



# Agricultural loess soils along a climosequence evidenced different susceptibility to acidification by simulated N-fertilization

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## ABSTRACT

Agricultural loess soils of the central region of Argentina show acidification evidences linked to both climatic conditions and N-fertilization. Because of that, simulations to estimate the future acidification trends under continuing N-fertilization, considering the different neutralization capacities of the soils in this region, were performed. An equivalent number of protons to that produced by a constant application of 180 kg urea ha<sup>-1</sup> year<sup>-1</sup> (84 kg N ha<sup>-1</sup> year<sup>-1</sup>) during 1, 10, 30 and 50 years of fertilization, was added to unfertilized topsoil samples of agricultural Haplustolls, Hapludolls and Argiudolls. Mostly proton additions did not modify neither CEC nor the contents of both amorphous and crystalline Al, Mn and Fe oxides. However, the Hapludolls, located in the transition zone of the climosequence, showed decreases in their phyllosilicates crystallinity with the most acidifying treatments equivalent to 30 and 50 years of N-fertilization. This effect was less pronounced in those soils placed in both the driest (Haplustolls) and the moist (Argiudolls) environments, due to the amount and composition of the substances and/or systems with acid neutralizing capacity that prevailed. Thus, the Haplustolls were the less affected soils by acidification due to their high amount of free lime-and soil organic matter (SOM) as well as the smectitic mineralogy of their fine mineral fractions, clay and silt. The Argiudolls were the soils with stronger neutralizing mechanisms given by both their high SOM and fine mineral fractions contents, though illitic. Therefore, the Hapludolls were the most susceptible soils to being acidified if N-fertilization continues, according to the low quantity of SOM and fine mineral fractions of illitic mineralogy. From these results, the development and validation of mathematical models were assessed in order to predict the soil buffer capacity and the future pH of the soils. The soil buffer capacity was explained 78% by both the cation exchange and dissolution reactions of minerals accumulated in clays and silts, while pH values were explained 75% by the cation exchange capacity as well as by the SOM, free-lime and clay and silt contents. The pH that the soils would have in the future was predicted with an accuracy of 75% by the outcomes of the simulations, and in a 57% by the pH values of no-tilled and urea fertilized soils.

## 1. Introduction

N-fertilizers are widely used in agricultural systems around the world, particularly in no-tilled soils (Díaz-Zorita et al., 2002; Ruisi et al., 2016). Urea is the N-fertilizer whose use is most widespread in the agricultural loess soils of the central region of Argentina (Montoya et al., 1999; Díaz-Zorita, 2005), where soil acidification was evidenced due to its application (Iturri et al., 2011; Iturri and Buschiazzo, 2016). However, the question prevails on how the chemical and mineralogical properties would evolve over time, under continuous N-fertilizer supply at the current dates.

The use of urea has been extended throughout the cultivated areas in Argentina and in the world (Smil, 2002; Galloway et al., 2008) due to its high nitrogen concentration (46-0-0) (Finck, 1979) as well as its relative low cost. During the nitrification process of urea, per mol of ammonium belonging to each N-amidic, 2 mol of protons are released (Chien et al., 2001; Bouwman et al., 2002). Although other N-fertilizers, such as the ammonium sulfate, have a higher acidity index, this experiment was developed with urea, since it is the most commonly used fertilizer. However, the calculations performed here can be referred to any other N-fertilizer, considering the protons generated during its nitrification.

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pH affects either directly or indirectly some soil properties, influencing plant growth (Malhi et al., 1998; Rice and Herman, 2012). As a result of the acidification, some damaging effects may appear in the soil, such as the depletion of exchangeable calcium and magnesium (Van Breemen et al., 1983; Dubiková et al., 2002) as well as a substantial increase in iron and manganese solubility (Watmough et al., 2007; Rust Neves et al., 2009). When pH decrease is pronounced, an irreversible process of soil degradation occurs, the denaturation of mineral structures, which not only leads to a higher soil acidification, but to the development of some phytotoxicity, due to the release of aluminium from the crystalline structures to the soil solution (Drábek et al., 2005; Lieb et al., 2011). Though soil acidification has been studied in both field and laboratory scale experiments (Gandois et al., 2011; Kopittke et al., 2012), most of these studies were conducted in tropical (Abreu et al., 2003) or forest acidic environments (Amiotti et al., 2000). Considering arable lands, Mollisols are the most widespread soils where agricultural practices are developed, representing 7% and 12% of the ice-free land surface on Earth and Argentina, respectively (FAO, 2004). Besides, these are the soils where N-fertilization is most extended in order to replace the extraction of this nutrient that has been produced as a consequence of several decades of no-till. Thus, Mollisols turn out to be appropriate to study acidification trends by continuous N-fertilization.

In most studies performed in tropical or forest acidic soils, the mineralogy defines the acidity (Vendrame et al., 2013). However, in agricultural soils, a decrease of soil pH would affect the crystallinity of the clay minerals, due to the release of aluminium from the crystalline structures when pH values are below 5.2 (Zapata Hernández, 2004). Moreover, clay minerals can change in short time scales being able to record a rapid clay mineral evolution (Turpault et al., 2008; Iturri and Buschiazzo, 2016). Therefore, to investigate if the input of protons from N-fertilization affects the chemical properties and the clay mineralogy of agricultural soils, laboratory experiments are needed to identify the prevailing buffer mechanisms and to develop a model to estimate the future acidification trends.

In this study we simulated the effect of the input of protons produced by the nitrification of urea on agricultural loess soils located along a climosequence. The aims were: 1. to evaluate the impact of acid loads on the chemical and mineralogical properties of unfertilized no-tilled Mollisols; 2. to identify the prevailing substances and/or systems with acid neutralizing capacity and 3. to develop a mathematical model to estimate the acidification trend of these soils if N-fertilization continues.

## 2. Materials and methods

### 2.1. Studied area and soils

Triplicate samples of the uppermost 20 cm were taken from triplicate no-till and unfertilized 10 m<sup>2</sup> plots at 13 sites of the Central Region of Argentina. All the studied plots belonged to experimental stations of the National Institute for Agricultural Technology (INTA) and the Regional Consortium of Agricultural Experimentation (CREA), where controlled long-term conservative tillage has been developed. The main characteristics of the sampled soils and their management practices are shown in Table 1.

All the studied soils classified as Mollisols (Soil Survey Staff, 1999), evolving in a vast range of climatic conditions, from semiarid to humid, as follows: four Haplustolls (1. EH-I, 2. OH, 4. TH-I and 5. EH-II), three Hapludolls (3. TH-i, 7. TH-ii and 10. TH-iii) and six Argiudolls (6. TA-I, 8. TA-II, 9. AA, 11. TA-III, 12. TA-IV and 13. TA-V) (Table 1). All soils developed on the same parent material, namely loess-like sediments, of pleistocenian and holocenian ages which contain variable amounts of volcanic glasses, accumulated during the frequent volcanic eruptions that occurred during these periods (Teruggi, 1957; Buschiazzo, 1988; Zárate, 2003). One of the last volcanic events happened in 1932, when

the eruption of the Andes-Quizapu volcano deposited a 10 cm-thick ash layer along a 1000 km-long W-E oriented area in the semiarid Pampas of Argentina (Larsson, 1936). Because of the transportation of aeolian materials by winds of different energies and the deposition of variable amounts of different dense minerals at different depths (Buschiazzo and Taylor, 1993), the mineralogy of this parent material is qualitatively but not quantitatively homogeneous. Thus, soils of the driest extreme of the sampled climosequence contain some amounts of volcanic glass, while those of the more humid extreme are volcanic glass free soils (Iturri and Buschiazzo, 2014).

### 2.2. Soil characterization

To perform a preliminary characterization of the soils, we determined the following properties in air-dried and sieved (< 2 mm) soil samples by triplicate:

- pH in both deionized water (pH<sub>w</sub>) and KCl 1 eq dm<sup>-3</sup> (pH<sub>KCl</sub>) (1:2.5 soil:liquid in both) (Page, 1982),
- the soil organic matter (SOM) content by wet digestion (Walkley and Black, 1934), and
- the free-lime content (expressed as calcium carbonate, CaCO<sub>3</sub>) by gasometry (Page, 1982).

In composite soil samples, we determined the particle size distribution by the combined Robinson's pipette and sieving methods (Gee and Bauder, 1986).

### 2.3. Simulated acidification experiment

We simulated the acidification produced by the release of protons during the nitrification of N-fertilizers. For that, we put 25 g of air-dried and sieved through 2 mm soil sample in contact with 75 mL of acid dissolutions, prepared from a 0.1 eq dm<sup>-3</sup> HCl<sub>(aq)</sub> dissolution, which contained 3024, 30,240, 90,720 and 151,200 eq H<sup>+</sup> dm<sup>-3</sup>. According to Finck (1979), the addition of these proton concentrations to each soil sample simulates the fertilization with 180 kg urea ha<sup>-1</sup> (84 kg N ha<sup>-1</sup>) during 1, 10, 30 and 50 years, respectively. A dose of 180 kg urea ha<sup>-1</sup> was chosen because it is the most used dose in no-till soils of the central region of Argentina (Díaz-Zorita, 2005) in order to replace the extraction of N caused by crop production. The resulting soil suspension (1:2.5 soil:liquid) was stirred at 150 rpm, room temperature and darkness, in three periods of 8 h each until 24 h were completed to assure the contact between the phases. The same procedure was performed on soil samples in contact with deionized water (1:2.5 soil:liquid) in order to represent a reference condition, i.e. no proton addition, for each soil. All the procedures were performed by triplicate.

The pH was measured in each soil suspension of both, reference and treatments, before the stirring period and every 8 h until 24 h were completed to assure its stabilization and to monitor its evolution over time (Table A-1). The soil buffer capacity (β<sub>H+</sub>), defined by the slope (the ratio Δn<sub>H+</sub>:ΔpH) of the neutralization curve (Sposito, 1994) was determined in each soil by the simulated acidification, where greater and negative slope values indicate a higher β<sub>H+</sub>.

### 2.4. Variables assessed in the soils resulting from the simulated acidification experiment

Each soil sample resulting from simulations was divided into two sub-samples: one which was dried at 35 °C, to avoid the phyllosilicates denaturation, for its subsequent analysis of some chemical properties, and another one which stayed as suspension, in order to separate its clay particles for X-ray diffraction analysis (XRD).

In the soil samples dried at 35 °C we determined the following properties:

**Table 1**  
Main characteristics of the soils.

Soil	Classification <sup>a</sup>	Geographic location	MAP <sup>b</sup>	MAT <sup>b</sup>	Period of no-till	Crops sequence	Granulometry			SOM	Free-lime
			mm	°C			years	Clay	Silt		
							%			% ± SD	
1. EH-I	Entic Haplustoll	S 36°30' W 64°00'	600	14.5	13	C-W/S	12	23	65	2.5 ± 0.03	1.2 ± 0.02
2. OH	Oxic Haplustoll	S 27°05' W 61°06'	951	20.8	5	S-Sg-Ct-C	21	1	78	2.9 ± 0.04	1.4 ± 0.03
3. TH-i	Typic Hapludoll	S 34°51' W 62°45'	775	16.9	13	C-S-Sf-W	13	23	64	2.8 ± 0.03	0.4 ± 0.02
4. TH-I	Typic Haplustoll	S 26°49' W 64°51'	1000	19.3	20	C-W/S	19	57	24	1.9 ± 0.02	0.4 ± 0.01
5. EH-II	Entic Haplustoll	S 26°34' W 64°50'	785	15.0	10	O-S/W	21	32	47	3.2 ± 0.03	0.7 ± 0.03
6. TA-I	Typic Argiudoll	S 32°43' W 60°60'	900	16.9	5	C-W/S	21	70	9	2.5 ± 0.02	0.1 ± 0.01
7. TH-ii	Typic Hapludoll	S 33°30' W 62°38'	863	16.0	7	C-W/S	17	34	49	2.2 ± 0.01	0.1 ± 0.01
8. TA-II	Typic Argiudoll	S 32°10' W 61°49'	850	15.0	5	C-W/S	28	64	8	3.3 ± 0.02	0.4 ± 0.02
9. AA	Aquic Argiudoll	S 32°38' W 61°20'	850	15.0	9	C-W/S	25	63	12	2.3 ± 0.02	0.1 ± 0.01
10. TH-iii	Typic Hapludoll	S 34°09' W 61°36'	908	15.8	6	C-W/S	14	30	56	1.7 ± 0.03	0.6 ± 0.02
11. TA-III	Typic Argiudoll	S 33°56' W 60°34'	989	16.4	8	C-W/S	21	5	74	3.0 ± 0.04	0.4 ± 0.03
12. TA-IV	Typic Argiudoll	S 33°53' W 61°27'	1100	16.5	12	C-W/S	34	48	18	3.4 ± 0.05	0.6 ± 0.03
13. TA-V	Typic Argiudoll	S 37°45' W 58°18'	932	13.6	18	C-W/S	21	33	46	5.3 ± 0.06	1.0 ± 0.02

MAP: mean annual precipitation; MAT: mean annual temperature; C: corn; W: wheat; S: soybean; Sg: sorghum; Ct: cotton; Sf: sunflower; O: oat; SOM: soil organic matter content; Free-lime: free lime content expressed as calcium carbonate; SD: standard deviation.

<sup>a</sup> Soil Survey Staff (1999).

<sup>b</sup> Servicio Meteorológico Nacional.

- the cation exchange capacity (CEC) by saturation with an 1 eq dm<sup>-3</sup> ammonium acetate dissolution at pH 7 (Rhoades, 1982),
- the aluminium, manganese and iron content from amorphous (Al<sub>o</sub>, Mn<sub>o</sub> and Fe<sub>o</sub>, respectively) and crystalline oxides (Al<sub>c</sub>, Mn<sub>c</sub> and Fe<sub>c</sub>, respectively), were extracted for 2 h with oxalic acid at room temperature and darkness, and for 6 min with boiled oxalic acid, respectively (Schlichting et al., 1985), and their concentrations were quantified by atomic absorption spectrometry (AAS). The ratios between amorphous and crystalline forms (Al<sub>o</sub>:Al<sub>c</sub>, Mn<sub>o</sub>:Mn<sub>c</sub>, Fe<sub>o</sub>:Fe<sub>c</sub>) were then calculated; higher values of these ratios indicate lower crystallinity of these oxides,
- the exchangeable aluminium (Al<sub>ex</sub>) was extracted with a 1 eq dm<sup>-3</sup> KCl dissolution at pH 7 (McLean, 1982) and its concentration was quantified by AAS, and
- the exchangeable acidity, i.e. the acidity corresponding to aluminium and protons (Al<sub>ex</sub> + H<sub>ex</sub><sup>+</sup>), was extracted following the same procedure than for Al<sub>ex</sub>, but its concentration was quantified by titration with a 0.01 eq dm<sup>-3</sup> NaOH dissolution (McLean, 1982). The exchangeable protons (H<sub>ex</sub><sup>+</sup>) were then calculated by difference between both Al<sub>ex</sub> + H<sub>ex</sub><sup>+</sup> and Al<sub>ex</sub>.

From each suspension, clays, i.e. particles with a diameter < 2 μm, were separated and concentrated by centrifugation and syphoning. The settling times were selected according to the methodology provided by Tanner and Jackson (1947). Mineralogical analysis of the clays was performed by X-ray diffraction (XRD). For this determination, a diffractometer with a Cu anticathode (λ = 1.54 Å), operating at 45 kV and 40 mA was used. The angular interval was scanned between 3° and 17° 2θ at 0.02° 1.5 s<sup>-1</sup>. The semi-quantitative determination 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, 1985).

## 2.5. Statistical analysis

A two-way ANOVA and a LSD test were performed, within each studied soil, to test for significant differences in pH values between the acidifying treatments and the reference condition as well as between the treatments. Moreover, between the variables investigated for acid neutralizing capacity (CEC and the contents of SOM, free-lime, clay and silt) of all the samples resulting from the simulation experiment, least-squares simple and multiple linear regression analyses, were performed.

To estimate the future acidification trend of the soils under continuous N-fertilization, we adjusted least-squares multiple linear regression models which considered the prevailing buffer substances and/or systems of each soil. These models included some soil parameters with acid neutralizing capacity deduced in this study and, moreover, in order to predict the pH that the soils would reach, the protons added during the simulations. The validation of the models was performed using both the pH values of the soils resulting from the simulation experiments as well as the pH values of long-term no-till and urea-fertilized paired soils (Table 2), assessed in former studies (Iturri et al., 2011; Iturri and Buschiazzo, 2016).

All mathematical and statistical analysis were performed, respectively, by means of Microsoft Excel/2016 version and the InfoStat/Professional version 1.1 (α = 0.05) (Di Rienzo et al., 2002) programs.

**Table 2**  
Mean pH<sub>W</sub> and pH<sub>KCl</sub> values of no-tilled and urea-fertilized paired soils<sup>a,b</sup>.

Soil	pH <sub>W</sub>	pH <sub>KCl</sub>
1. EH-I	6.5	5.1
2. OH	6.9	6.0
3. TH-i	6.4	5.2
4. TH-I	5.8	5.6
5. EH-II	5.9	5.2
6. TA-I	5.6	4.6
7. TH-ii	5.9	4.8
8. TA-II	5.8	4.7
9. AA	5.8	4.8
10. TH-iii	5.8	4.4
11. TA-III	5.6	4.8
12. TA-IV	5.7	4.7
13. TA-V	5.2	4.3

pH<sub>W</sub>: pH 1:2.5 soil:distilled water; pH<sub>KCl</sub>: pH 1:2.5 soil:1 eq dm<sup>-3</sup> KCl dissolution. Both in McLean (1982).

<sup>a</sup> Paired soils refers to the same no-till soils used in this study but fertilized during the middle-long time with urea.

<sup>b</sup> Both pH<sub>W</sub> and pH<sub>KCl</sub> values are mean of three soil replicates and belong to former studies about soil acidification evidences in no-till and urea fertilized soils of the central region of Argentina. For further details about these studies Iturri et al. (2011) and Iturri and Buschiazzo (2016) can be consulted.

**Table 3**

pH values of the reference condition (no proton addition) and the acidifying treatments simulating a N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup> during 1, 10, 30 and 50 years, in each soil.

Soil	0	1	10	30	50
1. EH-I	6.6 a	6.4 b	6.3 b	6.1 bc	4.9 c
2. OH	6.6 a	6.6 b	6.4 b	6.2 b	5.4 c
3. TH-i	6.2 a	6.2 b	6.0 bc	5.8 c	4.4 c
4. TH-I	6.5 a	6.4 b	6.3 c	6.0 cd	4.4 d
5. EH-II	6.2 a	6.1 b	6.0 bc	5.8 bc	4.8 c
6. TA-I	5.9 a	5.9 b	5.5 c	5.3 d	3.8 d
7. TH-ii	6.0 a	6.0 b	5.8 bc	5.5 c	4.3 c
8. TA-II	6.2 a	6.1 b	6.0 c	5.6 c	4.4 c
9. AA	6.1 a	6.1 b	5.9 bc	5.6 c	4.3 c
10. TH-iii	6.1 a	6.1 b	5.7 c	5.4 d	4.0 d
11. TA-III	6.0 a	5.9 b	5.7 bc	5.5 cd	4.3 d
12. TA-IV	6.1 a	6.2 b	6.2 b	5.9 b	4.7 c
13. TA-V	5.8 a	5.8 b	5.5 bc	5.3 cd	4.3 d

0, 1, 10, 30 and 50 indicate equivalent years of N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup>.

Different lowercase letters indicate, within each soil, significant differences between the acidifying treatments and the reference condition and between the acidifying treatments (LSD test,  $\alpha = 0.05$ ).

Values are mean of three replicates.

### 3. Results

#### 3.1. Impact of acid loads on chemical and mineralogical properties of the soils

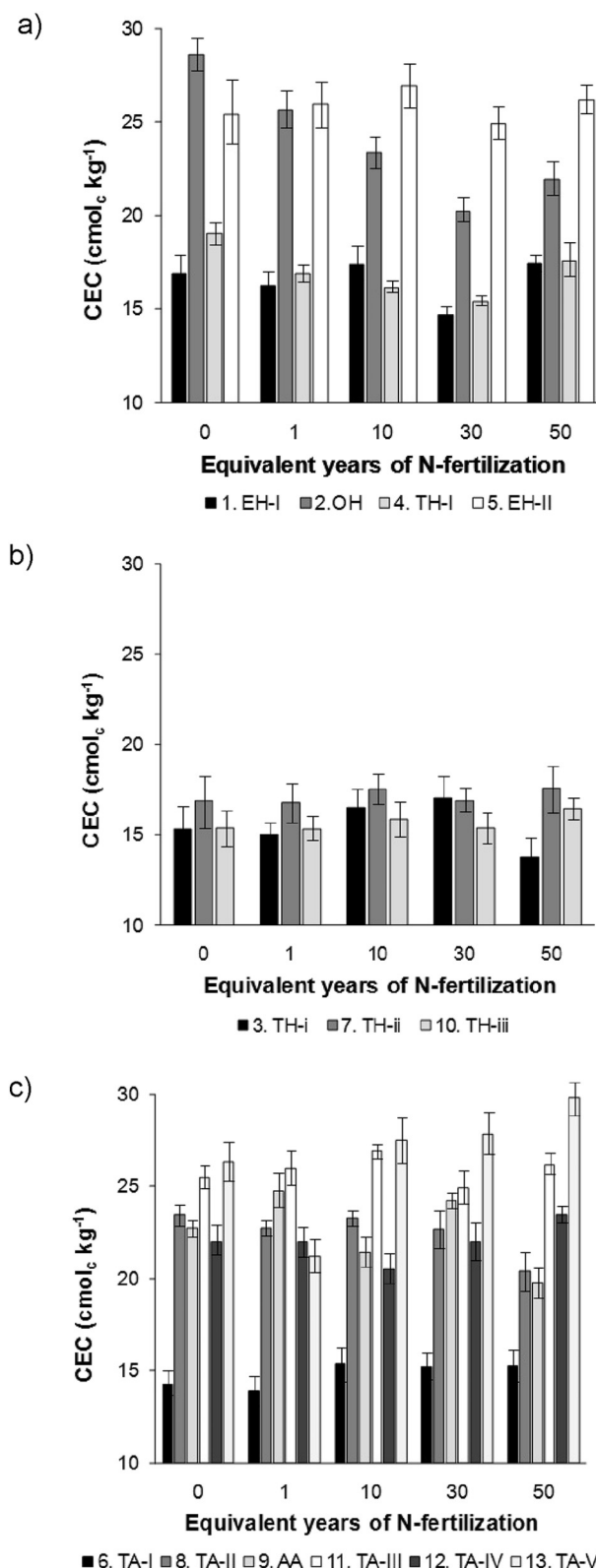
The pH values of the soils in the reference condition (no proton addition) were significantly different ( $p < 0.05$ ) between them, being higher in Haplustolls (mean pH 6.5) than in Argiudolls and Hapludolls (6.0 in both). In general, for all the soils and acidifying treatments, pH decreased with increasing levels of protons added, being the pH values of the acidifying treatments significantly lower ( $p < 0.05$ ) than those of the reference condition (Table 3). Moreover, within each soil, pH values of the acidifying treatments were significantly different ( $p < 0.05$ ) between them (Table 3).

A proton addition equivalent to 1 year of N-fertilization with 180 kg urea ha<sup>-1</sup> significantly decreased ( $p < 0.05$ ) the pH values in all the studied soils (Table 3). Similarly, but with a 10- and 30-year-long simulated N-fertilization, pH values of all the studied soils also decreased significantly ( $p < 0.05$ ), with the exception of the 2. OH and 12. TA-IV, where no significant differences ( $p > 0.05$ ) were registered between these treatments. Finally, in the most acidifying treatment, equivalent to 50 years of N-fertilization, pH values of all the studied soils decreased significantly ( $p < 0.05$ ), being these values higher in Haplustolls (mean pH 4.8) than in Argiudolls (4.3), and these in turn higher than in Hapludolls (4.2).

The pH decreases caused by the acid inputs simulating the proton release from the nitrification of N-fertilizers, generated changes of different magnitude in some chemical and mineral soil properties. When no protons were added, the CEC of Haplustolls and Argiudolls was significantly higher (mean CEC, 22.3 cmol<sub>c</sub> kg<sup>-1</sup> in both;  $p < 0.05$ ) compared to that of Hapludolls (15.7 cmol<sub>c</sub> kg<sup>-1</sup>) (Fig. 1). The CEC of Haplustolls decreased significantly up to 3.0 cmol<sub>c</sub> kg<sup>-1</sup> after the lowest level of proton addition, with a trend to continue decreasing as the treatments became more acidifying, reaching decreases of up to 5.8 cmol<sub>c</sub> kg<sup>-1</sup> (2. OH) (Fig. 1). However, after the same levels of proton addition, the CEC of Hapludolls and Argiudolls remained invariable ( $p > 0.05$ ) (Fig. 1).

The contents of amorphous oxides of Al (Alo, which oscillated between 275 and 1586 mg kg<sup>-1</sup>), Mn (Mno, 156 to 5851 mg kg<sup>-1</sup>) and Fe (Feo, 309 to 3835 mg kg<sup>-1</sup>), as well as those of the crystalline oxides, Alos (2459 to 13,079 mg kg<sup>-1</sup>), Mnos (379 to 903 mg kg<sup>-1</sup>) and Feos (271 to 1722 mg kg<sup>-1</sup>), fluctuated widely between the no acidified soils (Table A-2)

and no trends relating to the increasing levels of protons added were found. Because of that, we analyzed the ratios between the summed amorphous and crystalline forms of these oxides in each of the acidification treatments (Alo + Alos, Mno + Mnos and Feo + Feos) and those of the reference condition (Alo<sub>0</sub> + Alos<sub>0</sub>, Mno<sub>0</sub> + Mnos<sub>0</sub> and Feo<sub>0</sub> + Feos<sub>0</sub>), i.e., Alo + Alos:Alo<sub>0</sub> + Alos<sub>0</sub>, Mno + Mnos:Mno<sub>0</sub> + Mnos<sub>0</sub> and Feo + Feos:Feo<sub>0</sub> + Feos<sub>0</sub>.

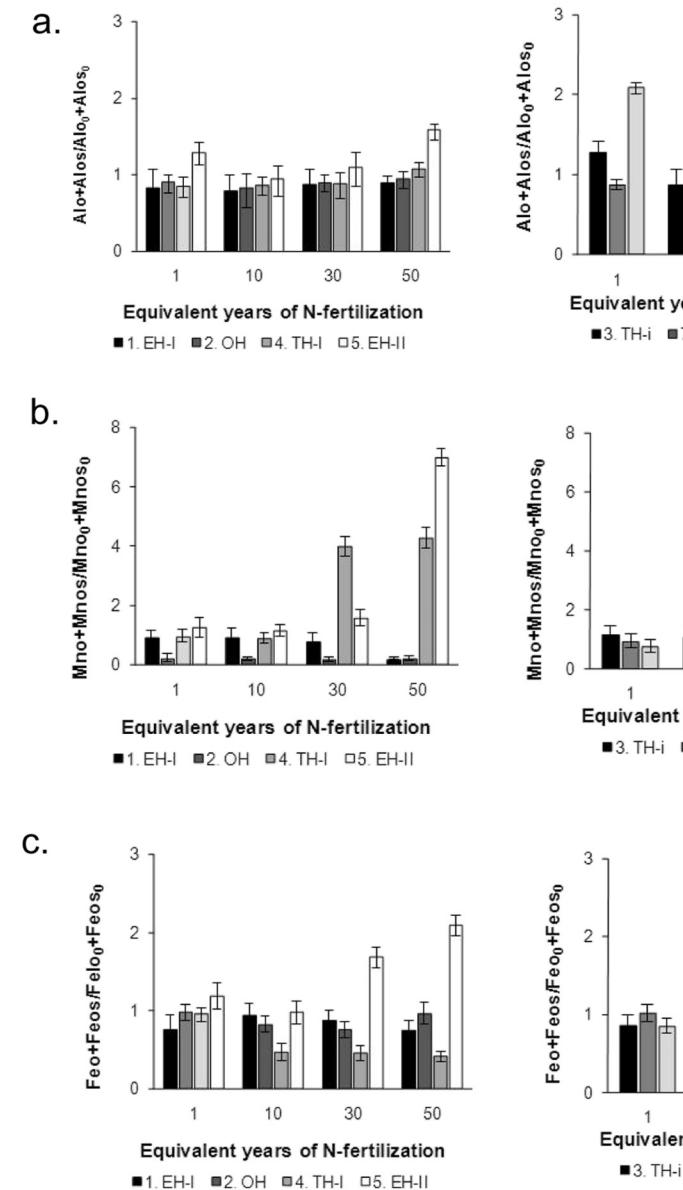
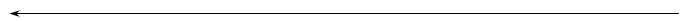


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**Fig. 1.** Cation exchange capacity (CEC) of a) Haplustolls, b) Hapludolls and c) Argiudolls in the reference condition (no proton addition) and the acidifying treatments simulating a N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup> during 1, 10, 30 and 50 years.

0, 1, 10, 30 and 50 indicate equivalent years of N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup>.  
 1. EH-I: Entic Haplustoll I from site 1; 2. OH: Oxic Haplustoll from site 2; 3. TH-i: Typic Hapludoll I from site 3; 4. TH-I: Typic Haplustoll I from site 4; 5. EH-II: Entic Haplustoll II from site 5; 6. TA-I: Typic Argiudoll I from site 6; 7. TH-ii: Typic Hapludoll ii from site 7; 8. TA-II: Typic Argiudoll II from site 8; 9. AA: Aquic Argiudoll from site 9; 10. TH-iii: Typic Hapludoll iii from site 10; 11. TA-III: Typic Argiudoll III from site 11; 12. TA-IV: Typic Argiudoll IV from site 12; 13. TA-V: Typic Argiudoll V from site 13.  
 Values are mean of three replicates.



**Fig. 2.** Ratios between the amorphous and the crystalline a) Al (Alo + Alos:Alo<sub>0</sub> + Alo<sub>s0</sub>), b) Mn (Mno + Mnos:Mno<sub>0</sub> + Mno<sub>s0</sub>) and c) Fe (Feo + Feos:Feo<sub>0</sub> + Feo<sub>s0</sub>) oxides in each of the acidification treatments regarding the reference condition (no proton addition) in Haplustolls, Hapludolls and Argiudolls.

1, 10, 30 and 50 indicate equivalent years of N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup>.

1. EH-I: Entic Haplustoll I from site 1; 2. OH: Oxic Haplustoll from site 2; 3. TH-i: Typic Hapludoll I from site 3; 4. TH-I: Typic Haplustoll I from site 4; 5. EH-II: Entic Haplustoll II from site 5; 6. TA-I: Typic Argiudoll I from site 6; 7. TH-ii: Typic Hapludoll ii from site 7; 8. TA-II: Typic Argiudoll II from site 8; 9. AA: Aquic Argiudoll from site 9; 10. TH-iii: Typic Hapludoll iii from site 10; 11. TA-III: Typic Argiudoll III from site 11; 12. TA-IV: Typic Argiudoll IV from site 12; 13. TA-V: Typic Argiudoll V from site 13.

Values are mean of three replicates.

In most of the soils, the ratios of the acidifying treatments remained similar ( $p > 0.05$ ) to those of the reference condition (Fig. 2), despite the increasing levels of added protons. However, in both the 5. EH-II and the 10. TH-iii, the ratios of Al increased up to 1.5 times, the ratio of Mn up to 4, 7 and 2 times respectively in the 4. TH-I, the 5. HE-II and the 6. TA-I, and the ratio for Fe, 2 times in the 5. EH-II and 2.5 times in the 7. TH-ii, but decreased 1.5 times in 4-TH-I (Fig. 2). A different trend was followed by the 13. TA-V, in which the ratios for the three elements initially increase with the levels of protons added simulating 10 and 30 years of N-fertilization, to then return, in the most acidifying treatment, to values similar to those of the reference condition (Fig. 2).

Fig. 3 shows that the mineralogical composition as well as the crystallinity of the clay fraction of the soils, recorded changes due to the simulated acidification. The clay fraction of the non-acidified 1. EH-I

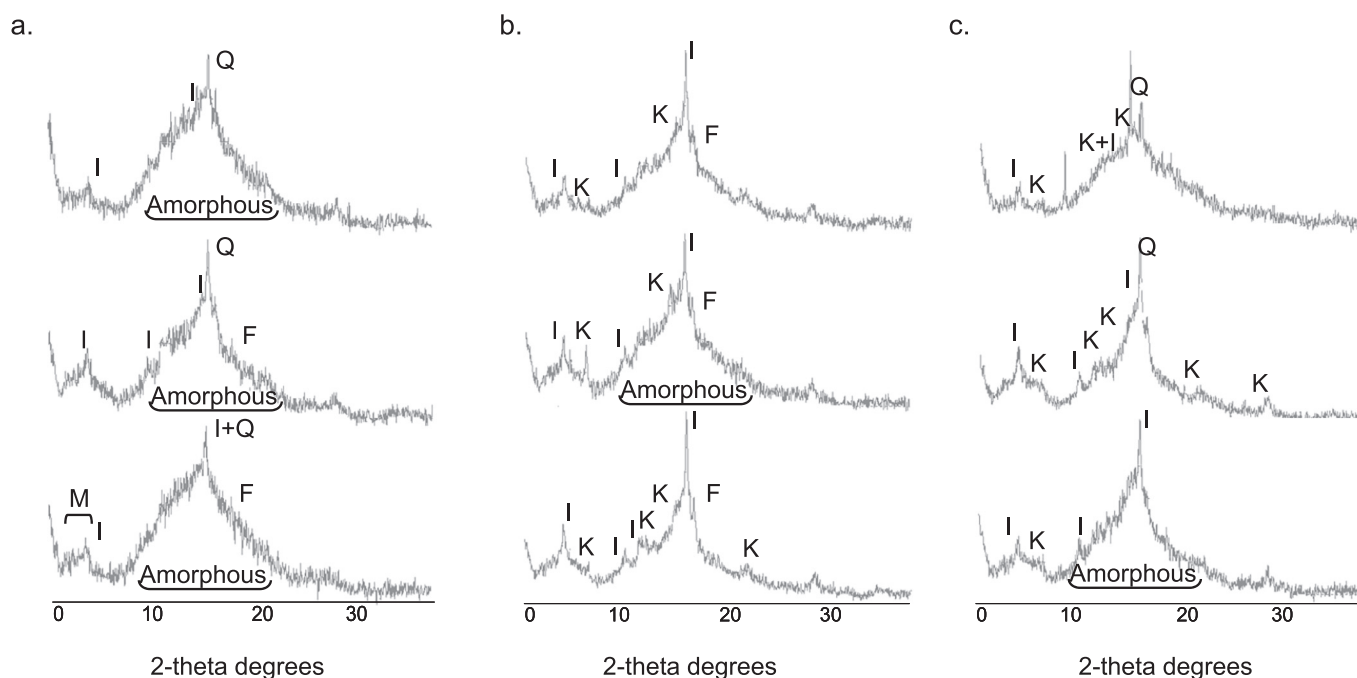


Fig. 3. X-ray patterns of natural oriented clays of a) the Entic Haplustoll of site 1 (1. HE-I), b) the Typic Hapludoll of site 3 (3. HT-i) and c) the Typic Argiudoll of site 11 (11. TA-III). X-ray patterns at the lower, middle and upper part correspond to 0, 10 and 50 years of simulated N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup>. Q: quartz; I: illite; M: montmorillonite; K: kaolinite; F: feldspar; Amorphous: amorphous minerals.

was mainly composed by poorly crystallized illite and montmorillonite as well as some amorphous materials (Fig. 3). After a 10-year-long simulated acidification, poor crystallized illite still prevailed, although in the most acidifying treatment equivalent to 50 years, a lower crystallinity was detected. Illites also predominated in the clay fraction of the 3. TH.i, as well as some subordinated amount of kaolinite (Fig. 3). In comparison to the reference condition, less crystallized illite and kaolinite were detected in its clay fraction as a result of the treatment simulating 10 years of N-fertilization. Moreover, in the 50-year-long simulated acidification, we found wide and devious reflections in the diffractograms, indicating the possible denaturalization of these clay minerals. The clay fraction of the 11. TA-iii was composed mainly by illite and subordinated amounts of kaolinite and amorphous minerals as well. After the simulation of the acidification that may be produced by 10 years of N-fertilization, we still clearly detected a smaller amount of illite and kaolinite than in the reference condition, while in the simulated 50-year-long treatment, less crystallized illite prevailed with some traces of kaolinite. Extremely acute reflections detected at 5.57, 3.54 and 2.88 Å of the diffractogram obtained from the clay fraction of the 11. TA-iii, belong to certain iron and aluminium phosphates.

### 3.2. Soil buffer capacity

In all soils, pH values remained almost constant until a certain addition of protons, above which they decreased sharply (Fig. 4). Additionally, all the soils presented significant differences ( $p < 0.05$ ) in their mean  $\beta_{H+}$ , oscillating from  $-5.5 \cdot 10^5$  to  $-5.1 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup> (Fig. 4), being  $-1.5 \cdot 10^5$  eq kg<sup>-1</sup> pH<sup>-1</sup> the average value for all of them. The  $\beta_{H+}$  mean values were higher in Argiudolls ( $-1.8 \cdot 10^5$  eq kg<sup>-1</sup> pH<sup>-1</sup>) than in Haplustolls ( $-1.5 \cdot 10^5$  eq kg<sup>-1</sup> pH<sup>-1</sup>) and these in turn higher than in Hapludolls ( $-1.1 \cdot 10^5$  eq kg<sup>-1</sup> pH<sup>-1</sup>).

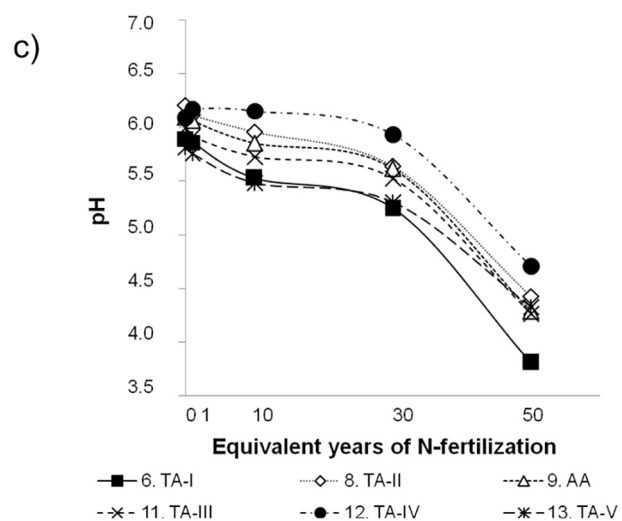
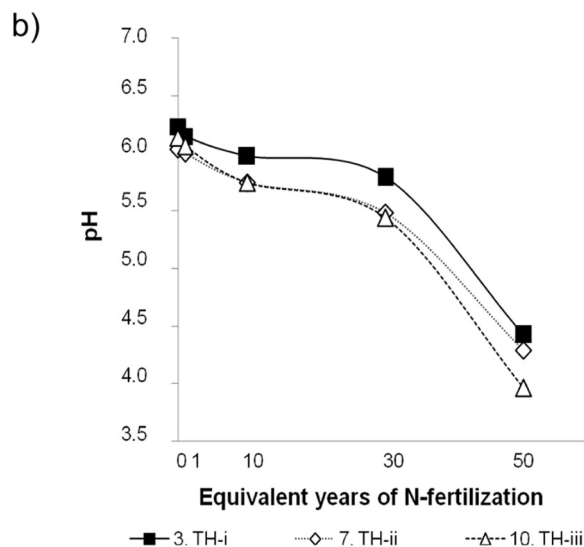
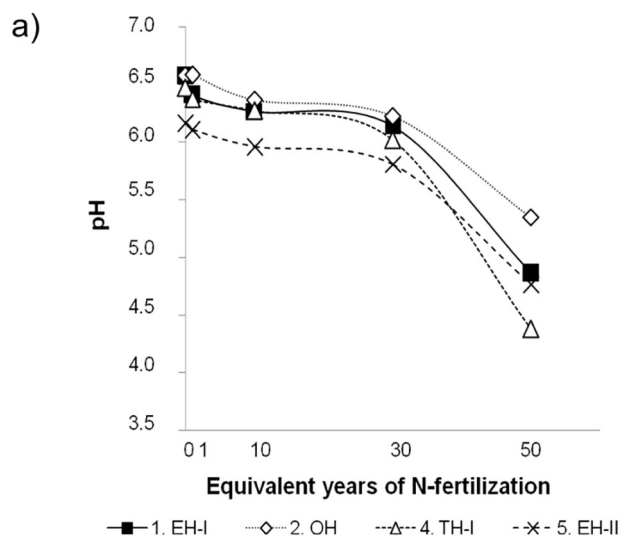
Differences in  $\beta_{H+}$  for each N-fertilization period simulated, i.e. between 0 and 1, 1 and 10, 10 and 30 and 30 and 50 equivalent years, were also significant ( $p < 0.05$ ) in all the soils (Fig. 4). In the range equivalent to up to 1 year of N-fertilization,  $\beta_{H+}$  of the Haplustolls ( $3.1 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup>) was higher than in Argiudolls ( $1.0 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup>), and this in turn higher than in Hapludolls ( $-3.3 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup>) ( $p < 0.05$ ). For the range

representing the period between 1 and 10 years, a different trend was shown by  $\beta_{H+}$ , being that of Argiudolls ( $-4.1 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup>) the highest, compared to that of Haplustolls ( $-1.9 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup>) and Hapludolls ( $-1.2 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup>) ( $p < 0.05$ ). Then, in the two most acidifying periods simulated,  $\beta_{H+}$  followed a similar trend between soils than the one described for the shortest period of up to 1 year. Thus, when a N-fertilization with 180 eq kg<sup>-1</sup> during 30 and 50 years was performed,  $\beta_{H+}$  was significantly higher ( $p < 0.05$ ) in Haplustolls ( $-3.9 \cdot 10^4$  and  $-5.3 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup>, respectively) than in both Argiudolls ( $-2.6 \cdot 10^4$  and  $-4.9 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup>) and Hapludolls ( $-2.5 \cdot 10^4$  and  $-4.5 \cdot 10^4$  eq kg<sup>-1</sup> pH<sup>-1</sup>), being similar ( $p > 0.05$ ) between the last two.

### 3.3. Development of mathematical models for acidification trends estimation

Table 4 shows the results of the regression analysis between the pH values of the soils without proton addition, as well as of their mean  $\beta_{H+}$ , with different substances and/or systems with acid neutralizing capacity (the CEC, SOM, free-lime and clay and silt contents) (Sparks, 2000; Rice and Herman, 2012). We did not find significant correlations ( $p < 0.05$ ) neither for pH nor  $\beta_{H+}$ , when the regression analysis involved all the soils (Table 4). However, pH was significantly explained ( $p > 0.05$ ) by the CEC (80%), the clay + silt- (94%) and the silt content (99%) in Hapludolls, and by the clay content (94%) in the Argiudolls. On the other hand, CEC (68%) and the SOM (53%), clay (94%) and silt (79%) contents contributed to  $\beta_{H+}$  mean in Haplustolls, and the SOM (99%) and clay (74%) contents, respectively, in Hapludolls and Argiudolls.

Considering the greater or lesser influence of those substances and/or systems with acid neutralizing capacity that contributed to the pH and  $\beta_{H+}$ , linear multiple regressions were performed, in order to achieve mathematical models to calculate the acidification susceptibility of agricultural loess soils. Thus, the CEC as well as the SOM, free-lime and the summed and separated clay and silt contents of the non-acidified soils, were determined as the independent variables, while pH and  $\beta_{H+}$ , as dependent variables (Eqs. (1) and (2)):



**Fig. 4.** Neutralization curves arising from the acidification experiment simulating a N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup>, performed in a) Haplustolls, b) Hapludolls and c) Argiudolls.

0, 1, 10, 30 and 50 indicate equivalent years of N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup>.

1. EH-I: Entic Haplustoll I from site 1; 2. OH: Oxic Haplustoll from site 2; 3. TH-i: Typic Hapludoll I from site 3; 4. TH-I: Typic Haplustoll I from site 4; 5. EH-II: Entic Haplustoll II from site 5; 6. TA-I: Typic Argiudoll I from site 6; 7. TH-ii: Typic Hapludoll ii from site 7; 8. TA-II: Typic Argiudoll II from site 8; 9. AA: Aquic Argiudoll from site 9; 10. TH-iii: Typic Hapludoll iii from site 10; 11. TA-III: Typic Argiudoll III from site 11; 12. TA-IV: Typic Argiudoll IV from site 12; 13. TA-V: Typic Argiudoll V from site 13.

Values are mean of three replicates.

**Table 4**

Regression coefficients ( $r^2$ ) between both the pH in the reference condition (no protons addition) and the mean buffer capacity ( $\beta_{H+}$ ) with the contents of substances and/or systems with acid neutralizing capacity, in all the soils.

	N	$r^2$					
		SOM	CEC	Free-lime	Clay + silt	Clay	Silt
<b>pH</b>							
All soils	13	0.195	0.007	0.293	0.100	0.063	0.086
Haplustolls	4	0.341	0.068	0.336	0.175	0.255	0.117
Hapludolls	3	0.341	0.804*	0.414	0.944*	0.175	0.999*
Argiudolls	6	0.215	0.020	0.135	0.174	0.944*	0.088
<b><math>\beta_{H+}</math></b>							
All soils	13	0.011	0.025	0.002	0.068	0.474	0.242
Haplustolls	4	0.527*	0.677*	0.057	0.207	0.945*	0.785*
Hapludolls	3	0.987*	0.077	0.017	0.231	0.038	0.017
Argiudolls	6	0.006	0.000	0.018	0.052	0.743*	0.274

CEC: cation exchange capacity; SOM: soil organic matter content; free-lime: content of free-lime expressed as calcium carbonate.

\* Indicates significant correlations ( $p < 0.05$ ).

$$pH = 6.19 - 0.21 \text{ SOM} + 0.01 \text{ CEC} + 0.46 \text{ free-lime} + 0.001 c + s + 0.001 s + 0.0004 s$$

$$r^2 = 0.753; n = 13; p < 0.05$$

(1)

$$\beta_{H+} = -1.9 \cdot 10^4 + 2.1 \cdot 10^4 \text{ SOM} + 1.9 \cdot 10^4 \text{ CEC} - 1.3 \cdot 10^5 \text{ free-lime} - 2.8 \cdot 10^4 c + s + 3.0 \cdot 10^4 c + 3.0 \cdot 10^4 s$$

$$r^2 = 0.783; n = 13; p < 0.05$$

(2)

being  $pH$  the pH of the soils in the reference condition (no proton addition),  $\beta_{H+}$  the mean buffer capacity, expressed in  $\text{eq kg}^{-1} \text{ pH}^{-1}$ ;  $SOM$  the soil organic matter content, in percent;  $CEC$  the cation exchange capacity, in  $\text{cmol}_c \text{ kg}^{-1}$ ;  $free-lime$  the free-lime content expressed as calcium carbonate, in percent;  $c + s$  the summed clay and silt content, in percent;  $c$  the clay content, in percent; and,  $s$  the silt content, in percent.  $SOM$  content (negatively) and the presence of certain amounts of free lime (positively), were the parameters which better explained  $pH$ , while  $CEC$ ,  $SOM$  and both summed and separated clay and silt content (positively), were those which better explained  $\beta_{H+}$ .

Furthermore, a linear multiple regression to predict the final pH values of the soils after the proton input generated during the nitrification of N-fertilizers, was performed (Eq. (3)). This model indicated, similarly to Eqs. (1) and (2), the influence of  $CEC$  and the  $SOM$ , free lime, summed and separated clay and silt contents, as well as of the added protons (independent variables), on the  $pH$  (dependent variable) values of all soils:

$$pH = 6.19 - 0.21 \text{ SOM} + 0.01 \text{ CEC} + 0.46 \text{ free-lime} + 0.001 c + s + 0.001 c + 0.0004 s - 2.45 \cdot 10^{-8} H^+$$

$$r^2 = 0.7553; n = 65; p < 0.05$$

(3)

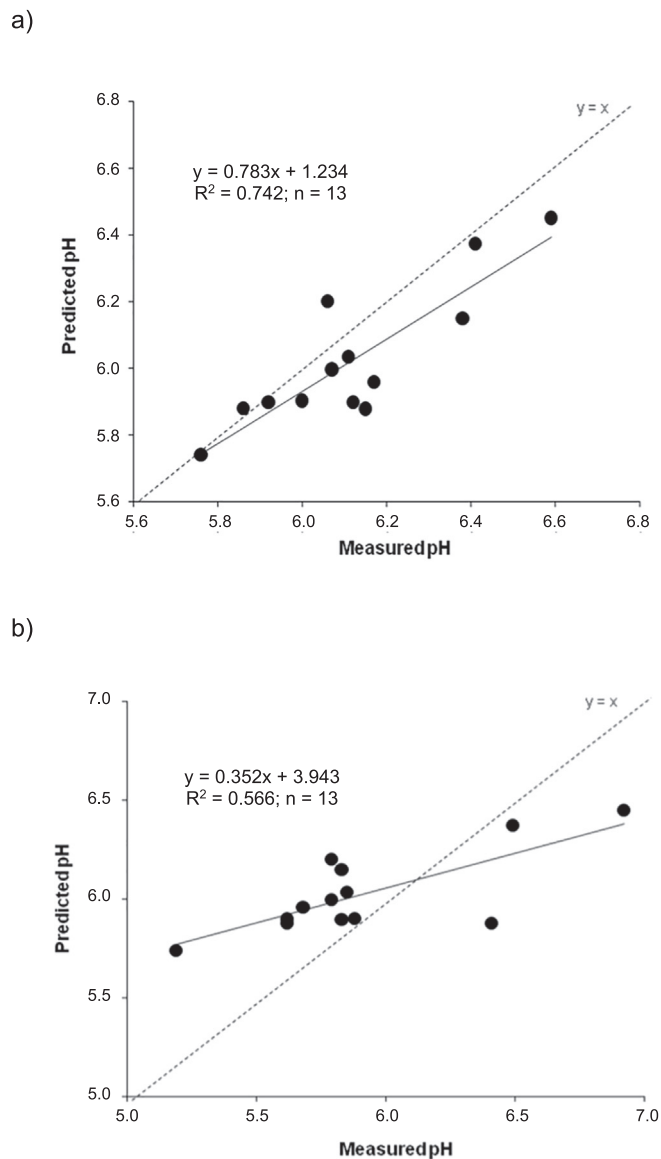


Fig. 5. Linear regressions between pH predicted by the model and a) pH measured after the simulated acidification performed on non-fertilized soils, and b) pH measured in urea-fertilized no-till paired soils. In all cases  $\alpha = 0.05$ .

being  $pH$  the pH of the soil after the different levels of protons added simulating the fertilization with  $180 \text{ kg urea ha}^{-1}$  during 1, 10, 30 and 50 years;  $SOM$  the soil organic matter content, in percent;  $CEC$  the cation exchange capacity, in  $\text{cmol}_c \text{ kg}^{-1}$ ;  $free\text{-lime}$  the calcium carbonate content, in percent;  $c + s$  the summed clay and silt content, in percent,  $c$  the clay content, in percent; and,  $s$  the silt content, in percent. Besides, this model was performed considering the number of protons added ( $H^+$  in Eq. (3), expressed in  $\text{eq H}^+$ ) in all the acidification treatments and for all the soils.

The model was validated with the pH values of the soils that resulted from the simulations, explaining 74% of pH variations (Fig. 5). Besides, the pH values of soils fertilized with urea during the long-time (Table 2; Iturri et al. (2011), Iturri and Buschiazzo (2016)) were used, explaining 57% of pH variations (Fig. 5).

#### 4. Discussion

The higher pH values of Haplustolls compared to those of Hapludolls and Argiudolls, would be explained by their higher content

of free-lime (Table 1), whose presence in the uppermost soil layer has been described for soils of the semiarid region of Argentina (Buschiazzo, 1988; Iturri and Buschiazzo, 2016). Further, the pH decreases of different magnitude found due to the same levels of protons added, showed the distinct responses that the soils have (Table 3; Fig. 4), in agreement with results described for different regions (Bowman and Cleveland, 2008; Cai et al., 2017). Moreover, some chemical and mineralogical properties of the soils registered some changes as a consequence of these pH decreases.

The higher CEC of the no acidified Haplustolls and Argiudolls compared to Hapludolls was given by their finer texture and higher SOM content (Table 1). As the treatments became more acidifying, the CEC of Haplustolls decreased, though it remained constant in Hapludolls and Argiudolls (Fig. 1). The decline of the CEC of the Haplustolls can be a consequence of the denaturation of mineral structures that proton addition may have produced (Barak et al., 1997; McGahan et al., 2003). Because of that, the ratios between the amorphous and the crystalline oxides of Al, Mn and Fe were used as indexes of the degree of denaturation of the mineral structures (Fig. 2), due to the amorphous form increases while the crystalline structures decrease as a result of the addition of protons (Hell and Stephan, 2003; Drábek et al., 2005; Rust Neves et al., 2009). In general, neither increases in the contents of amorphous oxides of Al, Mn and Fe nor decreases in the crystalline structures due to increasing levels of protons added were found (Fig. 2). Despite the acidification did not generate significant changes in the crystalline structures of most of the soils, the increasing ratios found mainly in the 5. EH-II and 7. TH-ii after the most acidifying treatments (30 and 50 years of N-fertilization), indicate evidences of an enrichment in the amorphous form. Thus, the crystalline structures of these oxides would have denaturated as a consequence of proton addition, leading to an increase in their amorphous structures. Results found for the 7. TH-ii may be explained because of the absence of mechanisms of response to proton addition, according to its low SOM and fine fractions contents (Table 1), while those for the 5. EH-II did not agree with its high contents of SOM and fine fractions, clay and silt (Table 1). The exceptional trend found for the ratios between the amorphous and the crystalline oxides of Al, Mn and Fe of the 13. TA-V, seem to be caused by their total transformation after the highest level of protons added simulating 50 years of N-fertilization with  $180 \text{ kg urea ha}^{-1} \text{ year}^{-1}$  (Uehara and Gillman, 1981; Sposito, 1989). These results agreed with the outcomes of the X-ray diffraction analysis of the acidified soils. Clay minerals of the Hapludolls showed the greatest depletion of their crystallinity compared to those of Haplustolls and Argiudolls. Even in the treatment equivalent to 10 years of simulated N-fertilization, the clay minerals of Hapludolls showed a clear depletion of their crystallinity to continue decreasing as the treatments became more acidifying. On the other hand, the clay minerals of Haplustolls and Argiudolls only exhibited changes in their crystallinity when they were submitted to the highest level of proton addition (Fig. 3). Furthermore, quartz and feldspar were recognized in all clay samples, being their reflections more intense, and minor the reflections of clay minerals, as the levels of protons increased. The iron and aluminium phosphates detected in the 11. TA-III can be explained by their precipitation in acid conditions (Dixon et al., 1985).

The different soil responses to the same levels of protons added were possible to explain through the neutralization curves, since they allowed identifying which substances and/or systems with acid neutralizing capacity prevailed in each soil. According to the amount and composition of these buffering species, the soils behaved different in each N-fertilization period simulated (Fig. 4). In the period of up to 1 year, the higher  $\beta_{H^+}$  of Haplustolls compared to those of Argiudolls and Hapludolls, would be explained by the dissolution of the free-lime (Table 1), accordingly to results found by Yang et al. (2012), which demonstrated that free-lime supplies the primary buffering capacity in loess-like soils developing in the semi-arid regions. This is because the presence of free-lime in the soil defines a fast-kinetic reaction to the



addition of protons (Sparks, 2000), determining pH values between 6.5 and 7.0, approximately. In the period between 1 and 10 years, the Argiudolls showed the highest  $\beta_{H+}$ , which may be due to both the cation exchange reactions and the dissolution of organo-metallic complexes (Vázquez et al., 2009; Weaver et al., 2004; Zapata Hernández, 2004). Thus, the greater acid neutralizing capacity of the Argiudolls compared to Haplustolls and Hapludolls, can be attributed to their high SOM and fine mineral fractions contents, which are known to contribute in a high proportion to their CEC (Iturri and Buschiazzo, 2014). In the periods between 10 and 30 years and 30 to 50 years, the buffering systems that prevailed were explained by the different composition of the clay minerals of the clay and silt fractions of the soils, defining a slow kinetic reaction (Porta Casanellas et al., 1999; Sparks, 2000; Zapata Hernández, 2004). In these two N-fertilization periods simulated, the highest  $\beta_{H+}$  of the Haplustolls was due to the mainly smectitic composition of their fine mineral fractions, while they are predominantly composed by illites in Hapludolls and Argiudolls (Fig. 3). Even though the  $\beta_{H+}$  of Argiudolls and Hapludolls behaved similarly in the period between 10 and 30 years (Fig. 4), in the most acidifying treatment, the higher  $\beta_{H+}$  of Argiudolls compared to that of Hapludolls (Fig. 4) would be explained by their higher amount of illitic fine mineral fractions. Therefore, the same input of protons that completely saturated the negative charges of the illites in Hapludolls, did it partially in Argiudolls.

Thus, the Argiudolls were the soils with the highest content of acid neutralizing substances according to their high SOM and illitic fine mineral fractions contents (Table 1, Fig. 3). Though the Haplustolls contain less SOM and fine mineral fractions compared to Argiudolls, the presence of free-lime (Table 1) and mainly smectitic clay minerals (Fig. 3) seems to contribute to their relatively high  $\beta_{H+}$ . The Hapludolls were the soils with the lowest contents of substances and/or systems with acid neutralizing capacity, due to the smallest amount of SOM and fine mineral fractions of illitic mineralogy (Table 1). Therefore, the response of the studied Hapludolls to the increasing levels of proton added may be mostly explained by the  $\text{CO}_2/\text{H}_2\text{O}$  buffer system. The dissolution of  $\text{CO}_2$  occurs in all soils, defining pH values near 6.0 when no other substances and/or systems with acid neutralizing capacity prevail (Zapata Hernández, 2004).

From the analysis of the three sets of soils (Haplustolls, Hapludolls and Argiudolls) it was possible to distinguish the quantitative contribution to both pH and  $\beta_{H+}$ , of the substances and/or systems that defined the different responses that the soils had to the acid addition (CEC, SOM, free-lime and/or clay and silt contents) (Table 4). The pH was not explained by SOM contents (Table 4), being the weak correlations found explained, on the one hand, by the relation between the amount of humified material and soil texture. Therefore, because the higher the content of fine mineral fractions, clay and silt, the higher the proportion of humified compounds (Galantini et al., 2004), is that the use of the total SOM in this study, may have included an additional source of variation. On the other hand, Hevia et al. (2003) found that significant relations between pH values and SOM exist for soils similar to the soils studied here. So, the weak correlation found would also be explained by the reduced number of soils from different climatic environments used and, therefore, with diverse levels of SOM in their topsoils (Table 1). However, the contribution of the SOM content to the  $\beta_{H+}$  in both Haplustolls and Hapludolls was significant (Table 4). Therefore, not only the humified material of SOM contributed to pH (Hevia et al., 2003) but also to  $\beta_{H+}$ . Additionally, since the lower content of SOM of Hapludolls ( $p < 0.05$ ) compared to Haplustolls and Argiudolls (Table 1), the significance of the linear regression for these soils adjusted with  $n = 3$ , could be overestimated, and the assessment of the composition of their SOM would serve to support their  $\beta_{H+}$ . Moreover, the exchange properties of the clay and silt fractions of Haplustolls contributed to the  $\beta_{H+}$  (Table 4) because of their predominantly smectitic composition though their low proportion (Table 1). On the other hand, results from the regression analysis

performed using the content of silt showed that in the Argiudolls was their high proportion not its mineralogical composition, mainly illitic, which contributed to their acid neutralizing capacity, agreeing with former results of Iturri and Buschiazzo (2014) for similar soils.

Neither pH nor  $\beta_{H+}$  were explained by the contribution of free-lime (Table 4), although the high pH values found in the Haplustolls agreed with the presence of some higher amounts of free-lime compared to Hapludolls and Argiudolls (Table 1). However, Yong et al. (1990) reported that the presence of calcium carbonate confers illites a higher buffer capacity than both illites in their natural state and smectites, by the increase of their sorption capacity. Thus, not only would the smectitic clay minerals in the fine mineral fractions of these soils have contributed to their acid neutralizing capacity, but the increase of the exchange properties of the illitic minerals by the free-lime.

Considering the different magnitude contributions of the buffering species, we developed linear multiple regressions to estimate the susceptibility to acidification of agricultural loessic soils, due to continuous N-fertilization at similar doses and frequencies to those used currently (Eqs. (1) and (2)). These models demonstrated that, since pH was determined mainly by the exchange reactions of SOM and the dissolution reactions of free-lime, the lower SOM and higher free-lime contents, the greater the pH. Therefore, the highest pH values were found in Haplustolls compared to Hapludolls and Argiudolls (Table 3). On the other hand, since  $\beta_{H+}$  was defined by the cation exchange and mineral dissolution reactions of the clay and silt fractions, the higher their proportion and/or the greater their cation exchange capacity, the higher the buffer properties. This agreed with the higher acid neutralizing capacity found in both Haplustolls and Argiudolls compared to Hapludolls. Furthermore, the pH of the soils was better predicted by the model (Eq. (3)) when the validation was performed with the number of protons equivalent to the pH measured in the soils after the simulated N-fertilization, than when they were calculated from the pH values of the no-till and urea-fertilized soils assessed in former studies (Iturri et al., 2011; Iturri and Buschiazzo, 2016) (Fig. 5). The model (Eq. (3)) underestimated the predicted pH values when the pH measured in the soils after the simulation experiment was higher. On the other hand, when the pH values measured in no-till and urea-fertilized soils were lower, the effect of proton input was overestimated by the model, but it was underestimated when the pH was high. Possibly, some other effects not considered in this experimental approach developed to understand the acidification due to N-fertilization, such as the proton input by rainfall (Cai et al., 2017; Iturri et al., 2011; Rice and Herman, 2012), are also contributors to the acidification process of these soils.

## 5. Conclusions

- The studied Haplustolls, Hapludolls and Argiudolls reacted differently to the same additions of protons.
- In general, the simulated acidification did not modify the CEC of the soils, but some evidences of denaturalization of clay minerals and crystalline Al, Mn and Fe oxides were found in all the Hapludolls as well as in the most acidified Haplustolls and Argiudolls.
- The most susceptible soils to acidification would be those with low SOM content, coarse texture and predominantly illitic clay minerals.
- If the N-fertilization continues, the Hapludolls would be the most susceptible soils to acidification, since their lower capacity to resist changes in pH, due to their small contents of SOM and illitic fine mineral fractions.
- Even though the Argiudolls are the most acidified nowadays, these are also the soils with more substances and/or systems to resist pH decreases due to proton inputs, because of their high contents of SOM, clay and silt.
- The Haplustolls receive the smallest inputs of protons as a consequence of the smaller doses of N-fertilizers supplied. Moreover, their relative high buffering properties were due to both some relatively high amounts of free-lime and smectitic mineral fractions.

Therefore, if the current trends in N-fertilization continue, the Haplustolls will show the lowest susceptibility to acidification.

- Management practices that reduce SOM contents would affect more the Argiudolls. On the one hand, pH increases would be generated in consequence but, on the other hand, the variable charges would decrease, declining the soil buffer capacity.

### 5.1. Methodological conclusions

- The simulation procedures performed were partially representative of the dose of N-fertilizers that the Haplustolls could receive in the mid to long term. So, possibly, the reaction generated in this study by the addition of different levels of protons, may have been too intense and little representative of the real conditions that these soils can experience in the future. However, this fact did not modify the observed results, as the Haplustolls resulted to be the least susceptible soils to acidification.
- The simulation experiments were performed by the addition of protons belonging to the total dissociation of a strong acid, but not

from a N-fertilizer. Because of that, the kinetics experienced and described in this study, are not strictly the same that can occur due to fertilization. If N-fertilizers would have been used, on the one hand, the reaction would have been had slower kinetics because of the functional groups involved and, on the other hand, the pH decreases would have been smaller than the ones experienced by the simulated acidification.

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## Appendix A

Table A-1

Soil pH evolution during the 24 h-stirring period of the simulation experiment performed. Linear regressions parameters (b: slope; a<sub>1</sub>, a<sub>2</sub> and a<sub>3</sub>: intercepts corresponding to the range between 0 to 8, 8 to 16 and 16 to 24 h-stirring period) between pH and the stirring time for each level of protons added.

Soil	Linear parameter	0	1	10	30	50
1. EH-I	b = pH <sub>0</sub>	6.5	6.4	6.2	5.8	3.8
	a <sub>1</sub> = (pH <sub>8</sub> -pH <sub>0</sub> )/(8-0)	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub> = (pH <sub>16</sub> -pH <sub>8</sub> )/(16-8)	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub> = (pH <sub>24</sub> -pH <sub>16</sub> )/(24-16)	0.0	0.0	0.0	0.0	0.0
2. OH	b = pH <sub>0</sub>	6.6	6.6	6.3	6.0	4.7
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
3. TH-i	b = pH <sub>0</sub>	6.2	6.0	5.8	5.3	3.4
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
4. TH-I	b = pH <sub>0</sub>	6.5	6.4	6.4	5.8	3.8
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
5. EH-II	b = pH <sub>0</sub>	6.2	6.0	5.9	5.6	4.2
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
6. TA-I	b = pH <sub>0</sub>	5.7	5.6	5.2	4.8	3.2
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
7. TH-ii	b = pH <sub>0</sub>	5.9	5.9	5.6	5.1	3.4
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
8. TA-II	b = pH <sub>0</sub>	5.8	5.8	5.5	5.1	3.4
	a <sub>1</sub>	0.0	0.0	0.0	0.1	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
9. AA	b = pH <sub>0</sub>	5.9	5.8	5.5	5.0	3.3
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0

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Table A-1 (continued)

Soil	Linear parameter	0	1	10	30	50
10. TH-iii	b = pH <sub>0</sub>	6.0	5.8	5.5	4.8	3.0
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
11. TA-III	b = pH <sub>0</sub>	5.7	5.7	5.4	4.9	3.3
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
12. TA-IV	b = pH <sub>0</sub>	5.7	5.7	5.6	5.1	3.3
	a <sub>1</sub>	0.1	0.1	0.1	0.1	0.2
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0
13. TA-V	b = pH <sub>0</sub>	5.7	5.6	5.3	4.9	3.6
	a <sub>1</sub>	0.0	0.0	0.0	0.0	0.1
	a <sub>2</sub>	0.0	0.0	0.0	0.0	0.0
	a <sub>3</sub>	0.0	0.0	0.0	0.0	0.0

pH<sub>0</sub>: pH value at the beginning of the 24 h-stirring period; pH<sub>8</sub>, pH<sub>16</sub> and pH<sub>24</sub>: pH value after 8, 16 and 24 h-stirring period; 0, 1, 10, 30 and 50 indicate equivalent years of N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup>.

1. EH-I: Entic Haplustoll I from site 1; 2. OH: Oxic Haplustoll from site 2; 3. TH-i: Typic Hapludoll I from site 3; 4. TH-I: Typic Haplustoll I from site 4; 5. EH-II: Entic Haplustoll II from site 5; 6. TA-I: Typic Argiudoll I from site 6; 7. TH-ii: Typic Hapludoll ii from site 7; 8. TA-II: Typic Argiudoll II from site 8; 9. AA: Aquic Argiudoll from site 9; 10. TH-iii: Typic Hapludoll iii from site 10; 11. TA-III: Typic Argiudoll III from site 11; 12. TA-IV: Typic Argiudoll IV from site 12; 13. TA-V: Typic Argiudoll V from site 13.

Values are mean of three replicates.

Table A-2

Amorphous (Alo, Mno and Feo) and crystalline (Alos, Mnos and Feos) oxides of Al, Mn and Fe, and exchangeable aluminium and protons (Al<sub>ex</sub> and H<sub>ex</sub><sup>+</sup>) contents in the reference condition (no proton addition) and the acidifying treatments simulating a N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup> during 1, 10, 30 and 50 years.

Soil	Alo				
	mg kg <sup>-1</sup>				
	0	1	10	30	50
1. EH-I	1586	1788	1800	1800	2133
2. OH	275	525	275	262	240
3. TH-i	304	866	1051	1114	1103
4. TH-I	745	510	637	469	619
5. EH-II	1286	1659	1286	1782	1617
6. TA-I	456	469	601	469	469
7. TH-ii	793	650	625	465	322
8. TA-II	532	563	809	771	793
9. AA	542	303	548	569	575
10. TH-iii	316	1075	1325	1486	1486
11. TA-III	1216	1005	1286	1250	1075
12. TA-IV	767	775	520	745	775
13. TA-V	1059	1122	1122	1300	1111

Soil	Mno				
	mg kg <sup>-1</sup>				
	0	1	10	30	50
1. EH-I	4688	4422	4293	3400	297
2. OH	3478	350	3791	304	289
3. TH-i	259	261	259	213	265
4. TH-I	377	346	329	2958	3156
5. EH-II	258	272	246	310	3349
6. TA-I	5851	6216	6093	671	684

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Table A-2 (continued)

Soil	Mno				
	mg kg <sup>-1</sup>				
	0	1	10	30	50
7. TH-ii	268	240	242	233	229
8. TA-II	5455	5967	6212	6181	6573
9. AA	593	621	609	680	678
10. TH-iii	265	185	178	225	203
11. TA-III	415	388	393	403	400
12. TA-IV	364	365	362	370	376
13. TA-V	156	215	202	210	214
Soil	Feo				
	mg kg <sup>-1</sup>				
	0	1	10	30	50
1. EH-I	3835	2523	3815	3346	2809
2. OH	309	332	246	243	269
3. TH-i	2907	2382	2249	2083	1306
4. TH-I	327	326	299	204	233
5. EH-II	2522	2702	2341	3844	3578
6. TA-I	1655	1787	2223	2164	2080
7. TH-ii	364	634	402	195	2481
8. TA-II	2214	2231	1893	1751	1636
9. AA	1442	1858	1784	1571	1299
10. TH-iii	2098	1477	2598	2319	1658
11. TA-III	1526	1162	1751	1217	963
12. TA-IV	1418	1658	1507	1507	1545
13. TA-V	3629	4210	3412	3815	3510
Soil	Alos				
	mg kg <sup>-1</sup>				
	0	1	10	30	50
1. EH-I	12,092	9640	9000	10,256	10,159
2. OH	2995	2451	2451	2694	3090
3. TH-i	12,850	15,931	10,417	11,250	13,480
4. TH-I	3762	3357	3286	3544	4232
5. EH-II	13,079	16,863	12,380	13,994	21,254
6. TA-I	2459	2788	3408	2108	2983
7. TH-ii	4792	4232	3415	4502	4442
8. TA-II	4825	5325	5210	5394	5841
9. AA	4880	3808	4825	5023	3995
10. TH-iii	4276	8490	9075	11,075	10,368
11. TA-III	9975	7995	9387	10,325	7748
12. TA-IV	3490	4775	4728	4233	4191
13. TA-V	6190	6790	17,593	15,616	8147
Soil	Mnos				
	mg kg <sup>-1</sup>				
	0	1	10	30	50
1. EH-I	773	624	659	772	708
2. OH	581	478	419	412	514
3. TH-i	351	435	393	401	396
4. TH-I	489	469	432	490	549

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Table A-2 (continued)

Soil	Mnos				
	mg kg <sup>-1</sup>				
	0	1	10	30	50
5. EH-II	382	542	484	668	1126
6. TA-I	847	827	976	839	876
7. TH-ii	601	569	477	459	413
8. TA-II	903	934	828	862	986
9. AA	850	735	903	1023	850
10. TH-iii	379	301	327	306	256
11. TA-III	576	571	451	657	523
12. TA-IV	527	580	559	496	550
13. TA-V	360	406	986	953	407

Soil	Feos				
	mg kg <sup>-1</sup>				
	0	1	10	30	50
1. EH-I	1722	1706	1438	1528	1337
2. OH	529	497	449	396	534
3. TH-i	795	801	617	901	850
4. TH-I	558	530	116	203	142
5. EH-II	1073	1556	1204	2211	3967
6. TA-I	271	336	475	226	360
7. TH-ii	1361	1134	1114	1202	1719
8. TA-II	1138	1195	1010	974	1122
9. AA	1149	795	1138	1013	749
10. TH-iii	1520	1587	925	1042	884
11. TA-III	870	800	1022	949	1263
12. TA-IV	1032	1358	1478	1211	1133
13. TA-V	1098	1207	4190	3895	1284

Soil	Al <sub>ex</sub>				
	cmol <sub>c</sub> kg <sup>-1</sup>				
	0	1	10	30	50
1. EH-I	0.7	0.0	0.7	0.7	0.0
2. OH	0.0	0.7	0.0	0.7	0.0
3. TH-i	0.2	0.2	1.3	0.2	0.0
4. TH-I	1.1	0.4	0.4	0.4	0.4
5. EH-II	0.0	0.0	0.0	0.0	0.0
6. TA-I	1.1	0.4	1.1	1.1	1.1
7. TH-ii	0.2	0.2	0.2	0.0	0.2
8. TA-II	0.0	0.0	0.0	0.0	0.7
9. AA	0.7	0.7	0.7	0.4	0.4
10. TH-iii	0.2	0.2	0.0	0.0	0.0
11. TA-III	0.7	0.7	0.8	0.7	0.0
12. TA-IV	0.0	1.1	1.1	0.4	0.4
13. TA-V	0.0	0.0	0.1	0.0	0.7

Soil	H <sub>ex</sub> <sup>+</sup>				
	cmol <sub>c</sub> kg <sup>-1</sup>				
	0	1	10	30	50
1. EH-I	0.1	0.7	0.1	0.2	0.7
2. OH	0.5	0.2	0.5	0.3	0.4

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Table A-2 (continued)

Soil	$H_{ex}^+$				
	$cmol_c kg^{-1}$				
	0	1	10	30	50
3. TH-i	0.4	0.3	0.9	0.5	0.7
4. TH-I	0.6	0.	0.6	0.4	0.1
5. EH-II	1.1	0.3	0.8	0.6	0.6
6. TA-I	0.6	0.0	0.7	0.8	0.7
7. TH-ii	0.2	0.5	0.5	0.7	0.5
8. TA-II	0.5	0.7	0.7	0.6	0.1
9. AA	0.3	0.2	0.1	0.1	0.3
10. TH-iii	0.7	0.7	1.1	1.2	1.1
11. TA-III	0.1	0.1	0.1	0.1	0.6
12. TA-IV	0.3	0.5	0.3	0.2	0.3
13. TA-V	0.8	0.9	0.8	0.7	0.4

Al<sub>o</sub>: amorphous Al oxides. Mn<sub>o</sub>: amorphous Mn oxides. Fe<sub>o</sub>: amorphous Fe oxide. Al<sub>s</sub>: crystalline Al oxide. Mn<sub>s</sub>: crystalline Mn oxides. Fe<sub>s</sub>: crystalline Fe oxides. Al<sub>e</sub>: exchangeable aluminium.  $H_{ex}^+$ : exchangeable protons.

0, 1, 10, 30 and 50 indicate equivalent years of N-fertilization with 180 kg urea ha<sup>-1</sup> year<sup>-1</sup>.

1. EH-I: Entic Haplustoll I from site 1; 2. OH: Oxid Haplustoll from site 2; 3. TH-i: Typic Hapludoll I from site 3; 4. TH-I: Typic Haplustoll I from site 4; 5. EH-II: Entic Haplustoll II from site 5; 6. TA-I: Typic Argiudoll I from site 6; 7. TH-ii: Typic Hapludoll ii from site 7; 8. TA-II: Typic Argiudoll II from site 8; 9. AA: Aquic Argiudoll from site 9; 10. TH-iii: Typic Hapludoll iii from site 10; 11. TA-III: Typic Argiudoll III from site 11; 12. TA-IV: Typic Argiudoll IV from site 12; 13. TA-V: Typic Argiudoll V from site 13.

Values are mean of three replicates.

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