DYNAMICS OF SOIL LIMING MATERIALS BROADCAST ON A THAPTOARGIC HAPLUDOLL SOIL IN ARGENTINA

MABEL VÁZQUEZ[1*]; ANTONIO TERMINIELLO[1]; GUILLERMO MILLÁN[1]; INÉS DAVEREDE[2] & ESTEBAN BARIDÓN[1]

ABSTRACT

Soils of temperate Argentine pampas have been undergoing a gradual acidification due to the application of nitrogen fertilizers without replacement with basics nutrients. Although liming has been widely adopted, the acidification process is difficult to revert in depth under no-tillage systems. The aims of this study were to evaluate the effect of surface-applied gypsum added to calcitic and dolomitic limestones on the downward movement of HCO_3^-/Ca^{2+}/Mg^{2+}, the cation exchange capacity (CEC) and the actual/potential acidity on a Thaptoargic Hapludoll. The following treatments were assigned to undisturbed soil columns (20 cm): control (C_0), 1000 kg ha^{-1} $CaCO_3$ (C1000), 1000 kg ha^{-1} of a mixture of $CaCO_3$/$MgCO_3$ (D1000), treatment C1000 + 500 kg ha^{-1} $CaSO_4.2H_2O$ (C1000g) and treatment D1000 + 500 kg ha^{-1} $CaSO_4.2H_2O$ (D1000g). Water (6.8 mm) was applied weekly and leachates were collected during 16 weeks. The soil was divided into three depths for analysis. The presence of Ca^{2+}/Mg^{2+} in depth both in absolute numbers and proportionally to the amount added was greater in D1000, C1000g, and D1000g compared to C1000 and the control. CEC and the Ca:Mg ratio increased in C1000 at the 0-13 cm-depth, which would reflect a greater Ca availability in the short term. The amendments generally increased the actual/potential pH, as well as the exchangeable Ca^{2+}/Mg^{2+} concentrations at all depths, but the increases were always greater in the 0-6.5 cm soil layer. Gypsum addition increased the downward movement of liming materials after 16 weeks and is recommended in no-tillage scenarios.

Key words. Dolomitic and calcitic limestones, calcium sulphate, gypsum, leaching.

DINÁMICA DE LA DIFUSIÓN DE MATERIALES DE ENCALADO EN UN SUELO HAPLUDOL THAPTOÁRGICO EN LA ARGENTINA

RESUMEN

Los suelos de la pampa templada argentina han sido sometidos a una acidificación gradual, debido a la aplicación de fertilizantes nitrogenados sin reposición de nutrientes básicos. Aunque el encalado ha sido ampliamente adoptado, este proceso es difícil de revertir en profundidad en sistemas sin laboreo. Los objetivos de este trabajo fueron: evaluar el efecto de la aplicación superficial de yeso junto a calizas dolomíticas y calcáreas, en el movimiento descendente de HCO_3^-/Ca^{2+}/Mg^{2+}, la capacidad de intercambio catiónico (CIC) y la acidez real/potencial, en un Hapludol Thaptoárgico. Los siguientes tratamientos fueron aplicados en columnas de suelo no disturbado (20 cm): control (C_0), 1000 kg ha^{-1} $CaCO_3$ (C1000), 1000 kg ha^{-1} de una mezcla de $CaCO_3$/$MgCO_3$ (D1000), el tratamiento C1000 + 500 kg ha^{-1} $CaSO_4.2H_2O$ (C1000g) y el tratamiento D1000 + 500 kg ha^{-1} $CaSO_4.2H_2O$ (D1000g). Se agregaron semanalmente 6,8 mm de agua y los lixiviados fueron recogidos durante 16 semanas. El suelo se dividió en tres profundidades para el análisis. La presencia de Ca^{2+}/Mg^{2+} en profundidad, tanto en valores absolutos como en proporción a la cantidad añadida, fue mayor en D1000, C1000g y D1000g, en comparación con el C1000 y el control. La CIC y la relación Ca:Mg aumentaron en C1000, en la profundidad de 0-13 cm, lo que reflejaría una mayor disponibilidad de Ca en el corto plazo. Las enmiendas generalmente aumentaron el pH real/potencial, así como las concentraciones de Ca^{2+}/Mg^{2+} intercambiables en todas las profundidades, pero los incrementos fueron siempre mayores en la capa de 0-6,5 cm del suelo. El yeso adicionado aumentó el movimiento descendente de los materiales de encalado luego de 16 semanas y se recomienda en escenarios de labranza cero.

Palabras clave. Calizas dolomíticas y cálcicas, sulfato de calcio, yeso, lixiviación.

1 Facultad de Ciencias Agrarias y Forestales. Universidad Nacional de La Plata. Av. 60 y 119, La Plata (1900) CC (31). Argentina.

2 Facultad de Ciencias Agrarias. Universidad Católica Argentina Cap. Gral. Ramón Freire 183, Ciudad Autónoma Buenos Aires (C1426AVC). Argentina.

* Autor de contacto: mvazquez@agro.unlp.edu.ar

INTRODUCTION

Soil chemical fertility is reduced in long-term cropping and cattle-raising systems when exported nutrients are not replaced in a balanced manner (Juo *et al.,* 1995; Cruzate and Casas, 2004; Gelati and Vázquez, 2004; Vázquez, 2007; Vázquez *et al.,* 2010; Millán *et al.,* 2010). In the Argentine pampas region, N and P fertilizers are regularly applied, while other elements, like Ca and Mg bases, are seldom replaced. In addition, the use of soil-acidifying fertilizers together with atmospheric industry pollutant deposits (Juo *et al.,* 1995; Barak *et al.,* 1997; Jandl *et al.,* 2004; SAGPyA, 2007) and natural acidifying processes like leaching of bases (Irurtia *et al.,* 2004) have contributed to the progressive acidification of some soils (Vivas, 2004; Vázquez, 2007). According to the latter authors, mild acidification of soils cause nutritional imbalances, not Al or Fe toxicity.

In Argentina, liming with calcitic ($CaCO_3$) and dolomitic ($CaCO_3/MgCO_3$) limestones are common practices used to treat mildly acidified soils. These minerals have low solubility and mobility in soils, especially when they are not incorporated, as in no-tillage systems. In Argentina, no-tillage comprises more than 70% of the cropping systems and a large percentage of cattle-raising systems (AAPRESID, 2009). In this context, the combination of these minerals with gypsum ($CaSO_4 \cdot 2H_2O$), a mineral with higher solubility, could appear as a better option to improve limestone solubility. In addition, the presence of S in gypsum could increase yields of leguminous species, characterized by their high S requirements and low tolerance to acidic soils.

When liming products come into contact with the soil, basic ions interact with the solid and liquid soil phases, exchanging ions with the colloidal complex. The exchange dynamics are affected by the progressive modification of the soil pH due to the variable charges introduced with the liming materials, as well as by the concentration of the original and imported ions present in the soil solution (Blake *et al.,* 1999). In addition, exchange dynamics will vary in soils with different soil textures and mineral properties.

The quality of calcareous materials, including gypsum, can vary greatly according to the chemical composition, purity and granulometry. Therefore, in Argentina, IRAM developed standards 22.451/97 and 22.452/06 that define the parameters for classifying calcareous materials and gypsum, respectively.

Our hypothesis is that adding gypsum to calcitic and dolomitic limestones ($CaCO_3$, $CaCO_3/MgCO_3$) should increase the downward movement of bases. The objectives of this study were to evaluate the effects of gypsum added to calcitic and dolomitic limestones on the downward movement of HCO_3^-, Ca, and Mg and on the soil's cation exchange capacity (CEC), actual and potential acidity when broadcast on a Thaptoargic Hapludoll under no-tillage.

MATERIALS AND METHODS

Field characteristics

Soil samples were collected from a fine, loamy, mixed, thermic Thaptoargic Hapludoll of the Ortiz de Rozas series in Roberts, Lincoln district, NW Buenos Aires province, Argentina. Soil characteristics are described in Table 1. The region has a subhumid template climate, with an annual average temperature of 16.5 °C and a regular yearly rainfall pattern that averages 900 mm.

Liming trial

Experimental units consisted of 20-cm long by 10-cm wide undisturbed soil columns. Samples were collected using a polyvinyl chloride (PVC) cylinder inserted in a cylindrical soil sampler. Paraffin was applied on the soil-tube interface to avoid preferential flow between the PVC cylinder and the soil. A filter paper and a metallic mesh were attached at the bottom of each column to avoid soil losses. Treatments were assigned to the soil columns in a completely randomized design with three replications as follows: control (C_0), 1000 kg ha^{-1} $CaCO_3$ (C1000), 1000 kg ha^{-1} of a mixture of 54% $CaCO_3$ and 46% $MgCO_3$ (D1000), treatment C1000 + 500 kg ha^{-1} $CaSO_4 \cdot 2H_2O$ (C1000g) and treatment D1000 + 500 kg ha^{-1} $CaSO_4 \cdot 2H_2O$ (D1000g). High-purity laboratory compounds (analytical reagents) were used as powders to avoid particle size variability and foreign

Table 1. Select physical and chemical properties of the studied soil (0-20 cm).

Tabla 1. Propiedades físicas y químicas seleccionadas del suelo estudiado (0-20 cm).

pH-H$_2$O (1:2.5)	pH-KCl 1N (1:2.5)	EC	CEC	Ca^{2+}	Mg^{2+}	Na$^+$	K$^+$	OM	N	Textural classes
		(dS m^{-1})	——————— (cmol$_c$ kg^{-1}) ———————					(g kg^{-1}) -		
5.7	5.2	0.49	14.1	7.9	1.4	0.1	2.0	25	1.35	loam

EC: electrical conductivity; CEC: cationic exchange capacity; OM: organic matter.

impurities. The limestone used in this study could be classified as IRAM standard 22.451 Type I and dolomite as Type II, both with 100% efficiency according to the particle size. The gypsum used in our study could be classified as IRAM standard 22.452 as agricultural powdered gypsum (Type I).

Treatments were surface-applied; columns were then maintained at 90% field capacity (0.03 MPa) with distilled water. After 15 days, 6.8 mm of water were applied weekly and leachates were collected weekly during 16 weeks. Finally, the soil was divided into three depths (0-6.5; 6.5-13, and 13-20 cm) for subsequent analysis.

Soil analyses

The following soil analyses were performed:
- actual pH (1:2.5 soil:water),
- electrical conductivity (EC) on a saturated soil extract,
- cationic exchange capacity (CEC) and exchangeable cations by ammonium 1N pH 7 acetate methods, CEC determination by Kjeldahl distillation, Ca^{2+} and Mg^{2+} by redox chelatometry, K^+ and Na^+ by flame photometry,
- organic matter (OM): redox volumetry,
- total N: Kjeldahl method,
- texture: Bouyoucus sedimentation method, and
- water field capacity: using the Richards equipment at 0.03 Mpa.

Soil leachates were analyzed for Ca^{2+}, Mg^{2+} (chelatometry with EDTA), CO_3^{2-}, HCO_3^- and SO_4^{2-} (acid-base titration). At the end of the experiment, the three soil-column sections were analyzed for actual pH (soil:water 1:2.5), potential pH (soil:KCl 1N 1:2.5), cation exchange capacity and exchangeable cations (Ca^{2+}, Mg^{2+}) according to the methodology previously described. The analytical methods follow the argentinean standardized methodology (SAGPyA, 2004).

Statistical analyses

Data variances were checked for homogeneity and residuals for normality; subsequently, an analysis of variance was performed on every measured variable and multiple comparisons were conducted according to the Least Significant Differences (LSD) method at the 0.05 probability level.

RESULTS

Ion masses in soil leachates

Table 2 presents the ion masses collected in the soil leachates during the 16 week-period. The movement of ions in-depth in the control treatment varied from 2.2 mg for Mg^{2+} to 12.2 mg for Ca^{2+}, which is equivalent to 0.02 and 0.11 mg mm^{-1} of rain, respectively. A local precipitation of 900 mm would represent losses of 221 kg Ca^{2+} ha^{-1} yr^{-1} and 40 kg Mg^{2+} ha^{-1} yr^{-1} for the same 0-20 cm soil layer.

Ion mobility was not proportional to the amounts added with each treatment. For example, treatment D1000 produced similar amounts of Ca^{2+} in the soil leachate compared to treatment C1000, despite having applied almost half the amount of Ca^{2+} in the former treatment. This was probably due to the higher $MgCO_3$ solubility (10.6 mg 100 ml^{-1}) compared to the much lower $CaCO_3$ solubility of 1.3 mg 100 ml^{-1}. The greater $MgCO_3$ solubility should have increased the $CaCO_3$ solubility in D1000 due to the common ion effect. In fact, the proportion of Ca^{2+} ion applied that was lost from the 0-20cm layer was 2.7% in the D1000 treatment, more than four times compared to C1000, which averaged 0.6% (Table 2). Similarly, gypsum

Table 2. Total ion masses (expressed as mg per kg soil) collected in soil-column leachates for a period of 16 weeks. Values are the means of three replicates.
Tabla 2. Masa total de iones (en mg por kg de suelo) colectados en la columna de lixiviación del suelo para un periodo de 16 semanas. Valores promedio de tres repeticiones.

	Treatment								
	C0	C1000		D1000		C1000g		D1000g	
	(mg)^A	(mg)	(%)^B	(mg)	(%)	(mg)	(%)	(mg)	(%)
Ca^{2+}	12.2 a	13.5 ab	0.6	14.6 b	2.7	18.5 c	2.6	18.9 c	4.0
Mg^{2+}	2.2 a	1.8 a		2.9 b	1.2	3.3 b		4.0 c	3.0
CO_3H^-	5.6 a	12.6 bc	2.4	13.0 bc	2.4	14.0 c	3.0	10.8 b	1.8
SO_4^{2-}	6.8 a	6.0 a		6.9 a	23.4 b		12.0	26.2 b	14.6

A: mgkg^{-1} B: (Total mass of leached ion from treated columns - total ion mass leached from untreated columns)/mass of ion applied to columns x 100.

addition to both liming materials increased the percentage of Ca^{2+} added that leached (2.6% in C1000g *vs* 0.6% in C1000; 4% in D1000g *vs* 2.7% in D1000; Table 2). On the other hand, the percentage of Mg applied that leached after adding gypsum increased from 1.2% in D1000 to 3% in D1000g. Figures 1 to 4 depict the ion masses found in weekly leachates during the 16-week period after the application of treatments. The leached ion masses varied throughout the experiment, reflecting a superposition of ion exchange and solubilization processes.

The greater leaching of SO_4^{2-} compared to HCO_3^- could explain that the greater solubility of gypsum is the main cause of the deep movement of Ca^{2+} (Table 2; Figs. 3 and 4). However, the solubilization of carbonates caused by gypsum must not be ignored, reflected by the increased leaching of Mg in D1000g compared to D1000, considering that gypsum does not contain Mg (Table 2).

The addition of gypsum to the liming materials (C1000g and D1000g) produced a sharp increase in the downward movement of Ca^{2+} during the first five weeks of the experiment, having received an average of 34 mm of water (Fig. 1). After this moment, differences between treatments with and without gypsum decreased and were often non-significant. Magnesium ion masses showed smaller differences between treatments compared to Ca^{2+}, but these differences were more extended in time (Fig. 2).

The weak SO_4^{2-} bonding in gypsum can be observed in Fig. 3, where sulfates were rapidly leached from the soil columns. Bicarbonate weekly leachings were erratic, and it was not possible to recognize a marked effect of gypsum on the downward movement of this anion (Fig. 4).

Treatment effects on soil properties

The actual pH increases in the superficial soil layer (0-6.5 cm) were significant and ranged from 0.58 to 0.89 when soil amendments were applied (Fig. 5a). The actual pH values in the amended treatments surpassed the critical soil pH (6.5) levels for important local species, like alfalfa (*Medicago sativa* L.) (Vázquez *et al.*, 2010). Although no significant differences were found among treatments, there was a tendency to a higher increase in the actual pH for D1000 in the superficial layer. This could be attributed to the greater acid-neutralizing effect of dolomites ($CaCO_3$/ $MgCO_3$) at comparable granulometries (IRAM 22.451/97).

Figure 1. Calcium ion masses found in weekly leachates during a period of 16 weeks after treatment application. Different letters within weeks represent significant differences among treatments ($\alpha=0.05$), arranged in the following order from top to bottom: Control, C1000, D1000, C1000g, D1000g.
Figura 1. Masa del ion calcio encontrada en la lixiviación semanal, durante un período de 16 semanas luego de la aplicación del tratamiento. Letras diferentes dentro de las semanas representan diferencias significativas entre tratamientos ($\alpha=0,05$), dispuestos en el siguiente orden de arriba abajo: Control, C1000, D1000, C1000g, D1000g.
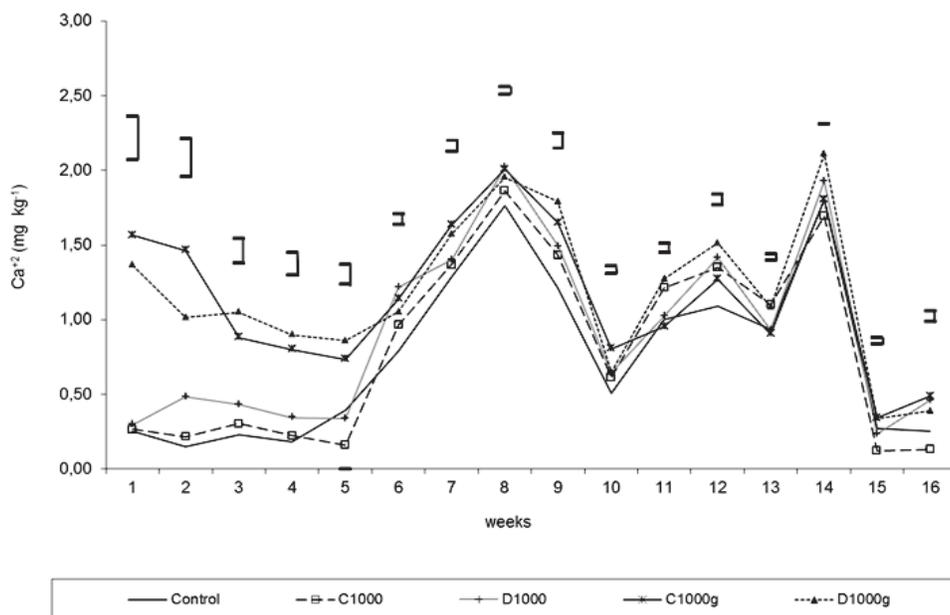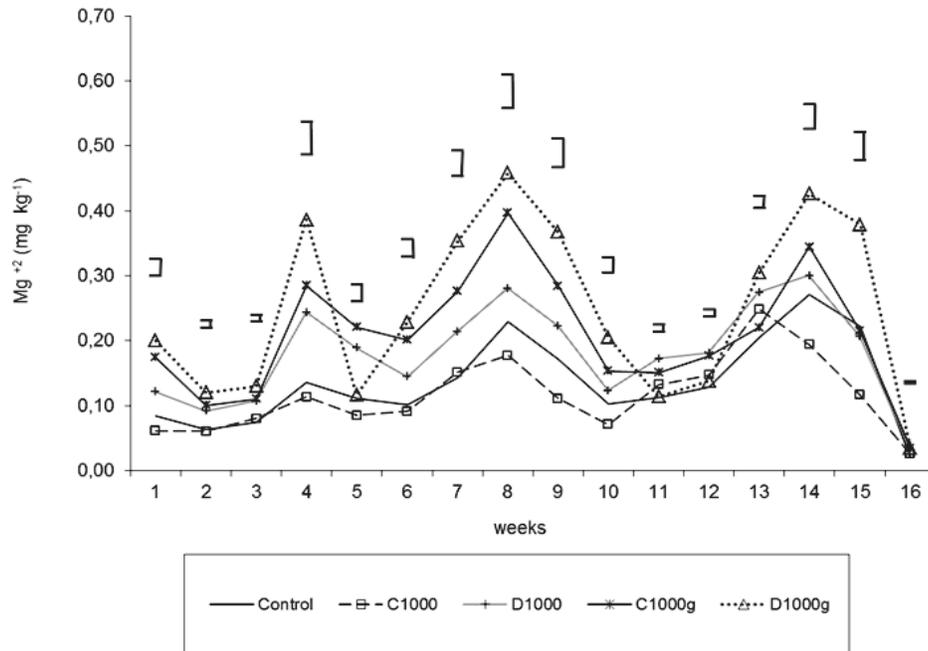
Figure 2. Magnesium ion masses found in weekly leachates during a period of 16 weeks after treatment application. Different letters within weeks represent significant differences among treatments ($\alpha=0.05$), arranged in the following order from top to bottom: Control, C1000, D1000, C1000g, D1000g.

Figura 2. Masa del ion magnesio encontrada en la lixiviación semanal, durante un período de 16 semanas luego de la aplicación del tratamiento. Letras diferentes dentro de las semanas representan diferencias significativas entre tratamientos ($\alpha=0,05$), dispuestos en el siguiente orden de arriba abajo: Control, C1000, D1000, C1000g, D1000g.

Figure 3. Sulfate ion masses found in weekly leachates during a period of 16 weeks after treatment application. Different letters within weeks represent significant differences among treatments ($\alpha=0.05$), arranged in the following order from top to bottom: Control, C1000, D1000, C1000g, D1000g.

Figura 3. Masa del ion sulfato encontrada en la lixiviación semanal, durante un período de 16 semanas luego de la aplicación del tratamiento. Letras diferentes dentro de las semanas representan diferencias significativas entre tratamientos ($\alpha=0,05$), dispuestos en el siguiente orden de arriba abajo: Control, C1000, D1000, C1000g, D1000g.
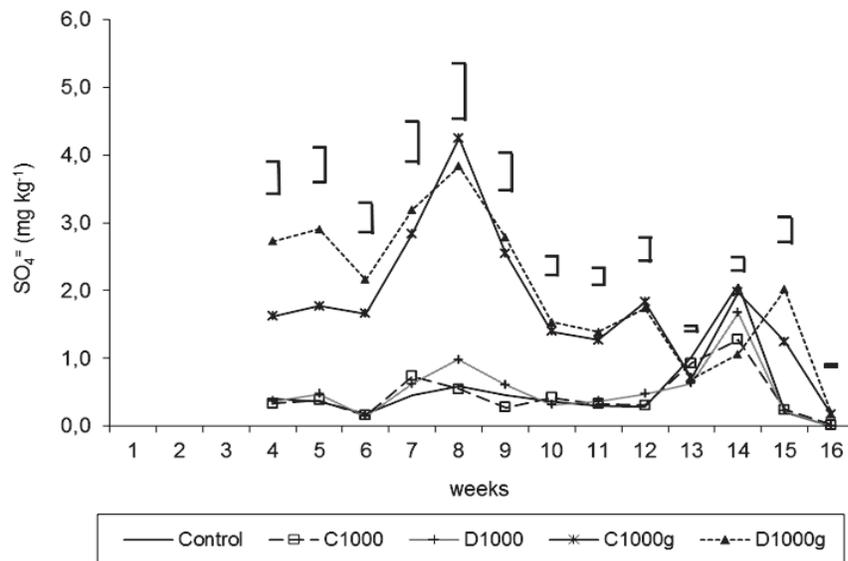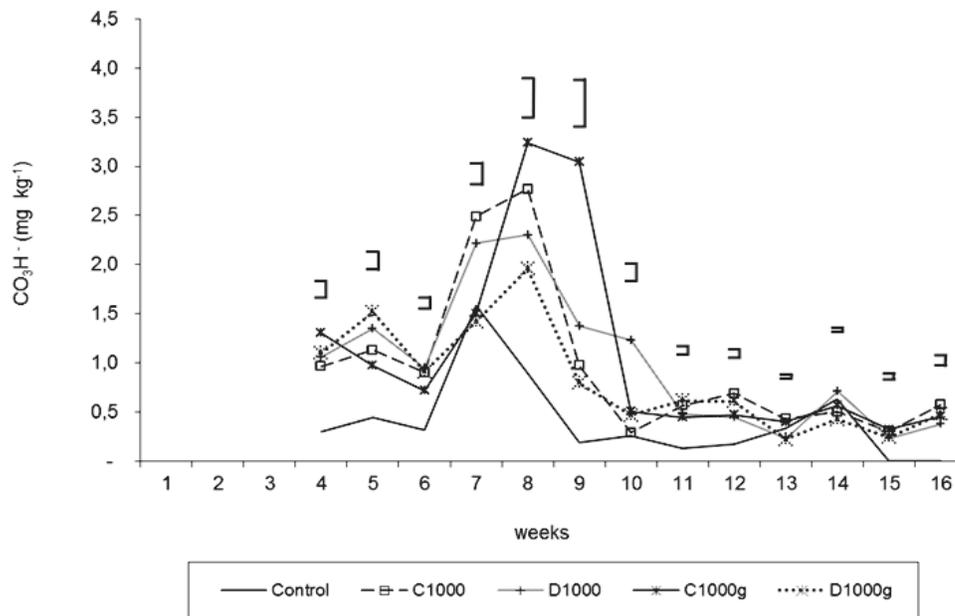
Figure 4. Bicarbonate ion contents found in weekly leachates during a period of 16 weeks after treatment application. Different letters within weeks represent significant differences among treatments (α=0.05), arranged in the following order from top to bottom: Control, C1000, D1000, C1000g, D1000g.

Figura 4. Masa del ion bicarbonato encontrada en la lixiviación semanal, durante un período de 16 semanas luego de la aplicación del tratamiento. Letras diferentes dentro de las semanas representan diferencias significativas entre tratamientos (α=0,05), dispuestos en el siguiente orden de arriba abajo: Control, C1000, D1000, C1000g, D1000g.
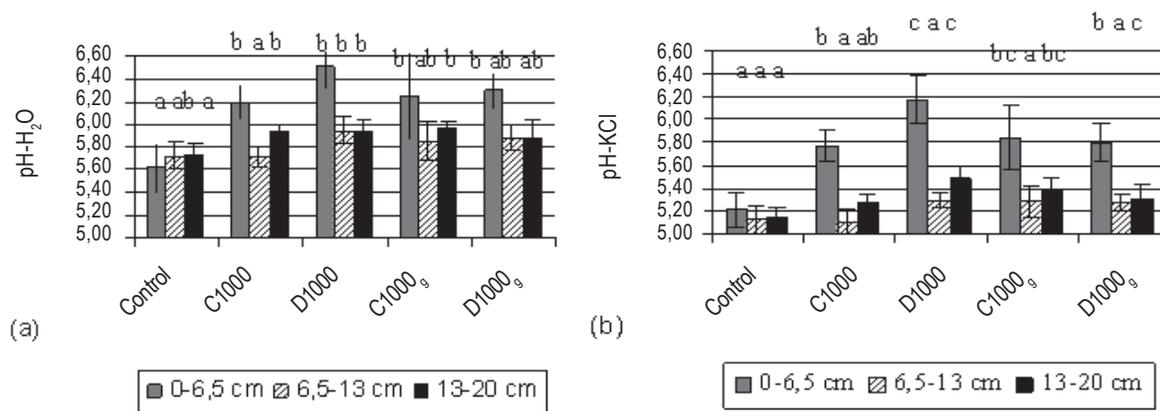

Figure 5. Soil actual pH-H$_2$O (a) and potential pH-KCl (b) for the different treatments and depths after a period of 16 weeks of weekly leachings with 6.8 mm distilled water. Different letters within each depth represent significant differences among treatments (α=0.05).

Figura 5. pH actual del suelo, pH-H$_2$O (a), y pH potencial, pH-KCl (b), para los diferentes tratamientos y profundidades, luego de un período de 16 semanas de lixiviación semanal con 6,8 mm de agua destilada. Letras diferentes dentro de cada profundidad representan diferencias significativas entre los tratamientos (α=0,05).

Actual pH increases in subsuperficial layers were much smaller compared to the superficial layer and did not surpass 0.24 units. In general, no significant differences were found between pH increases caused by the combination of limestones and gypsum (C1000g and D1000g) compared to limestones without gypsum (C1000 and D1000).

The treatment effects on the soil potential pH are depicted in Fig. 5b. As observed for the actual pH, the greater

potential pH changes were also observed in the superficial soil layer, ranging from 0.56 to 0.96 pH units, the latter value corresponding to D1000. Although D1000 produced a greater increase in the potential pH in the superficial layer compared to the control (C_0), this increase was significantly smaller compared to D1000g, coinciding with a greater leaching of bases in D1000g. Bakker *et al.* (1999) found similar results on a Dystrochrept soil using higher amendment rates. Additionally, Peregrina Alonso *et al.* (2006) found that the initial soil pH decreased after the first leaching event due to the salt effect caused by gypsum. Subsequently, pH increases were observed when most of the sulfates were leached. As observed in this study, changes in potential pH were less significant subsuperficially.

CEC increased significantly in C1000 compared to C_0 in the first two soil layers (0-13 cm; Fig. 6a) with differences between treatments averaging 1.2 and 2.8 cmol$_c$ kg^{-1} for the 0-6.5 and 6.5-13 cm depths, respectively. In contrast, there were no defined tendencies in CEC among the other treatments. The CEC increases in this experiment were considerably lower than those found by Vázquez *et al.* (2005) in a clay loam soil, with a higher clay content and CEC at the same study site. Ion retention varied depending on each treatment. Compared to C_0, amendments produced exchangeable Ca^{2+} increases in the first layer that ranged from 0.21 to 1.88 cmol$_c$ kg^{-1} (Fig. 6a). Soils receiving additional Ca^{2+} rates with gypsum did not show increases in CEC in the first layer compared to treatments without gypsum (C1000g *vs.* C1000 and D1000g *vs.* D1000). Furthermore, treatment D1000g presented significantly lower exchangeable Ca^{2+} compared to D1000.

Dolomite application produced a significant increase in exchangeable Mg^{2+} in the first soil layer. This increase was greater for the D1000 treatment, without gypsum addition.

Figure 6. Ca^{2+} (a), Mg^{2+} (b), and CEC (c), from the soil exchange complex for each treatment after 16 weeks of leaching in the three sections in which the column was cut.
Figura 6. Ca^{2+} (a), Mg^{2+} (b), CEC (c), del complejo de intercambio del suelo, de acuerdo al tratamiento luego de 16 semanas de lixiviación en las tres secciones en que se cortó la columna.

DISCUSSION

The increase in leached Ca^{2+} caused by the addition of gypsum to calcitic and dolomitic limestones (Table 2) was in accordance with the addition of a more soluble source of Ca (gypsum). The greater downward movement of Ca^{2+} from dolomitic limestone compared to calcitic limestone reflected the higher solubility of the former. Comparatively, the proportion of Mg^{2+} that leached increase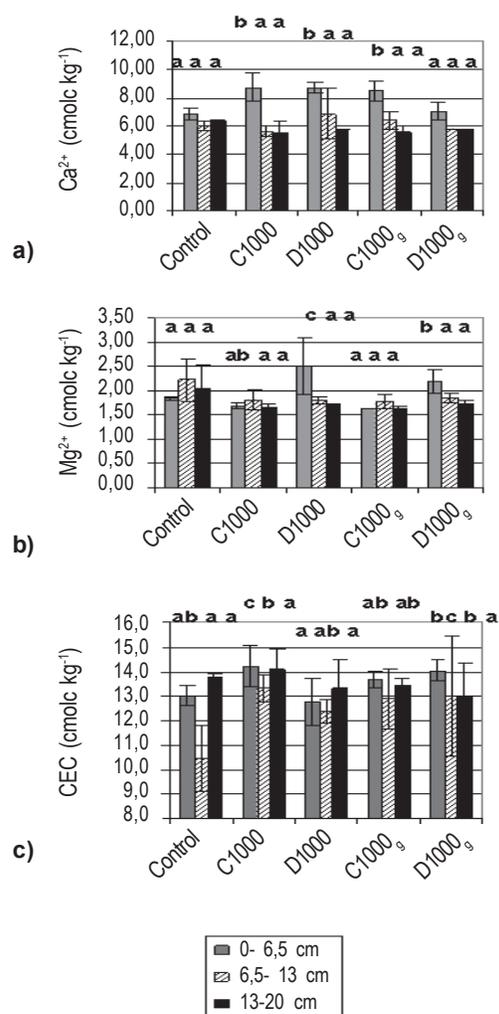d with the addition of gypsum to both calcitic and dolomitic limestones, resulting from the materials' different solubilities, neutralizing powers, and interaction with the soil exchangeable complex. The increase in the downward movement of ions in strongly acid soils caused by the addition of gypsum to liming materials was observed by Saigusa *et al.* (1996), Pearce and Sumner (1997), Saigusa and Toma (1997), Salvada Wadt and Oliveira Wadt (1999), Farina *et al.* (2000), and Ernani *et al.* (2001).

In another study, Davis and Burgoa (1995) reported a positive effect in the adsorption of Ca^{2+} due to SO$_4^{2-}$

compared to other ions such as Cl⁻ and NO₃⁻. According to the authors, this could have been caused by the specific adsorption (ion pairs) as well as non-specific adsorption (variable charge effect) produced by SO_4^{2-}, which would not be enough to compensate for the higher leaching losses compared to CO_3^{2-}. It is well-known that soil CEC is the result of negative permanent electrostatic charges originating from clay isomorphic substitution as well as from variable charges that depend on soil pH. Gypsum, being a salt from a strong acid and having a cation that may interact with the soil exchangeable complex or precipitate, could produce an alteration of variable charges in the site of its dissolution, increasing the leaching of bases. In addition, the higher content of Ca in gypsum and its higher solubility compared to calcitic and dolomitic limestones could promote its movement in depth, in agreement with the study reported by Shamshuddin and Ismael (1995). The released Ca^{2+}, having a high affinity to the soil exchangeable complex, could produce desorption of other bases such as Mg^{2+}. Loess is the parent material of the soil under study, composed primarily of clays with high affinity to Ca^{2+} such as illite, vermiculite, and montmorillonite (Imbellone and Giménez 1998).

The higher HCO_3^- lixiviation in treatment C1000g compared to treatment C1000 was probably due to the presence of SO_4^{2-} ions in treatment C1000g that could have produced a dissolution effect on CO_3^{2-} ions. Similar results were found by Hernández *et al.* (2003) in soils with natural calcitic minerals. Under our study conditions, it is possible that liming materials may not have moved downward without previous dissolution, explanation supported by the fact that no CO_3^{2-} was found in the leached solution. In contrast, Amaral *et al.* (2004) found a downward movement of liming particles without dissolution, possibly due to the acidic soil matrix (pH=4.7).

Soil buffer capacity is also modified by amendments, apart from pH, ion type and concentration. The buffer capacity can vary under different pH ranges producing different adsorption-desorption dynamics of bases, causing the erratic tendency of ion leachings in Figs. 1 to 4.

The ion variations observed in the exchangeable complex after the addition of the liming materials coincide with the trends observed for the actual and potential pH values. Davis and Burgoa (1995) found that the role of anions is critical in the regulation of the leaching of bases in limed soils and their accumulation in the exchangeable complex. However, we consider that these effects depend on the amount of variable charges present in the soil exchangeable complex, in agreement with the study conducted by Shamshuddin and Ismael (1995). According to Hernández *et al.* (2003), sulfates are frequently used to amend calcareous soils in order to leach part of the Ca^{2+} present and to decrease the soil pH. In another study on limestone application to crops, Carran (1991) attributed the different crop responses to the variation in the soil Ca:Mg ratio caused by the accompanying anions present in the liming materials. The presence of carbonates in the soil solution tend to increase the soil pH and consequently increase soil negative variable charges, producing higher Ca^{2+} adsorption and increasing the soil Ca:Mg ratio. In contrast, liming materials containing SO_4^{2-} and Cl⁻ promote Ca^{2+} leaching and cause a decrease in the soil Ca:Mg ratio.

The soil Ca:Mg ratio plays an important role in plant nutrition according to Muñoz Hernández and Silveira,
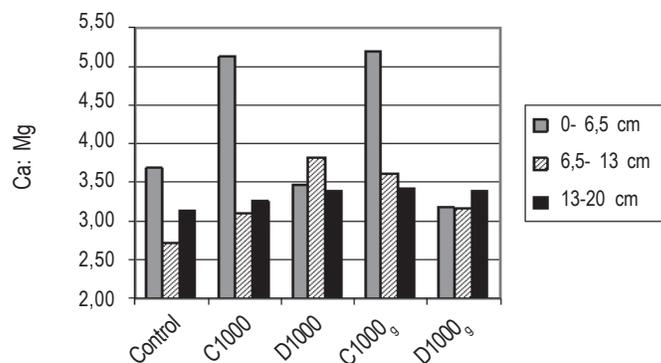

Figure 7. Effect of the added amendments on the exchangeable Ca:Mg ratio for the different soil-column depths.
Figura 7. Efecto de los correctores aplicados en la relación al Ca:Mg intercambiable a diferentes profundidades.

(1998), Büll *et al.* (1998), Anjos Reis *et al.* (1999), Bakker *et al.* (1999), Borie *et al.* (1999), Demanet *et al.* (1999), and Loide (2004). According to these authors, optimum Ca:Mg ratios range from 3:1 to 15:1 for different soils and crops. Therefore, the increase in the soil Ca:Mg ratio observed in treatments C1000 and C1000g (Fig. 7) could improve Ca^{2+} availability and promote plant growth.

The combined application of calcitic and dolomitic limestones with gypsum could be a valuable alternative for increasing the pH in acid soils under no-tillage due to the impact on the downward movement of Ca^{2+} and Mg^{2+}. However, more research should be conducted in this subject to assess the optimum application rates to avoid the leaching of bases that could eventually generate a higher soil acidification in the medium to long term, particularly in soils with a coarse texture under repeated liming applications. The application of limestones and gypsum combined would be very useful in cases where the movement of bases in the short term is sought, for example in annual cropping systems. In contrast, in cases where soil acidity should be corrected in the long term, like in perennial pastures, calcite and/or dolomite without gypsum seem to be the better option. Care should be taken when fertilizing with gypsum as a S-source to coarse-textured soils that are susceptible to acidification; this is the case of extensive areas in the Argentine pampas cropped with soybeans (*Glycine max* L.).

The results observed in this study are very promising; however, more research is needed to validate the results under field conditions. Variations in soil temperature and moisture conditions in the field, as well as the particular water movement under natural soil porosity could produce differences in ion lixiviation in soils.

CONCLUSIONS

The addition of gypsum to calcitic and dolomitic limestones increased the downward movement of Ca^{2+} and Mg^{2+} in soils compared to the control and to calcite alone, both in absolute terms and relative to the amount applied. This effect was concomitant with the increase in CEC in the top two soil layers (0-13cm). Calcite application increased the soil exchangeable Ca:Mg ratio, implying an increase in Ca^{2+} availability in the short term, although only superficially.

The amendments increased the real and potential soil pH as well as the exchangeable Ca^{2+} and Mg^{2+} concentrations, particularly in the 0-6.5 cm layer. The less pronounced and

more variable effects observed in the subsuperficial layers of the soil colloidal complex at the end of the experiment could represent the slow vertical dynamics of the applied limestones, which were partially counteracted with the addition of gypsum. Therefore, the application of gypsum in combination with carbonatic liming materials could be particularly convenient on surface applications without incorporation, for example on annual crops under no-tillage. However, more research should be conducted to adjust the optimum combination of liming material rates to avoid the leaching of bases that could increase the process of soil acidification in the medium to long term.

REFERENCES

AAPRESID (Asociación Argentina de productores de siembra directa. 2009. Siembra directa, su evolución en Argentina. http://www.aapresid.org.ar/apadmin/img/upload/evolucion.xls. 9/5/07.

Amaral, AS; I Anghinoni; R Hinrichs & I Bertol. 2004 Movimentação de partículas de calcarío no perfil de um Cambissolo em plantío direto. *Rev. Bras. Ciênc. Solo* 28(2): 359-367.

Anjos Reis, RP; C Rezende Fontes; JC Lima Neves & N Terra Santos. 1999. Total soil electrical conductivity and critical soil K+ to Ca2+ and Mg2+ ratio for potato crops. *Sci. Agric.* 56(4): 993-997.

Bakker, MR; R Kerisit; K Verbist & C Nys. 1999. Effects of liming on rhizosphere chemistry and growth of fine roots and of shoots of sessile oak (Quercus petracea). *Plant Soil* 217: 243-255.

Barak, P; BO Jobe; AR Krueger; LA Peterson & DA Laid. 1997. Effect of long-term soil acidification due to nitrogen fertilization inputs in Wisconsin. *Plant Soil* 197: 61-69.

Blake, L; KWT Goulding; CJB Mott & AE Johnston. 1999. Changes in soil chemistry accompanying acidification over more than 100 years under woodlandygrass at Rothamsted Experimental Station, UK. Eur. J. *Soil Science* 50: 401-412.

Borie, BF; FA Gallardo; MLG Mora & JC García. 1999. Sensibilidad y tolerancia a la acidez de los cultivos en condiciones de campo. *Frontera Agríc.* 5(1-2):19-28.

Büll, LT; RL Villas Boas & J Nakagawa. 1998. Variações no balanço catiônico do solo induzidas pela adubação potássica e efeitos na cultura do alho vernalizado. *Sci. Agric.* 55(3): 456-464.

Carran, RA. 1991. Calcium magnesium imbalance in clovers: A cause of negative yield response to living. *Plant Soil* 134: 107-114.

Cruzate, G & R Casas. 2004. Balance de nutrientes. *Fertilizar.* Special Publication No. 8, Sostenibilidad. Argentina.

Davis, JG & B Burgoa. 1995. Interactive mechanism of anion adsoption with calcium leaching and exchange. *Soil Sci.* 160(4): 256-264.

Demanet, RF; BM Schnettler & MLG Mora. 1999. Efecto del encalado y su relación con los nutrientes sobre la producción de pasturas en suelos ácidos. *Frontera Agríc.* 5(1-2): 95-110.

Ernani, PR; M Schurmann Ribeiro & C Bayer. 2001. Modificações químicas em solos ácidos ocasionadas pelo método de aplicação de corretivos da acidez e de gesso agrícola. *Sci. Agríc.* 58(4): 825-831.

Farina, MPW; P Channon & GR Thibaud. 2000. A comparison of strategies for ameliorating subsoil acidity: I. Long-term growth effects. *Soil Sci. Soc. Am. J.* 61: 646-651.

Gelati, P & M Vázquez. 2004. Exportación agrícola de nutrientes básicos en la zona N de la Pcia. de Buenos Aires y el costo de su remediación. *In:* ´Proceedings Segundas Jornadas de la Asociación Argentino Uruguaya de Economía Ecológica (ASAUEE) 2004.pp. 12 (Colonia, Uruguay).

Hernández, JC; DL Orihuela; S Pérez-Mohedano; L Marijuan & NR Furet. 2003. Efecto de la modificación del pH sobre la lixiviación de cationes en columnas de suelos calizos. *Estudios de la Zona No Saturada del Suelo* 6: 99-104.

Imbellone, PA & Giménez. 1998. Parent materials, buried soil and fragipans in northwestern Buenos Aires Province, Argentina. *Quaternary International* 51-52: 115 -126.

INTA (Instituto Nacional de Tecnología Agropecuaria) (1993) ´Carta de suelos 3563-24 Roberts' (Buenos Aires, Argentina).

IRAM (Instituto Argentino de Normalización y Certificación) (1997) ´NORMA 22451. Materiales calcáreos para uso agropecuario' (Buenos Aires, Argentina). 19 p.

IRAM (Instituto Argentino de Normalización y Certificación) (1997) ´NORMA 22452. Yeso para uso agrícola´ (Buenos Aires, Argentina). 32 p.

Irurtia, C; E Rivero & R Michelena. 2004. Pérdidas de nutrientes por lixiviación y escurrimiento en siembra directa. *In:* Proceedings XVI Congreso Latinoamericano de Suelos 2002' (Cartagena, Colombia. CD-room).

Jandl R, Alewell C, Prietzel J (2004) Calcium loss in Central European Forest Soil. Soil Sci. *Soc. Am. J.* 68: 588-595.

Juo, ASR; A Dabiri & K Franzluebbers. 1995. Acidification of a kaolinitic Alfisol under continuos cropping with nitrogen fertilization in West Africa. *Plant Soil* 171: 245-253.

Loide, V. 2004. About the effect of the contents and ratios of soil's available calcium, potassium and magnesium in liming of acid soils. *Agron. Res.* 2(1): 71-82.

Millán, G; M Vázquez; A Terminiello; D Santos & D Sbuscio. 2010. Efecto de las enmiendas básicas sobre el complejo de cambio en algunos suelos ácidos de la región pampeana. *Ciencia del Suelo* 28(2): 131-140.

Muñoz Hernández, RJ & RI Silveira .1998. Efeitos da saturação por bases, relações Ca:Mg no solo e níveis de fósforo sobre a produção de material seco e nutrição mineral do milho (*Zea mays* L.). *Sci. Agric.* 55(1): 79-85.

Pearce, RC & ME Sumner. 1997. Apparent SALT sorption reactions in unfertilized acid subsoil. *Soil Sci. Soc. Am. J.* 61: 765-772.

Peregrina Alonso, F; J Santano Arias; R Ordonez Fernández; P González Fernández & R Espejo Serrano. 2006. Agronomic implications of the supply of lime and gypsum by-products to Palexerult from western Spain. *Soil Sc.* 171(1): 65-81.

SAGPyA (Secretaría de Agricultura, Ganadería, Pesca y Alimentación de la Nación Argentina) (2004). ´Sistema de Apoyo Metodológico a los Laboratorios de Análisis de Suelos (SAMLA)'. (Dirección de Producción Agrícola. Buenos Aires, Argentina. CD-room)

SAGPyA (Secretaría de Agricultura, Ganadería, Pesca y Alimentación de la Nación Argentina). (2007) Insumos Agropecuarios. Fertilizantes. Available at: www.sagpya.mecon.gov.ar.

Saigusa, M; M Toma & M Nanzyo. 1996. Alleviation of subsoil acidity in non-allophanic Andosols by phosphogypsum application in topsoil. *Soil Sci. Plant Nutr.* 42 (2): 221-227.

Saigusa, M & M Toma. 1997. Mechanism of reduction of exchangeable aluminium by gypsum application in acid Andosols. *Soil Sci. Plant Nutr.* 43(2): 343-349.

Salvada Wadt, PG & LH De Oliveira Wadt. 1999. Movimentação de cátions em amostras de um Latossolo Vermelho-Amarelo incubadas com duas fontes de cálcio. *Sci. Agric.* 56(4): 1157-1164.

Shamshuddin, J & H Ismael. 1995. Reactions of ground magnesium limestone and gypsum in soils with variable-charge minerals. *Soil Sci. Soc. Am. J.* 59: 106-112.

Vázquez, M. 2007. Calcio y Magnesio del suelo. Encalado y enyesado. *In:* ´ Fertilidad de suelos y fertilización de cultivos ´ (*eds* H Echeverría & F García) pp 161-188. (INTA, Buenos Aires, Argentina)

Vázquez, M; P Gelati & D Santos Sbuscio. 2005. Efecto del agregado de calcio y magnesio sobre el complejo de cambio de un Argiudol Típico y su relación con el rendimiento de alfalfa. *In:* ´ Proceedings Simposio Uruguayo-Argentino Impacto de la Intensificación Agrícola en el Recurso Suelo 2005' (Colonia, Uruguay, CD-room).

Vázquez, M; A Terminiello; A Casciani; G Millán; P Gelati; F Guilino; J García Díaz; J Kostiria & M García. 2010. Evaluación del efecto de enmiendas básicas sobre la producción de alfalfa (*Medicago sativa* l.) y propiedades edáficas en ámbitos templados argentinos. *Ciencia del Suelo* 28(2): 141-154.

Vivas, H. 2004. Fertilización con fósforo, calcio y azufre en la producción de alfalfa y soja. *In:* ´ Proceedings Primera Jornada Nacional de Ca y Mg en la producción agropecuaria 2004´ (La Plata, Argentina, CD-room).