



Patterns and mechanisms of soil acidification in the conversion of grasslands to forests

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Abstract. Grassland to forest conversions currently affect some of the world's most productive regions and have the potential to modify many soil properties. We used afforestation of native temperate humid grassland in the Pampas with eucalypts as an experimental system to 1) isolate forest and grassland imprints on soil acidity and base cation cycling and 2) evaluate the mechanisms of soil acidification. We characterized soil changes with afforestation using ten paired stands of native grasslands and *Eucalyptus* plantations (10–100 years of age). Compared to grasslands, afforested stands had lower soil pH (4.6 vs. 5.6, $p < 0.0001$) and ~40% lower exchangeable Ca ($p < 0.001$) in the top 20 cm of the soil. At three afforested stands where we further characterized soil changes to one meter depth, soil became increasingly acidic from 5 to 35 cm depth but more alkaline below ~60 cm compared to adjacent grasslands, with few differences observed between 35 and 60 cm. These changes corresponded with gains of exchangeable acidity and Na in intermediate and deeper soil layers. Inferred ecosystem cation balances (biomass + forest floor + first meter of mineral soil) revealed substantial vertical redistributions of Ca and Mn and a tripling of Na pools within the mineral soil after afforestation. Soil exchangeable acidity increased 0.5–1.2 $\text{kmol}_c\text{Ha}^{-1}\text{yr}^{-1}$ across afforested stands, although no aboveground acidic inputs were detected in wet + dry deposition, throughfall and forest floor leachates. Our results suggest that cation cycling and redistribution by trees, rather than cation leaching by organic acids or enhanced carbonic acid production in the soil, is the dominant mechanism of acidification in this system. The magnitude of soil changes that we observed within half a century of tree establishment in the Pampas emphasizes the rapid influence of vegetation on soil formation and suggests that massive afforestation of grasslands for carbon sequestration could have important consequences for soil fertility and base cation cycles.

Introduction

Plants influence the earth surface through the uptake, transformation and redistribution of materials in the atmosphere, pedosphere and lithosphere (Simonson 1959; Likens et al. 1977; Schlesinger 1997). Although all plants leave such an imprint (e.g., input of organic matter and respired CO_2 , enhancement of rock weathering, etc.), variations in size, growth rate, life span, allocation, tissue chemistry, and many other attributes affect cycling patterns and the properties of soils differently (Alban 1982; Finzi et al. 1998; Jackson et al. 2000; Jobbágy and Jackson 2000). The widely applied state factor model of soil formation recognizes such effects and includes

vegetation as a master control of pedogenesis (Jenny 1941, 1980). However, isolating the effects of vegetation on soil development in the field is confounded by covarying interactions of vegetation and other important influences of soil functioning, including climate, topography, and history (Ugolini et al. 1988).

Understanding the feedback of vegetation type on soils is important because current rates of vegetation change are high and may lead to further biotic changes through soil modifications (Roberts 1987; Jackson et al. 2002). Shifts from grasslands to forests (afforestation and tree invasion/encroachment) affect some of the most productive areas still covered by native vegetation globally, especially in the Southern Hemisphere (Rudel and Ropel 1996; Richardson 1998; Geary 2001). In the native grasslands of the Pampas, afforestation with pines and eucalypts is becoming increasingly common. In the last decade Uruguay and Argentina have increased their afforested areas five- and two-fold, respectively, in this region (MAGP 1998; SAGPyA 2000), with even higher afforestation rates expected for the coming decades (Wright et al. 2000). In such systems, most base cations are essential plant nutrients and play a key role balancing ecosystem acidity (Aber and Melillo 1991). Soil acidity in turn is a master control of soil fertility (Marschner 1995) and affects many important biogeochemical processes, such as rock weathering and nitrification (Richter and Markewitz 2001). In this paper we use the chronosequence of forested sites compared to native grasslands as a controlled experiment for isolating the imprint of eucalypt afforestation on soil acidity and base cation cycling.

Spatial comparisons of areas historically dominated by trees and grasses indicate that soil pH and base saturation tend to be lower under forests with similar parent materials and climates (Jenny 1941; Geis et al. 1970; Ugolini et al. 1988). Such comparisons do not address the rate and mechanisms of vegetation effects on soil properties and are usually unable to rule out other controls that influence vegetation and soils together (Richter et al. 1994). Nonetheless, such studies suggest soil acidification as a likely outcome of the conversion of grasslands to forests.

Direct manipulations of vegetation can also yield mechanistic insights into the ecological consequences of grassland-to-forest conversions. Studies examining the shift of native grasslands to forests reveal various degrees of surface soil acidification after tree establishment (Davis and Lang 1991; Musto 1991; Davis 1995; Quideau and Bockheim 1996; Parfitt et al. 1997; Alfredsson et al. 1998; Amiotti et al. 2000). As expected, the largest decline in pH is associated with the loss of exchangeable base cations, particularly Ca, and increases in exchangeable Al.

We propose three basic mechanisms of soil acidification following the afforestation of grassland ecosystems (Figure 1): 1) organic acid inputs 2) soil respiration, and 3) sequestration and redistribution of cations. In the first mechanism, organic acids produced by plants are the acidifying agent. In contrast to grasses, many trees have acidic litter, canopy leachates, and decomposition products. This acid input, usually negligible under grassland vegetation, could cause cation leaching and a decline in soil pH after tree establishment (Ugolini et al. 1988). A second mechanism of soil acidification is carbonic acid inputs derived from soil respiration. Carbonic acid is an important agent of weathering in soils (Richter and Markewitz 1995), and higher carbonic acid production has been linked to increased base cat-

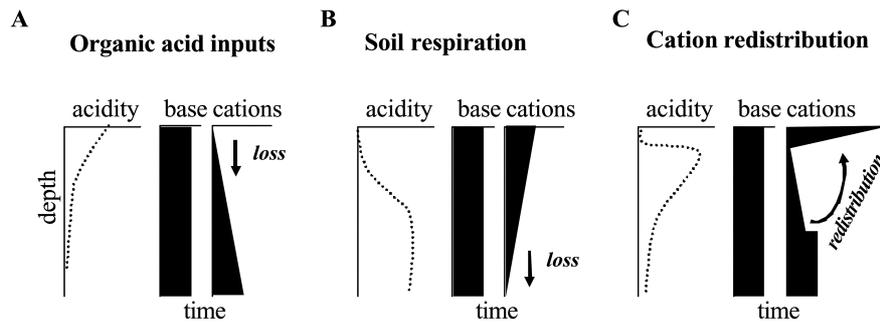


Figure 1. Three potential mechanisms of soil acidification and their imprint on soil profiles after afforestation: A) organic acid inputs, B) soil respiration, and C) cation redistribution. Figures show the vertical distribution of acidity accumulation and base cation pools before and after afforestation. For purposes of illustration, base cation pools are assumed to be homogeneously distributed under grassland vegetation. The first two mechanisms cause a net ecosystem loss of base cations, the third yields no net change in cation pools but redistribution from intermediate depths to the topsoil.

ion leaching in forests (Andrews and Schlesinger 2001). In order to acidify grassland soils by this mechanism, forests should have higher root respiration and/or enhanced microbial respiration compared to grasslands. Contrary to this suggestion, recent reviews suggest that soil respiration rates tend to be lower in forests (Raich and Tufekcioglu (2000); see also Chen et al. (2000) and Tate et al. (2000), Saviozzi et al. (2001)). The third potential mechanism is the sequestration and redistribution of cations within the ecosystem after tree establishment. Trees can store cations in excess of anions in both aggrading biomass and in the organic floor (litter + organic soil). This difference in charge should in turn be balanced by a net gain of protons in the soil (Nilsson et al. 1982). Even when forests approach a steady state of cation gain and loss, soil cations may be redistributed within the soil as a result of intense cycling by trees, leading to localized acidification in some layers (Jobbágy and Jackson 2001).

If each of these mechanisms acts singly in controlling soil acidification, different soil vertical patterns and ecosystem balances should develop. If organic acid inputs drive acidification, they should be observed either in throughfall or in forest floor leachates, causing maximum acidification in the surface soil (Figure 1a). If soil respiration drives acidification, maximum acidification should not occur in the surface soil where CO_2 partial pressures are lower, but at depth; there, the loss of cations would be observed without signs of acidity in throughfall or forest floor leachates (Figure 1b). In both of these cases, cations will be lost from the ecosystem. In contrast, in the third mechanism cation redistribution should dominate the process of acidification. Maximum acidification should then occur where root nutrient uptake is relatively high but inputs from litterfall and throughfall are low – below the first ten centimeters of the mineral soil profile (Figure 1c) (see Jobbágy and Jackson (2001)). No net ecosystem loss of cations should be observed in this case, as forest sequestration will balance soil losses. In all likelihood, such mechanisms will operate in concert.

In this paper we characterize the effects of afforestation on soil chemistry in the Pampas of Argentina, measuring soil changes in paired grassland and afforested sites of 10 to 100 years of age. We evaluate the proposed mechanisms of acidification in these systems and explore potential feedbacks of soil changes after afforestation on the nutrition of trees and grasses.

Study system

The Pampas region covers ~50 million ha of Argentina (Figure 2). The word "Pampa", derived from the Quechua language, indicates a flat, treeless extension of land (Bravo 1967). The climate lacks a dry season and is temperate and sub-humid to humid (mean annual T ranges from 17 °C to 14 °C north to south; Hall et al. (1992)). Average annual rainfall ranges from 600 mm in the southwest to 1000 mm in the northeast, but during the last three decades increased rainfall in the drier areas of the west has erased this regional gradient (Podesta et al. 1999) (Table 1). Dominant soils are Mollisols developed on loess-like sediments deposited throughout the late Pleistocene and the Holocene (Teruggi 1957; Tricart 1973).

The natural vegetation of the Pampas is a mixture of C3 and C4 grasses (Soriano 1991). One of its most conspicuous original features was a complete lack of trees over most of the region, an observation noted by early travelers such as Azara (1796) and Rosas and Senillosa (1825), and Darwin (Barlow (1933); see also Garavaglia (1999)). Phytoliths indicate that grasses dominated the region throughout the period of soil genesis (Tecchi 1983). The limitations to plant growth in the Pampas include poor drainage and Na accumulation in lower landscape positions (Soriano 1991).

With European settlement, plantations ranging from 0.1 to 100 ha were established for shade, windbreak, and aesthetics. Most plantations were unfertilized and had little wood extraction or soil disturbance. Soon after the mid 1800s, Eucalypts became common in rural plantations (Senillosa et al. 1878; Zacharin 1996), which today are primarily composed of *E. camaldulensis*, *E. viminalis*, and *E. globulus*. The cumulative replacement of natural communities in the region with annual grain crops and cultivated pastures ranges from 30% in the Flooding Pampas to 90% in the Rolling Pampas (INDEC 1988). Most areas occupied by natural grasslands are devoted to cattle ranching, where irrigation, fertilization, and feed supplementation are almost universally absent (Soriano 1991).

The Pampas region offers an ideal opportunity to test the mechanisms of soil acidification, both because throughout pedogenesis most of the region lacked woody species and because it has low anthropogenic inputs of acids and N which might otherwise confound the effect of vegetation on soil chemistry (Lavado 1983; Bouwman et al. 1997). We used fence-line comparisons to assess the effect of vegetation change on soil attributes, identifying adjacent paired Eucalypt stands and native grasslands throughout the major subregions of the Pampas using aerial photographs (1:50000) (INTA 1989) and Landsat imagery (1:250000) (IGM 1997).

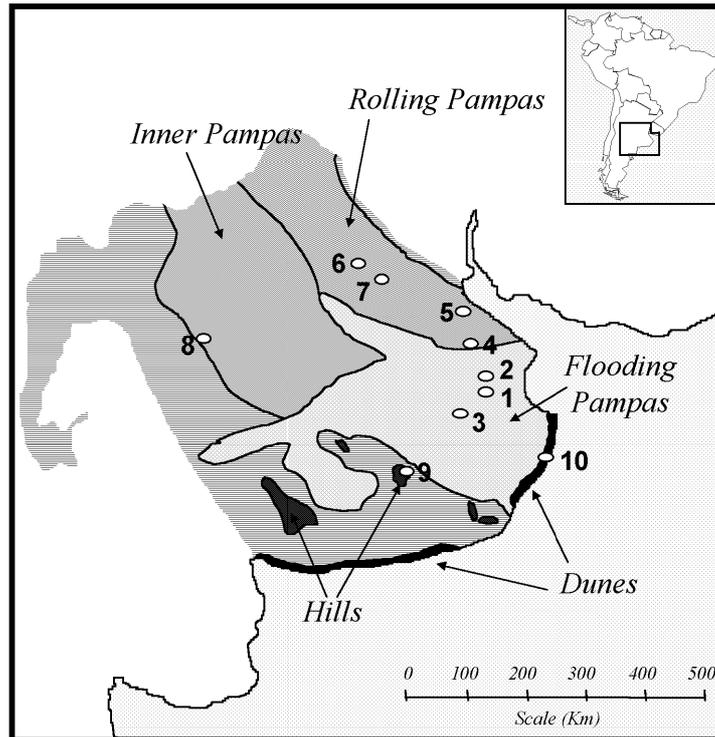


Figure 2. Location of study sites in the Pampas. Each site includes a grassland and tree plantation stand. The major subregions covered by this study are indicated. Sites are: 1, Castelli; 2, Guerrero; 3, Pila; 4, Chascomús; 5, Pereyra; 6, Rojas; 7, Rancagua; 8, América; 9, Tandil; and 10, Pinamar.

Materials and methods

Site description

We selected 10 paired sites representing the most typical upland soils of the region (Figure 2, Table 1): The Castelli, Guerrero, and Pila sites represent one of the most common soil series of upland soils in the Flooding Pampas, Hapludolls over-laying an older eroded soil that constitutes a textural B horizon at 30 to 60 cm depth. The horizon sequence is: A-AC-IIBt-IIC and the soils were derived from loess sediments that were locally redistributed by wind in the Holocene. The Rojas and Rancagua sites correspond to the most conspicuous soil series of uplands in the Rolling Pampas. These soils are considered among the best agricultural soils of the continent and have an A-Bt-C horizon sequence with a 40 cm thick A horizon. The Pereyra site is located in the transition between the Flooding and Rolling Pampas. It was located in an Argialboll (planosol) with an A-E-Bt-C sequence with a textural B at 30 cm of depth. The Chascomús site is also in the transition between the

Table 1. List of study sites. Each site includes a grassland and a *Eucalyptus* stand. Latitude and longitude correspond to the center of the tree stand. Mean annual precipitation (MAP) and temperature (MAT) values were obtained from the closest available (< 30 km) meteorological stations. Soil series denomination and soil classification to subgroups (USDA 1998) were derived from 1:50000 soil cartography and from local observations. Initial tree density was derived from the original planting grid; in the case of irregular planting patterns it could not be estimated (NA). Current tree density was sampled in the field.

Site	Lat (S)	Long (W)	MAP (mm)	MAT (C°)	Soil series	Soil subgroup	Tree species	Age (yrs)	Density (stems/Ha)	
									Initial	Current
<u>Flooding Pampas</u>										
Castelli	36°02.0'	57°50.3'	980	15.3	Pila	thapto Hapludoll	<i>E camaldulensis</i>	50	1666	783
Guerrero	35°58.4'	57°51.1'	980	15.3	Pila	thapto Hapludoll	<i>E camaldulensis</i>	95	NA	545
Pila	36°28.4'	58°11.8'	895	15.0	Pila	thapto Hapludoll	<i>E camaldulensis</i>	36	1111	1022
<u>Flooding/Rolling Pampas</u>										
Chascomús	35°25.3'	58°02.4'	970	15.4	Abbott	aquic Argiudoll	<i>E camaldulensis</i>	47	1111	767
Pereyra	34°51.9'	58°09.0'	1010	15.7	Numancia	vertic Argialboll	<i>E viminialis</i>	11	1111	1067
<u>Rolling Pampas</u>										
Rojas	34°11.0'	60°55.5'	990	16.6	Rojas	typic Argiudoll	<i>E camaldulensis</i>	44	1111	1002
Rancagua	34°07.6'	60°34.8'	990	16.8	Rojas	typic Argiudoll	<i>E camaldulensis</i>	89	NA	220
<u>Inner Pampas</u>										
América	35°30.6'	62°59.2'	745	16.5	América	entic Haplustoll	<i>E camaldulensis</i>	41	833	599
<u>Hills</u>										
Tandil	37°20.7'	59°02.7'	900	12.3	Tandil	lithic Hapludoll	<i>E camald.vimin.</i>	42	625	1125
<u>Coastal dunes</u>										
Pinamar	37°05.1'	56°51.3'	837	14.5	No name	typic Udipsamment	<i>E camald.vimin.</i>	41	767	690

Flooding and Rolling Pampas and occupied an aquic Argiudoll with an A-Bt-C sequence. A temporarily perched water table over a textural B located at 35 cm is commonly observed in this type of soils (INTA 1989). The América site corresponds to the most typical upland pedon of the Inner Pampas, which is a deep sandy soil with no B horizon (A-AC-C sequence). Like soils sampled in the Flooding Pampas, these soils developed on sediments transported by wind in the Holocene. The Tandil site is located on the typical soil of slopes and hilltops on the few isolated hills of the Pampas. The horizon sequence is A-AC-rock. The soils developed on a thin loess layer over-laying Precambrian granite rock that formed a solid boundary at 40 cm depth in the study site. The Pinamar site is located on the coastal strip of sand dunes formed in the Holocene. Calcium carbonate from shell fragments represents 20 to 40% (mass) of the sediments, and there is no horizon differentiation in these young Udipsamments.

Adjacent forest and grassland sites shared the same soil unit (deduced from 1:50000 soil maps and on-site inspection of soil profiles) and were always located in uplands. All forest stands were dominated by *E. camaldulensis* or *E. viminalis*, were > 10 Ha in area and ungrazed, and, as confirmed with the owners or managers (and consistent with common regional practices), were never fertilized or irrigated. Biomass was not harvested from these forest stands except at Pila (see below), where the stand was clearcut and left to regrow for 15 years before sampling, and at Guerrero and Pinamar, where 20–50% of the trees were cut previously. Grassland stands were neither fertilized nor irrigated but were generally grazed. None of the grasslands was plowed except at Castelli, Chascomús, and América, with no plowing in the last 20 years.

Tree stands had little or no grass understory, with *Cynodon dactylon* being the only understory species present at a few sites. For the eucalypt stands > 40 years of age, *Celtis tala*, *Morus alba*, and *Ligustrum* sp. occasionally formed a sparse woody understory. Grassland stands were dominated by plants of the genera *Paspalum*, *Bothriochloa*, *Bromus*, *Stipa*, *Piptochaetium*, and *Festuca*. At the coastal dune site the native C₃ grass *Cortaderia selloana* was the only dominant grass species.

Soil and plant analyses

We performed three classes of analyses at the study sites. At all sites we sampled soil to 20-cm depth and analyzed exchangeable nutrient pools, pH, organic C and total N. Examining three paired sites (Guerrero, Castelli, and América) in more detail, we extended the above sampling throughout the first meter of soil and also measured exchangeable acidity, soluble Cl, extractable P, and total element pools. A full accounting of tree biomass and forest floor elemental pools was also performed at these three sites. Finally, at Castelli we sampled the vegetation more intensively and conducted repeated measurements of wet + dry deposition and throughfall in the forest and grassland between July 2001 and January 2002 to examine in more detail the mechanisms of soil acidification.

To avoid potential edge effects, sampling areas were > 50 m away from fences or borders. At each stand we randomly located five soil pits (1 m wide × 0.5 m

deep) along a transect parallel to the grassland-forest edge. The soil pits were > 0.5 m away from the nearest tree and > 10 m away from each other. Mineral soil was sampled at depth intervals of 0–5, 5–10, 10–20, 20–35, 35–50, 50–75, and 75–100 cm. Above 50 cm, individual samples were composited from material along a 1 m horizontal strip of the pit wall. Below 50 cm, samples were obtained with a 10-cm diameter auger. We obtained 250-ml volumetric soil samples at each depth interval for bulk density estimates in two soil pits per stand (Elliot et al. 1999). Litter and organic soil layers (only present in forest stands) were sampled in each soil pit using 20 × 50 cm frames. Mineral and organic soil samples were air-dried and aggregates were broken to pass a 2-mm sieve; no stones were observed except at Tandil. Soil pH was measured with an electrode on the supernatant of a 1:1 soil-water extract (Thomas 1996). We analyzed samples for exchangeable Ca, Mg, K, Na, and Mn using extracts of 1 M ammonium acetate (pH 7) with a 1:5 soil-water ratio, shaking 5 minutes and equilibrating 24 hours (Robertson et al. 1999). Concentrations in the extracts were measured using inductively coupled plasma emission spectrometry (ICP, Soltanpour et al. (1996)). Total organic C and N were measured using dry combustion and a CHN autoanalyzer system (Gill et al. 2002). For samples having carbonates in the deeper layer, we ran combustion at 550 °C and 650 °C and estimated organic C as the difference between readings (Robenhorst 1988). Carbonates were detected only below 75 cm of depth at some of the sites.

For the additional soil analyses at Castelli, Guerrero, and América, we determined exchangeable acidity with an alkaline titration of 1 M KCl extracts (Robertson et al. 1999), Cl concentrations on 1:1 water extracts using an ion selective electrode (Frankenberger et al. 1996), and Olsen extractable P colorimetrically (Kuo 1996). We measured total elemental soil pools using ICP after a HNO₃/H₂O₂/HCl acid – microwave digestion (EPA-3050A, see Chen and Ma (1998)). We also estimated forest nutrient accumulation from the product of biomass and elemental concentration. The forest components analyzed were leaves, bark, wood, roots, and forest floor, divided into litter and organic soil. We used allometric equations developed with seven trees to estimate leaf, wood and bark biomass from basal area and height measurements at each site. We used a ratio of 0.19 for below to above-ground biomass as determined from published equations that link belowground biomass to aboveground biomass, stand age, and latitudinal region (Cairns et al. 1997). Basal area and tree height measurements were taken in five 0.1-ha plots at each site; within each plot we collected five samples of fully expanded sun leaves, bark, and wood from three randomly selected individuals.

We also sampled shoots of *Cynodon dactylon* as a bioindicator of soil changes. Five randomly selected individuals were collected whenever the species was present in both forest and grassland stands. Plant, litter, and organic soil samples were oven-dried at 70 °C, ground (0.5 mm sieve), and HNO₃/H₂O₂-digested for ICP elemental analysis. Carbon and N concentrations were determined by dry combustion with an autoanalyzer (Gill et al. 2002).

Deposition and throughfall measurements

At Castelli we measured wet + dry deposition and throughfall in the forest and grassland stands. For wet + dry deposition, we installed three 17-cm diameter PVC funnel collectors with glass wool filters and 5-L glass bottles. Collectors were located 3.5 meters above the ground in the grassland 100 m away from the forest edge. We installed six collectors of the same type under the forest canopy, 60 cm above the ground. We made 9 collections during the sampling period, with the lag between rainfall events and collection always < 20 days. Collectors were replaced after each sampling. Collections covered a 184-day period and accumulated 498 mm of precipitation and 316 mm of throughfall in the forest. The release of acidity by the forest floor was evaluated in the lab with a 1:3 mixture of litter + organic soil and deionized water shaken for 15 minutes and filtered. By doing this we attempted to magnify any possible exchange between the forest floor and the percolating rain water that could take place in field conditions. We used rinsed Whatman 42 paper to filter precipitation, throughfall, and forest floor extract solutions and analyzed them using the above methods for soil extracts.

Element balances

We estimated transfers and gain/loss of base cations and protons following afforestation at Castelli, Guerrero, and América. For this purpose we used spatial differences between forest and grassland stands as a surrogate for temporal changes within forest stands established on native grasslands, assuming that forest stands were established on soils similar to those under our native grasslands stands. We based our estimates of changes on the observed differences between cation and proton pools in forest and grassland stands for the top meter of mineral soil, considering the product of bulk density and concentrations from acid digestion or titration. Although compaction or expansion of the soil after afforestation could have affected this calculation (Brimhall et al. 1991), soil volumetric contents of Ti (Jersak et al. 1995) did not differ between forest and grassland stands, suggesting that such effects were negligible (differences were always < 5% and statistically non-significant). The ecosystem balance for each base cation was estimated from the difference between forest accumulation and soil losses. We calculated excess cation accumulation (ECA) of tree plantations considering biomass and forest floor pools ($ECA = Ca + Mg + K + Na + Mn + Fe - S - P$). This methodology was adapted from Richter (1986).

True replication in our study was derived from the comparisons of effects across sites, which were evaluated using paired t-tests (Zar 1984). Statistical comparisons between stands within each site were also performed with a t-test in order to constrain error estimates. All pH values were transformed to H^+ concentrations for statistical calculations.

Results

Soils under forest and grassland vegetation displayed consistently different acidity and base cation composition across the study sites (Table 2). With the exception of Pinamar, located on calcareous sand dunes, soil pH from 0–20 cm depth was one pH unit lower on average under forests than grasslands (4.6 and 5.6, respectively; $p < 0.0001$ across sites, Table 2). Among base cations, Ca and Na showed the greatest differences. Exchangeable Ca was 40% lower on average under forest stands than under grasslands ($p < 0.001$ across sites, Table 2). Maximum differences were observed at Pila (75%), the only forest that had been completely harvested in the past. Exchangeable Na showed the opposite trend and was higher under forests at all sites except Chascomús, Tandil, and Pinamar ($p < 0.05$ within sites, $p = 0.0038$ across sites, Table 2). Exchangeable Mg and K showed variable trends with significant differences occurring in both directions between forest and grassland stands. All forests, except Pila, had higher soil organic C (SOC) ($p < 0.05$ within sites, $p = 0.0096$ across sites, Table 2), with forest stands on average having $\sim 30\%$ more SOC in the top 20 cm of mineral soil.

Soils under trees and grasses also showed consistently different vertical patterns to one-meter depth (Figure 3). Soil pH under grasslands ranged from 5.5 to 6.5 and decreased slightly with depth (Figure 3). In all cases forest stands had significantly lower soil pH between 5 and 50 cm depth ($p < 0.01$ within sites, $p = 0.0088$ across sites), with the lowest values observed between 10 and 35 cm at Castelli and América and closer to the surface in Guerrero. All three sites had a distinct cross-over point at ~ 60 cm, below which soil pH became more alkaline under forests than grasslands (Figure 3). This was particularly evident at América, where the same forest profile displayed pH values < 4 at intermediate depths and > 8 at one meter. The pH of the organic soil horizon was ~ 5.7 at all three sites.

The effective cation exchange capacity (ECEC) of soils also differed under forests and grasslands (Figure 3). Guerrero soils displayed lower ECEC under forests throughout the top 50 cm of the profile, but at Castelli this occurred only between 20 to 35 cm depth. Differences disappeared below 50 cm with the occurrence of the B horizon. At América significant differences were observed in the top 5 cm only ($p < 0.01$). Soils under all three grasslands had 100% base saturation. Base saturation decreased to as little as 80% under forest vegetation within 10–35 cm depth ($p < 0.05$ within sites, $p = 0.0024$ across sites). We analyzed the relationship between soil pH and ECEC in more detail for the A horizon (0–35 cm) at Castelli and Guerrero, which shared the same parent material. ECEC of individual samples was significantly and positively associated with organic C content ($r^2 = 0.29$), and pH ($r^2 = 0.26$) ($n = 80$ and $p < 0.0001$ in both cases). The residuals of the ECEC-organic carbon content regression showed a stronger relationship with pH ($r^2 = 0.56$, $p < 0.0001$). This regression analysis indicated that a decline of pH from 6 to 5 corresponded with an average ECEC loss of 2.24 cmol_c/kg, a 20% decline.

The composition of the exchange complex also differed markedly between grassland and forest soils. After afforestation, exchangeable acidity and Na displaced Ca at all sites (Figure 4), with changes in exchangeable Ca smallest in the surface soil.

Table 2. Chemical properties of the top mineral soil (0–20 cm) under native grasslands (G) and *Eucalyptus* forests (F). The sampled depth was completely in the A horizon except at Pinamar where no horizon differentiation was observed. Soil pH_{water} was measured in a 1:1 soil-water ratio. Exchangeable (Exch) base cations were determined by ICP using extracts of 1 M NH_4OAc at pH 7. Organic C and total N were obtained by dry combustion.

Site	pH_{water}		Exch Ca (mg/Kg)		Exch Mg (mg/Kg)		Exch K (mg/Kg)		Exch Na (mg/Kg)		Org C (%)		Total N (%)	
	G	F	G	F	G	F	G	F	G	F	G	F	G	F
<i>Flooding Pampas</i>														
Castelli	5.60	4.60*	1783	1191*	248	271	602	442*	0	42*	2.9	3.9*	0.25	0.30*
Guerrero	5.70	4.30*	1362	679*	224	203*	458	316*	4	84*	2.5	2.9*	0.23	0.23
Pila	5.58	4.42*	1229	305*	383	218*	403	244*	50	89*	2.7	2.2*	0.24	0.18*
<i>Flooding/Rolling Pampas</i>														
Chascomús	6.15	5.76*	1134	1100	187	345*	656	473*	43	31	2.5	3.5*	0.22	0.25*
Pereyra	5.29	4.59*	1703	1013*	193	191	364	247*	0	17*	2.1	2.4*	0.19	0.20
<i>Rolling Pampas</i>														
Rojas	5.17	3.73*	1962	887*	258	183*	809	603*	9	100*	1.7	2.9*	0.21	0.29*
Rancagua	5.29	4.37*	1756	833*	259	176*	760	916*	12	49*	1.9	2.6*	0.19	0.31*
<i>Inner Pampas</i>														
América	5.76	4.22*	944	604*	256	353*	355	344	14	78*	1.3	1.5*	0.11	0.11
<i>Hills</i>														
Tandil	5.80	5.21*	1038	790*	227	310*	133	109*	9	13	3.8	4.1*	0.30	0.30
<i>Coastal dunes</i>														
Pinamar	7.76	7.97	10861	12811	53	95	119	298*	103	159	nd	nd	nd	nd

* Significant differences within sites, $p < 0.05$

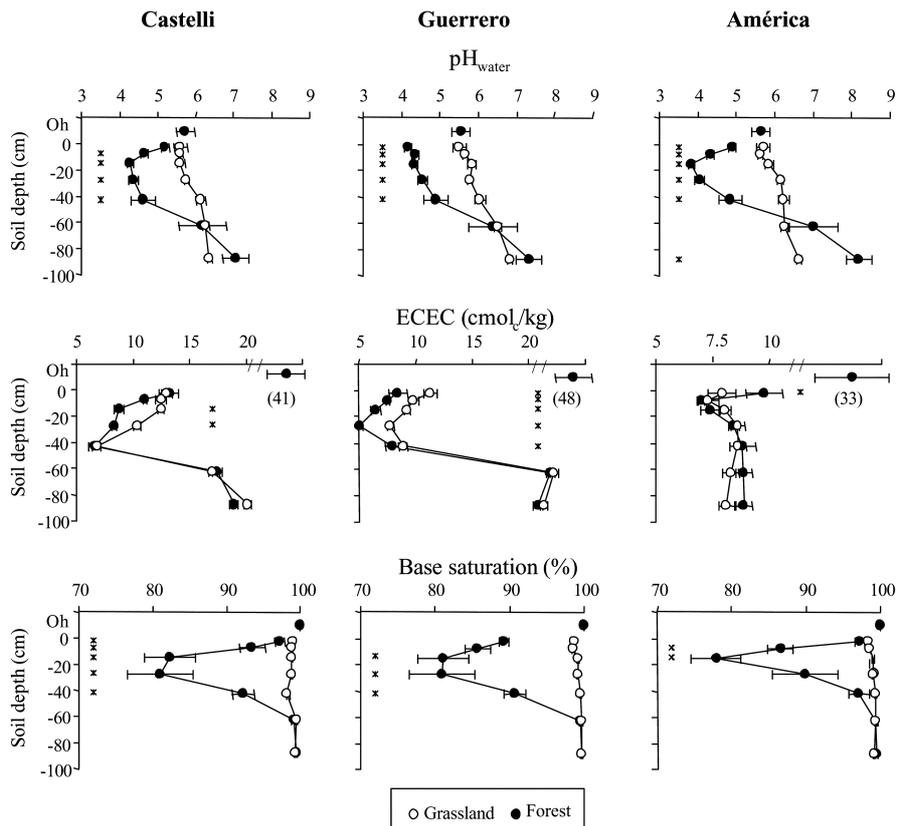


Figure 3. Soil properties under native grassland and eucalypt forests for the top meter at three sites (mean + S.D, $n = 5$ for each pair). A) Soil pH measured in 1:1 water-soil extract. B) Effective cation exchange capacity (ECEC) obtained from the sum of NH_4OAc -exchangeable base cations and KCl -exchangeable acidity. C) Base saturation of the effective cation exchange complex. Values for the organic soil horizon (present only under forests) are indicated in the top of the panel. Asterisks indicate significant differences between stands at $p < 0.05$.

At intermediate depths, the contribution of Ca to the exchange complex decreased to $< 50\%$, mainly as a result of gains in acidity. Below 50 cm, Ca was increasingly replaced by Na (Figure 4). Exchangeable Na, barely detectable in grassland soils, accumulated under forests to 16 to 24% of saturation.

Organic matter accumulation in forest stands was ~ 500 to 750 Mg/Ha for the tree, litter, and organic soil pools (Table 3). Two-thirds of this accumulation was in wood. Despite contributing only 15% of accumulated biomass, bark accounted for 60 to 90% of base cation sequestration by forests (data not shown). Ca was the dominant cation in forest biomass, followed by K, Mn, Mg, and Na, with mean sequestration across sites of 5.6, 0.72, 0.29, 0.28, and 0.19 Mg/Ha, respectively (Table 4).

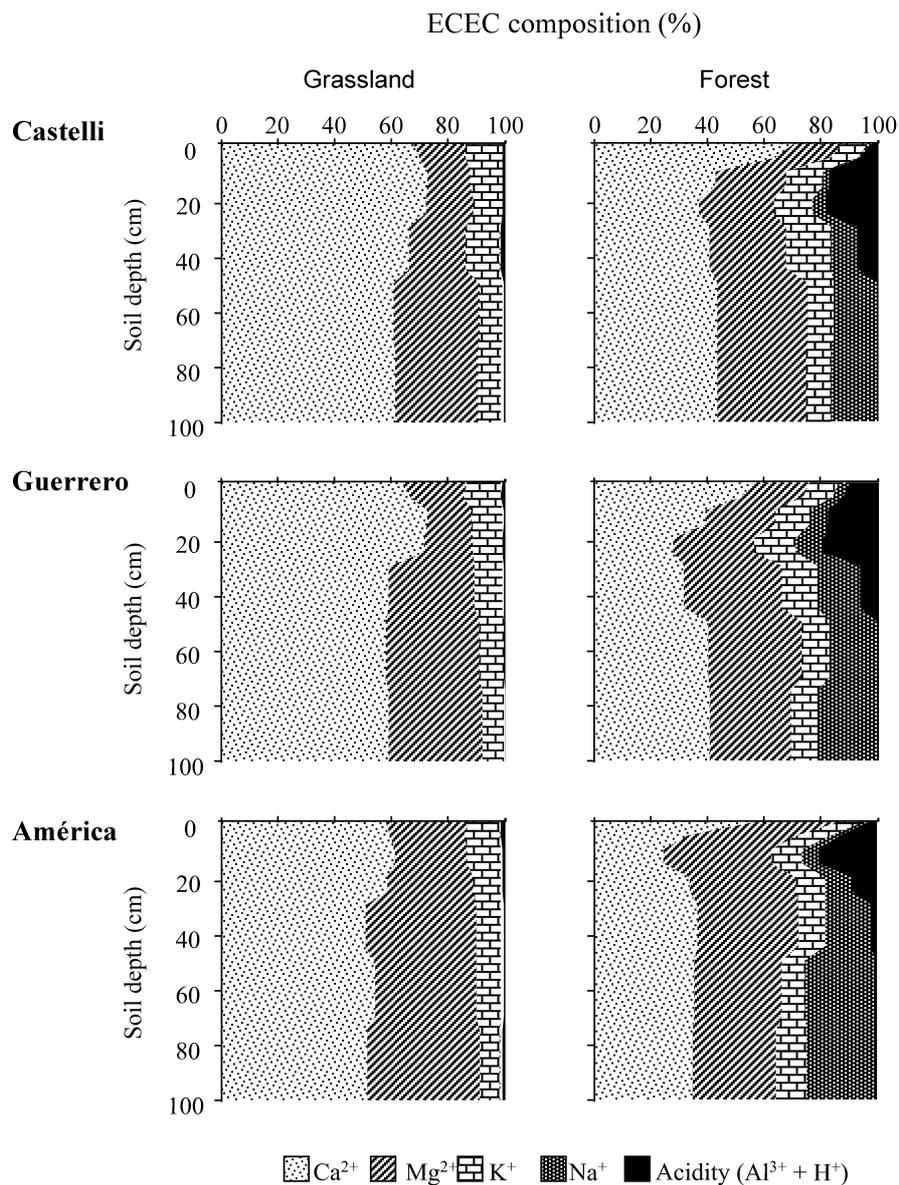


Figure 4. Relative composition of the exchange complex in the top meter of mineral soil under native grasslands and *Eucalyptus* forests ($n = 5$). The values for NH_4OAc -exchangeable base cations and KCl -exchangeable acidity sum to 100%, with proportions calculated on a charge basis ($\text{mol}_c/\text{mol}_c$).

With the exception of Na, cation pools in mineral soil displayed little or no change overall for grasslands and forests in the upper meter (Table 4). The differences between total elemental pools in the forest and grassland ecosystems sug-

Table 3. Forest biomass estimates at three sites: Castelli, Guerrero, and América (mean + S.D., $n = 5$ for each site). Leaf, bark, and wood biomass were estimated from measurements of tree basal area and height at each site and from allometric equations developed at Castelli. Basal area and tree height measurements were taken in five 0.1 Ha plots in each stand. Litter and organic soil biomass were measured in five 0.2×0.5 m plots.

	Biomass (Mg/Ha)		
	Castelli	Guerrero	América
<u>Trees</u>			
leaves	7.2 (3.2)	6.5 (2.5)	6.8 (3.6)
bark	116.9 (28.0)	86.5 (27.7)	71.0 (31.2)
wood	514.8 (123.6)	381.0 (121.9)	312.6 (137.5)
roots	97.8 (24.1)	72.4 (23.8)	59.4 (26.8)
<u>Floor</u>			
litter	9.6 (2.2)	11.4 (0.8)	12.2 (1.5)
organic soil	8.0 (4.7)	26.2 (2.1)	28.9 (6.0)
TOTAL	754.3 (129.1)	584.0 (127.3)	490.8 (143.7)

gested significant net ecosystem gains after forest establishment for Ca and Na at Castelli, for Na at Guerrero, and for all base cations at América. The only significant negative difference between forest and grassland ecosystem pools was observed for Mn at Guerrero (Table 4). When mineral soil changes were examined by depth intervals, important localized differences were revealed. All sites lost Ca from 5–50 cm depth and two gained Ca from 0–5 cm. Mn followed this trend with even bigger changes on a relative basis (Table 4). The large difference of total Ca observed from 5–50 cm depth between stands involved smaller pools of both exchangeable and non-exchangeable pools in the forests. Based on these differences, non-exchangeable Ca losses after afforestation could have reached 20% from 5–10 cm depth ($p < 0.001$ within sites, $p = 0.0097$ across sites, data not shown). In contrast with the rest of the cations, Na pools were three times higher under forest stands at all three sites (Table 4; $p < 0.001$ within sites, $p = 0.021$ across sites).

Estimates of proton releases from excess cation accumulation by trees were higher than actual proton accumulation in soils. While the first ranged between 300 ± 6 and 406 ± 33 $\text{kmol}_c\text{.Ha}^{-1}$ across sites, the second amounted 44 ± 14 to 53 ± 21 $\text{kmol}_c\text{.Ha}^{-1}$. Taking into account the age of the forest stands (Table 1) and their excess cation accumulation, mean annual rates of proton release by trees should have ranged from 3.1 to 9.9 $\text{kmol}_c\text{.Ha}^{-1} \text{. yr}^{-1}$, whereas exchangeable acidity accumulation should have ranged 0.5 to 1.2 $\text{kmol}_c\text{.Ha}^{-1} \text{. yr}^{-1}$. Deposition was more acidic than throughfall at all sampling dates ($p < 0.05$), indicating no acid inputs from the forest canopy. During the sampling period the mean pH of precipitation collections ranged between 5.6 and 6.9, whereas that of throughfall ranged between 6.7 and 7.2. Acidity deposition was 0.013 $\text{kmol}_c\text{.Ha}^{-1} \text{. year}^{-1}$. Our measurements of precipitation and throughfall yielded the following estimates for annual elemental fluxes (precipitation and throughfall respectively, in $\text{kg. Ha}^{-1} \text{. yr}^{-1}$): 5.9 and 10.1

Table 4. Differences in elemental pools between eucalypt plantation and native grassland stands in the Pampas. Negative values indicate losses (mean + s.d., n = 5). Asterisks show significant differences (p < 0.05) for mineral soil changes and net balances. Where mineral soil pools differed significantly, the percentage difference is shown. See Methods for details on the specific calculations.

Castelli	Pool size differences (Mg/Ha)											
	Ca		Mg		K		Na		Mn			
	mean	sd	%	mean	sd	%	mean	sd	%	mean	sd	%
Forest	5.9	0.1		0.27	0.02		0.66	0.02		0.20	0.02	
Trees	5.6	0.1		0.24	0.02		0.62	0.02		0.18	0.02	
Floor	0.5	0.0		0.06	0.00		0.08	0.00		0.02	0.00	
Mineral soil	-2.3	1.8		2.14	4.32		2.69	3.92		10.02	2.20*	192
0-5 cm	1.1	0.5*	49	0.05	0.02*	5	-0.08	0.03		0.08	0.02*	63
5-50 cm	-4.5	1.9*	-25	0.40	0.25		0.46	0.31		1.31	0.25*	82
50-100 cm	1.1	1.7		1.69	4.48		2.31	4.00		8.63	2.04*	246
BALANCE	3.7	1.8*		2.44	4.32		3.39	3.92		10.22	2.20*	
Guerrero												
Forest	4.6	0.1		0.25	0.02		0.57	0.02		0.14	0.01	
Trees	4.1	0.1		0.19	0.02		0.50	0.02		0.12	0.01	
Floor	0.6	0.0		0.06	0.00		0.07	0.00		0.03	0.00	
Mineral soil	-3.9	4.5		1.20	5.41		-0.85	4.63		15.13	2.12*	263
0-5 cm	-0.3	0.2		-0.08	0.04*	-7	-0.19	0.06*	-14	0.08	0.01*	49
5-50 cm	-7.1	1.3*	-34	-4.16	2.28*	-27	-5.43	2.28*	-30	2.04	0.69*	95
50-100 cm	3.5	4.1		5.44	4.25		4.78	3.42		13.01	1.78*	378

Table 5. Chemistry of *Cynodon dactylon* plants growing in grassland and forest stands. Values correspond to non-reproductive shoots and show the mean for grassland and forest stands (n = 5 in each stand) at six sites: Castelli, Guerrero, Dolores, Pereyra, Chascomús, and América. Percentage change from grassland to forest plants is indicated where differences are significant.

	Dry weight concentration (mg/kg)		Difference
	Grassland	Forest	
N	17796	16894	
P	1735	1503	
Ca	2975	3862*	30%
Mg	1375	1971*	43%
K	10965	11354	
Na	199	183	
Mn	70	201*	187%
S	2500	3087	
Al	151	107	
Fe	233	177	
Si	102	78	

for Ca, 1.5 and 3.1 for Mg, 4.9 and 27.6 for K, and 4.4 and 8.9 for Na. Forest floor leachates obtained in the lab had a mean pH of 6.2 (SD = 0.4) indicating a low contribution of protons by litter and organic soil.

The chemistry of *Cynodon dactylon* shoots differed significantly in grassland and forest stands (Table 5). *C. dactylon* plants from the forest had almost triple the Mn concentrations of those in grasslands ($p < 0.05$ within sites, $p = 0.033$ across sites), with Ca and Mg showing a similar but smaller change (Table 5; $p < 0.1$ within sites, $p < 0.05$ across sites).

Discussion

Soils under Eucalyptus plantations in the Pampas had substantially higher acidity than native grassland soils. Ten to 100 years after tree establishment, soils that developed originally under herbaceous vegetation were 1 pH unit more acidic on average and had lower exchangeable Ca in the surface soil (Table 2). This pattern was repeated at nine sites across soils typical of the region (Table 2). The differences in soil acidity that we observed in the Pampas matched observations in afforested grasslands of Africa and New Zealand (Davis and Lang 1991; Musto 1991; Davis 1995; Alfredsson et al. 1998), although the intensity of forest/grassland differences was greater in the Pampas (see also Amiotti et al. (2000)). Mirroring our results, a recent review of vegetation transitions in the Amazon basin revealed large pH and exchangeable Ca increases in Ultisols and Oxisols after the shift from native or secondary forest to pastures (McGrath et al. 2001; Krishnaswamy and Richter 2002).

Table 6. Synthesis of major results for the predicted imprint of soil acidification and the mechanisms proposed in this paper (see Table 1).

	H ⁺ inputs from throughfall & forest floor	Vertical location of acidification peak	Base cation pools, grassland/forest difference
Castelli	No H ⁺ inputs	10–35 cm	Ca higher in forest Mg no differences K no differences Na higher in forest
Guerrero	<i>no data</i>	10–35 cm	Ca no differences Mg no differences K no differences Na higher in forest
América	<i>no data</i>	10–20 cm	Ca higher in forest Mg no differences K no differences Na higher in forest

Soil acidification following afforestation can potentially be explained by three complementary mechanisms: 1) organic acids inputs, 2) increased soil respiration, and 3) cation sequestration and redistribution (Figure 1). The vertical patterns of soil acidification together with the estimated elemental balances and measurements of aboveground acidity suggest that the last mechanism dominates in the Pampas (Table 6). Vertical patterns of pH and exchangeable acidity indicated maximum acidification at intermediate soil depths (10–35 cm), as well as losses of exchangeable Ca (Figure 3). These vertical patterns suggest that organic acid inputs are unlikely to have caused the acidification observed; they would have entered the soil predominantly from the surface, causing maximum acidification in the top soil (Figure 1), and the throughfall and organic soil leachates were not acidic. Afforested stands showed pH values well below 5, suggesting that carbonic acid, if important, could not be the only agent of acidification since it would not be dissociated below that pH.

The differences of base cation pools between forest and grassland stands suggested that no net ecosystem losses occurred after afforestation (Table 4), and hence base cation sequestration and redistribution, rather than increased soil respiration and leaching, was the dominant mechanism of acidification in afforested plots (Table 6). An important redistribution took place within mineral soil from intermediate depths to the surface soil (Table 4). This vertical redistribution, particularly large for Ca, most likely reflects the intense cycling (uptake and release) of base cations by trees (Jobbágy and Jackson 2001). In the past, excess cation absorption and sequestration by trees has been proposed as a transient cause of acidification in forests, unless harvesting occurred (Nilsson et al. 1982). In the long term, cation

recycling was expected to balance uptake at some point, neutralizing any early acidification (Nilsson et al. 1982). We suggest that even when a long-term equilibrium is achieved, internal redistribution of cations from intermediate depths to the surface mineral soil could cause the transfer of charge and sustained localized acidification, with clear implications for mineral weathering in these layers. It is important to highlight that the substantial redistribution of Ca in afforested soils was not observed for Mg, suggesting that a "cation-specific" process such as root uptake, rather than a less specific mechanism like acid leaching, was operating.

In the Southeastern US, acidification accompanied an aggrading pine plantation on a previously limed and cultivated Ultisol, but acidification peaked in the surface soil and the system had significant Ca losses from leaching (Richter et al. 1994; Markewitz et al. 1998). A particularly interesting case is a cultivated pasture in Australia (formerly a forest soil) that was then reforested with *Pinus radiata* and *Quercus suber* (Noble et al. 1999). Soil pH under the oak stand showed the largest decrease and peaked at intermediate depths, whereas soils under the pine stand had smaller pH changes observed only in the surface soil (Noble et al. 1999). We suggest that these differences in acidification could result from shifts in the mechanism of acidification between forest types.

Additional mechanisms of acidification associated with nitrogen cycling may operate in afforested ecosystems but do not appear to be dominant in our systems. One possible source of acidity is enhanced nitrification coupled with net nitrate losses (Schlesinger 1997). Although feasible in our system, we believe that this mechanism is unlikely, given that afforested stands retained or gained rather than lost N, as indicated by the higher N contents of the top 20 cm of the soil in five afforested stands compared with their grassland pairs (Table 2). Increases in the ammonium/nitrate ratio of plant uptake after afforestation could be a source of acidity if the forest acts as a N sink (Richter (1986), see also Arnold (1992)). We made coarse estimates of net cation sequestration by tree stands assuming that all N was taken up either as ammonium or as nitrate, and our figures of potential proton release remained positive and large in all study sites under both scenarios (2 to 6 $\text{kmol}_c\text{.Ha}^{-1}\text{.yr}^{-1}$ assuming nitrate uptake and 4–9 $\text{kmol}_c\text{.Ha}^{-1}\text{.yr}^{-1}$ assuming ammonium uptake).

Soils under eucalypt plantations at our Pampas sites acidified with the same intensity as soils from heavily industrialized areas affected by acid rain (Andrews et al. 1996). The annual gain of exchangeable acidity that we estimated, 0.5 to 1.2 $\text{kmol}_c\text{.Ha}^{-1}\text{.yr}^{-1}$, is attributable solely to the influence of tree plantations; acid rain is effectively absent in the region, as shown both from our deposition and throughfall data and in other studies (e.g., Lavado (1983) and Bouwman et al. (1997)). Estimates of proton releases in plantations because of net cation sequestration exceeded observed exchangeable proton gains in the soil by 300 $\text{kmol}_c\text{.Ha}^{-1}$. These extra charges could have been consumed by weathering reactions. Assuming that feldspar, an abundant mineral in these loess soils (Teruggi 1957), was weathered to kaolinite, < 4% of the soil mass of a 20 cm-thick layer would need to be affected in a 50-year period to explain this proton consumption.

Soil chemical changes associated with afforestation had important feedbacks on plants. Soil acidification increases the mobility and bioavailability of Mn, potentially even leading to Mn toxicity (Gambrell 1996; Marschner 1995). We observed substantial mobilization of Mn under afforested stands (Tables 4 and 5), with reduced Mn at intermediate depths in the total mineral pool and higher Mn concentrations in the mineral surface soil and in the leaves of the bioindicator grass *C. dactylon*. This redistribution may have been caused by enhanced mineral release and mobility of Mn due to acidification and by the accumulation of Mn in the surface soil due to its intense uptake and cycling by Eucalypts (mean concentration in fully expanded leaves was 1420 mg/kg). Mn toxicity could potentially affect further agricultural use of afforested land, as suggested by Mn concentrations in *Cynodon* leaves, which in our forest stands reached levels that are considered toxic for other grass species (Edwards and Asher 1982).

The exchange capacity of soils is a critical aspect of soil fertility that may drive future modifications in afforested soils of the Pampas. Soils under eucalypt plantations showed a decline in effective exchange capacity, particularly at the oldest forest stand in Guerrero (Figure 3). A decline in the variable charge component of organic matter due to acidification is a likely cause of this trend together with mineralogical alterations (i.e., weathering) of clays. Effective cation exchange capacity declines could trigger irreversible nutrient losses in the future.

We suggest that the acidification described here could be expected under most broadleaf tree species that, like Eucalypts, cycle large amounts of Ca. Acidification should be even higher under commercial tree plantations experiencing regular biomass (and cation) removals, compared to stands, which in most cases were never harvested. The largest decreases in pH and Ca in our study occurred at the only site that had been clear-cut in the past (Table 2 – Pila). In contrast with tree-dominated systems, grasslands should not suffer significant Ca losses, even under intense forage harvesting and removal situations, because of their limited use of soil Ca.

Afforested stands had substantially higher exchangeable Na and more alkaline soil in deep layers (Figures 3 and 4) (see Parfitt et al. (1997)). The potential sources of this Na were atmospheric deposition, rock weathering, and groundwater. Atmospheric inputs are an unlikely source since the annual rates of deposition that we recorded explained < 10% of the accumulated Na. In addition, Na:Cl ratios of deep soil were four times higher than those of atmospheric inputs ($p < 0.001$; data not shown), suggesting either a different Na source or substantial Cl leaching. Rock weathering, enhanced by acidification, could potentially increase exchangeable Na pools, but not total Na pools as we observed (Table 4). We believe that groundwater was the most likely source of the Na accumulated in our afforested stands. Na accumulation is frequent in lowland soils and groundwater of the Pampas as a result of poor regional drainage (Tricart 1973; Lavado 1983; Bui et al. 1998). The pathway of Na movement from groundwater to the upland soils studied here is still uncertain. Physical transport resulting from enhanced capillary rise, decreased leaching under tree plantations, and root uptake from deeper soil layers are plausible mechanisms that deserve further study. Eucalypt leaves in Castelli, Guerrero, and América showed high Na concentrations (> 1000 mg/kg, data not shown).

Whether this increased Na uptake is a cause or a consequence of soil Na accumulation is uncertain, but potentially negative consequences of Na accumulation on forest production should be explored. Groundwater could also be the source for the apparent net Ca and Mg gains in afforested stands (Table 4).

Tree planting in the Pampas has been considered an aesthetically and even "ethically" correct practice since the beginning of European settlement, with any potential negative consequences rarely acknowledged (Sarmiento (1855) and Acosta (1873); but see Panario (1991)). The growing need for wood products in Argentina and the prospective global market for C sequestration both suggest that expansion of plantations will continue (Canadell et al. 2000; Wright et al. 2000). Furthermore, tree invasions (e.g., *Gleditsia triacanthos*, *Melia azedarach*) are increasing in the region (Ghersa et al. 2001; Mazia et al. 2001). The magnitude of soil alterations that we observed within half a century of tree establishment emphasizes the role of vegetation type as a dynamic factor of soil formation and suggests large potential feedbacks of vegetation change on soil fertility and biogeochemistry.

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