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Land use change in a temperate grassland soil: Afforestation effects on chemical properties and their ecological and mineralogical implications

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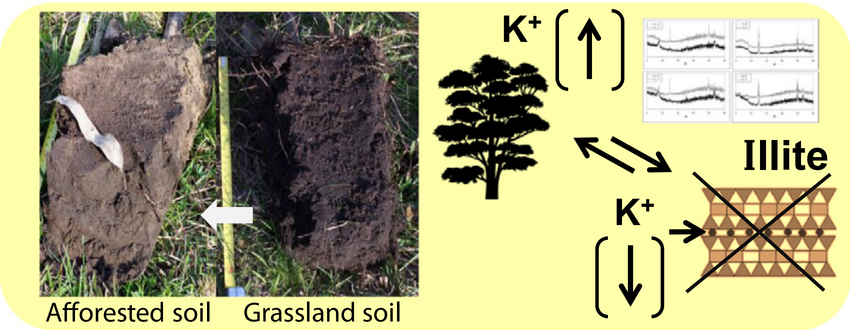
HIGHLIGHTS

- ► Eucalyptus afforestation in a grassland soil causes a loss in fertility.
- ► Potassium capture by trees irreversibly affects the mineral structure of illites.
- ► Other physicochemical variables are also affected by these changes associated with the mineralogy.
- ► The set of processes that occur under afforestation redirects pedogenesis.

GRAPHICAL ABSTRACT



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ABSTRACT

The current change in land use of grassland in the temperate region of South America is a process associated with the worldwide expansion of annual crops and afforestation with fast growing exotic species. This last cultivation has particularly been the subject of numerous studies showing its negative effects on soil (acidification, loss of organic matter and base cations, among others). However its effects on the mineral fraction are not yet known, as it is generally considered as one of the slowest responses to changes. This stimulated the present study in order to assess whether the composition of clay minerals could be altered together with some of the physicochemical parameters affected by afforestation. This study compares the mineralogical composition of clays by X-ray diffraction (XRD) in a grassland soil (Argiudolls) under natural coverage and under *Eucalyptus grandis* cultivation implanted 25 years ago in a sector of the same grassland. The tendency of some physicochemical parameters, common to other studies was also compared. XRD results showed, as a most noticeable difference in A_{11} and A_{12} subhorizons (~20 cm) under eucalyptus, the fall of the 10 Å spectrum minerals (illite-like minerals), which are the main reservoir of K in the soil. Meanwhile, the physicochemical parameters showed significant changes ($p<0.01$) to highly significant ones under eucalyptus, particularly in these subhorizons, where on average soil organic matter decreased by 43%; K^+ by 34%; Ca^{2+} by 44%, while the pH dropped to this level by half a point. Our results show that the exportation of some nutrients is not compensated due to the turnover of organic forestry debris; the process of soil acidification was not directly associated with the redistribution of cations, but with an incipient podzolization process; the loss of potassium together with soil acidification, leads to a drastic change in clay mineralogy, which would be irreversible.

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1. Introduction

The current expansion of tree cultivation with fast growing species (*Eucalyptus* sp. and *Pinus* sp.) is a worldwide phenomenon that has reached even temperate grassland ecosystems, such as the so called Pampa Biogeographic Province by Cabrera and Willink (1973) and Morrone (2001, 2006), in the southeastern region of South America.

At present there is a wealth of evidence indicating that growing large scale *Eucalyptus* sp. has a negative effect on soil fertility (Carrasco-Letelier et al., 2004; Céspedes-Payret et al., 2009; Jobbágy and Jackson, 2003; Nosetto et al., 2005, 2011; Pérez Bidegain et al., 2001; Vega et al., 2009). As with other changes in land use, potentially affected soil properties can be very diverse and even affect their own clay mineralogy (Bain, 1995; Barré et al., 2009; Drever, 1994; Farley et al., 2005; Hinsinger et al., 1992; Jobbágy and Jackson, 2004a; Kelly et al., 1998; Pernes-Debuyser et al., 2003; Velde and Peck, 2002; Verboom and Pate, 2006).

The main agricultural soils depend on illite as the source of K for crops (von Boguslawski and Lach, 1971). "Non-exchangeable" ions may represent the 90–99% of total K of many soils and may contribute to 80–100% of the supply of plant-available K (Hinsinger, 2002).

In the K^+ uptake process, plant roots release H^+ which reacts with the structure of clay minerals (Mengel and Steffens, 1982; Tributh et al., 1987). This enables plants to extract much more K than the K chemically defined as exchangeable (Barré et al., 2007a; Hinsinger, 2002; von Boguslawski and Lach, 1971). The permanent removal of this cation from soils, leads to degradation of illite (Tributh et al., 1987). This situation defines the importance of the inclusion of clay minerals in studies of land use change, as a key component of soil. These minerals are involved in the most important soil processes from the development of its structure to its cation exchange capacity (Barré et al., 2009; Wilson, 1999).

For the present study, grassland sandy soils under contrasting vegetation cover were selected (natural pasture vs. *Eucalyptus grandis* 25 year old plantation). Thus, the inclusion of the effects of agricultural use that has characterized the study region (soybean, wheat, maize, and sunflower) was avoided.

Based on such a background, we set as our first hypothesis that eucalyptus cultivation leads to a high demand of K^+, so it would also involve "non-exchangeable potassium". In addition to this, particular acidic conditions under this plantation also affect other relevant soil properties (pH, organic matter percentage, cation exchange capacity, base cations, soil moisture). Consequently, this allows us to suggest as a second hypothesis, that several years after the implantation of eucalyptus afforestation in sandy soil, the synergistic effect of such changes would make irreversible the alteration in dominant potassium clays such as illite. This study focused on testing both hypotheses.

The analysis focused on the detection of possible changes in the mineralogical composition of clays by X-ray diffraction (XRD). Additionally, we evaluated the behavior of some widely used physicochemical properties (pH, SOM, CEC, Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe_d, Fe_o). It seeks to determine whether this behavior was similar to the one recorded by background, both for the region (Jobbágy and Jackson, 2003), and for our area of study (Carrasco-Letelier et al., 2004; Céspedes-Payret, 2003; Richard, 2002).

2. Materials and methods

2.1. Characterization of the study area

The study area is located on the west region of Uruguay (32° 23′ S and 57° 36′ W, Fig. 1). It is an agricultural area which is being displaced by a high concentration of afforestation for commercial purposes, mainly *Eucalyptus* sp. Today these cultivations are managed with short terms. The climate in the region is temperate with an annual rainfall of 1200 mm yr^{-1} and a mean temperature of 18 °C. The geology of the area is dominantly composed by retransported Cretaceous sandstones.

The soil is Mollisol (Argiudoll) (Soil Survey Staff, 2010) developed on a relief of smooth hills with 1–6% slope. The thickness of the *solum* ranges from 120 to 125 cm, the sequence of horizons is A, Bt, and C. The texture of the A horizon is sandy loam to loamy sand, and Bt horizon is sandy clay with clear transition (Table 1).

The selected soil unit is located in a representative area of the Uruguayan territory assigned for *Eucalyptus* sp. afforestation. Efforts were made to ensure an old enough cultivation, in order to get a better record of its effects on the soil profile. This determined an exhaustive search in the west sedimentary basin of Uruguay, to identify a soil with both types of vegetation covers, a portion under grassland and adjacent eucalyptus afforestation implanted some decades ago (25 years), which had never been fertilized. Pits were excavated at the site, in order to describe and verify the similarity of the soil profiles under both vegetation covers.

2.2. Sampling strategy

Sampling was done by topographic levels (high, middle and low slope) and soil use (grassland and eucalyptus), 3 replicates in performing each of the 6 combinations (9 sampling points for each use and 6 for each 3 slope levels) (Fig. 1).

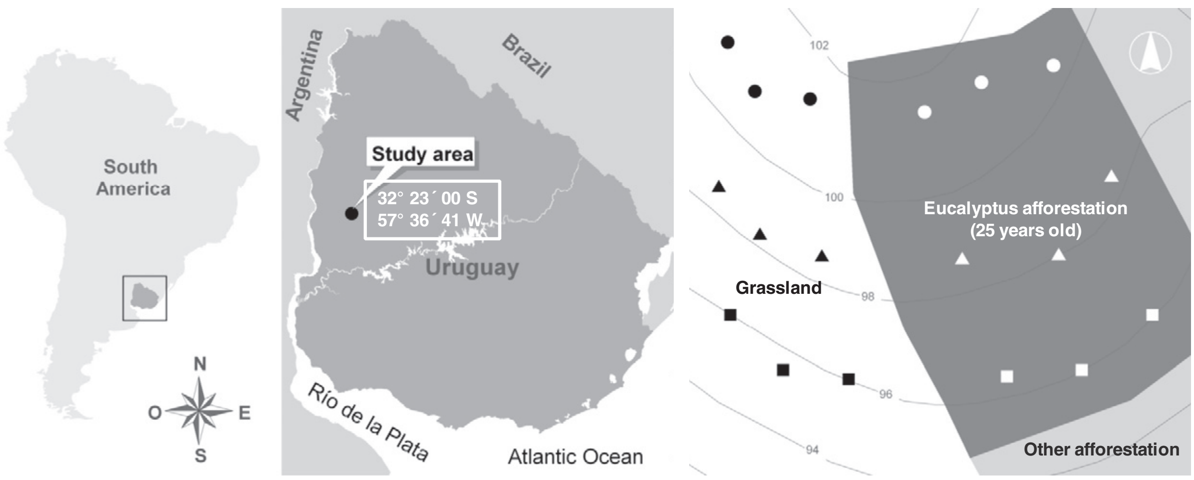

Fig. 1. Study area. Right: soil sampling point details. Key to symbols: black ones indicate grassland; white, afforestation; circles, high slope; triangles, middle slope; squares, low slope. Contour interval is 2 m.

Table 1
Average content of clay in the soil horizons.

Subhorizon	Depth (cm)	Average soil clay content (%)
A_{11}	0–5	19.2
A_{12}	5–18	17.6
A_3	18–38	17.6
B_1	38–45	26.3
B_2	45–80	40.1

The procedure was applied in 5 horizons (A_{11}, A_{12}, A_3, B_1 and B_2) and for each of the physicochemical parameters analyzed (pH, SOM, CEC, Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe_d, Fe_o).

2.3. Physicochemical analysis

The samples were dried at 40 °C, ground and sieved over 2 mm mesh. Standard methods of soil characterization were used in the analysis. Soil pH was measured in suspensions prepared with 10 g of soil in 25 ml of H_2O (pH meter, Hanna, Model HI 8424). The percentage of soil organic matter (SOM) was determined by the Walkley–Black modified method (Burt, 1996). 1 g soil samples are treated with 10 ml of 1 N $K_2Cr_2O_7$ solution to which 20 ml of concentrated H_2SO_4 is added. After shaking, reposing and spinning, the preparation is read through a 650 nm spectrophotometer (Spectronic, Model 401). Cation exchange capacity (CEC) was determined by the 1 M NH_4OAc method at natural soil pH. Exchangeable bases (Ca, Mg, Na and K) were determined by the 0.2 M NH_4Cl method (Sumner and Miller, 1996). Bases extracted from the supernatant were determined by atomic emission and absorption spectrophotometer (Perkin Elmer, Model 3110). Ca^{2+} and Mg^{2+} absorption was monitored at 422.7 and 285.2 nm wavelengths respectively. Na^+ and K^+ emissions were monitored at 589.0 and 766.5 nm respectively.

Residual substrate ions were displaced by a solution of 0.2 M KNO_3 and determined by titration. The exchangeable Al was extracted by 1 M KCl solution (McLean et al., 1958). The free iron oxide content (Fe_d) was evaluated by the Na dithionite–citrate–bicarbonate extraction (Mehra and Jackson, 1960), the amounts of Fe-amorphous oxides (Fe_o) by acid-ammonium oxalate dissolution in the dark (Schwertmann, 1964), and the amounts of Fe-amorphous oxides (Fe_o) by acid-ammonium oxalate dissolution in the dark (Schwertmann, 1964).

For mineralogical analysis of clay fraction, we selected those samples at the low slope, *a priori* considered to be more sensitive to possible changes in vegetation cover.

2.3.1. Clay analysis

Particle-size distribution in soils was determined by the pipette method (Burt, 1996). The clay fraction (<2 µm) was obtained from the soil after oxidizing the organic matter with dilute H_2O_2 and by dispersion with Calgon (sodium hexametaphosphate) and sedimentation in water. The clay fraction was flocculated (several drops of $SrCl_2$ solution) and deposited on a glass slide. No chemical treatment was performed on the material before the X-ray diffraction (XRD) in order to observe clays, particularly illite and kaolinite. Oriented specimens were analyzed by X-ray diffraction using Cu K-alpha radiation (1.54056 nm) on a Philips X' Pert diffractometer equipped with a theta–theta goniometer. X-ray scans were from 5 to 30° 2 theta and a 0.02° step size (at 1 s/step). These samples were taken in the A_{11}, A_{12}, A_3, B_1 and B_2 subhorizons. When these had a high tenor of iron oxide, they were removed with sodium dithionite in order to improve signal-to-noise ratio. In the diffraction patterns obtained, the kaolinite is identified by small broadening, symmetrical and strong (001) peaks near 0.70–0.71 nm and near 0.35 nm by (002) reflection

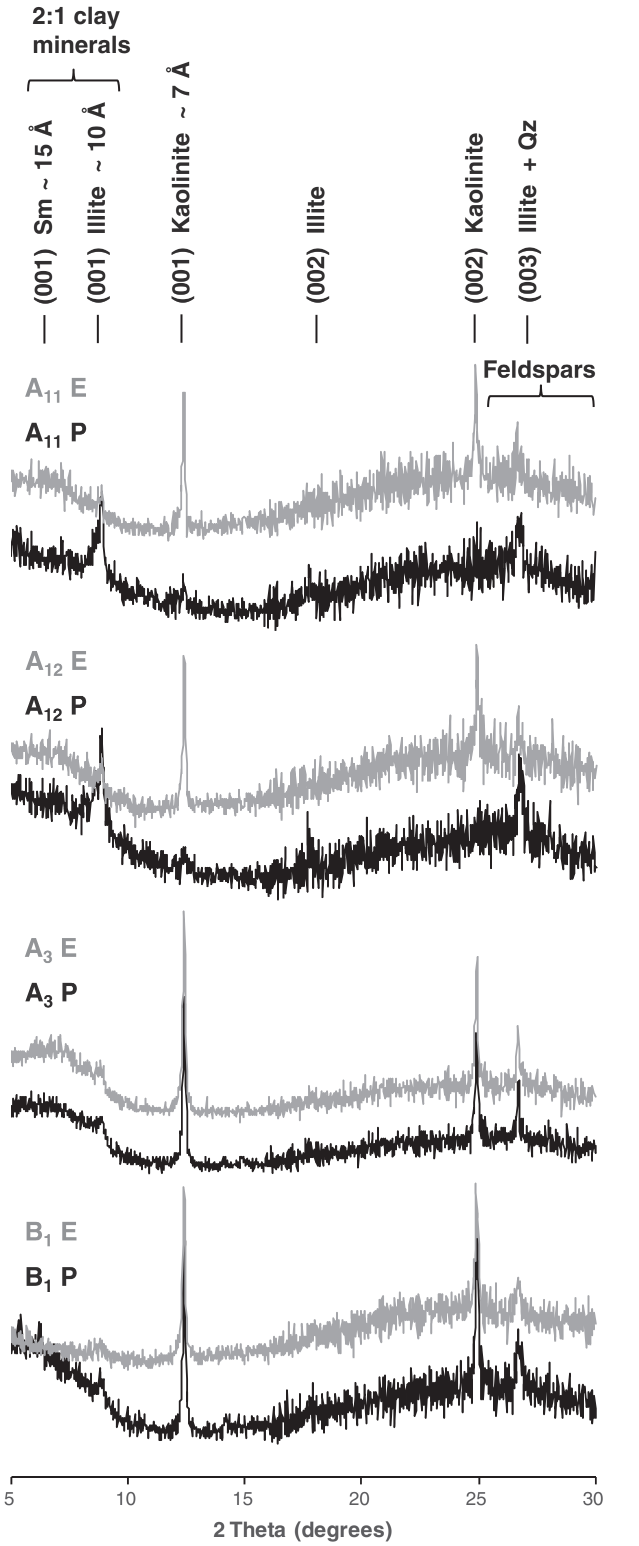

Fig. 2. X-ray diffractograms of the grassland soil (black) and of the afforested grassland soil (light gray) for horizons (A_{11}, A_{12}, A_3 and B_1).

(Note: the basal reflections of 2nd or 3rd order are expressed as theoretical distances). Kaolinite also presents a reflection (021) lower intensity near 0.38 nm. Meanwhile, the "illite-like" or "2:1 K-bearing minerals" (*sensu* Barré et al., 2007b) are identified by the reflections at 1.0 nm, 0.5 nm, and 0.33 nm, with a distinctive shoulder in the basal peak at 1.05 nm.

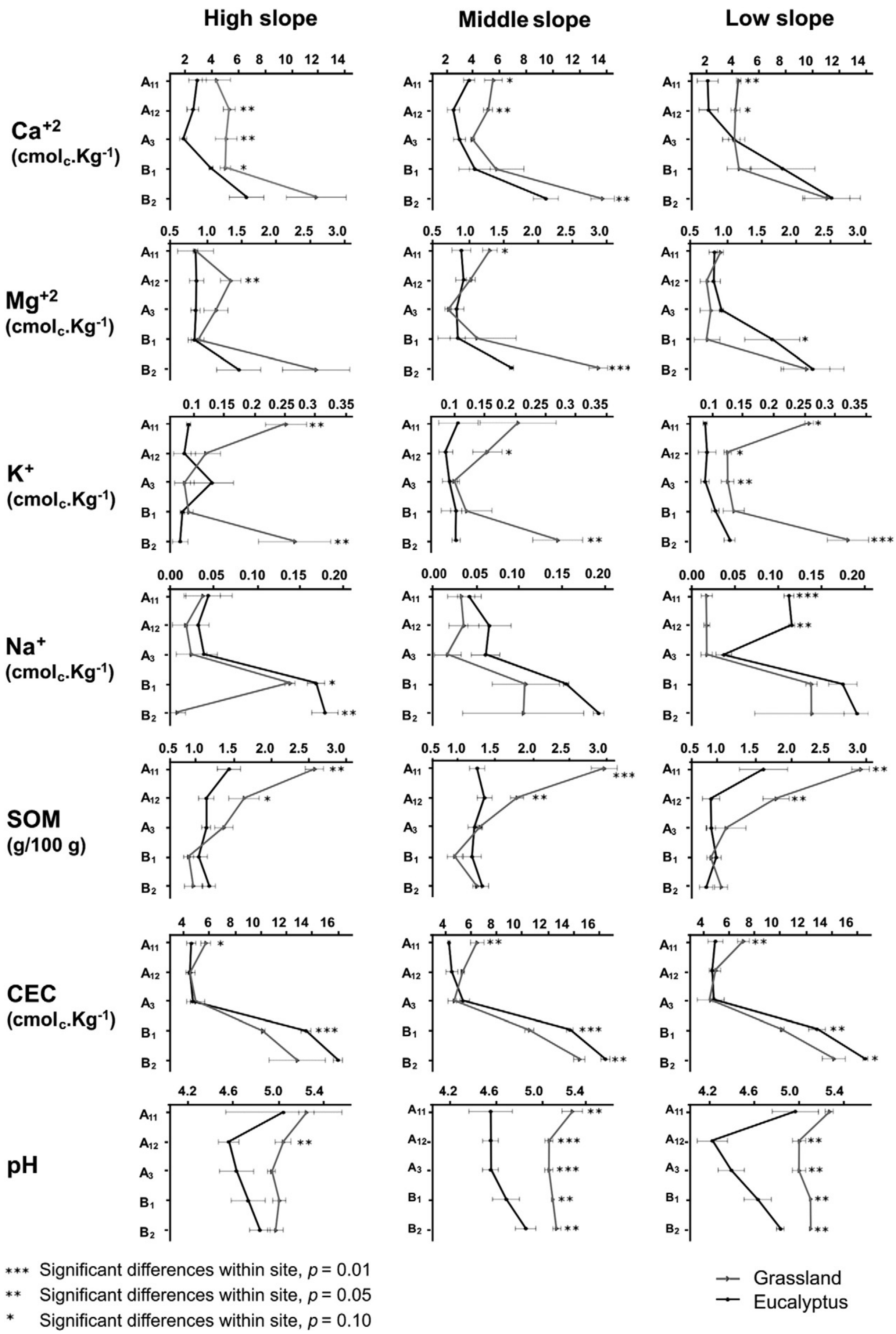

Fig. 3. A comparison of physicochemical parameters of soils, both under grassland and under plantations.

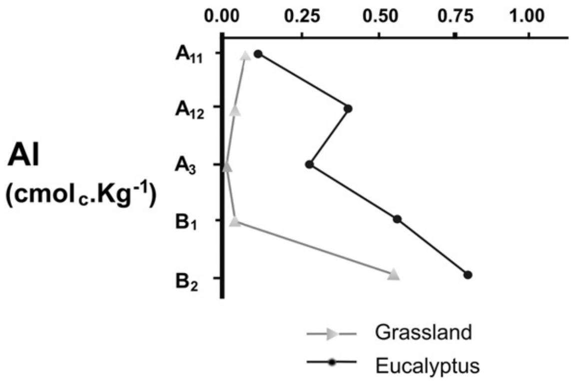

Fig. 4. Behavior of Al^{3+} in the soil profile both under grassland and under plantations.

2.4. Statistical analysis

Normality and homogeneity of variance were evaluated with Shapiro–Wilk and Levene's tests, with a rejection probability of $p<0.05$. When accepted, a one-way analysis of variance (ANOVA) was performed on factors (soil use and slope) with three replicates for each combination. Only the results of the two-way ANOVA were used for comparisons of means to minimize type I error. The comparison between uses was made with the Student's *t*-test in samples with normal distribution and with the Mann–Whitney *U* nonparametric test in the remaining. Statistical analysis was performed using the R Statistical Computing Environment (R Development Core Team, 2007).

3. Results

3.1. Clay mineralogy

In A_{11} and A_{12} subhorizons (0–20 cm) of grassland soil cultivated 25 years with eucalyptus, clay mineralogy recorded significant differences from the same horizons in soil under grassland vegetation. The most noticeable difference in the diffractograms is expressed in the relative magnitude of basal reflections (00l) of illite and kaolinite (Fig. 2).

In these subhorizons of the grassland soil, K-bearing clay minerals are dominant. Diffractograms show this through a ragged and very high peak (001) towards 10 Å accompanied by a clear peak (002) and another (003). In this soil the (001) and (002) kaolinite reflections are also present, although with lower intensities. In contrast to the soil under eucalyptus cultivation, kaolinite pattern is clearly dominant in both subhorizons as showed in the diffractogram, with stylized and narrow (001) and (002) peaks at 7 and 3,33 Å. K-bearing clay mineral pattern of reflections is less intense than in the grassland. This pattern consists of (001) and (003) peaks and a very weak (002) peak.

The A_3 and B_1 subhorizons, showed no significant differences between the diffractograms of natural grassland and the eucalyptus cultivation (Fig. 2). Kaolinite was the most important clay mineral in both cases, showing similar patterns in the two diffractograms, both in spacing and in the intensity of the reflections. In the case of B_1 horizon under eucalyptus, the diffractograms showed a low signal-to-noise ratio due to fluorescence of iron oxide. After treatment with dithionite, the diffractogram pattern was similar to the natural grassland.

3.2. Physicochemical properties

ANOVA assumptions were violated in limited opportunities, 1/35 in middle slope (Na^+ in B_1) and 6/35 cases in low slope (pH and K^+ in A_{11}; Na^+ in A_{12}; Mg^{2+} in A_3; Mg^{2+} and pH in B_2).

In most analyzed cases with two-way factorial analysis (ANOVA), topographic factor effect and its interactions were not significant, in contrast to land-use factor which certainly was, particularly in the surface horizons.

The significance of differences between uses (Fig. 3) for each slope sector and horizon indicates the (p) value of the differences between means calculated using the Student-*t* tests or Mann–Whitney *U* test when distribution is not normal.

In the first few centimeters (~20 cm), where mineralogical changes of clays are shown (A_{11} and A_{12} subhorizons), the number of affected parameters varied according to their location in the landscape; in order of importance, the sequence of these changes was as follows: low slope > middle slope > high slope, 10/14, 9/14 and 7/14, respectively. SOM under eucalyptus showed significantly lower values in the first subhorizons regarding grassland, throughout the entire slope.

Up to 20 cm, K^+ also showed a strong tendency to decrease in the lower part of the slope; this decrease reached almost the whole profile. Even though in the A_3 high slope subhorizon K^+ showed a tendency to increase, this was not statistically significant. With some differences Ca^{2+}, just as SOM presented significant changes in the first 20 cm of the profile, across the whole landscape. This trend of Ca^{2+} is inverted in low slope in depth (from subhorizon A_3), although its values are not statistically different from those of the grassland. Mg^{2+} did not show the same trend as Ca^{2+}, though it tended to get lost in subhorizons near the surface. On the contrary, Na^+ showed a smooth tendency to increase under the eucalyptus cultivation, though at different depths. In the high slope, it increased in depth (B horizon), while in the low slope, it did it near the surface (A_{11} and A_{12} subhorizons). CEC showed a similar behavior in the three topographic positions (high, middle and slow slopes), with a significant decrease near the surface (A_{11} subhorizon) and it increased in depth (B subhorizons). At the same time, in afforestation the pH decreased throughout the whole profile (A and B horizons), though it reached the most significant values in the middle and low slopes. This decrease in pH was accompanied by a significant increase in Al^{3+} (Fig. 4), especially in depth (B horizons).

The slope factor was not significant in most of the parameters, therefore it has not been considered in the discussion (Table 2).

4. Discussion

4.1. Clay minerals and land use change

The possibility that the vegetation cover may influence the stability of some clay minerals is recognized in the literature (e.g. Bain, 1995; Barré et al., 2007a; Drever, 1994; Hinsinger et al., 1992; Kelly et al., 1998), and some authors indicate that 2:1 clay minerals can react as fast as a biological system (Barré et al., 2007a). It would respond to nutrient demand established by plants in their life cycle, which determines a capture time that must necessarily be accompanied by the mineral fraction of the soil. Consequently, it is expected that the crystallochemical structure of minerals such as clays, changes according to demand.

Nevertheless a reversible character is commonly attributed to such modifications. In moderately degraded agricultural soils, the dominant mechanism in this process is the release of K, fixed or structural, from the phyllosilicates (Sparks and Huang, 1985).

The ability to fix or release K has led us to postulate that illitic clays behave as a reservoir of K in soils (Barré et al., 2007a). The K input made by crops can lead to the transformation of illites (Fichter et al., 1998). Simonsson et al. (2009) argue that the uptake by crops of up to 80% of "not interchangeable" K from illite layers of 10 Å, cannot be recovered by addition of K as a fertilizer. The results of our study indicate that the fall of K^+ values was accompanied by a significant decline in the

Table 2
Results of three-way ANOVA analysis with interactions (horizon, slope and soil use).

	Df	Sum Sq	Mean Sq	F value	Pr(>F)	Signif.
Ca^{2+}						
SLOPE	2	11.19	5.593	1.6535	0.19999	
USE	1	67.01	67.012	19.8091	3.78e−05	***
HORIZON	4	645.39	161.347	47.6951	<2.2e−16	***
SLOPE:USE	2	28.61	14.306	4.2288	0.01914	*
SLOPE:HORIZON	8	25.01	3.126	0.9240	0.50342	
USE:HORIZON	4	26.53	6.632	1.9603	0.11214	
SLOPE:USE:HORIZON	8	28.30	3.537	1.0455	0.41300	
Residuals	60	202.97	3.383			
Mg^{2+}						
SLOPE	2	0.1609	0.0805	0.5643	0.571730	
USE	1	0.7308	0.7308	5.1252	0.027209	*
HORIZON	4	20.7970	5.1992	36.4629	1.929e−15	***
SLOPE:USE	2	1.8891	0.9445	6.6241	0.002515	**
SLOPE:HORIZON	8	1.1379	0.1422	0.9975	0.447483	
USE:HORIZON	4	2.2690	0.5673	3.9783	0.006276	**
SLOPE:USE:HORIZON	8	1.4779	0.1847	1.2956	0.263175	
Residuals	60	8.5554	0.1426			
Na^{+}						
SLOPE	2	0.005480	0.002740	1.5635	0.2178	
USE	1	0.054022	0.054022	30.8244	6.783e−07	***
HORIZON	4	0.230576	0.057644	32.8908	1.621e−14	***
SLOPE:USE	2	0.001910	0.000955	0.5450	0.5827	
SLOPE:HORIZON	8	0.010698	0.001337	0.7630	0.6363	
USE:HORIZON	4	0.011000	0.002750	1.5690	0.1942	
SLOPE:USE:HORIZON	8	0.017425	0.002178	1.2428	0.2906	
Residuals	60	0.105155	0.001753			
K^{+}						
SLOPE	2	0.001520	0.000760	0.4283	0.6536	
USE	1	0.128974	0.128974	72.6868	6.249e−12	***
HORIZON	4	0.120003	0.030001	16.9078	2.475e−09	***
SLOPE:USE	2	0.002972	0.001486	0.8375	0.4378	
SLOPE:HORIZON	8	0.009574	0.001197	0.6744	0.7119	
USE:HORIZON	4	0.110692	0.027673	15.5958	8.411e−09	***
SLOPE:USE:HORIZON	8	0.008624	0.001078	0.6075	0.7679	
Residuals	60	0.106463	0.001774			
SOM						
SLOPE	2	0.2595	0.1297	2.4385	0.0959	.
USE	1	3.5561	3.5561	66.8432	2.458e−11	***
HORIZON	4	14.7366	3.6841	69.2494	<2.2e−16	***
SLOPE:USE	2	0.1009	0.0505	0.9484	0.3931	
SLOPE:HORIZON	8	0.5990	0.0749	1.4073	0.2121	
USE:HORIZON	4	6.9688	1.7422	32.7474	1.771e−14	***
SLOPE:USE:HORIZON	8	0.4335	0.0542	1.0186	0.4321	
Residuals	60	3.1921	0.0532			
CEC						
SLOPE	2	2.72	1.36	1.2957	0.281248	
USE	1	11.66	11.66	11.1227	0.001466	**
HORIZON	4	1617.06	404.27	385.5042	<2.2e−16	***
SLOPE:USE	2	0.92	0.46	0.4409	0.645539	
SLOPE:HORIZON	8	5.77	0.72	0.6873	0.701010	
USE:HORIZON	4	75.14	18.78	17.9125	1.001e−09	***
SLOPE:USE:HORIZON	8	2.59	0.32	0.3092	0.959677	
Residuals	60	62.92	1.05			
pH						
SLOPE	2	0.0327	0.0163	0.3349	0.7167724	
USE	1	3.7618	3.7618	77.1207	2.302e−12	***
HORIZON	4	1.2196	0.3049	6.2506	0.0002844	***
SLOPE:USE	2	0.2069	0.1034	2.1207	0.1288475	
SLOPE:HORIZON	8	0.3684	0.0461	0.9442	0.4876968	
USE:HORIZON	4	0.3049	0.0762	1.5626	0.1959276	
SLOPE:USE:HORIZON	8	0.2031	0.0254	0.5205	0.8364281	
Residuals	60	2.9267	0.0488			

Signif. Codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1.

illite content in the topsoil (A_{11} and A_{12} subhorizons) under eucalyptus afforestation. In turn, and as a characteristic of this culture, those cations of higher nutritional demand would be subject to a more rapid turnover and a greater retention time in their biomass, as expressed in the vertical pattern of K^{+} we have obtained (Fig. 3). These results coincide with a study in 2.5 year old of *E. grandis* cultivation, which has established that K^+ is the second most accumulated element after nitrogen: $N>K^+>Ca^{2+}>Mg^{2+}>P>Mn^{2+}>Fe^{3+}>Zn^+>Cu^{2+}$ (Poggiani et al., 1983). This greater accumulation of K^+ by the tree increases the residence time outside soil; situation that turns irreversible the process of destructuration of the illite. A positive feedback is thus produced and this way the K released by the biomass and eventually entered the soil, will not find illites in sufficient quantity to return to its structure and therefore be retained in the soil. This situation would in general turn negative the net balance of K^+ in soils under this cultivation; moreover when runoff and/or leaching losses possibly occur. In fact, the greatest effects were registered mainly in the low slope of soil under *E. grandis* (Fig. 3). Consequently Carrasco-Letelier et al. (2010) in eucalyptus afforestation in western Uruguay have observed an increase of K in water streams. These observations are confirmed by other authors for other regions and other tree species (e.g. Lickens et al., 1994; Romanowicz et al., 1996).

However, the action of organic acids provided by eucalyptus should not be dismissed. Even though the possibility of a vermiculitization or smectitization of illite has not been analyzed in this study, the dissolution by organic acids could also be a major mechanism in the fall of the spectrum of 10 Å minerals. Whatever the dominant mechanism, it can be argued that this phenomenon is irreversible, not only because there was a net loss of K, but also because simultaneously the content of illite decreased. This imbalance of K might be magnified when the plantation is harvested, the biomass exported, and the site re-forested.

In case these results are generalized to other land uses with similar characteristics, their repercussions would be remarkable considering that the illite is the main reservoir of mineral K in soils of temperate regions (Barré et al., 2007b; Hinsinger, 2002) which use is potentially agricultural.

4.2. Nutrient uplift model in eucalyptus afforestation

Changes in illitic clay mineralogy can be mainly explained by the effect of bio-cycling, particularly the K in the first centimeters of soil in both grassland (Barré et al., 2009) and afforestation (Tice et al., 1996). In other words, the activity of plants would enrich the upper soil profiles with inorganic elements they use to grow (e.g. Berner et al., 2005; Jobbágy and Jackson, 2001; Jongmans et al., 1997; Kleber et al., 2007; Wallander and Wickman, 1999). This phenomenon called "nutrient uplift", "translocation of elements" or "biological pumping" could counteract the loss of elements by leaching in surface soils (Jobbágy and Jackson, 2004b; Jobbágy and Jackson, 2001). This could gradually lead to increase the concentration of potassium and silica in the upper parts of soil profiles (Barré et al., 2007a; Jobbágy and Jackson, 2001). According to this model, cation cycling and redistribution by trees are also the dominant mechanisms of acidification in this system (Jobbágy and Jackson, 2003). However, in our study an increase of K in the topsoil was not observed (Fig. 3).

High biomass production of some forests may result in an increased accumulation of cations in this biomass and a depletion of chemical and mineralogical reserves of soil (Nordborg and Olsson, 1999). In this way, it is reasonable to assume that the stability of clay minerals in the upper soil horizons may be affected (Barré et al., 2009; Berner et al., 2005; Kleber et al., 2007; Lucas, 2001). Our results show the depletion of certain cations (K^+ and Ca^{2+}) centered in the first centimeters of the soil profile and the increase of others in depth, as Na^+ (Fig. 3). This would indicate that there is no real input of these cations (K^+ and Ca^{2+}) into the soil, which can be justified by the existence of a high turnover on the surface, in the organic horizon itself where the development of a dense network of thin roots at this level can represent 90–95% of the total length of the root system (Bowen, 1984), which then decreases exponentially in depth. This network of roots would operate as a "filter" to all those nutrients of greater demand, once they are returned by the aerial biomass. However, a possible input of K^+ into the soil profile could be counteracted by the loss through runoff and/or leaching in accordance with the results of Carrasco-Letelier et al. (2010) who determined an increase of K^+ in fluvial watercourses of basins afforested with eucalyptus in this region.

This limitation on the input of certain nutrients, might determine its deficit in the soil, so the *nutrient uplift model* (translocation or biological pumping) proposed by Jobbágy and Jackson (2004b) and also by other authors (e.g.; Lucas, 2001; Berner et al., 2005; Kleber et al., 2007), does not apply to a forest management with eucalyptus in these sandy soils.

4.3. Behavior of other physicochemical parameters

In the context of recorded mineralogical changes, it is expected that there is also a fall in the electrical charge of the soil in the first centimeters as the decrease in the content of illite and the comparative increase of kaolinite, which is larger, imply a decrement of the specific surface area (SSA) and a decrease of negative charges, which also are not permanent, but pH-dependent. Thus, the low CEC given by the predominance of kaolinitic clays would promote the leaching of K high enough to be lost in a considerable amount (Sharpley, 1990). Properties such as the turnover of the SOM can also be affected, as different clay minerals use different binding mechanisms in the complexation of organic matter.

The composition of organic matter and the differences in the mean residence time may be influenced by the type of predominant clay in the soil (Wattel-Koekkoek et al., 2001). Thus, for example, in accordance with Wattel-Koekkoek and Buurman (2004) who found that SOM associated with kaolinite has a faster turnover than with other clay minerals, the low values of SOM found under *E. grandis* and the fall of CEC in the topsoil could be explained (Fig. 3).

In soils dominated by 1:1 minerals, Al and Fe oxides are often found, which are strong flocculants, and can further reduce the area available for adsorption of the SOM (Six et al., 2002). Our results show a marked increase of Al^{3+} with increasing depth (Fig. 4). This process is related to increased acidity derived from the presence of organic acids of low molecular weight which come from the decomposition of litter, which as argued by Pai et al. (2004) can promote the rapid decomposition of clay minerals such as illite, releasing Fe and Al in soil solution. These acids acting as ligands make these metals susceptible to horizontal and vertical transport within the profile (Egli et al., 2008; Zanelli et al., 2007) which is characteristic of podzolization processes (Bloomfield, 1953). Soils with podzolic properties are characterized precisely by an accumulation of organic matter in the upper horizon and a high content of phases of amorphous or poorly crystalline Fe and Al (Zanelli et al., 2007).

The significant fall in pH registered in accordance with Jobbágy and Jackson (2003) may be associated with the loss of exchangeable cation bases, especially Ca, and the increase in exchangeable Al. In summary, a decrease in the concentrations of exchangeable cations can be attributed to the displacement by hydrogen ions, caused by acid deposition or capture of cations by roots (Johnson et al., 1994; Richter et al., 1994). The imbalance between the capture of cation and anion, and hence between H^+ and OH^- released to the solution, would determine the amount of free acidity that flows through the rhizosphere and is available to react with mineral surfaces (Gobran et al., 2005). The Al^{3+} has a much greater affinity for negatively charged surfaces than calcium, thus it can displace the absorbed calcium (Lawrence et al., 1995). Once captured by trees, this cation is partly immobilized as oxalate crystals and accumulated in their biomass (Johnson et al., 1988). As suggested by Turner and Lambert (2008), when the requirement is greater than the capture, the difference represents redistribution within the biomass, whereas when the capture is greater than the requirement, the difference represents the accumulation in excess, and this situation occurs with potentially immobilizable nutrients such as calcium. Studies of Kojima et al. (2002) in *Eucalyptus camaldulensis* indicate that the concentration of K in the sap of growing trees was much larger than that of calcium. But in the body of the plant throughout its growth, calcium accumulates more than potassium. Consequently, the nutrient that is likely to be scarcer in eucalyptus plantations is K (Hernández et al., 2009). The felling of trees could reduce the availability of calcium through the elimination of calcium stored in the biomass, which may reduce growth rates of regeneration of the stand (Federer et al., 1989; Hornbeck et al., 1990).

The behavior of these cations has led Jobbágy and Jackson (2003) to propose that the turnover and redistribution by the trees, rather than leaching of cations by organic acids or a greater production of carbonic acid in soil, are the dominant mechanisms of acidification in afforested native grasslands of a temperate and humid region such as La Pampa in Argentina. However this has not been verified in our study, and on the contrary, a net loss of cations was observed, particularly in the topsoil (Fig. 3), suggesting that the recorded acidification process is strongly conditioned by the leaching of organic acids. As it was mentioned, the predominance of kaolinite and Fe and Al oxides can further reduce, even more, the surface available for SOM adsorption, thus promoting leaching. Hence, there are also good reasons to expect a strong link between the quality of organic matter and the mobility of elements such as Fe and Al and its speciation in the solid phase (Zanelli et al., 2007). In turn, the sequence of mobilization processes of organic carbon, Al and Fe in the surface horizons of acid soils, followed by a vertical transport and subsequent immobilization in less acidic subsoils, is considered characteristic of a podzolization process (Sommer et al., 2001).

4.4. Effects on soil mineralogy

Replacement of grassland vegetation by planting eucalyptus would set a positive feedback loop starting from the input–output of some nutrients, from and to the soil, with the consequent re-adaptation of its cycle, affecting some structural nutrients. This directly affects the secondary minerals due to changes in structural elements such as the redistribution of Al^{3+}, Fe^{3+} or the loss of K. This process must particularly affect the mineralogy of illites within a comparatively short period of time (only 25 years). The high demand for K and its short time retained in the litter due to its rapid turnover could be one of the determining factors in the destabilization of this mineral. This "competition" down the trees for K, particularly in the first centimeters of the soil profile, conditions the destruction process of illite (2:1), with consequent relative increase of kaolinite (1:1). It is therefore reasonable to expect that the change given in the soil will become irreversible.

So after the final abandonment of the eucalyptus cultivation, in a hypothetical scenario in which the original grassland vegetation is restored, the restoration of the original mineralogical composition cannot be expected. The set of observed changes is consistent with a process of podzolization, conducive to developing an Alfisol; soil from which *E. grandis* is native. The results show the importance of considering the effects of land use change not only through the change of its properties, but also through the identification of thresholds of no return.

These results are a warning for the region because sandy soils are being heavily forested and especially in the case of Uruguay where they are promoted even by state policies that have designated soil units as "priority for afforestation" in the context of the regulation that has been established for such activity, and therefore they have even benefited from economic incentives or tax exemptions.

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