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ORIGINAL ARTICLE

Soil Organic Carbon vs. Bulk Density Following Temperate Grassland Afforestation

Carlos Céspedes-Payret[1] **· Bruno Bazzoni**[1] **· Ofelia Gutiérrez**[1] **· Daniel Panario**[1]

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Abstract Afforestation is part of a worldwide strategy to mitigate CO_2 emissions. However, afforestation in grassland soils may have the opposite effect by promoting the loss of native carbon. Potential effects of this land use change on the flow of organic carbon to and from the soil can be described through bulk density (Db). Nowadays the suitability of Db for this purpose is being questioned. In order to bring new elements to the discussion, we carried out a comparative study of soil in the western region of Uruguay. Based on the background information and our own data, collected for over a decade, we evaluated the fitness of Db as proxy soil organic carbon (SOC) stocks in grassland converted to tree afforestation. These data were also related to soil pH values. The sampling consisted of five plots afforested with *Eucalyptus grandis* paired with control plots under grassland. All samples were taken at depth (0–10 cm and 10–20 cm) except for Db samples (0–10 cm). In afforested sites, Db increased (1.62 vs 1.53 g/cm^3; $p \leq 0.01$) and SOC decreased (0–10 cm: 0.90 vs. 1.22%; $p \leq 0.08$). Db values were not significantly correlated with SOC content. As with SOC, pH values decreased after afforestation at both depths (0–10 cm: 4.92 vs. 5.62; $p \leq 0.01$; 10–20 cm: 4.76 vs. 5.54; $p \leq 0.01$). The high acidity generated in soils following afforestation, is enough to affect the interaction between mineral and organic fractions and, with them, the original Db values. According to a previous study in the same location, there is a change in the predominance of different clay minerals in the topsoil (0–20 cm). This qualitative change in the mineral fraction

✉ Ofelia Gutiérrez
oguti@fcien.edu.uy; gutierrez.ofelia@gmail.com

Carlos Céspedes-Payret
cespedes@fcien.edu.uy

Bruno Bazzoni
brunobazzoni@gmail.com

Daniel Panario
panari@fcien.edu.uy

1 UNCIEP, Instituto de Ecología y Ciencias Ambientales (IECA), Facultad de Ciencias, Universidad de la República, Igua 4225, C.P, 11400 Montevideo, Uruguay

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can affect the ability of the soil to retain organic carbon, and not be reflected in the recorded Db values. The non-reciprocity recorded between Db and SOC values warns about the need for restriction of the generic use of Db in calculation of SOC stocks estimation. In view of these results, we present a discussion of possible causes that explain the disparity between Db values and SOC measurements.

Keywords Soil organic carbon · Bulk density · Grassland afforestation · Soil acidification · Land use change · Uruguay

1 Introduction

Soil degradation affects large areas of cropland land, resulting in a general decline in agricultural productivity (Seenivasan et al. 2016). Such agricultural practices result in massive decrease of soil carbon, exacerbating the degradation of ecosystems, posing a serious threat to human society survival (Pu et al. 2014).

South American temperate grasslands, especially in Río de la Plata basin (Fig. 1), are being afforested (Vega et al. 2009) with fast-growing species (*Eucalyptus* spp. and *Pinus* spp.). In recent years, the expansion of forestry has experienced renewed growth due to agreements derived from the Kyoto Protocol (Clean Development Mechanism, CDM). Articles 3.3 and 3.4 allow countries to carry out tree plantations and reforestation (since 1990) to capture atmospheric carbon, in order to meet their goal of reducing greenhouse gas emission (Farley et al.

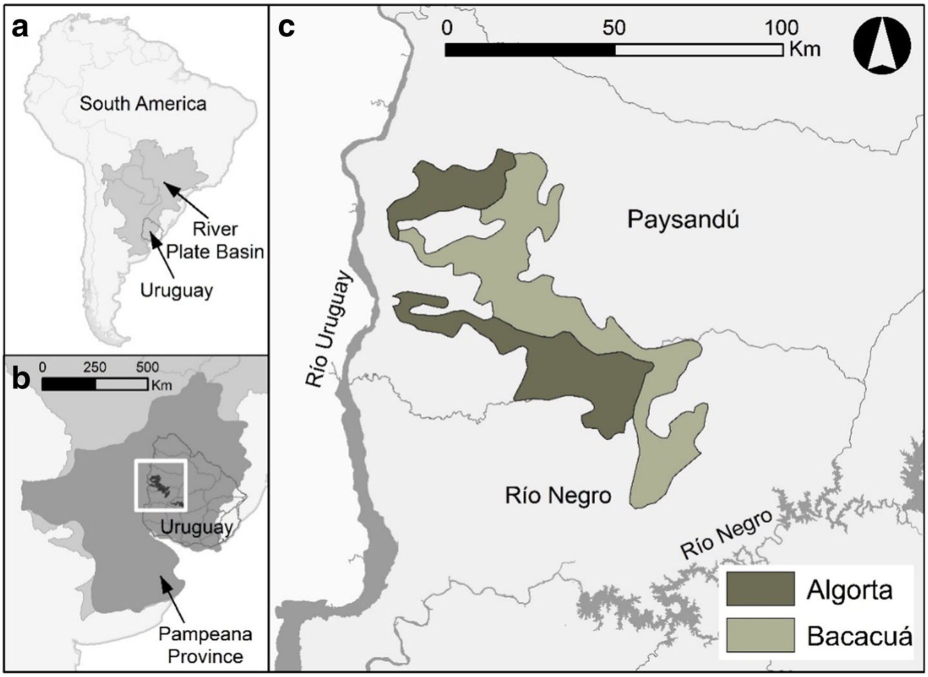

Fig. 1 **a** South America and de River Plate basin. **b** Uruguay and the Pampeana Province. The white rectangle shows the study area. **c** Western region of Uruguay with the study area: Algorta and Bacacuá soil unit of the uruguayan soil map, original scale 1:1,000,000 (Altamirano et al. 1976; Dirección de Suelos y Fertilizantes 1976)

2005). Actually, commercial tree plantations are also included. In the case of Uruguay, the national greenhouse gases budget clearly indicates that after implementation of the National Forestry Plan (in 1991), the country status has switched from carbon "source" to carbon "sink", mainly due to great absorption of CO_2 by woody biomass and soils (MVOTMA/DINAMA/UCC 2010). Nevertheless, the ability of tree plantations to accumulate soil organic carbon (SOC) remains a subject of debate (Post and Kwon 2000; Garten 2002; Paul et al. 2003; Kaiser and Guggenberger 2003; Carrasco-Letelier et al. 2004; Céspedes-Payret 2012). A major part of this debate is related to the suitability of bulk density (Db) as a descriptor parameter of SOC stocks estimates (Six et al. 1999; Denef et al. 2002; Gifford and Roderick 2003; Denef and Six 2006; Lee et al. 2009). It has been observed (in many soils) that the type of mineral composition is more important for soil carbon storage than the total clay amount (Veldkamp 1994; Torn et al. 1997; Percival et al. 2000).

This has led to question the validity and scope of Db in cases where land use change leads to the alteration of certain mineral components, and thus, to a change in the binding mechanisms with organic carbon entering to the soil. However, despite these questionings, institutions such as the Intergovernmental Panel on Climate Change (IPCC), proposed the inclusion of Db as a tool to calculate carbon stocks per surface unit (Watson et al. 2000). Yet, when a change in the soil mineral fraction occurs, the processes of organization of mineral and organic particles to form aggregates may be affected. For example, the interaction between mineral particles may occur without SOC as cementing agent (Denef et al. 2002; Denef and Six 2005). This means that the type of binding between particles is what would be conditioning SOC not to act as crucial linking agent (Six et al. 2000a). This is the case of soils with dominance of electrostatic interactions between kaolinite, oxides and vermiculite, in which structural stability is not so heavily dependent on SOC content (Six et al. 2000a). As known, clay SOC interactions are less stable in soils with 1:1 clay predominance compared to those with 2:1 clay predominance (Denef and Six 2006). Consequently, SOC associated with kaolinite has a faster turnover than with other clay minerals (Wattel-Koekkoek and Buurman 2004). Instead, the binding of SOC to smectite (2:1) is tighter than to kaolinite, and its turnover time is twice as long (Wattel-Koekkoek et al. 2003). In other words, soil mineralogical properties are highly relevant factors when determining the variation in SOC mean residence time (Wattel-Koekkoek et al. 2003). These observations are consistent with studies that have demonstrated that the ability of minerals to preserve organic matter may be the result of a combined influence of surface reactive sites and a large active specific surface area (Kögel-Knabner et al. 2008). Therefore, the amount and relative percentage of organic carbon in organo-mineral fractions may vary markedly, not only between soil types, but also between horizons within the same soil (Kögel-Knabner et al. 2008). Nevertheless, these variations may not be reflected on Db values obtained in the field.

Though most SOC dynamics models recognize the importance of clay minerals soil content (Saffih-Hdadi and Mary 2008), they fail to take into account the actual mechanisms by which the clay fraction stabilizes organic matter (Barré et al. 2014). This is the case of models of widespread application such as Roth-C and Century, in which SOC mineralization rates decrease with increasing clay-sized particles content (Barré et al. 2014 and references therein). Furthermore, these models do not contemplate the effect of stabilizing mechanisms on the possible variation of Db within the same soil type. For example, in soils with kaolinite predominance it has been observed that carbon concentrations do not increase with the size of aggregates (Six et al. 2000a). Therefore, the use of Db as an expression of the relationship between solid and porous space (Keller and Håkansson 2010), would not contemplate cases where the relationship between charge density of the mineral fraction and SOC content is affected by a change in land use. As mentioned above, land use change can induce an alteration in the solid soil constituents (Guo and Gifford 2002) and particularly affect the mineralogical composition of the clay fraction (Céspedes-Payret et al. 2012 and references therein). Consequently, if a change occurs in predominance from 2:1 to 1:1 clay minerals, it will cause soil reactivity to become pH-dependent (since organic matter is pH-dependent) affecting the natural process of flocculation/dispersion, and leading to an aggregation mechanism less dependent on organic carbon (Goldberg et al. 1990).

This background is in keeping with studies developed in grassland soils of Uruguay converted to Eucalyptus cultivation. The results of research conducted at the same location as the present study showed a change in predominance from 2:1 to 1:1 clay minerals after afforestation (Céspedes-Payret et al. 2012). These results showed a fall in SOC values in the top twenty centimetres of the soil profile, along with an increase in 1:1 clay minerals and marked reduction in pH (Céspedes-Payret et al. 2012). This increase in acidity and alteration of secondary minerals, with the subsequent liberation of Al and Fe and their translocation in soil, would indicate an incipient process of podzolization (Carrasco-Letelier et al. 2004; Zanelli et al. 2007; Céspedes-Payret et al. 2012).

One of the most commonly used species, *Eucalyptus grandis*, is native in the subtropical wet forest (1100–3500 mm rainfall) on the east coast of Australia (Boland et al. 2006; Céspedes-Payret 2012). Its implantation in a temperate grassland region as Uruguay can cause major pedological changes in response to their ecophysiological demand. Among other things, it may cause an alteration in the vertical distribution and bioavailability of mineral elements in the grassland soil profile (Jobbágy and Jackson 2004). According to Jobbágy and Jackson, plant uptake and subsequent cycling and transport of minerals (e.g., Ca, Mg, K, and P) to the soil surface, results in vertical distributions that are shallower for strongly cycled elements than for other elements. Based on the background information and data collected for over a decade in the study area, we sought to bring new elements to the discussion on the use of Db as a tool in SOC stocks estimates. For this purpose, the values of Db, SOC and pH were compared in five *E. grandis* plantations of different ages with their respective controls under grassland vegetation. The history of use of these controls was varied, allowing assessment of the cumulative effects of previous agricultural use on Db, SOC and pH, together with the effects of afforestation. In this way, independently of the history of use and its effect on these parameters, we investigated the consequences of the implantation of *E. grandis* over time. In addition, in light of current knowledge, we present a discussion of the possible causes that could explain the disparity between the obtained Db values and SOC records, and their relationship with soil pH.

2 Material and Methods

2.1 Study Area

The study area is in the littoral western region of Uruguay, between latitudes S 32°27′ - S 32°17′ and longitudes W 57°39′ - W 57°21′, on the border between the departments of Paysandú and Río Negro (see Fig. 1). This region is the largest area of eucalyptus afforestation in the country, and was the first to develop the forestry sector. The total area is approximately 28,400 km^2 and includes the Algorta Unit (9800 km^2) and the Bacacuá Unit (18,600 km^2)

shown on the Uruguayan Soil survey chart (Altamirano et al. 1976; Dirección de Suelos y Fertilizantes 1976). The geology is formed by Guichón, Mercedes and Asencio sedimentary formations, accumulated during the Cretaceous, eroded and redeposited during the Quaternary period. The Bacacuá Unit has pebbles and cobbles in the topsoil, due to differences in sedimentary transport processes (Dirección de Suelos y Fertilizantes 1979).

Both units include large areas of soil classified as "forestry priority" because they are suitable for practicing afforestation. These soils are very similar (Table 1) and are included in the U.S. Soil Taxonomy as Mollisols (Argiudol) (Soil Survey Staff 2010). The selected plots were formerly extensive agriculture units (100–200 ha) with different intensity of management, actually secondary succession of plant communities. The exceptions are two plots of more recent treatment, which were subject to extensive grazing. However, prior to their merging for forestry land use, they remained fallow for several years. In the case of the plots under pasture, grass cover was maintained until the time of sampling. As a result of their respective histories of use, the majority of plots under pasture had SOC contents below original levels.

Mean annual climate values are: temperature 17.8 °C, precipitation 1192 mm and evaporation 1893 mm. Vegetation mainly consists of C4 grass species. The main varieties grown are *Eucalyptus* spp. as with other "forestry priority" soil areas in the country.

2.2 Sampling Strategy

In order to study the effects of afforestation, sampling was intended in the first instance to identify eucalyptus plantations that were within an age range, and that were also adjacent to pasture plots with similar pedological and topographical characteristics. Under these conditions, five plots forested with *E. grandis* were identified, with ages between 10 and 30 years: E_{10}, E_{15}, E_{20}, E_{25} and E_{30}; Table 2). Only four pasture plots were identified ($P_{10–15}$, P_{20}, P_{25} and P_{30}), so one of them ($P_{10–15}$) had to serve as the control for two treatments (E_{10} and E_{15}). As mentioned above, due to their history of use, most of the grassland plots showed evidence of degradation/erosion, some even visible in the field, except for one plot which has natural pasture (i.e., without antecedent tillage). The conservation conditions of the control plots,

Table 1 Soil profiles description, Bacacuá and Algorta units (Dirección de Suelos y Fertilizantes 1979)

Horizon	Colour	Mottles	Texture	Structure	Pores	Root	Macro-fauna
A_{11}	10YR 3/1		fine sandy loam	granular, soft when moist	abundant	abundant	abundant
A_{12}	10YR 2/1		sandy loam	subangular blocks, soft when moist			
A_3	7.5YR 2.5/1		heavy sandy loam	subangular blocks, soft when moist			
B_1	10YR 2.5/1.5	7.5YR 3/4	light sandy clay	angular blocks, hard	common	common	common
B_2	10YR 2/1		sandy clay	angular blocks, very hard			

Complementary description of horizon A - B transition

Transition	**Bacacuá**	**Algorta**
Hor. A – Hor. B	abrupt with pebbles and boulders	gradual

Table 2 Study sites list. Each site corresponds to an afforestation and control plot. The status of "regenerated prairie" refers to recovery of much of the forest floor based on native species is considered, although not exempt from invasive alien species (e.g. *Cynodon dactylon*)

Site	Soil Unit (Altamirano et al. 1976)	Plantation age (years)	Previous land use	Control plot (current use)
E_{10}/P_{10}	Bacacuá	10	Grazing	Grazing
E_{15}/P_{15}	Bacacuá	15	Grazing	Grazing
E_{20}/P_{20}	Algorta	20	Fallow	Regenerated prairie
E_{25}/P_{25}	Algorta	25	Fallow	Regenerated prairie
E_{30}/P_{30}	Algorta	30	Fallow	Natural pasture

which are themselves very diverse (Table 2) would help us to make clear the extent to which eucalyptus afforestation had an effect in the soils, not only in SOC stock, but particularly in the values of Db. In other words, we have sought to assess the effects of afforestation with contrasting states of soil conservation, not pristine plots, but with a certain degree of impairment because of agricultural use.

Previous field surveys were carried out in order to verify similarity between paired plots, conducting soil profiles description by making soil pits and exploratory drillings (Table 1). Twelve points were randomly selected at each plot and independent samples were taken from the A-horizon in two depths (0–10 and 10–20 cm).

In the afforested plots, sampling included both the rows and inter-row. At greater depths, no significant changes were detected in SOC content between afforested paired plots and corresponding controls under grassland vegetation. Therefore, these data were not included in this study.

Forest management of the five sites with *E. grandis* corresponded, in general, to the regional model of multipurpose management (fast-growing varieties, high density stands, thinning and usually short shifts). While in the case of cellulose pulp production, management does not generally exceed 10 years, after each harvest the stand is re-planted (without tillage). As a result there is continuity over time which allows for a time window longer than the 30 years included in the present study. As for the paired sites under pasture, at the time of sampling and independently of the history of use, they had lain fallow for over 15 years and in two cases were under natural pasture (Table 2).

2.2.1 Bulk Density

Bulk density was determined by the cylinder method (method 3B6a of Soil Survey Staff, Burt 2004). A metal cylinder with 4.6 cm in diameter and 165.4 cm^3 in volume was used. Samples were taken in triplicate at each sampling point, with six sampling points per plot at each of the paired sites. Places with high root concentration or roots with diameters >1 mm were avoided, as were places with rock fragments greater than the gravel fraction (>4 mm). All samples were collected in the same day. They were placed in sealed bags, taken to the laboratory and dried in an oven at 105 °C for 24 h to achieve constant weight. They were then weighed at constant temperature (25 °C) and Db (g/cm^{-3}) was calculated as dry soil weight (g) × 100/cylinder volume (cm^{-3}). Coefficient of variation was used to evaluate the spatial variation of bulk density, as it is considered a practical indicator for comparing different observation set of the same soil property (Webster and Oliver 1990).

2.2.2 Soil Organic Carbon and pH

Samples were taken from the topsoil (0–20 cm) because at this depth the largest changes in SOC occur, so it is also expected there to have comparatively greater reductions in SOC stocks (Jones et al. 2004). Samples were dried at 40 °C, ground up and then sieved through a 2 mm mesh. Percentage of soil organic carbon (SOC) was determined by the Walkley-Black method with modifications (Burt 2004). 1 g of soil sample was treated with 10 mL of 1 N $K_2Cr_2O_7$ solution to which 20 mL of concentrated H_2SO_4 were added. After shaking, being allowed to settle and centrifugation, the solution was read in a spectrophotometer (Spectronic, Model 401) at a wavelength of 650 nm.

Soil pH was measured in suspensions prepared with 10 g of soil in 25 mL of H_2O (pH meter, Hanna, Model HI 8424).

2.2.3 Complementary Analyses

In order to verify some of the assumptions associated with pH decrease under eucalyptus, exchangeable aluminium and accumulation of iron oxides were also determined. The analyses were performed on composite samples taken by subhorizons (A_{11}, A_{12}, A_3 and B_1) and included only the oldest treatment and grassland Control (E_{30} and P_{30}, respectively):

- Interchangeable Aluminium: extracted in 1 M KCl solution (McLean et al. 1958).
- Exchangeable bases (Ca and K): determined by the 0.2 M NH_4Cl method (Summer and Miller 1996). Bases extracted from the supernatant were determined by atomic emission and absorption spectrophotometer (Perkin Elmer, Model 3110). Ca^{2+} absorption was monitored at 422.7 nm wavelengths and K^+ emission was monitored 766.5 nm, respectively.
- Iron Oxides: Clay fraction analysis by X-ray diffraction using Cu K-alpha radiation (1.54056 nm) on a Philips X'Pert diffractometer equipped with a theta-theta goniometer.

2.3 Statistical Analyses

The significance of changes in grassland soil was assessed by comparison at sites under *E. grandis.* True replication in our study was derived from the comparisons of effects across paired sites (prairie versus eucalyptus), which were evaluated using paired *t*-tests. Data were subjected to the Shapiro–Wilk test to check for normality of distribution, followed by the F-test to check for homogeneity of variances. The t-Student test or Mann–Whitney U-test (for non-normal distribution of data) was performed to show differences between paired plots, in order to constrain error estimates. Pearson's coefficient was used to determine whether there was a correlation between Db and SOC. *P*-values of less than 0.10 were considered significant.

3 Results

3.1 Soil Organic Carbon

Despite the low initial SOC content of sites with prairie vegetation most of these sites just recorded a significant decrease in SOC content compared with their paired plots (*E. grandis* vs. prairie) at both depths. In the first 10 cm (0–10 cm), all afforested plots had a lower average content of SOC ($p < 0.01$ within sites; Table 3), although not significant in P_{15}-E_{15} and P_{20}-E_{20}. Across sites, SOC registered a significant decrease (0.90% vs. 1.22%, $p = 0.083$, $n = 5$). Differences in SOC content at a deeper level (10–20 cm) within sites were statistically significant for four ages (P_{10}-E_{10}, P_{15}-E_{15}, P_{25}-E_{25} and P_{30}-E_{30}) ($p < 0.01$, within sites; Table 2). The only case with significant increase in the percentage of SOC (0.23%, $p < 0.01$; Table 3) was in site P_{20}-E_{20}, where prairie plot registered the lowest SOC content ($P_{20} = 0.54\%$). In the prairie sites, the highest averages on SOC content were found under no-tilled plots (P_{30} and $P_{15–10}$). At 10–20 cm depth, SOC under afforestation was also lower but not significant across sites (0.79% vs. 0.97%, $p = 0.18$, $n = 5$). As a result, SOC content was not significantly correlated to bulk density (Pearson's coefficient $r = -0.22$; $p = 0.53$).

3.2 Bulk Density

Db values increased in all plots under afforestation, recording significant differences across sites (1.624 vs 1.53 g/cm^3, $p < 0.01$, $n = 5$). It should be noted that the spatial variation of Db corresponds to minimum variability (CV < 15%) according to Wilding and Drees (1984). Therefore, this variation range is not an additional uncertainty factor. Neither was the sampling method used, nor the fact that the study compared paired sites. At the no-tilled prairie sites in the Bacacuá Unit ($P_{10–15}$), the highest Db values were associated with the presence of pebbles (Table 3).

3.3 pH

There were significant differences in pH between soils under afforestation and prairie. Plots under *E. grandis* had on average lower pH values than their paired prairie plots, in the first centimeters (0–10 cm: 4.92 vs. 5.62, $p < 0.01$ across sites, $n = 5$; Table 3), as well as at the next depth (10–20 cm: 4.76 vs. 5.54, $p < 0.01$ across sites, $n = 5$; Table 3). In almost every case, acidification in afforested soils reached mean values below pH 5.0, and in no case above pH 5.50. The younger plantations (E_{10}, E_{15} and E_{20}) experienced comparatively the largest decrease in pH (Table 3). As expected, Al^{3+} values registered under eucalyptus (E_{30}) almost trebled the grassland site values (P_{30}) (Fig. 2). Consistent with these values, strong fluorescence, produced by accumulation of iron oxides in the horizon B_1, was found (Fig. 3).

4 Discussion

4.1 Afforestation and Soil Acidification

The decrease in pH reaches average values below the normal range (slightly to moderately acidic) for a temperate grassland soil (Table 3). These pH values are similar to those found in several subtropical and tropical forest soils. This similarity with acidity levels recorded under *E. grandis* cultivation on grassland soils is given by the high nutrient demand and the control, not only over pH (Jobbágy and Jackson 2001), but also over the soil mineral fraction (Jobbágy and Jackson 2004). The possibility that vegetation cover might influence the stability of soil minerals, such as clays, is acknowledged in the literature (Barré et al. 2007b). This effect of vegetation on soil acidity can also affect soil structure through loss of clay fraction (Slattery et al. 1998). A decrease in pH values between strong acidic (pH 5.5–5.1) and very acidic (pH 5.0–4.5) is strong enough to induce large changes in clay minerals.

Table 3 Soil properties values of all sites (mean ± standard deviation). All samples were taken within A horizon (0–10 and 10–20 cm). Db values were only taken at 0–10 cm depth. Significant differences between *Eucalyptus* afforestation (E) and prairie control (P) plots are shown $*p \leq 0.05$, $**p \leq 0.01$

SITE	SOC (%)				Db (g/cm^3)		pH			
	0–10 cm		0–10 cm		0–10 cm		0–10 cm		10–20 cm	
	E	P	E	P	E	P	E	P	E	P
E_{10}/P_{10}	0.91 ± 0.05**	1.32 ± 0.08	0.91 ± 0.08**	1.24 ± 0.11	1.71 ± 0.08	1.63 ± 0.05	4.80 ± 0.13**	5.50 ± 0.13	4.85 ± 0.10**	5.55 ± 0.10
E_{15}/P_{15}	1.26 ± 0.10	1.32 ± 0.08	1.09 ± 0.09**	1.24 ± 0.11	1.69 ± 0.06	1.63 ± 0.05	4.65 ± 0.17**	5.50 ± 0.13	4.66 ± 0.13**	5.55 ± 0.10
E_{20}/P_{20}	0.88 ± 0.08	0.91 ± 0.12	0.77 ± 0.11**	0.54 ± 0.07	1.55 ± 0.04**	1.47 ± 0.03	4.62 ± 0.19**	5.68 ± 0.26	5.00 ± 0.29**	5.56 ± 0.28
E_{25}/P_{25}	0.63 ± 0.11**	0.94 ± 0.22	0.45 ± 0.13**	0.63 ± 0.12	1.67 ± 0.06**	1.53 ± 0.09	5.18 ± 0.30**	5.81 ± 0.18	4.63 ± 0.06**	5.67 ± 0.16
E_{30}/P_{30}	0.82 ± 0.20**	1.62 ± 0.09	0.72 ± 0.11*	1.18 ± 0.12	1.50 ± 0.18	1.40 ± 0.04	5.37 ± 0.27	5.60 ± 0.31	4.64 ± 0.12**	5.38 ± 0.12

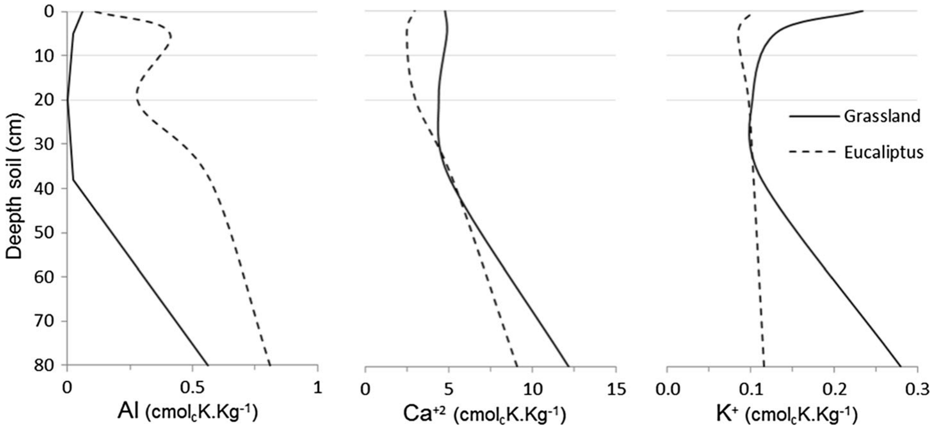

Fig. 2 Distribution in the soil profile of interchangeable Al, and exchangeable bases (Ca and K) under grassland and eucalyptus afforestation

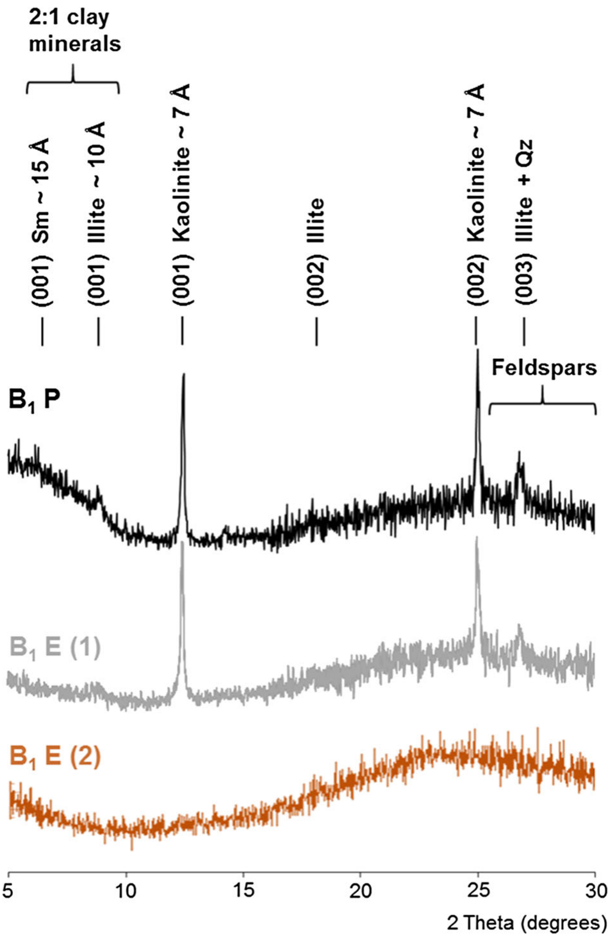

Fig. 3 Comparison of X-ray diffractograms of horizon B_1. Grassland soil (P) in black above; afforested grassland soil (E): down (2) in brown, diffractogram exhibits low ratio signal/noise due to fluorescence caused by the precipitation of iron oxy-hydroxide of low crystallinity; center (1) in gray, after removal iron oxy-hydroxide with sodium dithionite, the characteristic peaks are observed kaolinite, among others

The disintegration of these clay minerals provides a source of silica (SiO_2) (Sommer et al. 2006). When silica leaching is not complete, kaolinite (1:1) can become an important mineral in the soil (Sposito 2008; Caner et al. 2014). In this process, there is also loss of Al and, to a lesser extent, of Fe. In the case of Al, there is an increase in the relative amount of the ion $Al3^+$ (below pH 5.5) with respect to other Al forms in the soil (Ritchie 1989; Marschner 1995; Matzner et al. 1998). This allows Al^{3+} concentration (Fig. 2) to be used as an indicator of the alteration intensity of the mineral fraction in the same manner as the translocation and accumulation of Fe-oxides below the topsoil (Fig. 3).

Studies conducted in temperate grassland soils in the Pampas region, in the Río de la Plata basin, confirm the effects of the replacement of herbaceous vegetation for eucalyptus afforestation. Soils with *Eucalyptus globulus* show a higher content of dissolved silica in the A horizon (pH = 4.2) in relation to grassland soil (pH = 6–6.3) (Borrelli et al. 2010). Jobbágy and Jackson (2003) suggest that this increased acidity in temperate grassland soils converted to eucalyptus cultivation could be explained by the loss of exchangeable bases, especially Ca, and by increased exchangeable Al. This study suggests that cation cycling and their redistribution by trees is the dominant mechanism of soil acidification under eucalyptus afforestation. Consequently, according to the authors, massive grassland afforestation for carbon sequestration could have important consequences on soil fertility and base-cation cycles.

In Uruguay, which is part of the Pampas region, studies show similar results in relation to pH and SOC (Carrasco-Letelier et al. 2004; Céspedes-Payret et al. 2009; Céspedes-Payret et al. 2012). One of them analyses the effects of acidification ($pH < 5.0$) under *E. grandis* in the mineralogy of dominant clays of these grassland soils. Results show a decrease in the soil mineral fraction of 2:1 clay minerals, particularly illite, in the A horizon (Céspedes-Payret et al. 2012). According to these authors, the sharp decline in pH would affect certain phyllosilicates more than others. This is the case of illite, considered a major source of K in agricultural soils (Boguslawski and Lach 1971). In the process of K^+ uptake, plant roots release H^+ which reacts with the structure of clay minerals (Mengel and Steffens 1982; Tributh et al. 1987). In this exchange, plants are able to extract more K than that chemically defined as exchangeable K (Boguslawski and Lach 1971; Hinsinger 2005; Barré et al. 2007a). The sequence of changes that take place can be summarized in: 1) pH decrease and increase in solubilisation of minerals; 2) extraction of interlaminar "non-exchangeable" K from illite by plants; 3) fast cycling of K by trees and consequent collapse of the structure of illite; and 4) release and leaching of structural silica, associated with the release and translocation of Al and Fe.

In other words, starting with the decrease in pH, a set of changes that affect the colloidal particles of variable charge (2:1 clay minerals) occur, and ultimately, result in a reduction of the soil charge density. This mainly responds to an decrease in specific surface area (SSA) and to an alteration in the nature of the exchange complex (adsorbed ions) due to the increase of H, Al and Fe ions. As known, ion charge and diameter are the factors that determine the retention energy of the complex, and thus the following order is established: Al > Ca > Mg > K > Na. With a predominance of 1:1 clay minerals in the soil, Fe and Al oxides can act as flocculants and further reduce the available area for SOC adsorption (Six et al. 2002). It has also been suggested that kaolinite and iron oxides can interact when they are simultaneously present in a suspension. In the 4–7 pH range, Fe-oxides have positive surface charge and kaolinite surface charge is negative, allowing an electrostatic attraction which can lead to heterocoagulation and formation of aggregates (mottling) between kaolinite and Fe-oxides (Osei and Singh 1999; Tombácz et al. 2004; Hou et al. 2007). If oxides, instead of SOC, are the dominant agents for aggregate stabilization in degraded soils, the relationship between SOC and aggregation in these soils is not as strong as in soils with predominance of 2:1 clay minerals (Six et al. 2000b). As has been proposed, the interaction between particles may occur even without organic matter as cementing agent (Six et al. 2000a; Denef et al. 2002; Denef and Six 2005). This change could even increase soil aggregation (Denef et al. 2002) and not be reflected in the Db values. These soils would have comparatively greater aggregation at lower SOC levels than soils with mixed clays mineralogy, with more aggregation at higher levels of SOC (Denef et al. 2002). When SOC values are lower than 2%, significantly reducing its contribution to the structural stability of the soil, Db is not an adequate proxy for estimating SOC value (Kemper and Koch 1966; Greenland et al. 1975). Hence, structural stability measurements lose relevance in case of low SOC content.

4.2 Bulk Density and SOC

The heterogeneity of land use history in the control plots and of their Db values was not an impediment to record an increase in Db values after afforestation. The disparity between initial Db values used as reference is precisely what allowed us to attest that the increase in this parameter can only be attributable to the eucalyptus afforestation, regardless of the afforestation age in the studied sites. Comparison between sites (treatment vs control) make it clear that the increase in Db was significant. Furthermore, SOC values showed a similar behaviour with afforestation. In other words, the quantitative contribution of organic carbon from eucalyptus litter is insufficient to compensate for the export of native SOC. This suggests that the increase in Db is strongly related to a decreased soil capacity to accumulate and/or retain new contributions of organic carbon (Fig. 4). Field observations showed that the first 20 cm of soil under eucalyptus have a massive, friable structure, which breaks into angular blocks of light colour. This structure markedly differs from that found in grassland soils, which has granular nature and darker colour. The appearance of this new structure associated to the

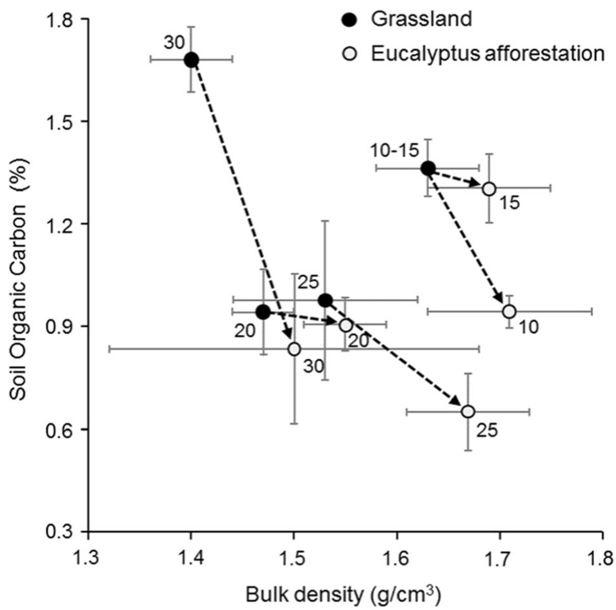

Fig. 4 Relation between SOC and Db at 0–10 cm depth in the topsoil is shown. No relation was found between SOC content and Db ($r = -0.22$, $p = 0.53$) within the value-range studied. *Eucalyptus* afforestation and paired grassland control are linked by an arrow, showing the direction induced by the treatment. *Eucalyptus* afforestation is visualized as a driver factor which modifies the relation between variables, increasing Db and diminishing organic carbon regardless initial control value

recorded increase in Db in the topsoil turned our attention to the secondary mineral components.

While knowledge about the role of Db in controlling organic carbon inputs to the ground are quite solid, it is not the same about its role in the retention of organic carbon in the soil. By definition, Db expresses the packing arrangement adopted by the soil mineral and organic components. Due to its origins, Db has been applied mainly in agronomic studies as an estimate of soil compaction. Since then, the accumulated data has statistically validated a certain level of correlation between Db values and SOC content, even with the soil clay fraction (Dexter 2004; Keller and Håkansson 2010). The widespread recognition of this relation between both parameters has validated the use of Db in SOC estimation calculations. Nevertheless, the finding of a high and statistically significant correlation between two parameters is not necessarily causal. For example, an increase in Db could be linked to the emergence of a new soil structure not associated with SOC content, as a result of a change in clay fraction mineralogy (and properties).

The nature of surface charges of the soil mineral particles is widely recognized as a relevant factor in the SOC-Db interaction. Nevertheless, studies aimed at understanding the relationship between the phyllosilicates mineralogy and SOC protection remain relatively scarce (Barré et al. 2014). Furthermore, according to Barré et al. (2014), those studies do not always reach the same conclusions.

To summarize, when the goal is to determine soil compaction for agricultural purposes, the non-inclusion of qualitative aspects that determine possible Db values would not be of much significance. Alternatively, when the aim is to establish the ability to retain and accumulate organic carbon in soil, some limitations arise. A major constraint is that Db does not always express the effective adsorption capacity of the soil mineral fraction to retain organic compounds. As mentioned before, a decrease in SSA of the most reactive mineral particles can qualitatively affect the soil mass without affecting its volume. So that, two soils expressing similar Db values may differ in their SOC adsorption and retention capacities due to differences in their electrochemical properties related to a change in the nature and amount of mineral particle charges.

In most soils, the adsorption capacity is of great importance because of the control exercised over the soil structure by the colloidal fraction and specifically their surface properties (Oades 1988). Some authors, like Kögel-Knabner et al. (2008), consider that the SSA would not always be a good predictor of C stabilization potential because of its discontinuous surface coverage.

Previous studies in the same soils of Uruguay have confirmed alterations in the mineralogical composition of soil under eucalyptus (Céspedes-Payret et al. 2012). These studies included XRD analysis where diffractograms show predominance of kaolinite and reduction of illite, along with an accumulation of Fe-oxides in the B_1 horizon (Fig. 3). This change in clay mineral predominance was associated with a significant pH decrease, but mainly to the fast cycling of K^+ by trees. Similar changes have already been reported under forestation. For example, in coniferous forest soils, Pai et al. (2004) observed rapid decomposition of illite and liberation of Fe and Al to the soil solution due to an increase in acidity.

At present, the prevailing view is that higher SOC content increases stability of aggregates, and thus, soil porosity, coupled with a decrease in Db values. Nevertheless, in this linear reasoning it is possible to foresee a reverse process: beginning with SOC loss, stability of aggregates, and consequently, soil porosity decrease, causing an increase in Db values. There is an assumption that the mass/volume ratio directly expresses the ability of soil to store organic matter, and vice versa. Consequently, behind this reasoning, the total pore volume emerges as a central factor in controlling organic carbon input/output. Nevertheless, upon a drastic change in land use and management, other factors could operate and control soil structure. Thus, several authors have already suggested that, in some soils, packing arrangement is more important than the amount of SOC (Loveland and Webb 2003), and that SOC distribution is more important than its quantity (Puget et al. 1995). Other studies found no correlation between SOC amounts and aggregate stability (Carter et al. 1994). Later studies in temperate soils indicate that interactions with mineral surfaces, and especially, Fe-oxide surfaces are the primary control for long-term organic carbon preservation in all the evaluated soils. According to Kögel-Knabner et al. (2008), the pedogenic oxides dominate the reactive surface area of the organo-mineral interactions, while recalcitrance, accessibility and aggregation seem to determine the turnover dynamics in the fast cycling organic carbon pool.

In the case of eucalyptus afforestation, the set of changes that could potentially happen with the replacement of herbaceous vegetation bring into question the main role assigned to SOC in the formation of aggregates, as well as soil ability to accumulate organic matter, now provided by eucalyptus cultivation. Differences between herbaceous and woody vegetation would allow explaining, not only why the soil under eucalyptus presents greater Db values (associated with lower soil porosity and a lighter colour), but also, why it has a lower SOC content. That is, why despite their huge aboveground biomass, organic carbon input did not compensate for the output of SOC accumulated by the previous grassland.

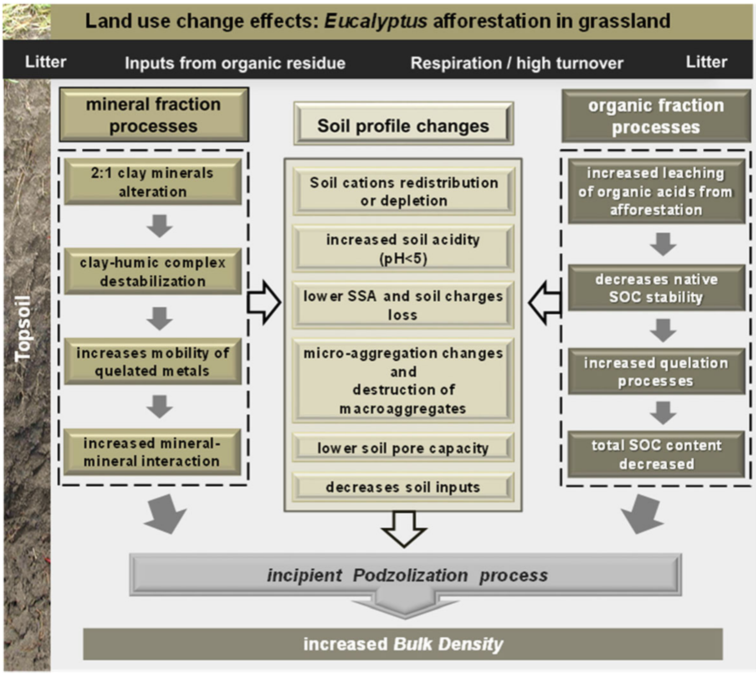

Fig. 5 Diagram showing the sequence of soil physicochemical changes that would be installed in the prairie topsoil (first 20 cm) after being afforested. In the *left box* are shown changes and interactions that act on the mineral soil, particularly on clay minerals. In the *right box*, are indicated the interactions and processes sequence that affect the soil organic fraction as a result of organic residues inputs from eucalyptus litter. In the *center box*, are outlined the soil profile changes resulting from the interaction between left and right box (a micro- and macro-structural level). The sum of changes and their interactions, finally lead to a podzolization process together with increased bulk density of the afforested soil

Based on this background, we considered the hypothesis that SOC values under eucalyptus afforestation would not be related to Db values, because aggregates formation is now less dependent on organic inputs to the soil. The aggregation of subproducts of illitic clay alteration (silica, Al- and Fe-oxides), mainly due to the low pH, would partially replace the role played by grassland SOC. Consequently, organic carbon incorporation and retention from now on would be conditioned by the new structure adopted by the soil depending on the new aggregation mechanisms. This would feedback the trend to increase Db under afforestation, resulting in lower infiltration and humidity in soils with Eucalyptus afforestation (Fig. 5).

To summarize, the increase in bulk density of soil under eucalyptus is in agreement with previous data, which demonstrate an increased predominance of 1:1 clays associated with a reduction in SOC content. From the data we have obtained, it is possible to explain this Db increase as the result of a decrease in soil electrical charge density. The decrease in pH and fast cycling of K by trees are two key factors to generate a change in clay mineralogy. These changes lead to a positive feedback process, and thus, to the establishment of an incipient process of podsolization due to the new vegetation cover (and not to a climate-dependent process).

5 Conclusions

The results obtained in the topsoil under eucalyptus showed a strong acidification process (pH <5.0). This pH range is low enough to promote instability of soil clay minerals. This pH activity is evidenced by an increase of exchangeable aluminium and Fe-oxides accumulation (B_1 horizon). Under these conditions, there is also SOC loss and decrease in organic carbon inputs to the soil from eucalyptus, which are not adequate to compensate for the losses. The set of factors that now interact are expressed in higher Db values, discordant with the SOC values. Lack of significant correlation between both parameters warns about the need for restriction of the generic use of Db in calculation of SOC stocks estimation. In fact, it is not possible to evaluate organic carbon accumulated in all afforested lands in the region from Db measures that do not reflect the ability of soil to accumulate carbon.

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