Groundwater and soil chemical changes under phreatophytic tree plantations

Esteban G. Jobbágy[1] and Robert B. Jackson[2,3]

[1]   The onset of groundwater consumption by plants can initiate a pathway of chemical inputs from aquifers to ecosystems, typically absent in groundwater recharge areas. We explored this biogeochemical transfer and its influence on soils in phreatophytic eucalypt plantations and native grasslands of the Pampas (Argentina). Groundwater and soil chemical observations at three grassland/plantation pairs were complemented with more detailed analyses along a 400-m-long grassland-plantation transect. Although tree plantations showed a widespread and homogeneous salinization of groundwater and soils at all study sites, chemical contrasts between the plantation edge and core were evident along the study transect. Nonsalty, slightly acidic, bicarbonate-dominated waters in the grassland changed sharply within the plantation, with dissolved chloride, sulfate, calcium, and magnesium peaking at the plantation core (200 m away from the grassland) and dissolved sodium, carbonate, bicarbonate, and pH peaking toward the edge (0–50 m away from the grassland) and declining toward the core. In agreement with these differences, soil alkalinization was the strongest at the plantation edge but absent in the core. Groundwater flow simulations using FLOWNET suggested trajectories of increasing length and depth and older groundwater ages (confirmed by tritium analyses) toward the plantation core, explaining the hydrochemical contrasts within the plantation. Flow simulations and chloride mass balances suggested discharges of 250–500 mm yr^{-1} to the plantations. In our sites phreatophytic discharge controlled solute transfers from groundwater through (1) altered flow within the aquifer, affecting solute transport to the rooting zone, and (2) water uptake plus solute exclusion, concentrating solutes in the rooting zone. While the first mechanism may be restricted to the core of large phreatophytic areas, the second is likely to occur more generally in phreatophytic ecosystems.

1.   Introduction

[2]   Biogeochemical exchange between terrestrial ecosystems and groundwater is predominantly unidirectional in upland zones, where downward water transport from ecosystems to aquifers (i.e., recharge) represents the only significant hydrological flux coupling both systems. This exchange, however, may become reciprocal and increasingly complex if water flows in the opposite direction (i.e., discharge), as in riparian or wetland zones where shallow water tables allow evaporative groundwater losses driven by capillary forces or plant water uptake (i.e., phreatophytic uptake) [*Freeze and Cherry*, 1979]. Far from being fixed attributes of different landscape positions, recharge/discharge patterns can switch as a result of hydrological and/or ecological change. Remarkably, vegetation shifts involving the establishment of plants with increased water access and use can initiate groundwater discharge in places where it was originally absent, opening a novel pathway of chemical inputs into the ecosystem and the possibility of complex feedbacks between vegetation, soils, and groundwater. In this paper we explore how the replacement of nonphreatophytic grasslands by phreatophytic trees influences the intensity and composition of solute transport from groundwater toward the surface and how these solutes accumulate and distribute in the soils and plants of the ecosystem.

[3]   The influence of groundwater use by plants on the amount, composition, and distribution of chemical inputs from aquifers to ecosystems can be conceptualized as the convergence of two independent types of processes: (1) aquifer effects associated with the influence of water discharge on hydraulic gradients and transport pathways of

[1]Grupo de Estudios Ambientales, Instituto de Matemática Aplicada San Luis, Universidad Nacional de San Luis and CONICET, San Luis, Argentina.
[2]Department of Biology, Duke University, Durham, North Carolina, USA.
[3]Nicholas School of the Environment and Earth Sciences, Duke University, Durham, North Carolina, USA.
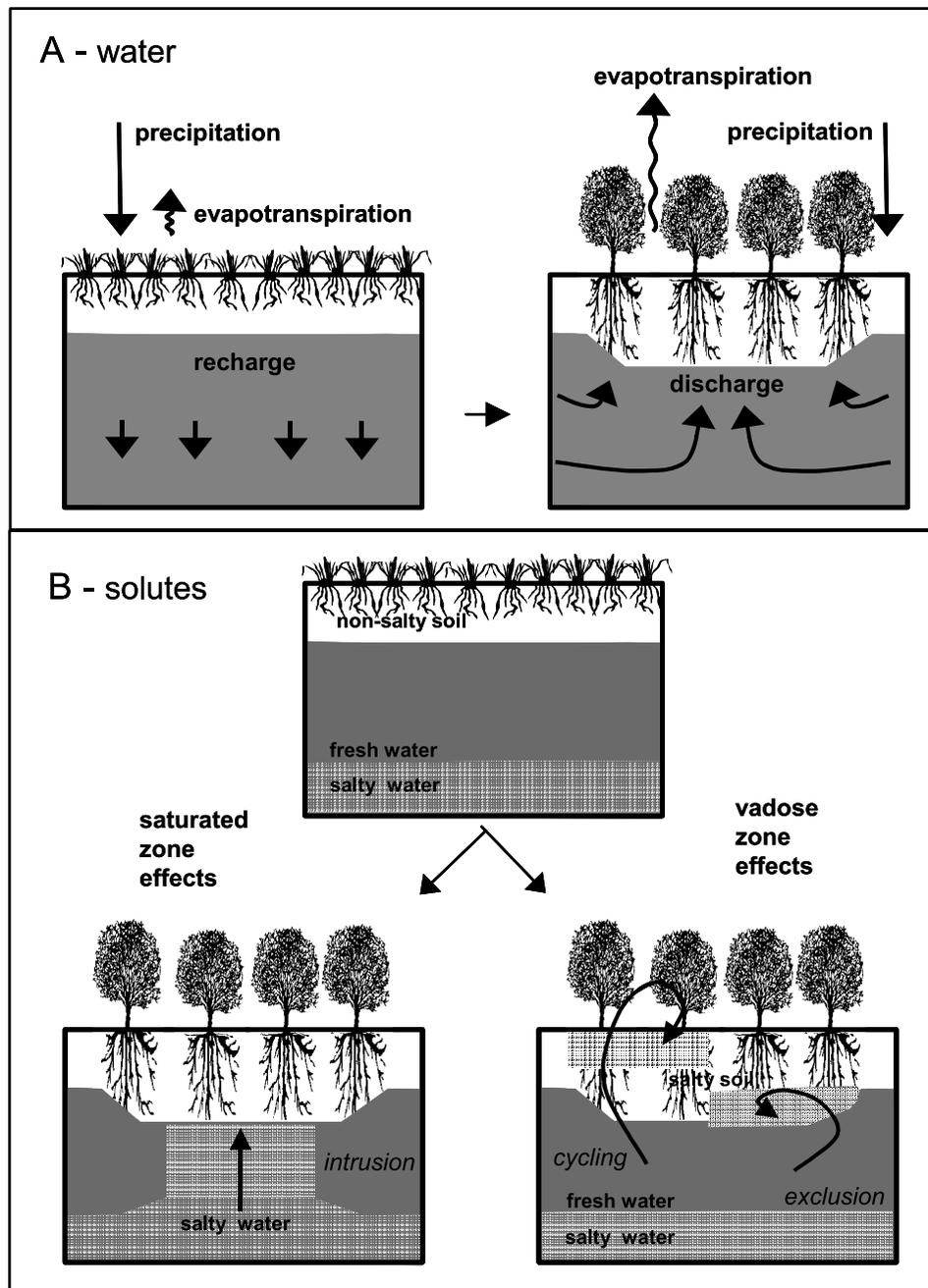
Figure 1. Schematic representation of the effects of phreatophytic discharge on solute fluxes. (a) Groundwater recharge under native grasslands that maintain evapotranspiration < precipitation compared with groundwater discharge under tree plantations with evapotranspiration > precipitation. (b) Solute composition changes in groundwater induced by tree establishment in the hypothetical situation of a fresh groundwater layer underlain by salty groundwater. Phreatophytic trees can alter groundwater chemistry if the discharge flow is strong enough to create an intrusion of salty water from greater depth (saturated zone effects). Additionally, solutes can accumulate in the vadose zone depending on the rates of water uptake and the relative coupling between water and solute absorption by plants (vadose zone effects). Solutes that are actively taken up will be cycled by the ecosystem, eventually accumulating toward the surface of the soil (left side), whereas solutes that are excluded by root membranes will tend to accumulate in the zone of groundwater absorption close to the water table (right side).

groundwater across the landscape, and (2) vadose zone effects resulting from solute uptake/exclusion by plant roots controlling the rates and pathways of transport from the aquifer to the ecosystem (Figure 1). Aquifer effects take place when the onset of a discharge regime alters the hydrological fluxes within the aquifer, influencing the amount and composition of solutes of the water that reach the phreatophytic stand. For example, recharge waters

initially occupying the phreatic zone may be consumed and replaced by deeper ground waters with a different chemical composition after the establishment of phreatophytic plants. This intrusion alone can explain ecosystem salinization if deeper waters are saltier [*Sapanov*, 2000] (Figure 1). Vadose zone effects involve the regulation of solute accumulation and distribution within the groundwater-ecosystem continuum by plants through the coupling or uncoupling of ion uptake and water absorption [*Tester and Davenport*, 2003; *Jobbágy and Jackson*, 2004]. Solutes being excluded by root membranes will tend to accumulate where groundwater enters roots, typically the upper portion of the aquifer and/or capillary fringe [*Jarrell and Virginia*, 1990; *Heuperman*, 1999] (Figure 1); in contrast, solutes that are absorbed by roots will enter plant tissues and accumulate in their biomass, eventually being recycled to the soil via litterfall and throughfall [*Tester and Davenport*, 2003; *Jobbágy and Jackson*, 2001] (Figure 1). A key difference between the aquifer and vadose zone effects of discharge on solute accumulation patterns is the spatial heterogeneity that can be expected from each process within stands using ground water. While vadose zone effects respond to interactions between plants and the soil solution that are likely to be constant across a stand with the same type of discharge regime, aquifer effects can create heterogeneous patterns of solute accumulation as a result of differences in the source and chemical composition of groundwater arriving at the edge (shallower sources) and the center (deeper sources) of discharging stands of vegetation.

[4] Transitions from grass- to tree-dominated vegetation often increase evapotranspiration as a result of increases in leaf area, canopy roughness, and rooting depth [*Kelliher et al.*, 1993; *Calder*, 1998; *Jackson*, 1999; *Schenk and Jackson*, 2002; *Nosetto et al.*, 2005]. This ecohydrological change can switch recharge to discharge zones in places where phreatic aquifers are near the surface, sometimes causing salinization of groundwater and soils [*Heuperman*, 1999; *Vertessy et al.*, 2000; *Sapanov*, 2000; *Jobbágy and Jackson*, 2004; *Engel et al.*, 2005; *Jackson et al.*, 2005]. The expansion of eucalypt and pine plantations over some of the remaining native grasslands of southern South America is currently accelerating [*Richardson*, 1998; *Geary*, 2001] and will very likely be reinforced by the prospective carbon sequestration market [*International Geosphere-Biosphere Programme*, 1998; *Wright et al.*, 2000]. Large evapotranspiration increases accompanying this land use change have already been documented in the region [*Nosetto et al.*, 2005], and groundwater discharge has been detected in areas where shallow and conductive phreatic aquifers are present [*Jobbágy and Jackson*, 2004; *Engel et al.*, 2005]. Groundwater use by trees has been linked to the salinization of the groundwater-ecosystem continuum observed under tree plantations of various species [*Jobbágy and Jackson*, 2004; *Farley et al.*, 2005]. As afforestation expands over areas with shallow ground water, the assessment of its impact on water and soil resources becomes increasingly important.

[5] To explore the pathways and rates of solute fluxes from groundwater to ecosystems and their impact on soils with grassland afforestation in the Pampas, we (1) characterized groundwater flow and hydrochemistry patterns at different positions in discharging tree plantations and their surrounding recharging grasslands, (2) assessed the fate and distribution of dominant groundwater solutes in the vadose-soil-ecosystem continuum, and (3) explored the impacts of these solutes on soil salinity, sodicity, pH, and Ca availability. For these purposes we combined hydrochemical observations at three paired grassland/plantation stands with more detailed hydraulic information at one stand derived from groundwater tritium dating and flow modeling along a grassland-plantation transect. At this site, solute inputs from groundwater after the establishment of trees were compared with observed elemental gains in the vadose zone, soil, and tree biomass.

2. Materials and Methods

2.1. Study Region and Sites

[6] The Pampas occupy a vast loessic plain in southern South America [*Zárate*, 2003] in which wind borne sediments were influenced by alluvial processes in some areas. Grasses have dominated this temperate humid and treeless environment for at least the last three thousand years [*Soriano*, 1991; *Prieto*, 1996]. The extremely flat topography and the imprint of wind erosion during the Quaternary created a poor drainage network that, combined with the current humid climate (800- to 1000-mm mean annual precipitation), results in shallow groundwater across most of the region [*Tricart*, 1973]. Although extremely flat, most landscapes of the Pampas host an array of upland and lowland areas displaying a "grain" size of tens to hundreds of meters and subtle elevation differences that, in spite of being in the order of tens of centimeters, are enough to create strong ecological contrasts [*Tricart*, 1973]. Our work focused on upland zones that behave naturally as recharge areas and have no accumulation of salts under natural conditions.

[7] In the Pampas, like in other humid to subhumid grasslands occupying poorly drained plains (e.g., Eastern Siberia, Great Hungarian Plain, Great Plains in Western Canada), alkaline phreatic waters with high carbonate/bicarbonate concentrations are widespread. These waters are responsible for the formation of dispersive, alkaline, and infertile soils in discharging lowlands that contrast with neighboring fertile soils occupying recharging uplands [*Bazilevich*, 1970; *Tricart*, 1973; *Sumner and Naidu*, 1998; *Logan et al.*, 1999; *Bui et al.*, 1998].

[8] Vast areas of the Flooding Pampas are still dominated by a combination of native grasslands and pastures [*Paruelo et al.*, 2001], but tree-dominated stands are present as a result of European settlers establishing plantations of 0.1 to 100 Ha since the 1800s and, more recently, forestry companies planting stands of more than 1000 Ha. Where sediments have sufficiently high saturated hydraulic conductivity, the high evapotranspiration rates of these plantations drive the onset of groundwater discharge in areas where recharge was the dominant vadose flux prior to afforestation, opening the pathway of solute inputs from the phreatic aquifer [*Jobbágy and Jackson*, 2003, 2004; *Engel et al.*, 2005].

[9] We studied three paired grassland and plantation (*Eucalyptus camaldulensis*) stands in upland positions of the Pampas region at Castelli, Guerrero, and América, Argentina, (Table 1). Castelli, the site we studied in the

Table 1. Location and Description of Study Sites Along With the Type of Observations Performed at Each Site[a]

Site	Latitude/Longitude	MAP mm/yr	Tree Density, Stems/Ha	Age, years	Soil Type (USDA System)	Water Table Depth, m
Castelli	−36°02.0′, −57°50.3′	987	600	50	Hapludoll with buried B horizon	1.5−2.5
Guerrero	−36°02.0′, −57°50.3′	987	550	96	Hapludoll with buried B horizon	1.5−2.5
América	−35°30.6′, −62°59.2′	745	850	42	Haplustoll	2−6

[a]MAP, mean annual precipitation; Age, age of the plantation stand.

greatest detail, is located in the Flooding Pampas. Guerrero is located in the same region, ~7 km away from Castelli, and has similar climate, topography, soil type, and hydrologic features. The surrounding native grassland at Castelli and Guerrero grows year round with a mixture of C_3 and C_4 grasses typical of upland communities in the Flooding Pampas [*Perelman et al.*, 2001]. América is located in the Inner Pampas on an upland position within a former dune landscape. All of the tree plantation and grassland/pasture stands were never fertilized or irrigated, as confirmed with land managers and consistent with regional practices. Biomass was not harvested from afforested stands except at Guerrero where ~50% of the eucalypts were cut previously; grassland stands were subject to cattle grazing. See *Jobbágy and Jackson* [2003, 2004] for further details.

2.2. Hydrochemical Patterns

[10] We explored the aquifer-level imprint of afforestation by sampling groundwater at different depths across the grassland-tree plantation flow system in Castelli and wells in the plantations and adjacent grasslands of Guerrero and América. At Castelli we sampled ground water at the water

table in 42 boreholes along three parallel 400-m transects and in 10 additional deeper boreholes and windmills located around and within the plantation (Figure 2). Boreholes were 0.1 m in diameter and were placed 0.5 to 1 m deeper than the water table. In order to characterize ground water below the rooting zone (1.8 and 5.5 m below the surface for grasses and trees, respectively [*Jobbágy and Jackson*, 2004]), additional water samples were obtained from four PVC-cased wells along the grassland-plantation transect (Figure 2). Three of them came from 6-m-deep wells that were sealed with bentonite plugs after hand-augering. An additional sample was obtained from an existing 16-m-deep cased well in the grassland. At Guerrero and América we sampled groundwater in grassland/plantation pairs 50 m away form each side of their boundary and 0.5 m below the water table level, using hand-augered boreholes.

[11] To characterize groundwater chemistry, we collected water samples from the boreholes and wells after flushing the volume of each well several times. Electric conductivity was measured in the field and pH in the lab within a week after collection. Dissolved Ca, Mg, K, Na, and S were measured after filtering the samples (syringe filter 0.45 μm)
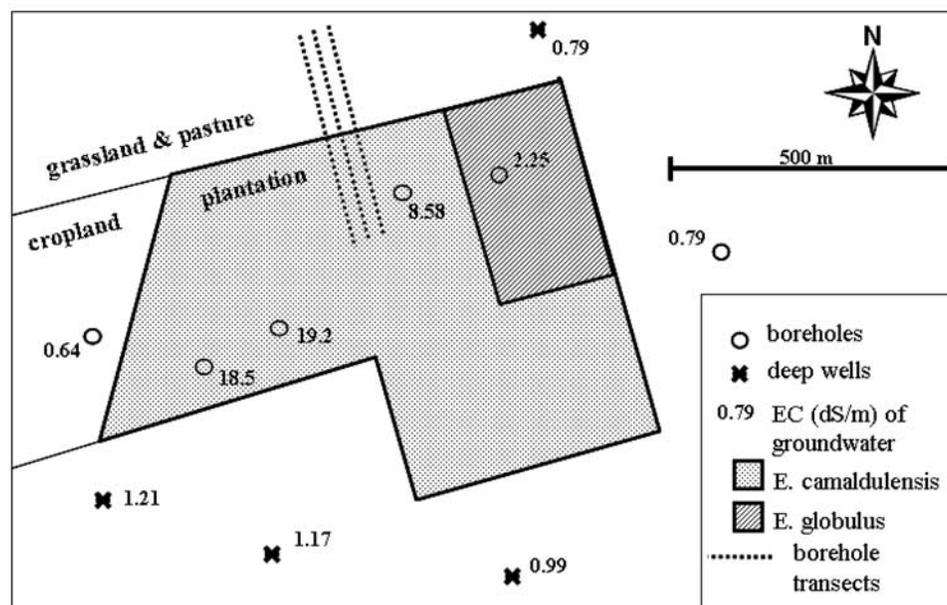

Figure 2. Diagram of the study site at Castelli. Ground water was sampled at the water table in 45 boreholes along the dotted transects and additional locations. Electrical conductivity (EC) values (dS/m) at the water table level are shown.

using inductively coupled plasma emission spectrometry (ICP [*Soltanpour et al.*, 1996]). Chloride was measured using a solid state ion selective electrode after adding sufficient 5M $NaNO_3$ solution to achieve uniform ion strength across samples [*Frankenberger et al.*, 1996]. Carbonate and bicarbonate were determined by titration. Our data analysis assumed that all S occurred as SO_4^{2-}. Charge imbalance in all samples was $< \pm 15\%$ (absolute mean = 6.4 %). We calculated the sodium adsorption ratio (SAR) and residual sodium carbonate (RSC) for groundwater in samples to characterize their potential to drive soil alkalinization and the associated dispersion of particles that leads to the deterioration of pore structure [*Sumner and Naidu*, 1998]. We estimated calcite saturation index and pCO_2 for groundwater samples using the NETPATH 2.0 routine [*Plummer et al.*, 1991]. For discharge phases we calculated evaporative concentration of solutes on the basis of Cl^- concentrations, assuming that this ion had a conservative behavior across the vadose zone and top meter of the aquifer [*Allison and Hughes*, 1983].

2.3. Hydraulic Patterns

[12] To interpret the aquifer-level effects of tree plantations on groundwater chemistry we explored their influence on groundwater fluxes at the landscape level. For this purpose we combined field measurements and a hydraulic model (FLOWNET [*van Elberg and Engelen*, 1986]) along the grassland-plantation borehole transect at Castelli (Figure 2), on the basis of groundwater levels, saturated hydraulic conductivity measurements, and stratigraphy for the region. FLOWNET simulates steady state groundwater flow in 2-D grids cell that represent a vertical plane of the terrain based on a finite-difference solution that approximates horizontal and vertical water fluxes into and out of each cell. Inputs are pressure-head values along open boundaries and saturated hydraulic conductivity and porosity of cells [*Spieksma et al.*, 1995; *Beckwith et al.*, 2003]. The model calculates groundwater age at discharge locations on the basis of flow-path length and porosity. We measured groundwater level, equivalent to pressure head in the unconfined aquifer at Castelli, in September 2002 (winter) and January 2003 (summer) across the transects described in the previous section (Figure 2). Surface elevation was measured using a water level. We used a 400-m by 30-m vertical plane comprised of two hundred cells (20 m wide, 3 m deep). Existing sediment cores from the area showed the presence of silty materials down to 8 to 10 m depth, followed by coarser sediments and then a silty clay layer at ~20 m [*Servicio Provincial de Agua Potable y Saneamiento Rural*, 1987]. On the basis of these cores we defined three layers and closed our modeled system at 30 m depth, within the silty clay layer (silt 0–9 m, silt and sand 9–21 m, and silty clay 21–30 m). The lateral boundaries were closed at the core of plantation and at the outer grassland (200 m from the edge in both cases). The only open boundary was the surface, and the pressure head of its cells was obtained by interpolating level measurements from the borehole transects. Saturated hydraulic conductivity (K) for the top layer was measured in situ by well tests (auger-hole method [*Amoozegar and Warrick*, 1986]) in September 2002 and January 2003 in four boreholes along the grassland-plantation transect (Figure 2; K = 1.0 ±

0.12 m/day). Hydraulic conductivity in the intermediate layer was obtained (piezometer method, [*Amoozegar and Warrick*, 1986]) in four supply wells tapping the 10- to 20-m depth range, located 3–4 km away from the study site [*Servicio Provincial de Agua Potable y Saneamiento Rural*, 1987] (K = 4.1 ± 1.2 m day^{-1}). We assumed a lower conductivity for the silty clay layer (K ≈ 0.1 m day^{-1}) on the basis of its fine texture and poor water yield [*Servicio Provincial de Agua Potable y Saneamiento Rural*, 1987]. On the basis of our bulk density measurements from hand-augered cores (6 m deep) and an assumed particle density of 2.65 g cm^{-3}, we used a volumetric porosity value of 0.46. The typical range for loess and aeolian sands is 0.40–0.57 [*Dingman*, 1993].

[13] Modeled groundwater trajectories derived from FLOWNET were qualitatively contrasted with age estimates for selected water samples derived from tritium measurements. Although the nuclear-derived spike of tritium in the precipitation of southern South America was 2 orders of magnitude lower than that reported for the Northern Hemisphere, anthropogenic tritium inputs shifted from background levels of 4 TU (TU = Tritium Units or 10^{-18} ^{3}H atoms per each ^{1}H atom) in the 1950s to 54.5 TU in 1966 [*Logan and Rudolph*, 1997]. Present precipitation approaches 4 TU, but values up to 15 TU are common owing to the regional influence of a nuclear power plant [*Ibarguren et al.*, 2001]. On the basis of the reconstruction of Tritium inputs in the vicinity of Buenos Aires by *Logan and Rudolph* [1997] and the decay rate of this radionuclide, we identified a threshold of <1 TU for water recharged prior to 1960, a range of 1–3.5 TU for water recharged between 1960 and 1963, and a threshold of >3.5 TU for water inputs that took place from 1963 to present. We obtained samples for tritium analysis in January and February 2002 and May 2003 from the water table in four boreholes and from greater depth in four cased wells. Tritium was determined at INGEIS (CONICET- Buenos Aires), where 0.5-L samples were enriched 15-fold by electrolysis and analyzed using liquid scintillation counting with a detection level of 0.8 to 1 TU.

2.4. Soil Chemistry and Elemental Mass Balances

[14] We explored changes in the abundance, distribution and composition of salts accumulated in the soil and vadose zone and their link with leaf chemistry of the trees. For this purpose, we sampled soils down to 6 m deep at three locations along the grassland-plantation transect in Castelli: grassland (100 m away from the plantation edge, n = 4), plantation outer belt (50 m away from the plantation edge, n = 5), and plantation core (175 m inside from the plantation edge, n = 4). We also sampled soils down to 1 m depth in both the plantations and grasslands at Guerrero and América, 50 m away from the boundary between grassland and plantation. Mineral soil was sampled in 0.5-m intervals to 6 m depth with a 10-cm-diameter auger. At each of the locations, cores were randomly located maintaining their distance to the plantation-grassland boundary within a range of ±5 m (Figure 2). Bulk density, estimated every 0.5 m of depth, ranged from 1.31 to 1.45 Mg m^{-3} and did not differ significantly among locations. Soil samples were analyzed for electrical conductivity and Cl concentration using a 1:2 soil/water ratio. Chloride was measured in the laboratory using an ion-selective electrode [*Frankenberger et al.*,

1996]. Soil pH was measured with an electrode on the supernatant of a 1:1 soil-water extract [Thomas, 1996]. Exchangeable Ca, Mg, K, and Na were measured after extraction with 1 M ammonium acetate (pH 7) and a 1:5 soil-water ratio followed by ICP analysis. Samples were shaken for 5 min and equilibrated 24 hours [Robertson et al., 1999]. The concentration of precipitated carbonates was measured on ground samples passed through a 150-μm sieve that were dissolved in 6M HCl and allowed to degas in a volumetric calcimeter [Loeppert and Suarez, 1996]. The presence of gypsum was qualitatively assessed by treating the supernatant of a 1:5 soil-water extract with an equal volume of acetone and recording the formation of precipitate [Loeppert and Suarez, 1996].

[15] In order to estimate water and solute inputs from the phreatic aquifer to the tree plantation ecosystem at Castelli, we used chloride as a conservative tracer, on the basis of the following balance equation:

$$GWuse = \frac{(\Delta Cl_{soil} + \Delta Cl_{bio} - Age*Cl_{atm})}{[Cl]_{gw}*Age}, \quad (1)$$

where GWuse (mm yr^{-1}) is the net annual groundwater uptake (total groundwater uptake – total deep drainage), ΔCl_{soil} (g m^{-2}) is the change in soil/vadose Cl (the difference in Cl stored in plantation and grassland soils and the vadose zone down to the maximum rooting depth of 6 m), ΔCl_{bio} (g m^{-2}) is the amount of Cl gained as biomass [Jobbágy and Jackson, 2003], Cl_{atm} (g m^{-2} yr^{-1}) is the mean annual atmospheric input of Cl (estimated by Jobbágy and Jackson [2003]), $[Cl]_{gw}$ (g m^{-3}) is the concentration of Cl in the groundwater arriving at the bottom of the root system (6 m depth), and Age (yr) is the age of the plantation stand (50 years at Castelli). Similar approaches have been applied by Jarrell and Virginia [1990] and Heuperman [1999]. We obtained ΔCl_{soil} by comparing the tree plantation and the grassland soils, assuming that the latter represented the initial condition of the former before tree establishment. We used values for ΔCl_{bio} (44 g m^{-2}) and Cl_{atm} (0.39 g m^{-2} yr^{-1}) obtained from our previous work at the same site [Jobbágy, 2002; Jobbágy and Jackson, 2003]. On the basis of this estimate of net groundwater uptake we were able to make an approximate quantification of the absolute flux of other dissolved species from groundwater to the ecosystem based on

$$\Delta E_{ecosystem} = GWuse* [E]_{gw}*Age, \quad (2)$$

where $\Delta E_{ecosystem}$ is the storage change in the whole ecosystem (biomass + soil, g m^{-2}) of a given element E and $[E]_{gw}$ is its concentration in groundwater arriving at the bottom of the root system (6 m depth). We compared these expected inputs with observed values of $\Delta E_{ecosystem}$ on the basis of our measurements of E pools in the soil (0–6 m depth) and the tree plantation biomass (tree biomass + forest floor). Soil storage changes were calculated as the difference between grassland and tree plantation pools, assuming that the first represented the preafforestation condition of the latter. In the case of calcium and carbonates the exchangeable + soluble soil pool was separated from the

precipitated pool. The chloride mass balance of equation (1) also allowed us to quantify the relative contribution of aquifer-level and stand-level effects of groundwater discharge on salt accumulation, with aquifer-level effects manifesting through solute load increases in groundwater reaching the bottom of the rooting zone of the plantation (changes in $[Cl]_{gw}$ between plantation and grassland), and stand-level effects manifest as solute gains in relation to the initial groundwater load either in deep soil, in the case of exclusion of solutes (ΔCl_{soil} in deep soil), or absorption and recycling (ΔCl_{soil} in surface soil and ΔCl_{bio}).

[16] To evaluate the potential feedbacks of soil changes on trees, we sampled E. camaldulensis leaves on a gradient from plants growing (1) isolated within the grassland (spontaneous trees located > 50 m away from the plantation and derived from its seed rain), (2) on the plantation edge, (3) on the plantation outer belt (50 m inside from the plantation edge), and (4) on the plantation core (175 m inside from the edge). Fully expanded sun leaves from five individuals at each position were collected, oven-dried at 70°C, ground (0.5-mm sieve), and HNO$_3$/H$_2$O$_2$-digested for base cation analysis using ICP.

3. Results

3.1. Hydrochemical Patterns

[17] Compared to their surrounding grasslands, tree plantations at Castelli, Guerrero, and América had shallow ground waters that were 15 to 30 times saltier (Figure 2 and Table 1). Shallow groundwater from grassland boreholes had low salinity (<1 dS m^{-1}), slightly acidic pH (6.5–6.9), high bicarbonate dominance among anions, and a relatively balanced composition of base cations (SAR ranging from 1 to 2.3), typical of recharge water in the region. Shallow groundwater chemistry sampled $\sim$50 m inside each plantation showed consistent shifts at all three study sites, including high salinity (>11 dS m^{-1}), slightly alkaline pH (7.3–7.43), and Cl-Na dominance, with relatively high bicarbonate contents (1250–1500 mg L^{-1}) (Table 2 and Figure 3). These ground waters were saltier but less alkaline than those observed in a small naturally discharging depression sampled at Castelli (Table 2 and Figure 3).

[18] The grassland-plantation transect at Castelli revealed hydrochemical shifts toward the interior of the afforested zone. Hydrochemical patterns were relatively constant along the grassland portion of this transect up to 30 m before entering the plantation. Beyond this point, salinity increased sharply, reaching its maximum at the plantation core, as did chloride, sulfate, calcium, and magnesium concentrations (Table 2). However, groundwater sodium, carbonate, and bicarbonate concentrations, and pH peaked in the plantation edge and outer belt, declining toward the core. As a result of these concentration changes, both the sodium absorption ratios (SAR), which indicate the dispersive effect of groundwater on soils, and residual sodium carbonate (RSC), which characterizes its alkalinization potential, increased from the grassland to the plantation edge but declined sharply toward the plantation core. In the case of RSC, it was reverted to negative values below those found in the grassland (Table 2).

Table 2. Groundwater Chemistry in Grasslands and Tree Plantations at Three Study Sites[a]

	Position, m	n	EC, dS/m	pH	Ca^{2+}, mg/L	Mg^{2+}, mg/L	Na^+, mg/L	K^+, mg/L	Cl^-, mg/L	SO_4^{2+}, mg/L	CO_3^{2+}, mg/L	HCO_3^+, mg/L	SAR	RSC, mol/L	Calcite, SI
							Castelli								
Boreholes															
Grassland	150 to 30	9	0.43	6.50	34	15	19	12	5.4	5.8	0.0	197	1.0	1.8	−1.52
Transition belt	30 to −10	15	9.62	7.34	105	149	2335	63	1991	390	98	1596	48.3	19.0	0.52
Plantation outer belt	−10 to −70	7	11.11	7.34	113	201	2352	76	2511	626	61	1471	43.2	14.1	0.48
Plantation core	−70 to−150	7	12.80	7.17	249	258	1934	84	4908	702	0.0	398	28.9	−12.9	0.01
Grassland (depression)	145	1	3.03	7.70	34	32	179	28	84	45	81	1843	7.5	29.8	−1.16
Cased wells															
Grassland, −6 m	100	1	0.87	7.73	58	28	46	38	15	11	12	537	1.7	6.4	0.53
Grassland, −16 m	100	1	1.24	7.77	40	26	161	34	70	36	14	725	6.8	10.0	0.50
Plantation outer belt, −6 m	−50	1	2.02	7.96	31	36	250	42	264	104	76	752	10.2	11.3	0.57
Plantation core, −6 m	−150	1	4.21	7.26	186	112	478	23	1165	216	0.0	387	9.5	−2.9	−0.45
							Guerrero								
Boreholes															
Grassland	100	1	1.01	6.77	80	56	78	58	8.7	28	0.0	660	2.3	6.5	−0.56
Plantation	−50	1	14.29	7.30	131	281	2135	180	4341	340	16	1248	34.1	5.9	0.59
							América								
Boreholes															
Grassland	100	1	0.63	6.91	40	45	49	28	7.6	11	0.0	510	1.8	5.5	−0.36
Plantation	−50	1	18.80	7.42	168	245	3074	164	5120	1225	11	1341	50.0	7.9	0.39

[a]All groundwater sampling points were located in uplands with the exception of a local discharge zone located in a small depression at the Castelli grassland. The first group of samples at Castelli and those at Guerrero and América were taken from boreholes at the water table, located 0.5 to 4.3 m below the ground level. The second group was taken from cased wells at the depths indicated between brackets. The position of the sampling points in relation to the plantation edge (zero value) is indicated with positive values for the grasslands and negative values for the plantation. The number of wells sampled for each class (n), water electric conductivity obtained in the field (EC), pH obtained in the lab, and concentration of major ions measured in filtrated samples are indicated. The sodium absorption ratio (SAR = $[Na^+]/([Ca^{2+}]+[Mg^{2+}]1/2)$) and residual sodium carbonate (RSC = $([HCO_3^-]+[CO_3^{2-}])-([Ca^{2+}]+[Mg^2_+]))$ are based on molar concentrations (mol/L). The logarithmic index of saturation for calcite mineral (Calcite SI) was calculated using the NETPATH 2.0 model.

3.2. Hydraulic Patterns

[19] Despite the slightly higher ground elevation of the plantation at Castelli, its groundwater level was lower than in the surrounding grassland in both winter and summer (Figure 4). Given its topographic position, the afforested area was most likely to behave as a recharge zone before tree establishment, but now had a depressed water table throughout the year, indicating a sustained discharge regime under trees. Relatively high and homogeneous water table levels were observed within the grassland section of the study transect in winter. In summer a ~15-cm water level depression developed toward the small lowland area suggesting a localized and temporary discharge at that position (Figure 4). Water levels declined within the plantation, showing the greatest slope at the plantation edge and the lowest absolute values at the plantation core, 31 and 75 cm below the highest levels in the grassland in winter and summer, respectively (Figure 4). The FLOWNET model simulated groundwater recharge, transport, and discharge rates within the grassland-plantation transect that were capable of explaining observed water level gradients under hydraulic equilibrium. These simulations suggested trajectories of increasing length and depth and older groundwater ages toward the plantation core (Figure 4). The summer simulation showed that trees located in the outer 50 m of the plantation received groundwater that traveled <70 m, reaching depths <10 m; in the plantation core this trajectory had a length of ~370 m and reached the bottom of the conductive sediment layer at 21 m of depth. These flow patterns

suggested that if solute upwelling (i.e., aquifer-level influences on solute accumulation) occurs, it is most likely taking place at the center of the plantation.

[20] While flow trajectories were very similar in winter and summer, flow rates changed with the water level gradient and were higher in summer than in winter. Assuming steady state conditions, the model suggested that the observed hydraulic gradients would have been attained with discharge rates under the tree plantation averaging 0.81 and 1.95 mm/day in winter and summer, respectively. These values are highly sensitive to the saturated conductivity values used in the model and they should be taken only as an indication of the order of magnitude and seasonal trend of discharge rates. Independent discharge estimates based on diurnal water level fluctuations and sap flow measurements obtained 100 m inside the plantation along the same transect by *Engel et al.* [2005] were in good agreement with the model estimate for wintertime (0.79 mm/day for the week before 12 September 2002) but greater for summertime (3.39 mm/day for the week prior to 8 January 2003). We assumed that the groundwater traveling time from recharge to discharge positions was equivalent to the average of those calculated by the model for winter and summer data, obtaining ages of <10, 35 and 65 years for groundwater discharging at the plantation edge, 50 m inside, and in the core, respectively.

[21] The estimates of groundwater age based on tritium data also suggested different groundwater origins at the plantation edge, outer belt, and core, supporting the model estimates (Table 3). Shallow groundwater had >3.5 TU at
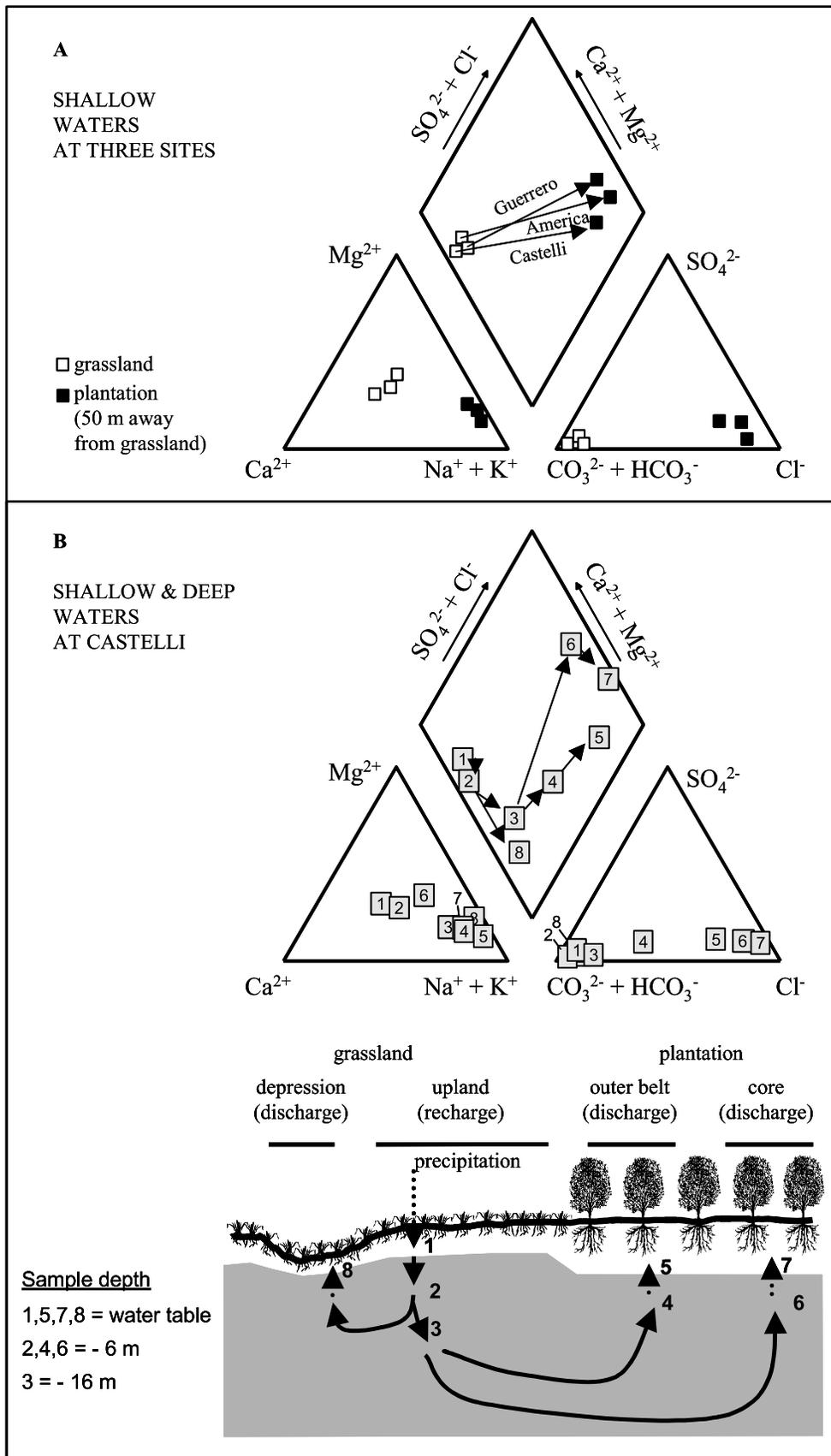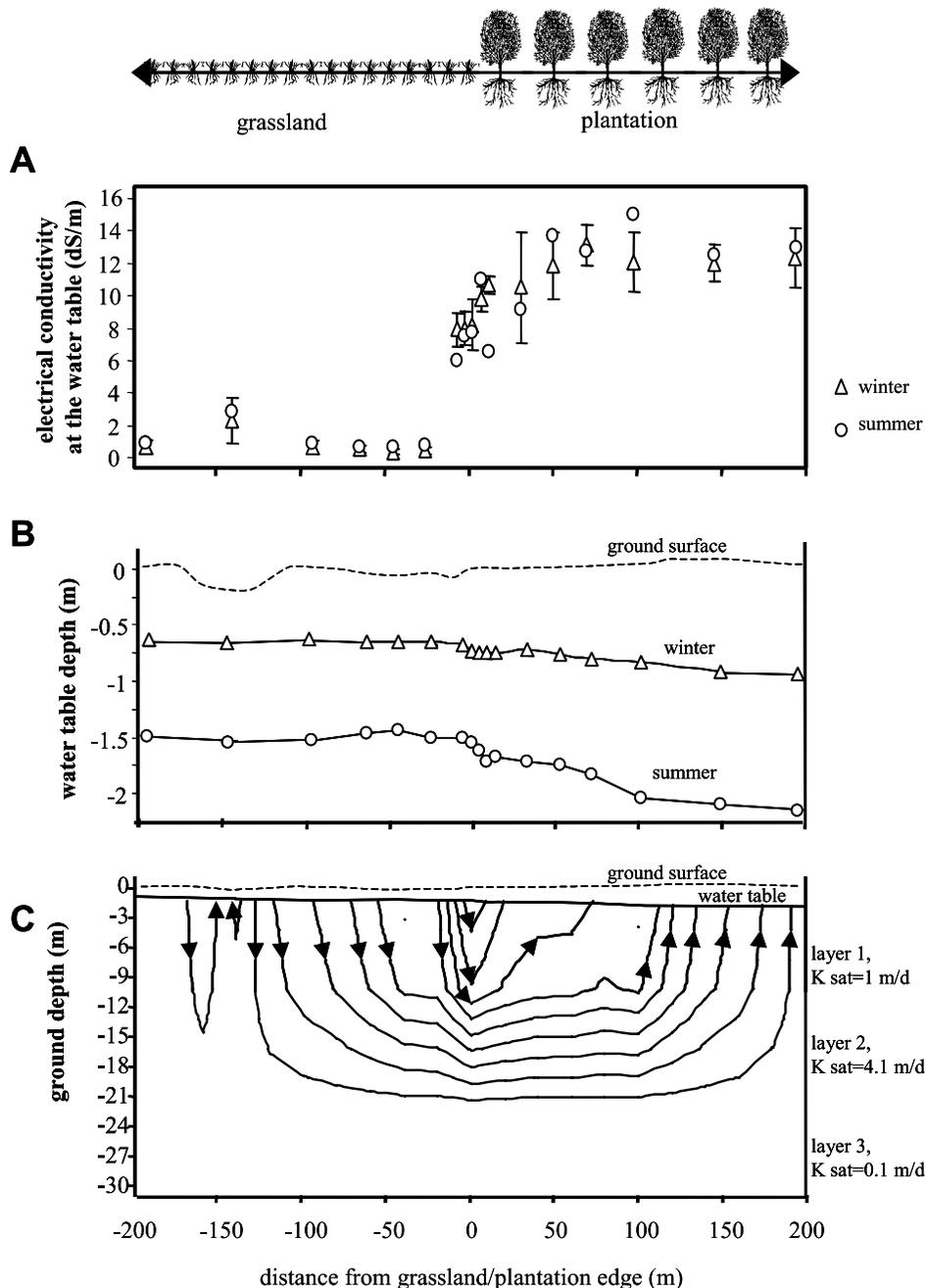
Figure 3

Figure 4. Groundwater salinity and flow across the grassland-plantation transect. (a) Groundwater salinity measured in winter (September 2002) and summer (January 2003). (b) Groundwater level for the same dates. (c) Two-dimensional representation of groundwater flow based on water levels of 8 January 2003, applied to the FLOWNET model [*van Elberg and Engelen,* 1986]. Streamlines (solid lines with arrows) are shown. Saturated hydraulic conductivity values (K, m/day) and sediment layers are represented. According to the model the plantation is experiencing a mean water discharge of 1.3 mm/day.

Figure 3. Piper diagrams showing changes in the ionic composition of ground water between grasslands and plantations. (a) Paired borehole samples taken at the water table at the three study sites. (b) Mean composition of shallow groundwater classes together with deep groundwater samples from cased wells. The direction of hydrochemical changes is suggested with arrows. Dotted arrows indicate recharge/discharge processes involving evaporative water losses. Numbers correspond to the representation of hydrological zones and groundwater fluxes along the grassland-plantation transect shown at the bottom.

Table 3. Tritium Concentrations in Ground Water for Selected Boreholes and Wells[a]

	Location	Tritium (TU)		
		08 Jan 2002	02 Feb 2002	30 May 2003
Boreholes				
Grassland	−100 m	11.9	6.4	6
Plantation edge	0 m	9.7	15.5	nd
Plantation outer belt	50 m	10.2	16.4	2.8
Plantation core	150 m	<1.0	<1.0	<1.0
Cased wells				
Grassland, −6 m	−100 m	nd	nd	6.7
Grassland, −16 m	−100 m	nd	nd	3.7
Plantation outer belt, −6 m	50m	nd	nd	1.5
Plantation core, −6 m	150 m	nd	nd	<1.0

[a]Details: nd, no data; detection limit = 1 TU; 1 TU = $^{3}H/H * 10^{18}$. Ground water was sampled at the water table in boreholes and at the indicated depths (m below ground level) in cased wells. Values correspond to individual samples taken at three different dates. Current precipitation in the area ranges between 4 and 15 TU (H. Panarello, personal communication, 2001). According to ^{3}H inputs from precipitation in Buenos Aires, reconstructed by *Logan and Rudolph* [1997] and accounting for radiogenic decay, only water recharged before 1960 would have <1 TU.

most locations and at all sampling dates, indicating that it could have entered the hydrological system at anytime from 1963 to present; in contrast, the plantation core did not show a "bomb signal" either at the surface or at 6 m of depth, suggesting that those waters were recharged prior to 1960. The outer belt of the plantation showed an intermediate pattern with waters being within the 1−3.5 TU range during May 2002, indicating that they entered the system between 1960 and 1963, or, more likely, that they resulted from the mixing of pre-1960 and modern waters. In all of these cases, positions inside the plantation showed older water than those at the plantation edge.

3.3. Soil Chemistry and Elemental Mass Balances

[22] Groundwater discharge at tree plantations was accompanied by a widespread and homogeneous soil salinity increase, whereas a more heterogeneous sodification (i.e., higher Na representation among exchangeable base cations) and alkalinization processes displayed their maximum intensity toward the tree plantation edges (Table 4). Salinity gains were greatest (>10-fold) at 0.5−1 m depth range. In the outer belt of tree plantations they were accompanied by

a significant increase in exchangeable soil Na (ESP, exchangeable sodium percentage), with soils that were initially nonsodic achieving ESP values >15% (a common threshold used to define sodic soils [*Sumner and Naidu*, 1998]) (Table 4). Soil pH shifts were more complex and combined a strong acidification in the top half meter (see *Jobbágy and Jackson* [2003] for additional background) with the alkalinization of the second half meter in the outer belt of tree plantations. The plantation core at Castelli contrasted with the rest of the plantation profiles, showing slighter sodium gains (ESP = ∼5%) accompanied with a pH decline rather than increases (Table 4).

[23] Deep soil/vadose data at Castelli showed the greatest changes in soil chemistry associated with tree establishment, occurring down to 3 and 4 m of depth in the plantation outer belt and core, respectively (Figure 5). Compared with the plantation outer belt, the plantation core showed a stronger salinization that involved higher Cl gains but a lower Na saturation of the exchange complex (Figure 5). Whereas the plantation outer belt experienced an alkalinization of maximum magnitude at 1 m of depth, the plantation core experienced no alkalinization, having neutral to slightly acidic pH values throughout the profile (Figure 5).

[24] Contrasts in precipitated and exchangeable calcium profiles suggests that in the outer belt of the plantation at Castelli a high proportion of calcium was lost from the exchangeable pool through precipitation, whereas in the plantation core this process was less intense. Exchangeable Ca losses peaked at the surface, reaching 43% and 33% in the top 0.5 m of the soil in the plantation outer belt and core, respectively; they then declined, peaking again at 2.5−3 m depth, where they reached 45 and 25% at both positions, respectively. These contrasts were in agreement with the residual sodium carbonate differences observed for the corresponding groundwater samples obtained at 6 m of depth (Table 2 and Figure 3), suggesting that aquifer-level effects created heterogeneous patterns of solute accumulation and soil change within this plantation. Soil in the plantation core revealed the presence of gypsum between 1.5 and 4.5 m of depth.

[25] Soil chemical changes left their imprint in the chemistry of eucalypts, as shown by the base cation composition of tree leaves across the grassland-plantation transect at Castelli (Figure 6). Isolated trees growing within the grassland had the lowest concentrations for all base cations (p < 0.01). Calcium and K concentrations in the leaves of

Table 4. Salinity, Sodium Saturation, and pH of Soils in Grassland and Plantation Stands at Three Study Sites[a]

		Castelli			Guerrero		América	
		Grassland	Plantation Outer Belt	Plantation Core	Grassland	Plantation Outer Belt	Grassland	Plantation Outer Belt
EC, dS/m	0−0.5 m	0.11 a	0.67 b	0.58 b	0.11 a	0.62 b	0.08 a	0.30 b
	0.5−1 m	0.17 a	1.92 b	1.78 b	0.12 a	1.83 b	0.17 a	1.80 b
ESP, %	0−0.5 m	0.3 a	10.6 c	3.7 b	0.8 a	10.3 b	0.0 a	6.0 b
	0.5−1 m	0.3 a	19.3 c	4.9 b	1.2 a	23.8 b	0.7 a	15.5 b
pH (1:1 water)	0−0.5 m	5.83 a	4.47 b	4.53 b	6.01 a	4.36 b	5.82 a	4.54 b
	0.5−1 m	6.37 a	7.06 b	6.01a	6.83 a	7.32 b	6.62 a	8.19 b

[a]All grassland and plantations measurements were taken 100 and 50 m away, respectively, from the plantation-grassland edge with the exception of the core of the plantation at Castelli which was located 175 m way from the plantation edge. Data for the 0−0.5 and 0.5−1 m depths are presented and letters depict significant differences (p<0.05) across stands within sites.
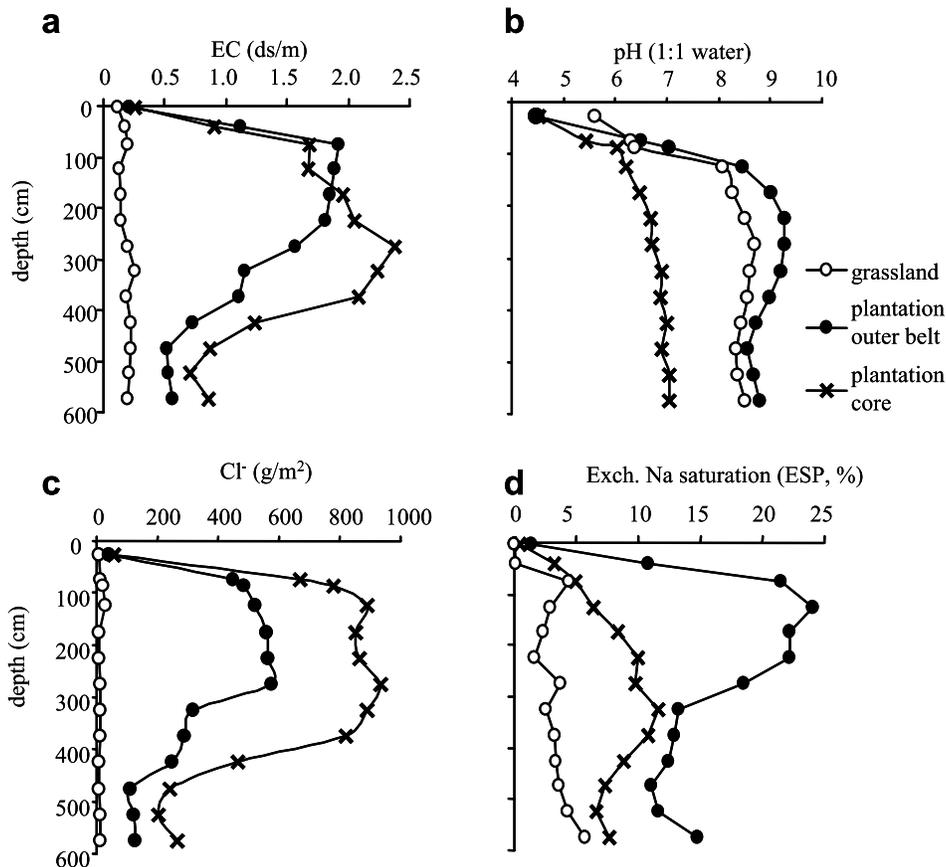
Figure 5. Soil salinity, pH, sodicity, and chloride content at three positions along the grassland-plantation transect at Castelli. (a) Salinity is characterized with electric conductivity in 5:1 soil-water. (b, c) A 1:1 soil-water ratio was used for pH and chloride measurements. (d) Sodicity is represented by the exchangeable sodium percentage (ESP) which indicates the proportion of the exchange complex that is saturated with that element. The grassland position is 100 m away from the plantation. The outer belt and core positions are located 50 and 175 m, respectively, toward the plantation interior.

eucalypts increased from the edge to the outer belt of the plantation and remained similar toward the core. Magnesium concentrations showed little variation across the plantation, whereas Na displayed the largest variability, peaking in the outer belt. The relative contribution of Na to the base cation pool in leaves was maximum in this position, doubling or tripling the values from the rest of the transect (Figure 6), and matching observed peaks of maximum groundwater and soil sodium concentrations along the same transect. In spite of this chemical imprint on leaf chemistry,
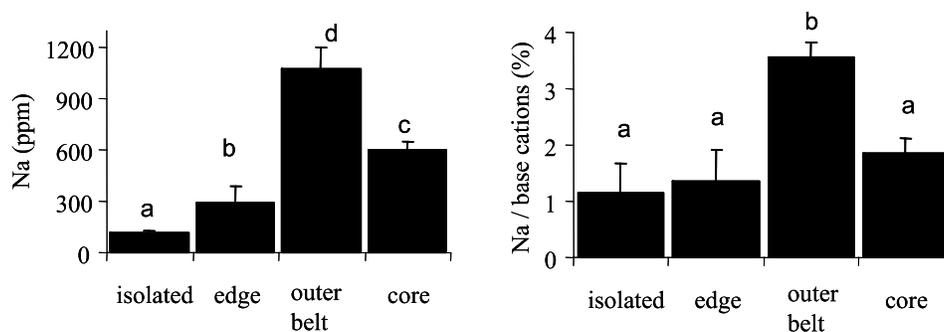
Figure 6. Sodium content in leaves of *Eucalyptus camaldulensis* trees growing along the grassland-plantation transect at Castelli. Both sodium concentrations as well as sodium proportion in the total base cation pool are shown. Isolated trees grow in the grassland >50 m away from the plantation. Trees in the edge correspond to the first row of trees in the northern boundary of the plantation. Trees in outer belt and core positions are located 50 and 175 m, respectively, toward the plantation interior. Mean values for fully expanded sun leaves from five individuals at each position are shown.

Table 5. Mass Balance for Sodium, Calcium, and Inorganic Carbon in the Tree Plantation Stand of Castelli at Two Locations[a]

		Outer Belt			Core		
		Na	Ca	IC	Na	Ca	IC
1: groundwater inputs	GW use * [E] gw * age, kg/m^2	3.59	0.44	2.34	2.87	1.12	0.46
2: ecosystem storage changes	soil exch + sol (0–6 m), kg/m^2	4.14	−6.38	0.13	3.34	−1.63	0.02
	soil precip. (0–6 m), kg/m^2	0.00	6.78	2.78	0.00	1.34	0.40
	forest biomass + floor, kg/m^2	0.02	0.46	0.00	0.01	0.56	0.00
	TOTAL, kg/m^2	4.16	0.86	2.91	3.35	0.22	0.42
3: difference	Groundwater inputs vs. Ecosystem storage changes, kg/m^2	−0.57	−0.42	−0.57	−0.48	0.85	0.04
	Idem, %	−15.9	−95.5	−24.4	−16.7	75.9	8.3

[a]Two locations are outer belt and core located 50 and 175 m away from the grassland edge, respectively. IC denotes inorganic carbon. Groundwater inputs were calculated using equation (2) and assume constant groundwater discharge and composition at each location throughout the plantation lifespan. Ecosystem storage changes are based on the addition of plantation versus grassland storage differences quantified for the soil pool (exchangeable + soluble and precipitated) for 0–6 m depth and ecosystem biomass including both plant tissues and litter + organic horizon (forest floor). In the case of inorganic carbon the soil pool encompasses soluble + precipitated pools. Differences between absolute inputs and observed storage changes are shown both in absolute terms and in relation to the inputs. Note that the large uncertainty in soil internal redistribution of Ca may explain the large relative differences observed for this element.

the growth of trees did not seem to be affected, since biomass accumulation rates did not differ across the gradient (data not shown).

[26] The Cl mass balance based on equation (1) suggested that, throughout the plantation lifespan, net groundwater discharge averaged 287 ± 61 and 120 ± 22 mm/yr at the outer belt and core, respectively, with error estimates stemming from the variability of soil Cl gains (3.8 ± 0.8 Kg/m^2 in the plantation outer belt and 7.0 ± 1.3 Kg/m^2 in the plantation core) (Figure 5). Estimates of long-term groundwater use based on chloride balances can have several sources of error that were not addressed directly in our study but are probably small in our system. First, our estimates of chlorine in biomass have uncertainties associated with the allometric equations used to scale up tissue concentration measurements; overall, however, the whole biomass component is small compared to the overwhelming role of groundwater inputs. This would not be the case in systems were external Cl inputs are derived only from atmospheric sources and biocycling of Cl can play a very significant role [Öberg and Sandén, 2005]. The lack of fires and foraging in the tree stands suggest that additional Cl losses through those pathways can also be discarded. Additional Cl inputs into the system may have occurred through the wastes of birds that perch preferentially in tree plantations. We anticipate that this flux is at least an order of magnitude lower than groundwater inputs even if we were to assume that we had one thousand 100-g birds per hectare importing Cl from outside the plantation. Another important limitation that needs to be highlighted for the Cl-balance is that it integrates groundwater use rates throughout the plantation lifespan, yielding a mean value that may not reflect instantaneous rates of groundwater use currently or in the past. Groundwater use may have been lower than average in the first years following tree establishment and could also have declined with time as groundwater became saltier [Jobbágy and Jackson, 2004].

[27] On the basis of the discharge estimates derived from Cl accumulation, we contrasted the estimates of sodium, calcium and inorganic carbon inputs based on equation (2) with observed accumulation in the ecosystem (Table 5). Sodium inputs were in relatively good agreement with observed gains in the exchangeable + soluble pool, the main reservoir for this element in the ecosystem (Table 5). Calcium inputs from groundwater were relatively small compared to the large internal redistribution associated with carbonate precipitation, particularly at the plantation outer belt (Table 5). Notably, however, Ca inputs from groundwater were similar or larger than Ca gains in forest biomass and floor, suggesting that this pathway can play a significant role for the ecosystem nutrient balance (Table 5). Our estimate of dissolved inorganic carbon inputs from groundwater indicated that ~2 and ~0.5 kg/m^2 of C entered the outer belt and core of the tree stand throughout the plantation lifespan, suggesting a close agreement with our independent estimate of inorganic C captured through calcite precipitation in the soil profiles (Table 5). For comparison, organic C capture by the tree plantation in the same period was 75 kg/m^2 [Jobbágy and Jackson, 2003].

4. Discussion

[28] The tree plantations examined here used groundwater intensely, triggering a large transfer of solute from the phreatic aquifer to the ecosystem. As a result of this exchange, plantations increased groundwater salinity to levels that were ~5 times higher than those commonly found in naturally discharging lakes of the same region and ~20 times higher than those observed in the upland grasslands that they replaced [Miretzky et al., 2000]. Soils became saltier, and in most cases more alkaline and sodic, particularly between 0.5 m of depth and the water table; they approached the conditions typically observed in lowland soils of the Pampas subject to natural groundwater discharge regimes [Istituto Nacional de Tecnología Agropecuaria, 1989]. This intense accumulation of solutes was associated with high groundwater discharge rates displayed by these eucalypt plantations in the order of ~250–500 mm/yr ($^1/_4$ to $^1/_2$ of mean annual precipitation), as suggested by our groundwater flow simulation (~500 mm/yr averaging winter and summer estimates) and our chloride mass balance (~290 mm/yr for the plantation lifespan) at the outer belt of the plantation in Castelli. These estimates are also in relative agreement with previous groundwater consumption estimates based on sapflow measurements and records of water table level fluctuations (~395 mm/yr [Engel et al., 2005]). It is important to highlight the high sensitivity of simulated discharge to the values of saturated conductivity used for the upper and intermediate sediment layers. In our case those values were obtained from various

field measurements and matched expected values for the sediment type and texture [*Dingman*, 1993], yet good estimates of saturated conductivity that capture possible variations with time due to chemical (e.g., carbonate precipitation or sodification) and biophysical effects (e.g., tree root channeling) of vegetation shifts remain as an important challenge for models coupling groundwater and plants [*Butler et al.*, 2007].

[29] Detailed groundwater sampling and flow-path modeling at Castelli suggested that both groundwater and vadose zone effects converged as drivers of salinization (Figure 1), although their relative importance varied across the plantation. Compared to groundwater in the recharge zone, the water reaching the base of the rooting zone (6 m deep) in the tree plantation outer belt and core was 2.3 and 4.8 times saltier, respectively (groundwater effect, Table 2). In its way from that position to the water table (~2 m deep), salinity increased 5.5 and 3 times in the tree plantation outer belt and core, respectively (vadose zone effect, Table 2). The vertical distribution of solutes under tree plantations pointed to solute exclusion as opposed to cycling (Figure 1) as the dominant vadose zone mechanisms driving salinization (Table 4 and Figure 5). Uptake may have been relatively important only in the case of calcium, given its large sequestration in the biomass and organic floor of these plantations (Table 5 [*Jobbágy and Jackson*, 2003]).

[30] Previous studies of tree plantations triggering soil/water salinization highlighted either groundwater intrusion or salt exclusion in the vadose zone as the driving mechanisms [*Heuperman*, 1999; *Sapanov*, 2000]; our results show that both coexist and can have varying intensities within a single tree plantation, suggesting that vadose zone effects dominate at the plantation edge and groundwater effects prevail toward the core, probably as a result of deeper flow paths reaching the core (Figure 4).

[31] The combination of groundwater and vadose zone effects in discharging plantations influenced the hydrochemical trajectories observed at Castelli (Figure 3) and played a significant role in determining soil chemical changes. While the concentrated solutions at the water table in the outer belt of the plantation maintained high carbonate/bicarbonate concentrations in molar excess over calcium and magnesium (positive RSC values, Table 2), typical of Pampas grasslands, the plantation core received waters of older age (Table 3) and had calcium/magnesium concentrations in excess over carbonate/bicarbonate (negative RSC values, Table 2). These hydrochemical contrasts were responsible for divergent soil chemical shifts in the plantation outer belt and core (Figure 7 [see *Van Breemen and Buurman*, 1998]).

[32] Particularly important for our system is the shift that follows calcite precipitation in concentrating solutions, yielding waters that either have or lack dissolved carbonates (Figure 7). In a simplified scheme in which potassium and magnesium are absent, if carbonates are in stoichiometric excess over calcium, they will accompany sodium in the concentrating solution, coupling Ca displacement from the soil exchange complex by Na with its further scavenging from the soil solution through calcite precipitation. This trajectory would lead to increased soil pH and intense Na saturation, as observed in the plantation outer belt; it also could be responsible for the formation of saline-sodic soils like those typically found in naturally discharging areas of the Pampas, such as Natraquolls, Natrudolls and Natraqualfs [*Istituto Nacional de Tecnología Agropecuaria*, 1989; *Van Breemen and Buurman*, 1998]. In contrast, solutions in which calcium is in stoichiometric excess over carbonates will consume the carbonates and maintain calcium ions in the solution upon concentration. This opens the possibility for gypsum formation and prevents the complete replacement of Ca by Na in the exchange complex [*Bui et al.*, 1998; *Van Breemen and Buurman*, 1998]. In this case the formation of saline nonsodic soils with precipitated gypsum, like those found in the plantation core, is likely.

[33] We speculate that the presence of a high Ca:carbonate ratio of waters at the plantation core, in a region in which this type of waters are rare, resulted from the unusually deep flow path of water reaching the plantation core in response to the steep hydraulic gradient maintained by trees (Figure 4). A long and deep flow path may have scavenged excess carbonate through continuous calcium/magnesium inputs but limited respiratory CO_2 inputs in deep sediments, causing the observed RSC shift between deep grassland and plantation core samples (Table 2). Alternatively, deep confined groundwater with a distinct composition may have emerged following a period of intense discharge and relatively little lateral replenishment at the plantation core. Either of these possible hydrochemical and/or hydraulic situations would not take place under the gentle hydraulic gradients and shallow groundwater depths observed in the grasslands [*Fuschini Mejia*, 1994]. Some discharging lakes in the Pampas do display buried layered deposits of gypsum in their sedimentary bottom, however, suggesting that the hydrochemical conditions observed at the plantation core may have taken place at natural discharge locations during dry periods throughout the Holocene [*Dangavs and Blasi*, 2002].

[34] Although groundwater consumption can greatly enhance the productivity of trees [*Vertessy et al.*, 2000; *Jobbágy and Jackson*, 2004], accompanying soil chemical changes may sometimes be detrimental in the long term. In our study, afforestation transformed initially fertile nonsaline mollisols (Hapludoll [*U.S. Department of Agriculture*, 1998]) into saline, sometimes sodic, soils [*Food and Agriculture Organization*, 1991] in less than half a century. High sodium saturation can have detrimental effects on the physical quality of soils through the reduction of water holding and infiltration capacity, among other attributes, that result from the dispersive effect of sodium on soil clay particles [*Sumner and Naidu*, 1998]. This can be expected in the outer belt of the plantations at the three study sites, given their high ESP values, but not in the plantation core at Castelli. In general, phreatophytic activity would lead to sodicity problems in these plantations as long as discharged water maintains the typical high residual sodium carbonate values that phreatic waters display throughout the region. However, if the composition of groundwater shifts, adopting negative residual sodium carbonate values, as we noticed at the plantation core in Castelli, salinization will not be accompanied by the deleterious process of sodification. Interestingly, the composition of eucalypt leaves manifested these trends in the relative importance of the sodicity problem within the Castelli plantation, with leaves displaying the highest Na:Ca ratios at the plantation outer belt (Figure 6).
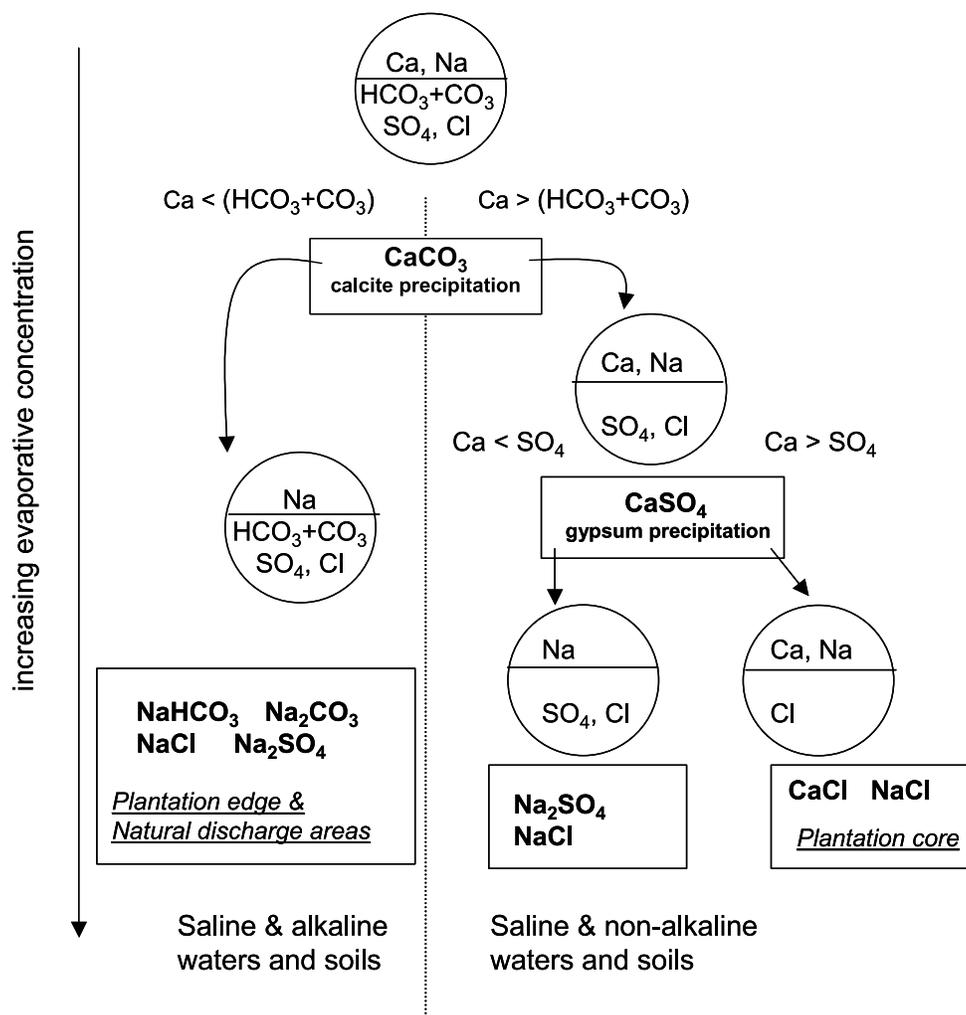
Figure 7. Precipitation pathways for evaporating solutions containing Na^+, Ca^{2+}, SO_4^{2-}, Cl^-, HCO_3^-, and CO_3^{2-}. Precipitation products are indicated in boxes and dissolved ions in circles. In this simplified analyses of possible precipitation trajectories Mg^{2+} and K^+ were not included but would behave closely to calcium and sodium, respectively. The molar ratios of Ca^{2+} to carbonates and Ca^{2+} to SO_4^{2-} play a key role determining precipitation products [after *Van Breemen and Buurman*, 1998].

[35] Our analysis shows that land use changes involving the onset of groundwater discharge can trigger rapid and complex changes in soil chemistry. In the case of plantations in the Pampas, the main impact has been an intense salinization and sodification of soils, particularly below 0.5 m depth. The changes documented here could not be predicted solely on the basis of stand-level processes and required a broader scale understanding of groundwater flow and hydrochemistry patterns. As shown here, ground water can link biogeochemical cycling in landscape positions that would otherwise be disconnected. Groundwater also likely played an important role supplying a highly demanded element like calcium to trees, although our budget for this element had large uncertainties [see *Jobbágy and Jackson*, 2003]. The role of groundwater supplying other limiting elements to the ecosystem including micronutrients awaits exploration.

References

Allison, G. B., and M. W. Hughes (1983), The use of natural tracers as indicators of soil-water movement in a temperate semi-arid region, *J. Hydrol.*, 60, 157–173.

Amoozegar, A., and A.W. Warrick (1986), Hydraulic conductivity of saturated soils: Field methods, in *Methods of Soil Analysis–Part 1: Physical and Mineralogical Methods*, edited by A. Klute, pp. 735–770, Soil Sci. Soc. Am., Madison, Wis.

Bazilevich, N. I. (1970), *The Geochemistry of Soda Soils*, 329 pp., Isr. Program for Sci. Transl., Jerusalem.

Beckwith, C. W., J. A. Baird, and A. L. Heathwite (2003), Anisotropy and depth-related heterogeneity of hydraulic conductivity in a bog peat. II: Modelling the effects on groundwater flow, *Hydrol. Processes*, 17, 103–113.

Bui, E. N., L. Krogh, R. S. Lavado, F. O. Nachtergaele, T. Tóht, and R. W. Fiztpatrick (1998), Distribution of sodic soils: The world scene, in *Sodic Soils: Distribution, Properties, Management and Environmental Consequences*, edited by M. E Sumner and R. Naidu, pp. 19–33, Oxford Univ. Press, New York.

Butler, J. J., G. J. Kluitenberg, D. O. Whittemore, S. P. Loheide, W. Jin, M. A. Billinger, and X. Y. Zhan (2007), A field investigation of phreatophyte-induced fluctuations in the water table, *Water Resour. Res.*, *43*, W02404, doi:10.1029/2005WR004627.

Calder, I. R. (1998), Water use by forests, limits and controls, *Tree Physiol.*, *18*, 625–631.

Dangavs, N. V., and A. M. Blasi (2002), Intrasedimentary gypsum deposits of El Siasgo Creek, Monte and General Paz districts, Buenos Aires Province, *Revista Asoc. Geol. Argentina*, *57*, 315–327.

Dingman, S. L. (1993), *Physical Hydrology*, 575 pp., Prentice-Hall, Upper Saddle River, N. J.

Engel, V., E. G. Jobbágy, M. Stieglitz, M. Williams, and R. B. Jackson (2005), Hydrological consequences of Eucalyptus afforestation in the Argentine Pampas, *Water Resour. Res.*, *41*, W10409, doi:10.1029/2004WR003761.

Farley, K. A., E. G. Jobbágy, and R. B. Jackson (2005), Effects of afforestation on water yield: A global synthesis with implications for policy, *Global Change Biol.*, *11*, 1565–1576.

Food and Agriculture Organization (1991), Global and National Soils and Terrain Digital Databases (SOTER), *World Soil Resour. Rep. 66*, Food and Agric. Org., Rome, Italy.

Frankenberger, W. T., M. A. Tabaitabai, D. C. Adriano, and H. E. Doner (1996), Bromine, chlorine and fluorine, in *Methods of Soil Analysis–Part 3: Chemical Methods*, edited by S. L. Sparks et al., pp. 833–868, Soil Sci. Soc. of Am., Madison, Wis.

Freeze, R. A., and J. A. Cherry (1979), *Groundwater*, 605 pp., Prentice-Hall, Upper Saddle River, N. J.

Fuschini Mejia, M. (1994), *El Agua en las Llanuras*, 58 pp., Programa Hidrol. Int., Montevideo.

Geary, T. F. (2001), Afforestation in Uruguay–Study of a changing landscape, *J. For.*, *99*, 35–39.

Heuperman, A. (1999), Hydraulic gradient reversal by trees in shallow water table areas and repercussions for the sustainability of tree-growing systems, *Agric. Water Manage.*, *39*, 153–167.

Ibarguren, S. P., H. Panarello, J. Ainchil, and G. M. Zuppi (2001), Isotope hydrology of the multilayer aquifer in N. E. Buenos Aires Province, Argentina, paper presented at International Symposium on Isotope Hydrology and Integrated Water Resources Management, Int. At. Energy Agency, Vienna.

International Geosphere-Biosphere Programme (IGBP) (1998), The terrestrial carbon cycle: Implications for the Kyoto Protocol, *Science*, *280*, 1393–1394.

Istituto Nacional de Tecnología Agropecuaria (1989), Mapa de suelos de la provincia de Buenos Aires, scale 1:500.000, 513 pp., Inst. Nac. de Tecnol. Agropec., Buenos Aires.

Jackson, R. B. (1999), The importance of root distributions for hydrology, biogeochemistry and ecosystem functioning, in *Integrating Hydrology, Ecosystem Dynamics and Biogeochemistry in Complex Landscapes*, edited by J. D. Tenhunen and P. Kabat, pp. 219–240, John Wiley, Hoboken, N. J.

Jackson, R. B., E. G. Jobbágy, R. Avissar, S. Baidya Roy, D. J. Barrett, C. W. Cook, K. A. Farley, and B. C. Murray (2005), Trading water for carbon with biological carbon sequestration, *Science*, *310*, 1944–1947.

Jarrell, W. M., and R. A. Virginia (1990), Soil cation accumulation in a mesquite woodland: Sustained production and long-term estimates of water use and nitrogen fixation, *J. Arid Environ.*, *18*, 51–58.

Jobbágy, E. G. (2002), The imprint of plants on the vertical distribution of soil resources, Ph. D. dissertation, 162 pp., Duke Univ., Durham, N. C.

Jobbágy, E. G., and R. B. Jackson (2001), The distribution of soil nutrients with depth: Global patterns and the imprint of plants, *Biogeochemistry*, *53*, 51–77.

Jobbágy, E. G., and R. B. Jackson (2003), Patterns and mechanisms of soil acidification in the conversion of grasslands to forests, *Biogeochemistry*, *64*, 205–229.

Jobbágy, E. G., and R. B. Jackson (2004), Groundwater use and salinization with grassland afforestation, *Global Change Biol.*, *10*, 1299–1312.

Kelliher, F. M., R. Leuning, and E. D. Schulze (1993), Evaporation and canopy characteristics of coniferous forests and grasslands, *Oecologia*, *95*, 153–163.

Loeppert, L. H., and D. L. Suarez (1996), Carbonates and gypsum, in *Methods of Soil Analysis–Part 3: Chemical Methods*, edited by S. L. Sparks et al., pp. 437–474, Soil Soc. of Am., Madison, Wis.

Logan, W. S., and D. L. Rudolph (1997), Microdepression-focused recharge in a coastal wetland, La Plata, Argentina, *J. Hydrol.*, *194*, 221–238.

Logan, W. S., W. P. Auge, and H. O. Panarello (1999), Bicarbonate, sulfate, and chloride water in a shallow, clastic-dominated coastal flow system, *Argentina, Ground Water*, *37*, 287–295.

Miretzky, P., V. Conzonno, and A. Fernandez Cirelli (2000), Hydrochemistry of pampasic ponds in the lower stream bed of Salado River drainage basin, *Argentina, Environ. Geol.*, *39*, 951–956.

Nosetto, M. D., E. G. Esteban, and J. M. Paruelo (2005), Land use change and water losses: The case of grassland afforestation across a soil textural gradient in central Argentina, *Global Change Biol.*, *11*, 1101–1117.

Öberg, G., and P. Sandén (2005), Retention of chloride in soil and cycling of organic matter-bound chlorine, *Hydrol. Processes*, *19*, 2123–2136.

Paruelo, J. M., E. G. Jobbágy, and O. E. Sala (2001), Current distribution of ecosystem functional types in temperate South America, *Ecosystems*, *4*(7), 683–698.

Perelman, S. B., R. J. C. Leon, and M. Oesterheld (2001), Cross-scale vegetation patterns of flooding Pampa grasslands, *J. Ecol.*, *89*, 562–577.

Plummer, L. N., E. C. Prestemon, and D. L. Parkhurst (1991), An interactive code (NETPATH) for modeling net geochemical reactions along a flow path, *U. S. Geol. Surv. Water Resour. Invest. Rep.*, *91*, 4078–4227.

Prieto, A. R. (1996), Late Quaternary vegetational and climatic changes in the Pampa grassland of Argentina, *Quat. Res.*, *45*, 73–88.

Richardson, D. M. (1998), *Ecology and Biogeography of Pinus*, 527 pp., Cambridge Univ. Press, New York.

Robertson, G. P., P. Sollins, B. G. Ellis, and K. Lajtha (1999), Exchangeable ions, pH and cation exchange capacity, in *Standard Soil Methods for Long-Term Ecological Research*, edited by G. P. Robertson et al., chap. 6, pp. 106–114, Oxford Univ. Press, New York.

Sapanov, M. K. (2000), Water uptake by trees on different soils in the northern Caspian region, *Eurasian Soil Sci.*, *33*, 1157–1165.

Schenk, H. J., and R. B. Jackson (2002), The global biogeography of roots, *Ecol. Monogr.*, *72*, 311–328.

Servicio Provincial de Agua Potable y Saneamiento Rural (1987), Perforaciones de explotación en las localidades de Castelli y Lezama, Provincia de Buenos Aires, Argentina, *Rep. 2419-2596/87*, Min. de Obras Públicas, Buenos Aires.

Soltanpour, P. N., G. W. Jonson, S. M. Workman, J. B. Jones, and M. O. Miller (1996), Inductively coupled plasma emission spectrometry and inductively coupled plasma mass spectroscopy, in *Methods of Soil Analysis–Part 3: Chemical Methods*, edited by S. L. Sparks et al., pp. 91–140, Soil Sci. Soc. of Am., Madison, Wis.

Soriano, A. (1991), Río de la Plata grasslands, in *Natural Grasslands: Introduction and Western Hemisphere*, edited by R. T. Coupland, pp. 367–405, Elsevier, New York.

Spieksma, J. F. M., J. M. Schouwenaars, and R. Van Diggelen (1995), Assessing the impact of water management options upon vegetation development in drained lake side wetlands, *Wetlands Ecol. Manage.*, *3*, 249–262.

Sumner, E. M., and R. Naidu (1998), *Sodic Soils: Distribution, Properties, Management and Environmental Consequences*, 207 pp., Oxford Univ. Press, New York.

Tester, M., and R. Davenport (2003), Na^+ tolerance and Na^+ transport in higher plants, *Ann. Bot.*, *91*, 503–527.

Thomas, G. W. (1996), Soil acidity and soil pH, in *Methods of Soil Analysis–Part 3: Chemical Methods.*, edited by S. L. Sparks et al., pp. 475–490, Soil Sci. Soc. of Am., Madison, Wis.

Tricart, J. L. (1973), *Geomorfologia de la Pampa Deprimida: Base Para los Estudios Edafologicos y Agronomicos, Colección Cient.*, vol. 12, 202 pp., Inst. Nac. Tecnol. Agropecuaria, Buenos Aires.

U. S. Department of Agriculture (1998), *Keys to Soil Taxonomy*, Nat. Resour. Conserv. Serv., U. S. Dep. of Agric., Washington, D. C.

VanBreemen, M., and P. Buurman (1998), *Soil Formation*, 357 pp., Springer, New York.

van Elburg, H., and G. B. Engelen (1986), Two-dimensional finite-difference modelling of groundwater flow systems on micro and personal computers, in *Developments in the Analysis of Groundwater Flow Systems, Publ. 163*, edited by G. B. Engelen and G. P. Jones, pp. 121–139, Int. Assoc. Hydrol. Sci., Wallingford, U. K.

Vertessy, R., L. Connell, J. Morris, R. Silberstein, A. Heuperman, P. Feikema, L. Mann, M. Komarzynski, J. Callopy, and D. Stackpole (2000), Sustainable hardwood production in shallow water table areas, *Publ. 00-163*, Rural Ind. Res. and Dev. Corp., Barton, Australia.

Wright, J. A., A. Di Nicola, and E. Gaitan (2000), Latin American forest plantations—Opportunities for carbon sequestration, economic development and financial returns, *J. For.*, *98*, 20–22.

Zárate, M. A. (2003), Loess of southern South America, *Quat. Sci. Rev.*, *22*, 1987–2006.

R. B. Jackson, Department of Biology, Duke University, Durham, NC 27708, USA.

E. G. Jobbágy, Grupo de Estudios Ambientales, Instituto de Matemática Aplicada San Luis, Universidad Nacional de San Luis & CONICET, San Luis 5700, Argentina. (jobbagy@unsl.edu.ar)