



Light acidification in N-fertilized loess soils along a climosequence affected chemical and mineralogical properties in the short-term



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ABSTRACT

Some evidences indicate that N-fertilization of crops decreased pH values of loess soils of the Argentinean Pampas in the last decades. We analyzed the A-horizons of four N-fertilized (F) and non-fertilized (NF) paired soils, developed on similar parent materials, within a climatic sequence (ustic to udic water regimes), and measured: 1) the extent of pH changes, 2) how these changes affected chemical and mineralogical soil properties and 3) how the soils, according to their H⁺ buffering substances, can react in the future if N-fertilization and acidification continue. Results indicated that all F- and NF soils were lightly acidified (differences between pH_W and pH_{KCl} higher than 1.0) and that fertilization produced pH decreases in all studied soils, but particularly in those with udic water regimes, in agreement with their longer N-fertilization histories. Fertilized ustic soils showed less crystalline illites and kaolinites and higher contents of amorphous Al oxides than NF soils. It remains unclear if the higher contents of amorphous Al are related with the dissolution of phyllosilicates, the transformation of the abundant volcanic glasses of these soils or both processes at the same time. The cation exchange capacity (CEC) and the percent of base saturation (V) did not change between F- and NF soils, probably due to the large influence of soil organic matter (SOM) in the studied soils. If N-fertilization, and consequently pH decreases continue, soils placed in both the moistest- (Argiudolls) and the driest extremes of the climosequence (Haplustolls) would be the less affected. This is because udic soils contain high SOM as well as illitic clays and silts while ustic soils contain free lime and high density charged clay minerals, which have high H⁺ neutralization capacity. The most affected soils by acidification should be those placed in the intermediate zone of the climosequence (Hapludolls), which have low amounts of substances with high buffer capacity.

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1. Introduction

Soil acidification has been mostly studied in soils of tropical and subtropical regions where natural conditions are the main driving factors of this process (Hulugalle, 1992; Eppinger and Fuge, 2009; Vendrame et al., 2013). Anthropogenic acidification has been also detected in highly industrialized regions, being acid rains its primary cause (Drever, 1997; Mather et al., 2004). Less information is available on soil acidification produced by continuous N-fertilization which seems to be occurring in agricultural loess soils of the Pampas of Argentina. In this region, N-fertilizers have been applied for more than 30 years since the introduction of no-till systems in the middle 1980s (FAO, 2004). As a matter of fact, some acidification evidences have been detected in these soils (Fabrizzi et al., 1998; Urricariet and Lavado, 1999; Iturri et al., 2011), but neither the effects of these pH decreases on other soil

properties, nor the resistance of soils against future N-fertilization inputs have been evaluated.

It is largely known that acidification can affect several soil properties, such as the decrease of the exchangeable bases (Darusman et al., 1991; Dubiková et al., 2002) or the increase of elements like Al, Mn and Fe in the soil solution (Hell and Stephan, 2003; Borůvka et al., 2005; Watmough et al., 2007; Rust Neves et al., 2009), which in high concentrations could be phytotoxic. When the acidification process is pronounced, the dissolution of clay minerals can also occur, leading to a higher acidification due to the release of aluminum ions from mineral structures to the soil solution (Barré et al., 2009; Céspedes-Payret et al., 2012).

The use of N-fertilizers, mainly urea, is carried out in loess soils of a wide range of climatic conditions but with similar fertilization histories within the Argentinean Pampas. This situation gives an opportunity to study the effect of pH decreases associated with N-fertilization on soils developing on similar parent materials and under similar fertilization histories but variable climatic conditions. It is known that associated with climatic conditions (ustic to udic soil moisture conditions), soils of the Pampas show different evolution rates (Teruggi, 1957). This is

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still a question how soils with different development rates can react to N-fertilizer inputs. Therefore, the purpose of this study was to evaluate the extent of pH decreases of N-fertilized soils of a climosequence of the Pampas, the effects of these pH changes on some chemical and mineralogical properties, and to estimate the reaction of the soils to future pH changes if N-fertilization continues.

2. Material and methods

2.1. Studied area and soils

All the studied soils have developed on the same parent material, loessic-like sediments, the so-called “Pampas-loess” of pleistocenian and holocenian ages (Teruggi, 1957; Buschiazzo, 1988; Zárate, 2003). The mineralogy of this parent material is qualitatively- but not quantitatively homogeneous, due to the fact that the sedimentation of aeolian materials by winds of different speeds, and therefore different transport energies, sedimented variable amounts of minerals with different densities at different depths (Buschiazzo and Taylor, 1993). These sediments contain variable amounts of volcanic glasses, accumulated during the frequent volcanic eruptions which occurred during those geological periods (Teruggi, 1957). One of the last volcanic events took place in 1932, when an eruption of the Andes-Quizapu volcano sedimented a 10 cm-thick-ash layer along a 1000 km-long W–E oriented strip in the semiarid Pampas of Argentina (Larsson, 1936).

Four sites placed in regions with different climatic conditions of the Argentinian Pampas (Fig. 1) were selected for this study. All studied plots are within experimental stations and belong to long-term experiments developed since several years in order to test the effect of N-fertilization on no-till produced crops. All analyzed soils were classified as Mollisols (Soil Survey Staff, 1999) and varied from dry to moist climatic conditions as follows: an Entic Haplustoll (EH), two Typic Hapludolls (TH-I and TH-II) and a Typic Argiudoll (TA). Soils EH and TH-I contain some amounts of volcanic glass while both, TH-II and TA,

are volcanic glass free soils. The main characteristics of the soils and their management practices are presented in Table 1.

At each site two different fertilization conditions were sampled: a non-fertilized (NF) plot and a urea- (46:0:0, Finck, 1979) fertilized plot (F). Triplicate topsoil samples were taken from triplicate 10 m² NF- and F plots at each site. Both NF- and F plots were located adjacently.

2.2. Laboratory procedures

Soil samples were air dried and sieved (<2 mm). The following determinations were carried out in each of them: 1) pH in both, water (pH_w) and 1 eq dm⁻³ KCl dissolution (pH_{KCl}) (1:2.5 soil:liquid ratio in both cases) (Mc Lean, 1982). Both pH values were determined in order to analyze the extent of the soil acidification process, considering that differences between both values higher than 1.0 indicate some degree of soil acidification (Gandois et al., 2011); 2) neutralization curves of all NF soils by volumetric titration (Vázquez et al., 2009), which included the contact of soil samples with different quantities of 0.1 eq dm⁻³ HCl_(ac) dissolutions for a period of 8 h, and the subsequent measurement of pH in the supernatant solutions; 3) the cation exchange capacity (CEC) by saturating the samples with a 1 eq dm⁻³ ammonia acetate dissolution at pH 7 (Rhoades, 1982); 4) the contents of exchangeable Ca, Mg (Lanyon and Heald, 1982), K and Na (Knudsen et al., 1982); with these data the percent of base saturation (V) was calculated; 5) the contents of soil organic matter (SOM), determined by wet digestion (Walkley and Black, 1934); 6) the contents of free lime (CaCO₃) (Schlichting et al., 1985); 7) the contents of amorphous Al-, Mn- and Fe oxides (Alo, Mno and Feo, extracted for 2 h in the darkness with oxalic acid) and crystalline Al-, Mn- and Fe oxide forms (Alos, Mnos and Feos, extracted for 6 min with boiled oxalic acid) (Schlichting et al., 1985). The ratios between amorphous- and crystalline forms (Alo:Alos, Mno:Mnos, Feo:Feos) were calculated; higher values of these ratios indicate lower crystallinity of these oxides, 8) the mineralogical composition of the clay fraction of each soil using X-ray diffraction analysis. This determination was carried

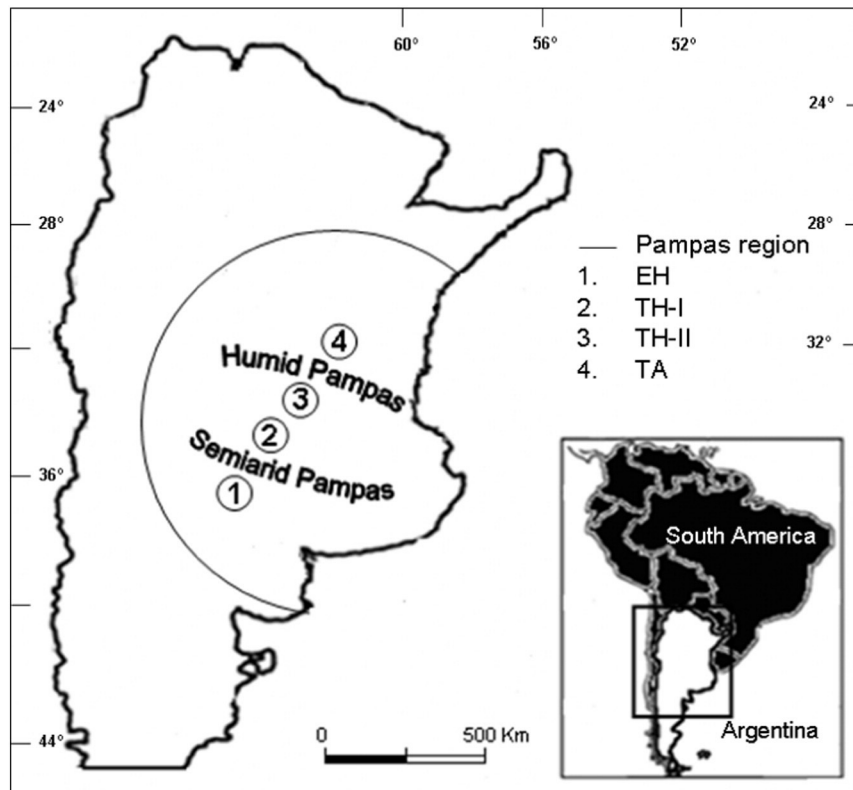


Fig. 1. Location of the studied sites. EH: Entic Haplustoll; TH-I: Typic Hapludoll I; TH-II: Typic Hapludoll II; TA: Typic Argiudoll.

Table 1
Main characteristics and management practices of the studied soils.

Denomination	Soil ^a	MAP ^b	MAT ^b	MAP MAT ⁻¹ ^b	Period of	Crops	Period of	Dose	Total
		mm	°C		no-till	sequence	fertilization ^b	of urea ^c	added N ^c
				yrs			yrs	kg ha ⁻¹ yr ⁻¹	kg ha ⁻¹
EH	Entic Haplustoll	600	14.5	41.4	13	W/S	13	80	1040
TH-I	Typic Hapludoll	775	16.9	45.9	13	C-S-Sf-W	15	130	1950
TH-II	Typic Hapludoll	863	16.0	53.9	7	C-W/S	9	171	1539
TA	Typic Argiudoll	850	15.0	56.7	5	C-W/S	9	171	1539

MAP: mean annual precipitation; MAT: mean annual temperature; N: nitrogen; C: corn (*Zea mays*); S: soybean (*Glycine max*); Sf: sunflower (*Helianthus annuus*); W: wheat (*Triticum aestivum*).

^a Soil Survey Staff (1999).

^b Servicio Meteorológico Nacional (2015).

^c In fertilized soils.

out on composite soil samples of each of NF- and F soils. The clay fraction (particles smaller than 2 µm in diameter) was first separated and then concentrated. The separation of this fraction was made on organic matter free samples that were dispersed with 1% sodium hexametaphosphate. The separation of clays was made by means of centrifugation, selecting the sedimentation times according to the methodology provided by Tanner and Jackson (1947). The X-ray diffraction analysis was performed on MgCl₂ saturated samples, by means of a diffractometer working with a Cu anticathode ($\lambda = 1.54 \text{ \AA}$) at 45 kV and 40 mA. The angular interval was scanned between 3° and 17° 2θ at 0.02° 1.5 s⁻¹. A semi-quantitative determination of clay species was performed by comparison of the spectra obtained from natural oriented samples, solvated with ethylene glycol and heated at 550 °C for 2 h (Brown and Brindley, 1984); and 9) the particle size distribution of clays (<2 µm in diameter), silts (2 to 50 µm) and sands (50 to 2000 µm) by means of the combined method of the pipette and wet sieving (Gee and Bauder, 1986).

2.3. Statistical analyses

A one way ANOVA was performed to test the differences between pH_W and pH_{KCl} between sites and fertilization treatments within each study site.

Linear multiple regressions were performed to assess the origin of pH_W and pH_{KCl} differences (ΔpH) between fertilized and non-fertilized treatments. This was done by considering the ratio between the mean annual precipitation and mean annual temperature of each site (MAP MAT^{-1} index; $x_{1,1}$) (Lang, 1920) and the equivalent of protons added with N-fertilization, calculated on the basis of doses- and years of fertilization ($\text{eq H}^+ \times \text{years}$; $x_{2,1}$) (Table 1).

Linear multiple regressions were also performed to explain the contribution of the acid neutralizing substances of each soil. The following variables were considered in this case: the contents of SOM and free lime (CaCO₃) and the proportion of clay + silt ($c + s$).

All mathematical and statistical analyses were performed, considering a significant level of 0.05 ($\alpha = 0.05$), by means of the following programs: Microsoft Excel/2003 and InfoStat/Professional version 1.1 (Di Rienzo et al., 2002).

3. Results and discussion

3.1. pH changes and soil properties

Table 2 shows that pH_W values averaged 6.4 in NF and 6.2 in F soils, while pH_{KCl} averaged 5.2 and 4.9, respectively. Results from the ANOVA analysis showed that the averaged pH_W values of all soils were significantly higher than pH_{KCl} values ($P < 0.05$) indicating the presence of some amounts of acidic ions adsorbed to their exchange complexes. Differences between pH_W and pH_{KCl} averaged 1.3 in NF and 1.2 in F. Differences between pH_W and pH_{KCl} higher than 1.0 indicate that an acidification process is in progress in all studied soils (Gandois et al., 2011).

The ANOVA analysis showed that the averaged pH_W and pH_{KCl} data of all studied soils differed ($P < 0.05$) between NF- and F pairs by 0.2 to 0.3 units. These results indicate that a weak acidification process is in progress due to N-fertilization. These results are in agreement with those of Iturri et al. (2011) who described that higher urea fertilization rates are accelerating soil acidification in Argiudolls of the Pampas. Similar results were also found in other parts of the world (Asadi et al., 2012; Ozgöz et al., 2013).

Table 2 indicates that EH-I has been less acidified than TA, TH-I and TH-II. Differences between pH_W and pH_{KCl} values were greater in EH and TH-I than in TH-II and TA while the absolute pH_W and pH_{KCl} values were lower in TA and TH-II than in EH and TH-I. pH values of udic soils (TH-II and TA) are low enough to affect nutrient availability and microbial activity, and probably crop productivity (Drábek et al., 2005; Stevens et al., 2009), as they are below the optimum pH levels.

A regression analysis showed that differences of both pH_W and pH_{KCl}, between F- and NF soils were larger in the moistest and more intensively fertilized sites (Eqs. (1) and (2)). This indicates that pH variations were produced by a superimposed effect of both climatic conditions and N-fertilization rates, which together explained 88 to 93% of the variance.

$$\Delta\text{pH}_W = -2.10 + 1.69 \cdot 10^{-5} \text{ eq H}^+ \times \text{years} + 0.035 \text{ MAP MAT}^{-1}$$

$$R^2_{\text{adjusted}} = 0.88; n = 12; P < 0.05 \quad (1)$$

$$\Delta\text{pH}_{\text{KCl}} = -1.98 + 1.18 \cdot 10^{-5} \text{ eq H}^+ \times \text{years} + 0.034 \text{ MAP MAT}^{-1}$$

$$R^2_{\text{adjusted}} = 0.93; n = 12; P < 0.05. \quad (2)$$

Results from the ANOVA analysis showed that CEC, the contents of exchangeable cations and the V values were similar between F- and NF pairs in all studied soils ($P > 0.05$) (Table 3), though it is largely known that these variables are highly sensitive to acidification (Sposito, 1989; Zapata Hernández, 2004).

Table 2

Mean values of pH_W and pH_{KCl} from triplicate samples taken from N-fertilized- (F) and unfertilized (NF) plots.

Soil	pH _W		pH _{KCl}		ΔpH	
	NF	F	NF	F	NF	F
EH	6.9 a, A	6.5 b, A	5.5 a, B	5.1 b, B	-1.4	-1.4
TH-I	6.5 a, A	6.4 a, A	5.2 a, B	5.2 a, B	-1.3	-1.2
TH-II	6.2 a, A	5.9 b, A	5.0 a, B	4.8 b, B	-1.2	-1.1
TA	6.0 a, A	5.8 b, A	4.9 a, B	4.7 b, B	-1.1	-1.1

EH: Entic Haplustoll; TH-I: Typic Hapludoll I; TH-II: Typic Hapludoll II; TA: Typic Argiudoll; ΔpH: difference between pH_{KCl} and pH_W within each site and fertilization treatment. Lowercase letters indicate significant differences ($P < 0.05$) between fertilization treatments within each site. Different capital letters indicate significant differences ($P < 0.05$) between sites and fertilization treatments.

Contents of Al_o, Mn_o and Fe_o (Table 3), which represent the amounts of amorphous oxides of these elements, were lower in NF- (910, 438 and 1599 mg kg⁻¹, respectively) than in F pairs (1028, 496, 1770 mg kg⁻¹) in all studied soils (P < 0.05). On the other hand, Fe_os contents (Table 3), the crystalline oxide forms of this element, were higher (P < 0.05) in NF- (18,106 mg kg⁻¹) than in F pairs (16,478 mg kg⁻¹). In general, the higher amounts of amorphous oxides in F than in NF, as well as the higher proportion of crystalline forms of Fe-oxides in NF than in F, indicate some degree of transformation of the crystalline forms into amorphous ones. These results were confirmed by the quotients Al_o:Al_{os} (Fig. 2), mainly for soils of the driest extreme of the sequence. The averaged Al_o:Al_{os} values for EH, TH-I and TH-II were higher in F than in NF pairs (P < 0.05). Opposite tendencies showed TA, the soil of the moistest extreme of the sequence. The Fe_o:Fe_{os} quotients showed similar trends than Al_o:Al_{os}, being highest in the F pair of the driest soil (EH) and lowest in the NF pair of both, TH-II and TA. No defined trends were found for Mn_o:Mn_{os} quotients between fertilization treatments, excepting TA, where the ratio was higher in F- than in NF. (Fig. 3.)

Decreases of the crystallinity of Al and Fe oxides of soils of the driest extreme of the climatic sequence would have occurred in a relatively short period of time, no more than 30 years. As these soils contain high amounts of volcanic glasses (Hepper et al., 2006; Iturri and Buschiazzo, 2014), it is possible that their weathering contributed to the increase of the amorphous Al oxides under the more acidic conditions of the fertilized soils (Table 3; Fig. 2). Hepper et al. (2006) demonstrated that amorphous Al oxides of soils of the semiarid Pampas of Argentina were produced by the fast weathering of volcanic glasses.

Table 4 shows the results of the semiquantitative X-ray diffraction analysis of the clay fraction of F- and NF soils. In general, the clay fraction was composed of highly crystallized illite and kaolinite as well as by poorly crystallized illite–smectite intergrades. The contents of both illite and kaolinite increased from soils of the driest – to those of the moistest extreme of the soil sequence, while the opposite occurred with the illite–smectite intergrades. F pairs of TH-I showed lower contents of illite than the NF pairs. Moreover, in TH-I, the crystallinity of illite in F- was lower than in the NF pair. Also, kaolinite contents were lower in F- than in NF pairs of TH-I. Though results from the X-ray-analysis are semiquantitative, a detectable depletion in the clay's crystallinity indicates some dissolution of phyllosilicates (Barré et al., 2009). Such change may produce amorphous Al oxides (Céspedes-Payret et al., 2012). Therefore, a deterioration of the phyllosilicate's crystallinity, probably linked to pH decreases that have taken place even in the short-term, may exist. Changes of phyllosilicate composition in the short-term in association with soil acidification have been described by several authors. Dubiková et al. (2002) found that clay minerals were formed and transformed mainly to amorphous Fe oxides after being submitted to an in vitro acidification experiment performed during 30 weeks. Céspedes-Payret et al. (2012) found that illite-like minerals decreased their crystallinity due to the release of K from mineral structures by acidification as a product of deforestation, producing an irreversible change of clay mineral structures. Changes in clay mineralogy due to fertilization were studied in soils of the long-term experiment of Rothamsted Classical Experiments (Tye et al., 2009). Results of these studies indicate that some illite–smectite minerals showed a considerable resilience to major changes.

Former results indicate that, in association with pH decreases, changes in the mineral composition of the clay fraction of the soils were detected, but not in some sensitive chemical properties like CEC and V. Similar results were found by Tye et al. (2009), who did not find definite trends in CEC and the specific surface area in N-fertilized and unfertilized soils but differences in the clay mineral composition. The lack of changes in CEC and V can be probably explained on the basis of the relatively high contribution of soil organic matter (SOM) to the cation exchange properties of the studied soils. As a matter of fact, Iturri and Buschiazzo (2014) demonstrated that SOM contents determined 46% of CEC in these soils.

Table 3
Main physical- and chemical characteristics of the studied soils. The values are means of the triplicate samples taken in each plot.

Site	Treatment	Grain size distribution					Exchangeable cations																												
		Clay %	Silt %	Sand %	SOM %	CEC cmol kg ⁻¹	Ca	Mg	K	Na	V %	CaCO ₃ %	Al _o mg kg ⁻¹	Fe _o	Mn _o	Al _{os}	Mn _{os}	Fe _{os}																	
HE	NF	13.0	na	21.5	na	65.6	na	2.2	na	19.4	ns	8.0	ns	2.3	ns	3.0	ns	0.5	ns	69.1	ns	1.2	na	1282	*	1903	*	179	*	4881	ns	20254	ns	19741	*
	F	12.3	23.4	64.2	2.6	18.8	8.2	18.8	8.2	18.8	8.2	8.0	ns	2.6	4.8	3.1	ns	0.4	ns	85.2	ns	1.2	na	1651	*	2100	*	215	*	4733	ns	21742	ns	19273	*
TH-I	NF	15.3	na	26.0	na	58.8	na	2.8	na	17.3	ns	7.7	ns	1.9	3.1	ns	0.1	ns	73.9	ns	0.4	na	175	*	1269	ns	324	ns	2120	*	468	ns	13184	*	
	F	12.5	22.8	64.7	2.7	16.4	7.6	19.9	7.6	16.4	ns	7.6	ns	1.9	3.4	ns	0.2	ns	79.3	ns	nd	nd	383	nd	1260	ns	305	ns	1632	ns	457	ns	11926	*	
TH-II	NF	17.0	na	34.2	na	48.8	na	2.2	na	24.0	*	8.2	ns	2.2	2.9	ns	0.2	ns	56.3	ns	0.1	na	1042	*	1464	*	440	*	5806	ns	2500	ns	27422	*	
	F	33.3	33.7	33.0	2.6	26.7	9.5	2.2	na	26.7	ns	9.5	ns	2.2	2.8	ns	0.2	ns	54.8	ns	0.4	na	1334	na	2311	ns	560	ns	6011	ns	2892	ns	22415	ns	
TA	NF	28.5	na	63.7	na	7.8	na	3.3	na	24.5	ns	8.5	ns	2.3	3.3	ns	0.2	ns	58.1	ns	0.4	na	1142	ns	1758	ns	809	*	4229	ns	1111	ns	12077	ns	
	F	36.8	53.0	10.2	3.3	23.6	8.9	2.4	na	23.6	ns	8.9	ns	2.4	3.1	ns	0.2	ns	61.4	ns	nd	nd	952	na	1408	ns	904	ns	5158	ns	961	ns	12296	ns	

HE: Entic Haplustoll; TH-I: Typic Hapludoll I; TH-II: Typic Hapludoll II; TA: Typic Argiudoll; NF: non-fertilized; F: F-fertilized; SOM: soil organic matter; CEC: cation exchange capacity; Ca, Mg, K and Na: exchangeable calcium, magnesium, potassium and sodium, respectively; V: percent of base saturation; CaCO₃: free lime; Al_o, Mn_o and Fe_o: aluminum, manganese and iron from amorphous oxides, respectively; Al_{os}, Mn_{os} and Fe_{os}: aluminum, manganese and iron from crystalline oxides, respectively; nd: non-determined; ns: indicates non-significant differences (P > 0.05) between fertilization treatments within each soil. *: indicates significant differences (P < 0.05) between fertilization treatments within each soil. na indicates that data were not analyzed to test for significant differences between fertilization treatments within each soil.

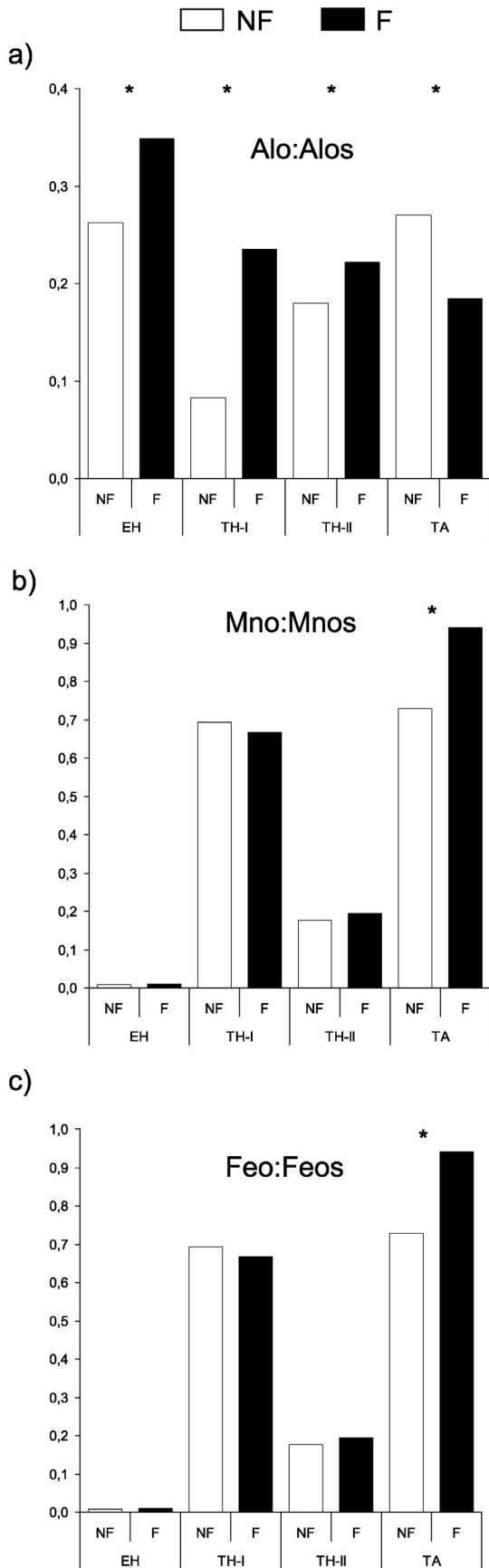


Fig. 2. Ratios a) Alo:Alos, b) Mno:Mnos, and c) Feo:Feos of the four non-fertilized- (NF) and fertilized (F) studied soils. Plotted values are means of triplicate samples. EH: Entic Haplustoll; TH-I: Typic Hapludoll I; TH-II: Typic Hapludoll II; TA: Typic Argiudoll. *Indicates significant differences ($P < 0.05$) between fertilization treatments within each soil.

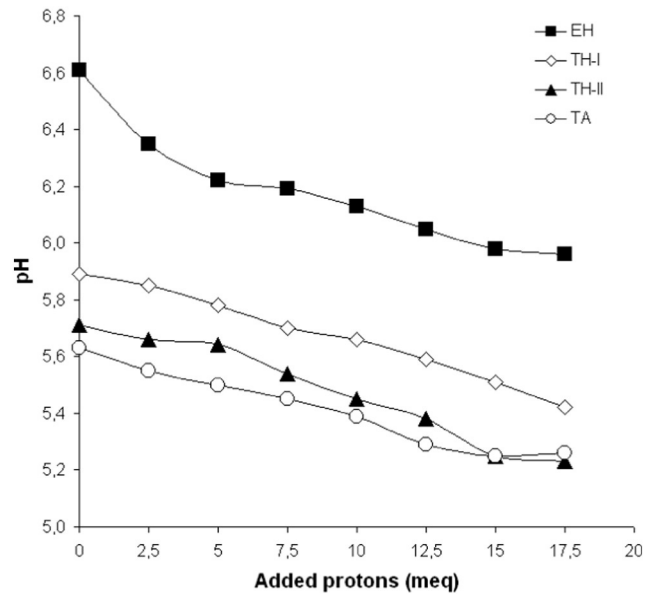


Fig. 3. Neutralization curves of the four NF studied soils. EH: Entic Haplustoll; TH-I: Typic Hapludoll I; TH-II: Typic Hapludoll II; TA: Typic Argiudoll.

It remains uncertain if the increase of Alo in fertilized and more acidified soils of the driest extreme of the climosquence is a product of the denaturalization of crystalline clay minerals, the accelerated transformation of volcanic glasses, or the superimposed effect of both processes.

3.2. Soil buffer capacities

Considering that N-fertilization is a management practice that will continue in the future in the studied region, it is important to know how soils can react against future H^+ inputs.

The neutralization curves show that pH values of EH decreased rapidly between 0 and 5 meq H^+ (slope -0.064). After 5 meq H^+ , pH changes were less pronounced (slope -0.026). The first part of the buffering curve can be attributed to the reaction of free lime (Table 3). The dissolution of this substance defines a fast-kinetic reaction against proton addition and determines soil pH values between 6.0 and 7.0, approximately (Sparks, 2000). However, according to these results, some other substances can buffer the H^+ addition in EH, because the dissolution reaction of free lime is not a so energetic neutralizing source as to explain completely the buffer properties of EH. Once free lime was neutralized, the major acid neutralizing capacity of the EH may be related to its fine textural fractions (Table 3). Such fractions are dominated by 2:1 minerals, not only in the clay- but also in the silt fraction (Iturri and

Table 4
Mineral composition of the clay fraction of the fertilized- (F) and unfertilized (NF) soils.

Site		I		Sm		Intergrades		Cl		K		Impurities
						I-Sm						
		%	C	%	C	%	C	%	C	%	C	
EH	NF	40	W	10	-	50	P	T	-	T	-	s:Q,F
	F	55	W	T	-	45	P	T	-	T	-	s:Q,F
TH-I	NF	65	VW	5	P	20	P	5	R	5	W	s:Q,F
	F	40	W	10	P	50	P	T	-	T	-	s:Q,F
TH-II	NF	65	W	T	-	30	P	5	R	T	-	s:Q,F
	F	65	W	5	P	20	P	5	R	5	W	s:Q,F
TA	NF	75	W	5	P	10	P	-	-	10	W	s:Q,F
	F	80	W	T	-	15	P	T	-	5	W	s:Q,F

I: illite; Sm: smectite; I-Sm: illite-smectite intergrade; Cl: chlorite; K: kaolinite; Q: quartz; F: feldspar; C: crystallinity; VW: very well; W: well; R: regular; P: poorly; T: traces; s: scarce; - : quantity below the detection limit of the X-ray diffractometer.

Buschiazzo, 2014) and, moreover, these soils presented the highest content of smectites in their clay fraction. In a former study, Iturri and Buschiazzo (2014) found that those smectites are a possible product of the transformation of the abundant volcanic glass in the parent material. Thus, the acid neutralizing capacity of EH is mainly explained by both free lime and the exchange properties of the high density charged clay minerals accumulated in its finer particle size fractions, clay and silt.

pH values decreased progressively in TH-I and TH-II, until a H⁺ addition of 15 meq (slopes -0.025 for TH-I and -0.031 for TH-II). Above 15 meq H⁺, pH values of TH-I continued to decline (slope -0.034) while in TH-II it remained almost constant above that H⁺ concentration (slope -0.030). However, it is still a question, what would have happened if H⁺ additions continued beyond 17.5 meq; possibly, the pH values of TH-I may have also approached a stable level. Between pH 5.0 and 6.0 the buffer mechanism which seems to prevail is the reaction of the exchangeable cations and, near 5.0, the dissolution of the crystalline Al and Fe compounds (Ulrich, 1986). TH-I and TH-II are both characterized by their low contents of free lime and also of both the mineral- and the organic fractions (Table 3). Moreover, in addition to their low clay and silt contents (Table 3), these mineral fractions are dominated by illitic minerals, which have low capacity for neutralizing H⁺ (Iturri and Buschiazzo, 2014).

In TA, the pH values decreased progressively until an H⁺ addition of 15 meq (slope -0.031 meq H⁺ pH⁻¹). Between 15 and 17.5 meq H⁺ TA presented a relatively small slope (0.006). As mentioned above, at pH values between 5.0 and 6.0 the buffer reactions are due to the exchangeable cations provided by both the mineral and the organic fractions. Near pH 5.0, the buffer capacity is due to the dissolution reactions of the crystalline Al and Fe compounds (Ulrich, 1986).

TA is enriched in fine mineral fractions, clay and silt (Table 3) in which illites predominate (Iturri and Buschiazzo, 2014). Thus, the acid neutralizing capacity of TA seems to be explained on one hand by its high clay and silt contents, though they are of illitic composition, with low buffer capacity, and by the high contents of SOM, on the other (Table 3).

These results indicate that TH-I and HT-II are the soils with less H⁺ neutralizing capacity due their composition. The behavior of these soils against H⁺ additions seems to depend mainly by the system CO₂/H₂O, which is responsible of pH values near 6.0 (Zapata Hernández, 2004) when no more energetic acid neutralizing substances and/or systems prevail.

Eqs. (3) and (4) demonstrate that the contents of SOM, free lime and clay and silt determined pH variations between fertilized and unfertilized soils.

$$\Delta\text{pH}_{\text{W}} = 1.44 - 0.11 \text{ SOM} - 0.39 \text{ CaCO}_3 - 0.01 \text{ c} + \text{s} \\ R^2_{\text{adjusted}} = 0.75; n = 12; P < 0.05 \quad (3)$$

$$\Delta\text{pH}_{\text{KCl}} = 1.03 - 0.05 \text{ SOM} - 0.22 \text{ CaCO}_3 - 0.008 \text{ c} + \text{s} \\ R^2_{\text{adjusted}} = 0.96; n = 12; P < 0.05 \quad (4)$$

The contents of SOM, free lime, clay and silt explain better pH_{KCl} than pH_W changes. Possibly, this may be due to the high variability of pH_W, which depends on factors not considered in the regression equation, for example CO₂ inputs with rains or microbial respiration, and the dissolution of different soil substances (Zapata Hernández, 2004). On the other hand pH_{KCl} is more stable as it depends on few variables acting in the long-term (SOM, free lime and finer size mineral fractions).

Our results indicate that EH shows low acidification risks, due not only to its relatively high initial pH values but its high buffer capacity, conferred mainly by the presence of free lime and smectitic clay minerals. TA shows also low acidification risks, though its pH values are already the lowest. Its buffer capacity seems to depend mainly on both its high contents of SOM and fine mineral fractions, clay and silt. TH-I and TH-II are the soils with the lowest capacity to resist acidification as the presence of all buffering substances in this soil (free lime, SOM and

fine textural fractions) is quite low. Besides this, predominant clays are illites, with low cation exchange capacity.

4. Conclusions

- Differences between pH_W and pH_{KCl} higher than 1.0 in both fertilized- and non-fertilized soils indicate that a general acidification process occurred due to environmental conditions.
- Fertilization produced slight pH decreases in all studied soils, more pronounced in soils with udic water regimes, in agreement with their longer N-fertilization history and higher fertilization doses.
- Fertilized and light acidified soils with ustic water regimes showed less crystalline illites and kaolinites and increases of the amorphous Al oxide forms. The occurrence of amorphous Al oxides can be attributed to either the transformation of phyllosilicates, the weathering of volcanic glasses existing in these soils or by a simultaneous superimposed effect of both processes.
- None of the fertilized and slight acidified soils showed changes in CEC- or in V-values. Apparently, this was due to the relatively high contents of SOM which make a high contribution to CEC.
- Soils of ustic water regimes contain free lime and high density charged clay minerals while soils of udic water regimes have abundant amounts of SOM and finer and illitic clays and silts. Thus, due to their composition, these soils seem to have high capacity to neutralize future H⁺ inputs.
- Soils placed in the mean part of the climosequence (Hapludolls) presented low amounts of buffer substances (SOM and clays and silts, which are illitic). This made them highly susceptible to acidification in the future.

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