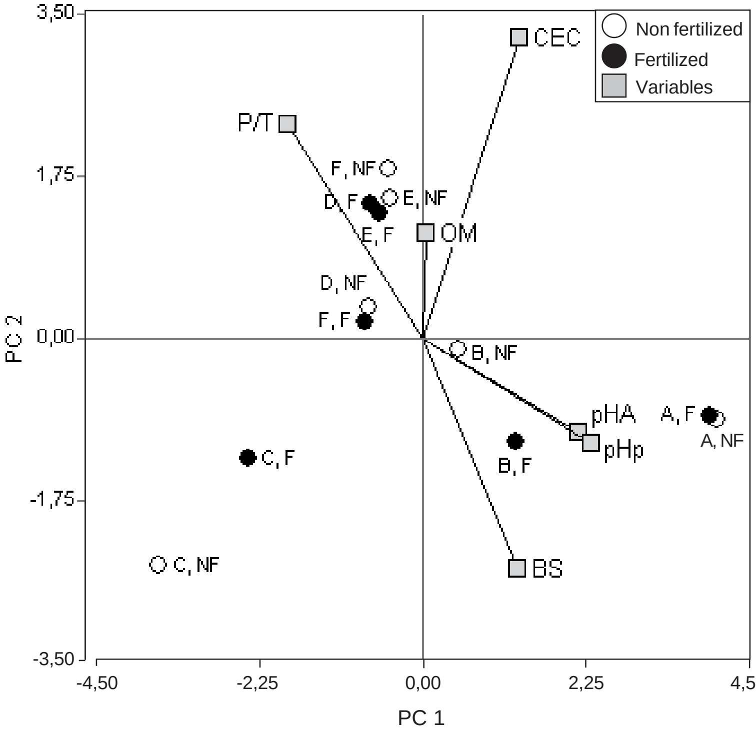

Figure 3. Principal components analysis. *Biplot* in the plane of the two first principal components (PCs).

Figure 3. Análisis de componentes principales. *Biplot* en el plano de las dos primeras componentes principales (PCs).

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