



Land use effects on soil carbon in the Argentine Pampas

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ABSTRACT

Our objective was to establish the pattern of variation of soil organic (SOC) and inorganic (SIC) carbon stored in surface and deep soil layers of the Argentine Pampas as affected by environmental conditions and land use. Eighty two farms, widespread over the region, were used for the study. At each farm paired treatments were sampled representing common land uses: trees, uncropped controls, seeded pastures, cropped fields and periodically flooded areas. Bulk density, SOC, SIC, texture, pH and electrical conductivity were determined to 1 m depth. Rainfall and temperature were obtained from climatic records. Significant differences were detected between treatments in SOC contents. Average SOC stocks to 1 m were: 131 t ha⁻¹ under trees > 101 t ha⁻¹ in uncropped control > 90 t ha⁻¹ in pastures = 86 t ha⁻¹ in cropped field > and 70 t ha⁻¹ in flooded sites. Compared with uncropped controls, SOC was significantly different in all soil layers under trees, to 75 cm depth in flooded sites and to 50 cm in pastures and cropped soils. Agriculture determined a reduction of 16% of SOC to 50 cm in sampled sites. In the 50–100 cm depth a decrease of 9% was observed, though not significant. The stratification pattern of SOC in depth was not affected by the treatments; implying that land use impacted the SOC sequestered in soil, but not its allocation in depth. SIC accounted for one third of total soil carbon, average SIC stock was 50 t C ha⁻¹ to 1 m. Both, its stock and distribution in the profile were not affected by the treatments; with greater SIC stocks founded in deep soil layers. An artificial neural network model was developed that allowed the estimation of SOC (R² = 0.64) based on climate, soil properties and land use. The model, linked to information from satellite image classification, was used for the estimation of present SOC stock of pampean soils, which accounted for 4.22 ± 0.14 Gt in an area of 48.2 Mha. Using soil surveys performed during the 1960–1980 period we estimated a SOC stock of 3.96 ± 0.22 Gt. Consequently, no change of total SOC stock seems to be produced in the last decades in the region. At smaller scale, counties with SOC content greater than 95 t ha⁻¹ to 1 m depth lost carbon; increases prevailed below this threshold. Apparently, SIC reservoirs seem have not change during the last decades.

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1. Introduction

In a context of climatic change, the focus of recent studies on soil organic carbon (SOC) attempts to determine its function as a sink for atmospheric carbon to mitigate the greenhouse effect by applying adequate management practices as well as its effect on soil productivity (Meersmans et al., 2008; Mishra et al., 2009). Many researches in the world are trying to estimate soil carbon sequestration potential by taking into account climate, soil and management factors (Liang et al., 2005; Schulp et al., 2008). Climate is the main controlling factor of SOC because it affects both carbon inputs to the soil, by regulating

net primary productivity, and losses, by controlling mineralization (Post et al., 1982). As the result of these influences, SOC is greater in humid than in arid regions, and in cold than in warm climates (Post et al., 1982). Soil texture is another factor that controls the SOC level by a double effect, impacting soil water holding capacity, and consequently plant productivity, and affecting mineralization. As fine particle content increases, soils have greater water holding capacity, which also is observed in deeper soils, leading to more dry matter production (Alvarez, 2009) and carbon inputs (Alvarez and Lavado, 1998). Fine particles have also a protective effect on microbial degradation (Hassink, 1997). The result of these two effects is that, generally, SOC increases as the content of fine particle in soil is greater (Burke et al., 1989). Net primary productivity is different between contrasting vegetation types. Generally, it is greater in forests than in grasslands, and grasslands usually have higher productivity than crops (Houghton et al., 1983). In agroecosystems, additionally, part of the net primary productivity is harvested. Consequently, carbon input to the soil is greater in natural ecosystems than under agriculture (Houghton et al., 1983). Carbon allocation into aboveground biomass and roots also change depending on vegetation (Jackson et

Abbreviations: SOC, soil organic carbon; SIC, soil inorganic carbon.

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al., 1996) and the pattern of root stratification is also affected by vegetation (Jackson et al., 1996). All these effects affect carbon inputs at different soil depths.

Soil organic carbon decreases with depth following the design of root distribution and carbon input (Jobbágy and Jackson, 2000). Meta-analysis of worldwide data showed that in forests 50% of the SOC sequestered in the upper 1 m of the profile is located in the 0–20 cm layer; SOC in grasslands is less stratified, with a ca. 40% located in the superficial layer (Jobbágy and Jackson, 2000). In cropped soils, SOC is usually less stratified than in natural ecosystems (Yang et al., 2007). This may be attributed to the well known effect of agriculture, which usually reduces SOC of surface soil under rainfed conditions (Davidson and Ackerman, 1993). Few studies have assessed the impact of cropping on deep SOC stocks, and these have shown that some soils lose deep SOC under cultivation, though these losses are lower than in surface layers (Guo and Gifford, 2002; Slobodian et al., 2002). Much of the work performed on the comparison of SOC profiles of different vegetation types and land uses was done using data from different biomes located worldwide. Consequently, climate and soil characteristics varied with vegetation type or land use. Regional comparisons of vegetation-land use effects on SOC reservoirs and their vertical distribution over depth, using paired situations under similar environmental conditions, are scarce.

In arid and semi-arid environments calcareous soils are found worldwide. Soil inorganic carbon (SIC) represents more than half of the total carbon content of these soils (Li et al., 2007). Lithogenic carbonate comes from parent material, while pedogenic carbonate, neofomed from CO₂ originated from the atmosphere and soil or root respiration precipitates continuously (Nordt et al., 1998). Changes of SIC content as the consequence of agricultural soil use have been reported. Soil inorganic carbon increases by irrigation with carbonates-rich water (Wu et al., 2009), and can decrease after tillage exposes previously buried soil to the atmosphere (Moreno et al., 2006), or acidification due to fertilization (Wu et al., 2009). Extensive research on the possible effects of land use on SIC has not been performed yet.

The Pampas is considered as one of the most suitable areas for grain crop production in the World (Satorre and Slafer, 1999). The effect of climate (Alvarez and Lavado, 1998) and cultivation (Alvarez, 2001) on SOC in surface soil layers has been assessed previously using soil survey data from the 1960–1980 period. No recent field information is available relating land use influences on SOC and SIC in surface and deep soil layers. Recently, concern has increased on the possible degradation effects of the cultivation expansion and especially the impact of soybean on SOC due to its low carbon input to the soil (Viglizzo et al., 2001). The goals of this research were (1) to determine the impact of land use on the amount and vertical distribution of SOC and SIC in the Pampas by comparing paired sites under similar climate and soil conditions, and (2) to estimate current regional soil carbon stock and compare it with estimated stock with data obtained from 30 to 50 years ago, before cultivation expansion.

2. Materials and methods

2.1. Region description

The Pampas is a vast plain of around 60 Mha which runs from 28 to 40 °S in Argentina. The relief is flat or slightly rolling with Mollisols, formed on loess-like materials, as predominant soils (Alvarez and Lavado, 1998). Its natural vegetation are grasslands in which graminaceous species predominate and forests are found in some areas. Annual rainfall varies from 200 mm in the west to 1200 mm in the east, and mean annual temperature ranges from 14 °C in the south to 20 °C in the north. Because of the eolian origin of sediments from southwest to northeast and the climatic gradient west–east, soils vary from sandy textured with little development in the west to fine textured and with more development in the

east, being illite the main clay mineral (Alvarez and Lavado, 1998). A petrocalcic horizon appears within the upper 1 m of the soil profile in many places along the east and the south ends of the region (Teruggi, 1957). Around 60% of the area, where annual rainfall is over 500 mm, is used for agriculture, usually on well drained soils, while areas with hydromorphic soils are devoted to pastures (Hall et al., 1992). Soybean (*Glycine max* (L.) Merr.), wheat (*Triticum aestivum* L.), and corn (*Zea mays* L.) are the main crops (MinAgri, 2010). Forests account for about 7% of the pampean surface in the humid portion of the region with planted trees, introduced 150 years ago and employed usually as wind barriers, occupying less than 0.2% of the surface (INDEC, 2002). These forested areas suffered minor changes over the last decades (Soriano, 1991). Since 1970, the agricultural use of soils intensified along with to the widespread adoption of soybean in rotations (Viglizzo et al., 2001). This crop occupies nowadays around 60% of the cropped area (MinAgri, 2010).

2.2. Sampling

Soil samples from 82 farms were collected from August 2007 to February 2008 along the humid and semi-arid portion of the Pampas (Fig. 1). Farms were selected because they were representative of common uses in each pampean subregion and because of their location in order to obtain a regional coverage. At each farm, five common land uses were selected: trees, uncropped controls, seeded pastures, cropped fields and flooded lands. Trees were usually *Eucalyptus* sp., *Pinus* sp., *Prosopis* sp. and *Acacia* sp., of at least 30 years old. Surfaces with trees ranged from 100 m² to hundreds of hectares; but generally their surface was around 1–2 ha. Uncropped controls were park grass surrounding houses in 60 of the farms and, in 22 farms, where they were available, natural grazing grasslands. In both cases graminaceous vegetation was dominant. Samples were taken far from the buildings and, as far as farm records indicated, all these sites were never cropped. Seeded pastures were cultivated soils that at the moment of sampling were in the pasture phase from a mixed rotation. They had been under pasture management for the last 3–4 years. Pasture composition was a mixture of leguminous and graminaceous species in nearly all sites, but only

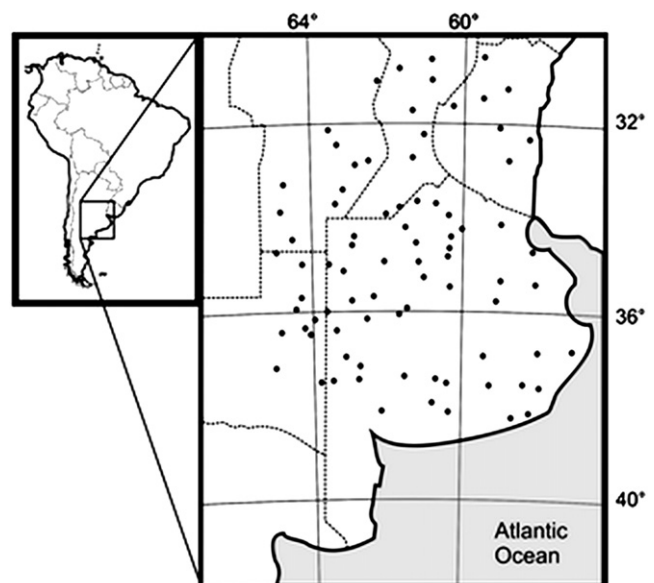


Fig. 1. Location of sampled farms within the Pampas of Argentina.

graminaceous ones in some cases. Cropped fields were selected to be representative of the most common rotation and tillage system used in each area, and the time since the last pasture period was at least three years. In many cases time since the last pasture period was 20–40 years. Flooded lands were lowlands which were never cropped and used for grazing. Soils were hydromorphic, Natracuolls and Natracualf generally, which suffered periodical flooding. Natural vegetation in the sampled sites was dominated by graminaceous vegetation.

In each site an area of 100 m² was delimited, georeferenced, and samples taken from the 0–25, 25–50, 50–75 and 75–100 cm soil layers with a corer, four samples at each depth. These areas were chosen because, as judging by eye, they were representative of the plots samples. Their surface was defined for the georeferencing equipment error in order to locate them in the future. When petrocalcic horizons were present, soils were sampled to their upper limit. Samples were composited by depth, air dried and sieved by a 2 mm mesh size. A total of 386 sites were sampled, because in some farms not all land uses were available, generating 1493 soil samples. The corer took samples of a known volume which allowed soil bulk density determination after oven dried (105 °C). Samples from nine petrocalcic horizons were also taken, dried, weighed, and their bulk density determined by the paraffin method. A part of the samples was ground to pass through a 2 mm sieve.

2.3. Analytical methods

Total carbon was determined by wet digestion with external heating using 0.5 g samples in 300 ml tubes (Amato, 1983). The CO₂ evolved from digestion was absorbed in NaOH and the excess of alkali titrate against phenolphthalein. SIC was assessed by acidification of 5 g soil samples in 200 ml flasks and volumetric determination of the CO₂ generated (Loeppert and Suarez, 1996). Soil organic carbon was obtained by difference and stocks estimated on an areal basis using soil bulk density data. Soil inorganic carbon in petrocalcic horizons was estimated assuming a mean layer thickness of 25 cm (Pazos and Mestelan, 2002). Texture was determined by the Bouyoucos method (Gee and Bauder, 1996) on 50 g samples. Soil was dispersed in 1 l bottles with a sodium hexametaphosphate solution overnight. The suspension was transferred to a stirring bottle machine and shaken for 2 min. Then transferred to a sedimentation cylinder and hand shaken previous to the hydrometer readings. Soil pH was assessed in a soil: water suspension (1:5). Electrical conductivity measurements were performed suspending 50 g of dried soil into 250 ml of water, shaking 1 h and determining conductivity after 24 h in the supernatant. This method was calibrated against the classical saturation extract technique (Rhoades, 1996) using 20 samples from a wide range of soil conditions with good results ($EC_{\text{saturation extract}} = 5.5 EC_{1 \text{ soil}:5 \text{ water}}$; $R^2 = 0.75$), and allowed the use of the same sample for measuring pH and conductivity.

2.4. Climate records and soil survey data

Mean annual rainfall and temperature of sampled sites were estimated using LocClim (FAO, 2006). This software has a database from the last ca. 50 years. The inverse distance method (IDW) of estimation was applied. This method uses climate data from the nearest weather stations to the site, giving to each station a weight that is inversely proportional to the distance from that site. Data from 10 stations, not farther than 300 km to each sampled site were used. A total of 120 weather stations of Argentina and Uruguay allowed estimations for the 386 sites sampled. The software performed good estimations of rainfall and temperature as indicated by the comparison between modeled values and true values from 18 weather stations of the Instituto Nacional de Tecnología Agropecuaria and the Servicio Meteorológico Nacional, with records of 80 or more years ($R^2 > 0.90$, F

test $P = 0.01$, ordinate not different from 0 and slope from 1, t test $P = 0.05$).

Soil classification (Soil Taxonomy, 1975) was obtained from the digital database of Argentinean soils for the georeferenced sites (INTA, 2010). Soils were grouped into four categories for statistical comparisons: 1) coarse textured soils of semi-arid zones, Haplustol, Argiustol, Calciustol, Torripsament and Ustipsament (23%); 2) coarse textured soils of humid zones, Hapludol (21%); 3) fine textured soils of humid zones, Argiudol, Peludert and Argialbol (36%); 4) hydromorphic soils, Natracualf, Natracuol and Natralbol (20%).

For the estimation of the past carbon stocks, soil data was obtained from surveys of the provinces of Buenos Aires (INTA, 1989), La Pampa (INTA, 1980), Córdoba (INTA, 2003), Santa Fe (INTA, 1981, 1983) and Entre Ríos (INTA, 1984) which occupy an area of ca. 74 Mha. These surveys were performed, mainly, between 1960 and 1980. More than 1000 soil profile descriptions with their corresponding influence area were used. Soil variables were reported from the soil surface to the bottom of the profiles or to the petrocalcic horizon, at different depth intervals, depending on genetic horizons. The variation in depth of the variables was modeled fitting different functions, using TableCurve 2D (Systat Software Inc.), with good results ($R^2 > 0.95$). The models adjusted were used for SOC, SIC, clay, silt and sand concentrations estimation in layers of 25 cm to 1 m depth or to the upper limit of petrocalcic horizons. Some surveys reported SOC and others organic matter. A correction factor of 1.72 was applied for transforming organic matter to SOC (Nelson and Sommers, 1996) as in all cases the Walkley–Black method was used for SOC determination. As the fraction of SOC oxidized in the Walkley–Black method decreases with depth, a correction equation, developed for pampean soils, was applied for adjusting the oxidation coefficient as a function of soil layer depth (Richter et al., 1973). Soil bulk density was estimated using soil texture and SOC data for each layer (Rawls, 1983) and variables were transformed to mass contents per area unit. The accuracy of the method was tested using our measured soil bulk density data. An overall overestimation of 4% (t test, $P = 0.05$) was detected so final estimations were corrected by this factor. Variables modeled at the profile level were integrated to the county level taking into account the corresponding areas (Alvarez and Lavado, 1998). Modeled texture variables at county scale were used later as inputs for the artificial neural network model for current SOC estimation (see Section 2.6 Statistical analysis). The effective area of each county used for the estimations was the result of the difference between the political boundaries and the area occupied by cities, lakes, lagoons, and salt mines (see explanation on classification of satellite images below). For SIC estimations a bulk density of 2.1 g cm⁻³, 6.4% of carbon content and a thickness of 25 cm were assumed for petrocalcic horizons (see Results section).

2.5. Modeling SOC and SIC profiles

The distribution of SOC and SIC in the profile was modeled using a potential model of the form (Bernoux et al., 1998):

$$C = A * d^B \quad (1)$$

where C represents the cumulate carbon mass (t ha⁻¹) to a depth d (m), A is the mass of carbon to 1 m (t ha⁻¹), and B describes the curvature of the function. As the model is not linear in the parameters, it can be liberalized by taking logarithms as follows:

$$\log C = \log A + B \log d \quad (2)$$

This form of the potential model has been successfully used previously for describing SOC in depth with worldwide data (Jobbágy and Jackson, 2000). Parameter B can be fitted using both untransformed and relative data. When $B = 1$, the model fits to a straight line and SOC mass is not stratified in the different soil layers. The modeling

was performed by least squares minimization using the Levenberg–Marquardt algorithm with TableCurve 2D facilities (Systat Software, Inc.). The R^2 and RMSE were calculated in each case and significance determined (F test, $P < 0.05$).

Soil organic carbon data were also transformed to equivalent soil mass to account for bulk density differences between sites. The estimations were performed for masses of 3000, 6000, 9000 and 12,000 $t\ ha^{-1}$. Three methodologies were tested. 1) A linear equation that adds or takes away a portion of soil to reach the desired soil mass assuming that transitions between soil layers are continuous and linear (Poulton et al., 2003):

$$MC_{MS_1} = MC_{P_1} + \left[(MS_1 - MS_{P_1}) \times \frac{MC_{P_2}}{MS_{P_2}} \right] \quad (3)$$

where MC_{MS_1} is SOC stock for the soil mass MS_1 , the mass of soil for SOC estimation, MC_{P_1} is cumulative SOC stock for the depth P_1 , MS_{P_1} is soil mass to P_1 , MC_{P_2} is cumulative SOC stocks to depth P_2 and MS_{P_2} is cumulative soil mass to P_2 . 2) A potential model similar to Eq. (1):

$$C = A * m^B \quad (4)$$

where C is the cumulative SOC ($t\ ha^{-1}$) to a cumulated soil mass m ($t\ ha^{-1}$), A is the SOC mass to the maximum soil mass sampled and B describes the curvature of the function. Parameters A and B were estimated for each site and 377 significant functions could be fitted (F test, $P < 0.05$). With the parameters adjusted to each site SOC to equivalent soil mass was estimated. 3) Spline functions (Bishop et al., 1999), take soil mass as independent variable and SOC as dependent variable. The performance of the three methodologies was tested by fitting observed vs. estimated data, using each technique for estimation of SOC for a 6000 $t\ ha^{-1}$ soil mass, adjusting models with data from smaller and greater soil masses and calculating the R^2 , and by visual inspection of residuals.

2.6. Land use area estimation

For estimation of current land use area when applying the artificial neural network model fitted for SOC stock prediction, which needs land use as an input (see Sections 2.6 Statistical analysis and Results), we used satellite image classification. For the Buenos Aires Province, which occupies around 50% of the area surveyed, SAC-C sensor images, with a spatial resolution of 175 m, were used. Considering previously tested criteria (Guerschman et al., 2003), the dates chosen for the analysis were: Path 228: May 24, 2003 and October 15, 2003, Path 226: May 26, 2003 and November 2, 2003, and Path 224: May 28, 2003 and September 1, 2003 (North Area), June 13, 2003 and November 4, 2003 (South Area). Supervised classifications, using the Maximum Likelihood Algorithm (Lillesand and Kiefer, 1994), were performed independently for path/area. The information used to classify were all the bands provided by the sensor of the two dates. Finally, a mosaic of classifications was made. The ground truth was obtained by GPS surveys between mid-November and mid-December 2003 (a total of 3620 observations). Each GPS waypoint was associated to a land use class. Assigning random values, information was divided by 70% for training and 30% to validate classification algorithms. The classification were summarized in three classes: cropped soils (summer and winter crops), continuously vegetated soils (trees and forage resource) and soils unsuitable for farm use (under water, cities and miscellaneous). The area of each land cover class was calculated per county, and the effective county area was determined as the sum of the classes: cropped soils and continuously vegetated soils. The accuracy of classification was determined through the coefficients derived from the confusion matrix (Congalton, 1991). The overall accuracy of the SAC-C classification of the Buenos Aires Province was 77%. The producer and user precisions for each class ranged between 66 and 86% depending on the class considered.

For the whole surveyed area (Provinces of Buenos Aires, Entre Rios, Santa Fe, Cordoba and La Pampa) the Normalized Differenced Vegetation Index (NDVI) value of the MOD13Q1 MODIS product, which spatial resolution is 250 m were used to perform a land use classification. The compounds used were those from July 2003 to June 2004. An unsupervised classification using k-means algorithm (Tou and Gonzalez, 1974) was applied. Three classes were determined by decision rules: cropped soils, continuously vegetated soils and soils unsuitable for farm use. Cropped soils were classified as those classes whose average NDVI curves showed one or two periods of active growth (NDVI greater than 0.4), followed by another period of low values of NDVI (lower than 0.2). In the classes that did not have a uniform or clearly bimodal trend, the separation criterion was based on the average NDVI annual value. Classes with average NDVI annual values greater than 0.2 were classified as continuously vegetated soils, while classes with average NDVI annual values under 0.2 were classified as soils unsuitable for farm use. The area of each class of land cover was calculated per county, and the effective county area was determined. Since there was no ground truth data to validate the classification, we analyzed the correlation between the area assigned to each class by the classification and the land use surface provided in the National Agricultural Census data for the year 2002 (NAC2002) (INDEC, 2002). The correlation of cropped soils and continuously vegetated soils between the classification MODIS data and NAC2002 data at county level was significant ($P < 0.001$) and with an R^2 of 0.96 in both cases. The correlations of the effective area surface, cropped soils surface and continuously vegetated soils surface between the two classifications for the Province of Buenos Aires were significant ($P < 0.001$) and had a R^2 of 0.99, 0.94 and 0.97 respectively; this indicated that results obtained by both methodologies were very similar. Data generated from the SAC-C images were used for the Buenos Aires Province and data generated from the MODIS images were used for the rest of the Pampean Region for carbon stock estimation.

The areas classified as continuously vegetated soils were spatially intersected with information on soil type from a soil map (SAGyP-INTA, 1990). From the intersection, two sub-classes were identified: lowland continuously vegetated soils, where the main limitation of the soil was alkalinity or salinity in the upper 50 cm of the profile, poor drainage, and susceptibility to flooding, and highland continuously vegetated soils otherwise. The first class was considered equivalent to flooded lands of the sampling, the second as equivalent to the sum of trees, pastures and uncropped controls. The information provided by the NAC2002 was used for calculating the participation of each land use in the sum. ENVI 4.1 and Arcview 9.1 software were used for data processing.

2.7. Statistical analysis

All variables were tested for normality using a modified Shapiro–Wilks test (Mahibbur and Govindarajulu, 1997). As in nearly all cases (except SOC in the 0–25 cm layer) there was evidence of non-normality ($P < 0.05$), data were transformed (logarithmic, potential, arcsine, exponential, and Box–Cox, Peltier et al., 1998). However, transformed data displayed not normality too. Notwithstanding this, as SOC, pH, bulk density and texture displayed near to normal distributions, untransformed variables were analyzed by mixed linear models (Littell et al., 1998) using more restrictive criteria on the size of the tests of hypothesis ($P < 0.01$). Variables displaying a bimodal distribution, SIC and electric conductivity (which included many cases with zero values), were analyzed by the Kruskal–Wallis test ($P < 0.05$) (Conover, 1999).

Data were analyzed with different mixed models. In the simpler of them the effect of land use treatment was considered a fixed effect and the effect of farms taken as a random effect. More complicated models considered climate and soil variables tested as covariates ($P < 0.01$), and were included in the model only if significant. The linear and quadratic effects of depth were nested within treatments and considered fixed. When comparing soil group effects on the determined variables, a term was introduced as a fixed effect, and its interaction with treatments

was tested for significance. As the treatment flooded lands was associated with a particular soil group (hydromorphic soils), which in turn would generate confounding effects, flooded lands were not included in these later models and only the other four land use treatments compared. Finally, for variables analyzed by the Kruskal–Wallis procedure, treatment was used as a classification variable and depth as a partition variable.

For an overall comparison of B parameters between vegetation types and land uses, the potential model (2) was adjusted to data on cumulative SOC by the following linear mixed model:

$$Y_{ijk} = \alpha_i + \beta_i d_{ijk} + a_j + \varepsilon_{ijk} \quad (5)$$

where: Y_{ijk} is the response variable; α_i ($i = 1, \dots, 5$) is the effect of land use treatment, which was considered a fixed effect; β_i (one for each land use) represents a fixed slope parameter for the regression on the k^{th} soil depth (d_{ijk}) nested within vegetation type (i) and farm (j), a_j ($j = 1, \dots, 82$) is the effect of farms taken as a random effect and ε_{ijk} is the random error. Notice that in model (4) the intercept for each treatment is the parameter α_i and that the transformation of Eq. (1) operates on the A parameter and on the d s but not on the B that is numerically equal to β_i in Eq. (4). The advantages of fitting a mixed model (4) are twofold. First, all parameters for the different land uses were simultaneously estimated, and second, the lack of independence among observations from the same farm was taken into account by using farm as a random effect. To test for heterogeneity of slopes estimable linear contrasts were employed (Searle, 1971). Tests for normality of the residuals in model (5) indicated that the distribution was somewhat skewed to the left and platykurtic. Therefore, a conservative view was taken of the size of the tests of hypothesis that were set to $P < 0.01$.

Regression and correlation analysis were performed for searching associations between variables, and the F test was used with $P < 0.05$. Multivariate analysis by polynomial linear regression and artificial neural networks methods were also used. Data were randomly partitioned into two sets, 70% for training and 30% for validation, fitting models using the training set and then testing them on the validation set in order to determine the generalization ability. Training and validation sets used for regression fitting were also used for network model development.

Second order polynomial multiple regression models, which included linear, quadratic and interaction terms (Shen et al., 2003), were fitted for SOC and SIC estimation, having as explanatory variables climate and soil covariates (rainfall, temperature, clay, silt, sand, pH, electrical conductivity). Treatment and depth layer were encoded and included in models as categorical variables (Kleinbaum and Kupper, 1979). Only linear and interaction effects were tested for categorical variables. Selection of variables in models was performed by the forward stepwise method. Terms were maintained in models only if they were significant ($P < 0.05$). Multicollinearity was checked by the VIF value (Neter et al., 1990).

Feed-forward artificial neural networks were adjusted using the back propagation algorithm for weight fitting (Rogers and Dowla, 1994). Network architecture, transfer functions, scaling methods, learning rate and epoch size were similar to those described previously (Alvarez, 2009). Maximum simplification of networks was looked for, reducing input variables and neurons in the hidden layers as much as possible without affecting the R^2 . In a first step, sensitivity analysis was performed to weight the effect of different inputs on SOC and SIC by calculating a sensitivity ratio (SR, Miao et al., 2006). As the value of the ratio increased, the impact of the input on the output was greater. Only variables with SR higher than 1 were preselected because a lower value indicates no impact of the variable on the ANN output (Miao et al., 2006). Selected variables were then tested as inputs by a stepwise procedure (Gevrey et al., 2003). All the same independent variables tested for regression analysis were initially used as inputs in ANN

development. Cross-validation was performed to avoid overlearning (Özesmi et al., 2006), by stopping the weight adjustment when R^2 from the validation set becomes lower than from the training set (Park and Vlek, 2002). Vegetation type-land use treatments and soil layer were encoded for neural networks fitting (Brouwer, 2004). Neural networks were fitted using Statistica (www.statsoft.com).

The utility of the potential model for estimation of SOC up to 1 m depth, when only data from the 0–25 cm layer are available, was tested and compared with the performance of artificial neural networks. Data were randomly partitioned into 70% for training and 30% for validation and a mean parameter B fitted using the training set. Then, for the validation set, cumulative SOC up to 1 m depth was estimated using SOC in the 0–25 layer and the B parameter. Neural networks were fitted using the same data sets for estimating SOC to 1 m depth with carbon content of the upper soil layer as input, joined to climate, texture, pH, conductivity and land use inputs.

Slopes and intercepts of predicted vs. observed data were compared by the t -test using IRENE ($P < 0.05$) (Fila et al., 2003). The determination coefficients of training and validation sets were contrasted (Kleinbaum and Kupper, 1979) for each modeling method ($P < 0.05$). Root mean square error (RMSE) (Kobayashi and Salam, 2000) was calculated for each method and significant differences between modeling methods were tested by contrasting the RMSE with an F -test ($P < 0.05$) (Xiong and Meullenet, 2006).

Uncertainty (0.5*95% confidence interval/average) analysis of SOC stocks was performed by a combination of expert knowledge and common error propagation methods (IPCC, 2006). For the 1960–1980 surveys, uncertainty of SOC concentration estimation in depth using regression models, the oxidation factor of the Walkley–Black method, and soil bulk density estimation by the Rawls method was assessed by Monte Carlo simulation. The combination of these uncertainties resulted in an estimation of SOC stock uncertainty at single profile level for each soil layer. Expert local knowledge (Marcos Angelini, per. commun.) was used for evaluation of probable error in soil surface cover estimation in soil maps. As average error was estimated at 50%, we adopted and uncertainty of 100% for areas corresponding to each soil type. The uncertainty of the SOC stock of the Pampas was a combination of each profile and soil layer uncertainty and its corresponding surface uncertainty at county scale. Consequently, around 3300 SOC stocks uncertainties were aggregated for estimating SOC stock uncertainty to 1 m depth. The uncertainty of the SOC stock for 2007–2008 survey was the combination of uncertainties of model inputs, structure and scaling (see Results for details on neural network model inputs and structure). Uncertainty of the inputs was estimated by land use and soil layer running the model fed with temperature, rainfall and texture data estimated at county scale. The probability density function of the output was plotted and its standard deviation and uncertainty calculated. Normal or triangular distributions were those which better fits to output density function, depending on land use and depth. Model uncertainty was assessed using the regression of observed vs. predicted SOC stocks by land use and soil layer of the validation data set. The 95% confidence interval of the ordinate and slope were calculated and their uncertainty estimated assuming normal distribution for the parameters, because residuals of the regression were normally distributed. The combination of inputs and model uncertainties were performed using the regression line of observed vs. estimated data by Monte Carlo simulation. Inputs uncertainty corresponded to the abscise uncertainty and model uncertainty to parameters uncertainty. Uncertainty of scaling was assessed by a similar approach, using the regression line of observed land use areas in NAC2002 against land use areas estimated by image classification. Soil organic carbon stock uncertainty at county scale for each land use and soil layer was combined with the uncertainty in the coverage area. Around 2700 SOC stocks were aggregated for

Table 1

Mean and range of climate and soil properties, as the average of the upper 1 m of 386 soil profiles.

Variable	Minimum	Mean	Maximum
Mean annual temperature (°C)	12.8	15.8	19.1
Mean annual rainfall (mm)	564	860	1156
Sampled depth (cm)	25	96	100
Bulk density (g cm ⁻³)	0.82	1.15	1.60
Organic carbon (t ha ⁻¹)	0.30	964	321.2
Carbonate carbon (t ha ⁻¹)	0.0	47.0	376.6
pH	4.90	640	9.47
Electrical conductivity (dS m ⁻¹)	0.20	1.90	27.00
Clay (g kg ⁻¹)	16	162	427
Silt (g kg ⁻¹)	8	336	590
Sand (g kg ⁻¹)	118	468	972

the estimation of overall pampayan SOC stock and uncertainty to 1 m depth.

3. Results

3.1. Treatment effects on stored SOC and SIC and other soil properties

Climate and soil properties had a wide range of variation between sampled sites (Table 1), with Mollisols present in 80% of the sites. It was not possible to sample to 1 m depth in some soils (11%) due to the presence of a petrocalcic horizon. Usually, the petrocalcic horizon appeared between 50 and 100 cm depth, but in 3% of the sites the horizon appeared at 25–50 cm depth. The petrocalcic horizon has a bulk density ranging from 1.9 to 2.3 g cm⁻³, with an average of 2.1 g cm⁻³. Its SOC was null and, as more than 50% was carbonate, the mean SIC content was 6.35%. As temperature and rainfall increased, the content of soil fine particles increased too (Table 2), but when considering data from different soil layers all together only a weak association was detected between texture properties and SOC concentration. This was due to the strong association between SOC and depth. In deep soil layers, SOC decreased, meanwhile SIC and clay or silt content were larger. Bulk density decreased in soils with greater SOC concentration. Soil inorganic carbon and pH were positively correlated.

There were no differences in bulk density between trees and uncropped controls for all soil strata. Average bulk density in these treatments increased from 1.13 g cm⁻³ in the 0–25 cm layer to 1.35 in the 75–100 cm layer. Cultivation (seeded pastures and cropped soils) determined a significant increase of 9–10% in bulk density to 50 cm depth, without differences between the pasture and the cropped phase of rotation. In flooded soils bulk density was similar to that measured under agriculture, and larger than in uncropped controls and trees.

Average clay content was greater between 25 and 75 cm depth than above or below this soil layer, silt decreased with depth, but sand showed no stratification in the soil profile. More than half of

the samples were of loam and sandy loam texture. Land use had little effect on texture. Some significant differences were detected in the upper 50 cm of the soil, where clay content was 2–3% greater in cultivated (pasture and cropped sites) and flooded soils than in trees and uncropped treatments. Conversely, no significant effect of cultivation was detected on silt and sand content at surface of deep soil layers.

Land use treatments had a strong impact on pH and electrical conductivity. Soil pH increased with depth (Fig. 2) being lower under trees and higher in flooded soils when compared with the other treatments. Conversely, conductivity showed different stratification patterns depending on land use (Fig. 2). Under trees it was greater than in pastures, cropped soil and uncropped controls, but lower than in flooded soils. Cropping (pastures and cropped soil) had no significant impact on both, pH and electrical conductivity, in relation to uncropped controls. Trees produced acidification and salinization of soils. Flooded sites accumulate salts, possibly including sodium salts, leading to pH increases.

Soil organic carbon was strongly influenced by land use (Fig. 3). Up to 1 m depth, SOC was significantly greater under trees (131 t ha⁻¹) than in uncropped controls (101 t ha⁻¹). Cultivated soils had lower SOC contents than controls, both when sampled during the pasture phase of rotation (pastures = 90 t ha⁻¹) or the cropped phase (cropped soil = 86 t ha⁻¹), but no differences were detected between rotation phases. Flooded sites had significantly lower SOC levels than cultivated soil (70 t ha⁻¹). The analysis by strata showed that significant effects of cultivation on SOC could be detected only up to 50 cm, that trees increased SOC in relation to uncropped controls up to 1 m, and that flooding impacted it to 75 cm. When compared to uncropped controls, the decrease of SOC by cultivation averaged 16% in the 0–50 cm layer. The range of differences in SOC between uncropped controls and cultivated soil was –22 to 64%. In 18% of the farms SOC was greater in cultivated soils than in uncropped controls. Below 50 cm, although not significant, SOC was on average 9% lower in soils under cultivation than in uncropped controls. Mean SIC content up to 1 m depth was 50 t ha⁻¹, and no differences among treatments were measured (Fig. 3). On average SIC was equivalent to 35% of total soil carbon, but in the semi-arid portion of the region it accounted for 80% of total carbon. Soil inorganic carbon stratification patterns were the inverse of SOC pattern, increasing with depth. When including in mixed models soil group for analysis of SOC variation, no interaction was detected between soil groups with land use treatment. Consequently, the effects of the treatments did not depend on this factor.

The three methodologies tested for transforming SOC data to equivalent mass gave acceptable results, but the spline technique resulted in the best fits. The linear method of interpolation produced larger errors of estimation than the other techniques when estimations were performed for soil mass much different to those present in soil layers, especially in the surface soil, where SOC stratification had a larger curvature (R^2 obs. vs. predicted data = 0.65). The potential model could be fitted to nearly all SOC profiles but tended to overestimate at surface and deepest soil layers, whereas it underestimates in intermediate layers (R^2 obs. vs.

Table 2

Pearson correlation coefficients between climate and soil variables determined in layers of 25 cm (n = 1493). ns: not significant, otherwise significant at P = 0.05.

	MAT	MAR	Depth	BD	SOC	SIC	pH	EC	Clay	Silt	Sand
MAT	1.00										
MAP	0.56	1.00									
Depth	ns	ns	1.00								
BD	0.32	ns	0.37	1.00							
SOC	–0.15	0.09	–0.61	–0.45	1.00						
SIC	–0.11	–0.14	0.16	0.19	–0.10	1.00					
pH	–0.08	–0.30	0.18	0.18	–0.31	0.17	1.00				
EC	–0.08	–0.10	ns	ns	–0.05	ns	0.36	1.00			
Clay	0.47	0.60	0.07	ns	ns	ns	–0.18	–0.07	1.00		
Silt	0.16	0.29	–0.14	–0.24	0.23	ns	–0.10	0.10	0.36	1.00	
Sand	–0.37	–0.53	ns	0.15	–0.13	ns	0.17	ns	–0.82	–0.83	1.00

MAT: mean annual temperature, MAR: mean annual rainfall, BD: bulk density, SOC: soil organic carbon, SIC: soil inorganic carbon, EC: electrical conductivity (units are similar than in Table 1).

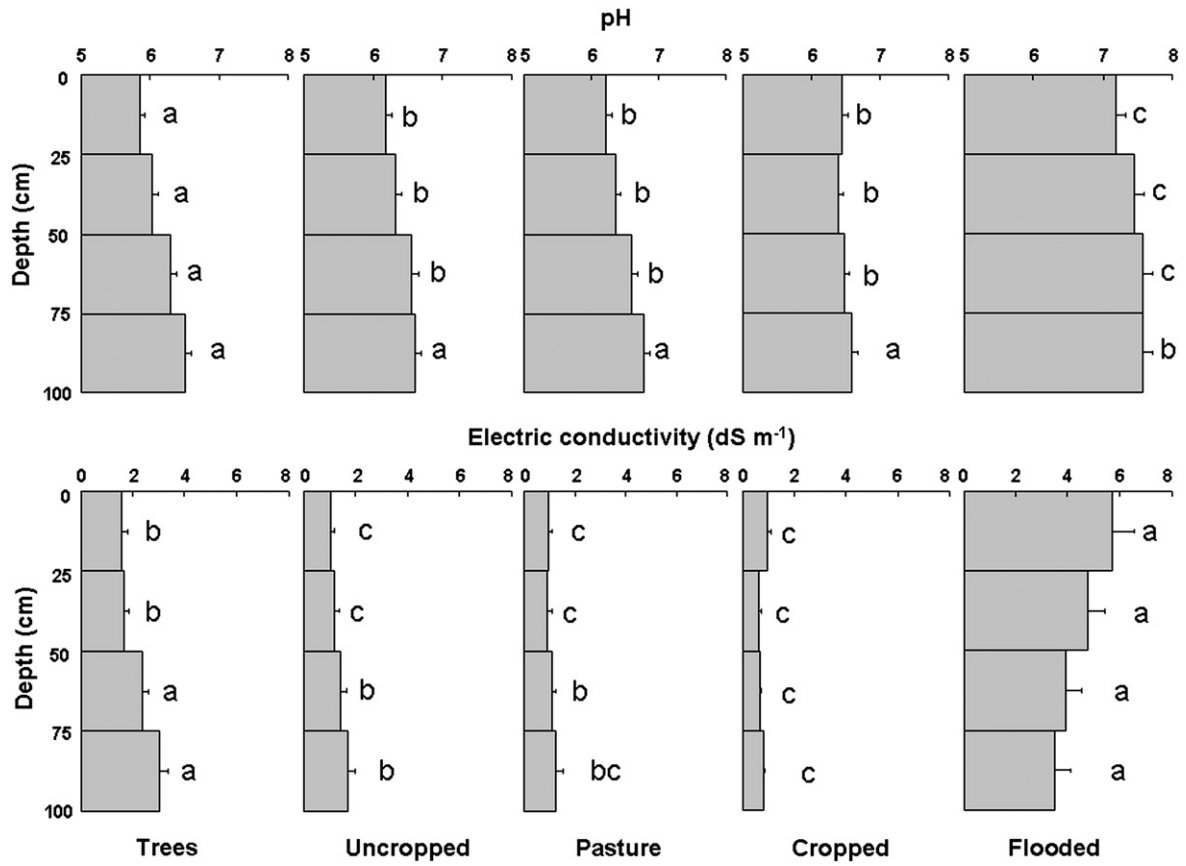


Fig. 2. Soil pH and electrical conductivity variation with depth associated to land use (mean + standard error). Different letters indicate significant differences between treatments for a same depth interval.

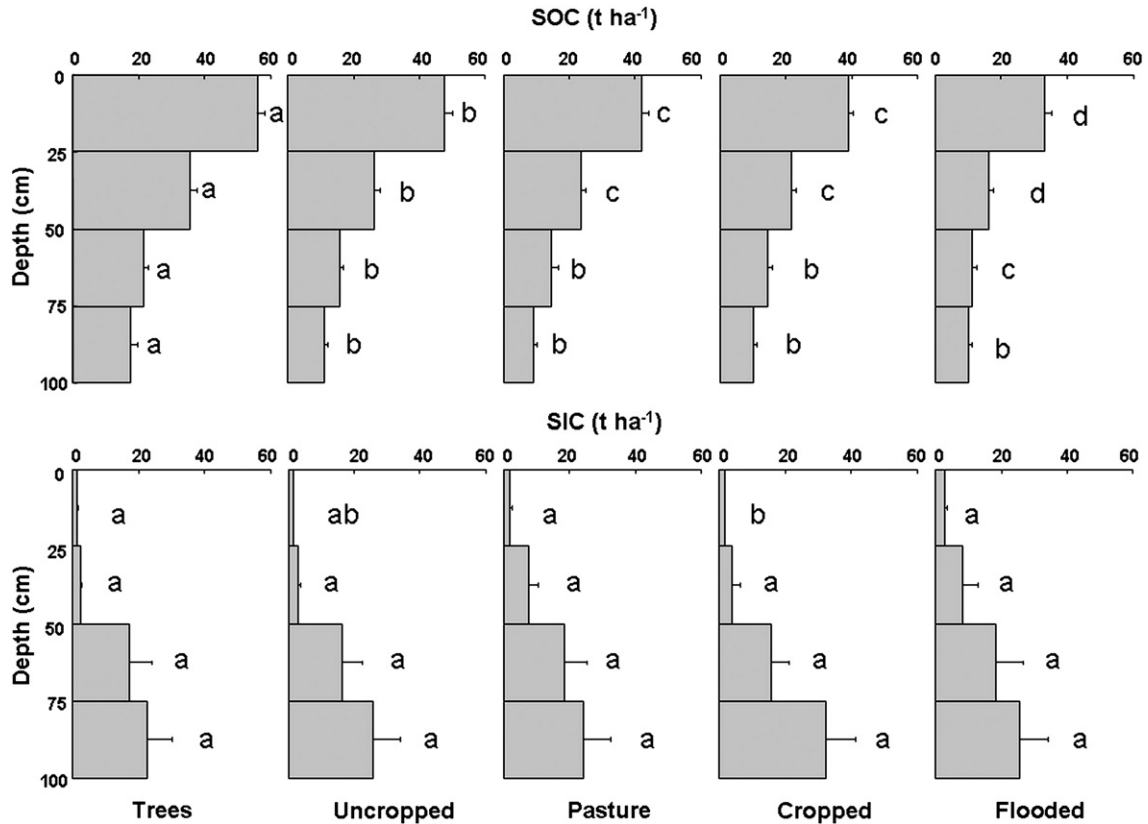


Fig. 3. Soil organic (SOC) and inorganic (SIC) carbon variation in depth associated with land use (mean + standard error). Different letters indicate significant differences between treatments for a same depth interval.

predicted data=0.89). Finally, the use of spline functions solved the problems of the previously mentioned methodologies, and could be fitted to all SOC profiles without over-estimation (R^2 obs. vs. predicted data=0.99). The statistical analysis of SOC storage using data transformed to an equivalent mass basis gave similar results to those reported previously for fixed depth soil layers (results not presented).

3.2. Stratification pattern of SOC

The potential model gave very good results for fitting cumulative SOC in depth being significant in 94% of the soils without petrocalcic horizon (Table 3). The model could be fitted adequately to SOC profiles of all treatments with RMSE rounding 3.5% of the means. The parameter A of the model was a very good estimator of SOC accumulated up to 1 m depth (Fig. 4). Averages of parameter B ranged from 0.53 to 0.60 between treatments. Conversely, a broad range of variation was observed in the values of B within each treatment, with the greater values being 4 to 16-fold larger than lower values. This indicated that SOC stratification varied strongly by causes other than land use. Moreover, no significant differences were detected among treatments for parameter B. Consequently, land use had no effect on the pattern of SOC accumulation in depth in the Pampas. In average for all the treatments 45 to 50% of SOC was accumulated in the 0–25 cm layer. In a few sites, mainly under hydromorphic conditions, B was greater than 1, indicating an inverse pattern of stratification, with more SOC in deep layers than at the surface.

The potential model allowed SOC estimation in depth with acceptable performance (Fig. 5). No differences were detected between R^2 and RMSE of training and validations sets, meanwhile intercepts and slopes of observed vs. estimated regressions did not differ from 0 and 1, respectively. RMSE was equivalent to 20% of the mean SOC of all sites. Artificial neural networks, despite their greater complexity, could not make a better job than the potential model (Fig. 5). Using the same training and validation sets, a network model could be fitted, with a R^2 and RMSE slightly better than those of the potential model, but not significantly different. The neural network used as inputs for SOC estimation up to 1 m depth, the content of SOC in the upper 25 cm of the profile, land use, temperature, rainfall, and soil clay and silt content.

3.3. Modeling the spatial distribution of SOC

The spatial distribution of SOC as a function of land use, and its distribution in depth, was modeled by polynomial regression and neural networks with similar performance (Fig. 6). Both methods generated models with R^2 and RMSE that did not differ between training and validation sets, showing good generalization ability. Intercepts and slopes were not different from 0 and 1, and no significant differences were detected between the R^2 and RMSE of the modeling methods. Variables in the regression were the same as the inputs for neural networks: land use, depth, temperature, rainfall, clay and sand. Models showed that SOC increased as site annual rainfall and clay content of the soil layer were larger, whereas it decreased in deeper soil layers and when site mean temperature or soil sand content

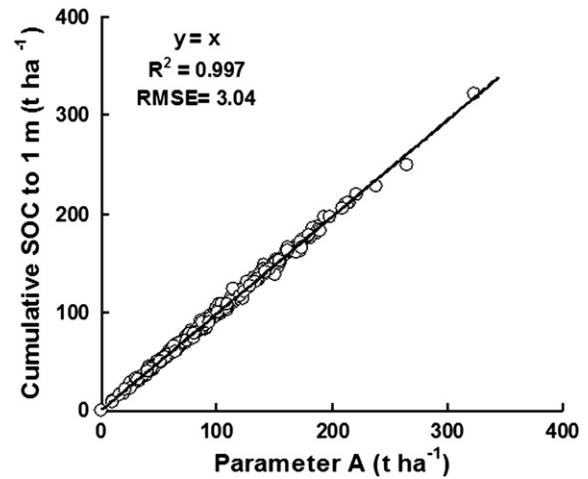


Fig. 4. Relationship between measured soil organic carbon (SOC) to 1 m depth and the parameter A of the potential model adjusted to 320 profiles of soils without petrocalcic horizon, to which the model fitted significantly.

increased. SIC could not be modeled adequately by any of the two methodologies ($R^2 < 0.20$).

Using data from soil surveys for an area of 74 Mha, performed mainly between 1960 and 1980, we estimated a SOC stock of 5.50 Gt and a SIC stock of 3.58 Gt up to 1 m depth for the whole Pampean Region (Fig. 7). Around 40% of the total soil carbon was present as inorganic compounds. The neural network model fitted to SOC data obtained in 2007–2008, linked to the results of satellite image classification, were used for estimation of SOC for an area of 48.2 Mha, corresponding to the humid and semi-arid portions of the Pampas. For this area, that includes the main cultivated portion of the region, SOC stock was 4.22 Gt. Soil survey information for this area during the 1960–1980 period indicated a SOC stock of 3.96 Gt. When comparing SOC in the 0–25 cm layer, SOC stocks were 2.04 Gt in 1960–1980 and 1.93 Gt in 2007–2008. At both moments, ca. 50% of SOC up to 1 m was allocated in the upper 25 cm of the profile.

Uncertainty of SOC stock estimations was low. When assessing for the cultivated portion of the Pampas the 1960–1980 stock in the 0–25 cm soil layer uncertainty was 9.8%, and 5.9% for the 2007–2008 survey, decreasing to 5.7 and 3.3% respectively for estimations of cumulative carbon to 1 m depth. In the 1960–1980 survey the main source of uncertainty was the area corresponding to each soil type described in soil maps. Uncertainty associated to the Walkley–Black method, modelization of SOC profiles in depth and soil bulk density estimation averaged 8% at the soil layer level. For the 2007–2008 estimation, model uncertainty and inputs uncertainty combined ranged from 35 to 49%, depending on land use and soil layer, meanwhile scaling uncertainty for average land use surface was around 68%. These results suggest that at regional scale SOC losses by cultivation in the Pampas were produced mainly before the 1960–1980 period and no significant differences are found during the last 30–50 years, because 95% confidence intervals of present and

Table 3

Performance of the potential model (Eq. (1)) fitted to cumulative organic carbon profiles of soils without petrocalcic horizon.

Vegetation type or land use cases	Cases	Significant cases (%)	R^2 range	RMSE (t ha ⁻¹)	Parameter A (t ha ⁻¹)			Parameter B			Cases with B > 1 (%)
					Min.	Mean	Max.	Min.	Mean	Max.	
Trees	74	99	0.94–0.99	4.1	36	131	324	0.24	0.58	1.00	0.0
Uncropped	74	95	0.95–0.99	3.2	31	104	213	0.13	0.53	1.05	2.7
Pasture	61	87	0.94–0.99	3.4	9.3	91	238	0.14	0.54	1.11	1.6
Cropped	72	93	0.95–0.99	3.1	16	88	173	0.24	0.57	1.65	1.4
Flooded	61	93	0.93–0.99	2.3	0.4	70	152	0.10	0.60	1.58	13.1

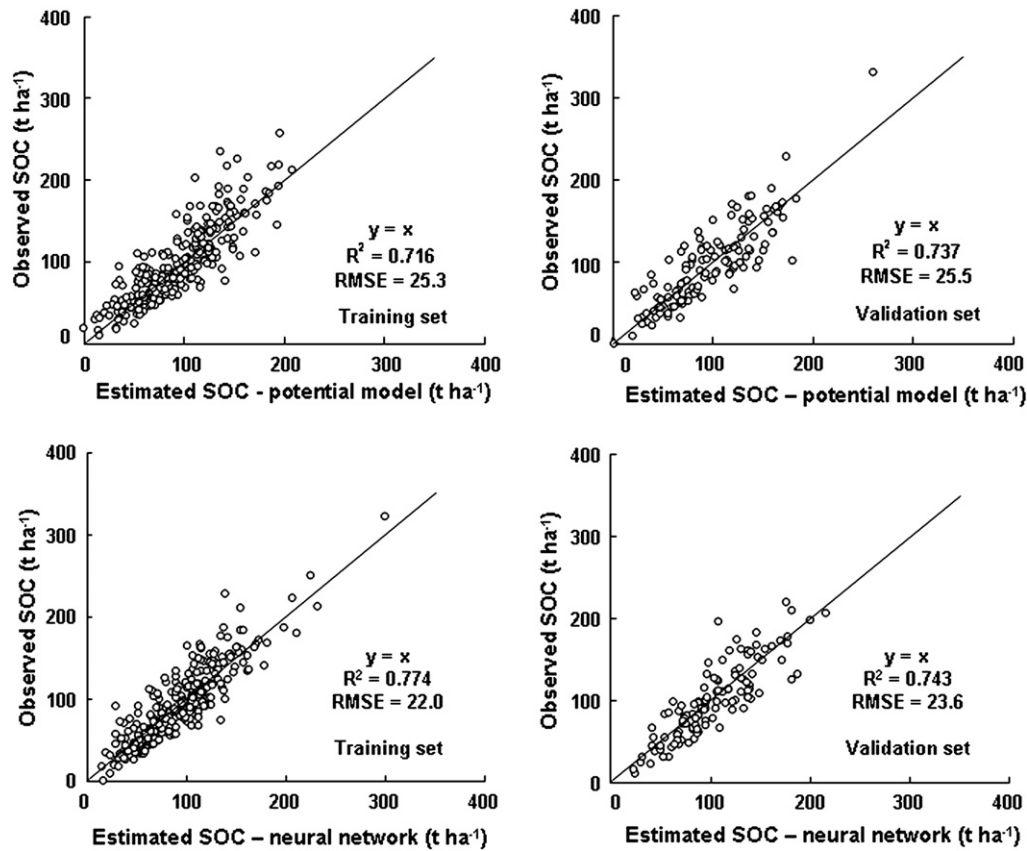


Fig. 5. Observed vs. estimated soil organic carbon (SOC) in the upper 1 m of soil profile using the potential model and an artificial neural network model.

past estimations overlaps. Conversely, when results were contrasted at county scale, soils with SOC content greater than 95 t ha⁻¹ tended to lose carbon. Meanwhile, below this threshold increases are more frequent (Fig. 8).

4. Discussion

Our uncropped control treatment should represent the soil conditions before the establishment of agriculture. In 22 farms controls were natural grasslands, but in 60 cases farm parks were used as controls. Local censuses have shown that plant species composition is very similar between farm parks and natural grasslands (R. León, unpublished data). The main difference between these two scenarios is that parks are not grazed and vegetation is periodically reaped. It was possible to compare paired situations of natural grasslands and parks in 11 farms, spread over the Pampean Region, using a paired t-test ($P < 0.05$). SOC was not different between natural grasslands and parks at any depth; neither significant differences were detected for the other variables addressed in this study; implying that parks seemed to be a good control treatment. Climatic environment was similar for all vegetation types and land uses at each farm and well drained soils of trees, uncropped, pasture and cropped treatments corresponded to the same Great Group of soils in all farms. For 50% of the farms information at the soil series level was available (INTA, 2010). In 95% of these farms the same soil series were found for trees, uncropped, pasture and cropped treatments. Consequently, climate and soil conditions were very similar under the contrasted vegetation types and land uses, except for hydromorphic soils, and comparison between treatments seemed not to be affected by these factors.

The densification observed in pampean soils subjected to agriculture could be caused by a combination of the effects of soil aggregates disruption by tillage (Carter, 1990), machinery transit (Richard et al.,

1999), and the decrease of SOC (Rawls, 1983). The small textural changes detected between treatments seem to be caused by erosion. Cropped soils have around 2–3% more clay in the upper soil layers than uncropped controls and trees. The loss of superficial soil by erosion and the mixing of the horizons by tillage may lead to this result. In the Pampas, B horizons are usually found in the 25 to 80 cm depth layer (INTA, 1981, 1983, 1989) and in areas where agricultural use of soils has been intensive for more than a century, the top 3–5 cm has been lost by erosion (Alvarez et al., 1995). Flooded soils are located in lowlands which receive eroded fine particles, leading to clay accumulation. Soil acidification and salt concentration increase under trees in relation to grasslands. These results can be attributed to differences in nutrient absorption, input of residues and water cycling between biomes (Jobbágy and Jackson, 2001, 2007). Cultivation usually reduces soil pH due to cation absorption and removal and also because of fertilizer reactions in soil, especially proton liberation by ammonia nitrification (Tisdale et al., 1993). This effect on pH was not detected in the Pampas where, depending on the subregion, cropping history is not longer than 60–130 years (Alvarez, 2001), and fertilizer use become important only a few years ago and at very low rates (FAO, 2004). SOC was 30% greater under trees than in the uncropped control. Similar results have been reported previously for other regions (Guo and Gifford, 2002) and it may be associated to a greater net primary productivity and carbon inputs of forests compared to grasslands (Dixon et al., 1994). In the Pampas some forested areas have been used as shelters for cows (Jobbágy and Jackson, 2007) which may produce an additional input of carbon from excretes. Agriculture usually determines a reduction of 30–50% of SOC in the upper 20–30 cm of the soil (Guo and Gifford, 2002). This effect is produced by the reduction of carbon inputs under cropping (Lauenroth et al., 2000) as a consequence of fallowing and harvesting, and higher soil temperatures of tilled soils (Grant et al., 1995), which increase mineralization. In the Pampas, estimated crop carbon inputs rounded

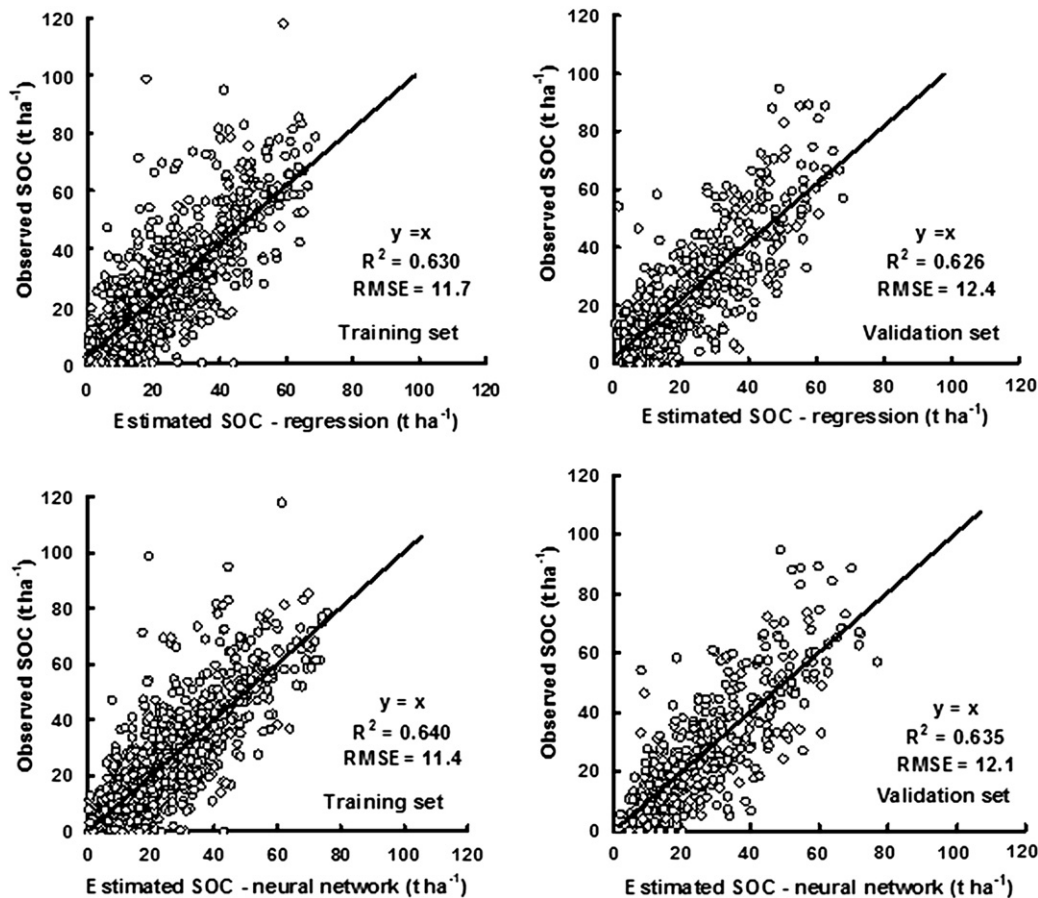


Fig. 6. Observed vs. estimated soil organic carbon (SOC), using a multiple regression model or an artificial neural network for all depth layer samples.

30–70% of grasslands inputs (Alvarez and Steinbach, 2010). This reduction of carbon inputs led to SOC depletion in the upper 1 m of soil profile, although significant differences could be detected only up to 50 cm. Soil erosion is also responsible for surface carbon losses in a central pampean subregion (the Rolling Pampa) in which an average lost of 4 cm of the A horizon has been estimated (Alvarez et al., 1995). In this subregion soil erosion would be responsible for a reduction of 8% of the SOC stock to 1 m depth.

Rotation phase has a small, not significant impact on SOC of around 5% in our sampled sites. Long-term experiments showed that in both, the humid (Casanovas et al., 1995) and the semi-arid (Galantini, 2005) subregions of the Pampas, few years under seeded pastures have a minor effect on SOC increasing mainly labile organic matter fractions. Net primary productivity is restricted in flooded soils of the Pampas and productivity is around 35% lower than in well drained soils (Paruelo et al., 2010). As a consequence, lower SOC levels may be expected in these soils than in controls, as observed in our study.

Despite differences in the mass of SOC sequestered under contrasting vegetation types and land uses, the stratification pattern was not significantly affected by treatments in the Pampas, as indicated by the estimated values of the *B* parameter from the potential model. The election of paired sites for sampling is a powerful technique that allows detecting SOC changes better than other methods (Heim et al., 2009). When climate and soil properties do not vary between paired treatments in the region, SOC followed a similar trend in depth, but with great variability. Studies performed in other regions of the World have modeled the effect of environmental variables on SOC stratification using neural networks to predict the value

of model parameters fitted to SOC profiles (Minasny et al., 2006). We could not model the *B* parameter satisfactorily ($R^2 < 0.20$) with regression methods and neural networks (results not presented). As a consequence, only the average *B* parameter can be used for SOC estimation in depth taking SOC in the 0–25 cm layer as an independent variable. Cropping impacted SOC significantly up to 50 cm but not deeper. Average SOC was also reduced by agriculture below 50 cm but, because of variability, significance was not attained. This may explain why the *B* parameter was not affected by land use. Our data suggested that the whole SOC profile up to 1 m was altered by management.

The three-dimensional spatial distribution of pampean SOC at the site level could be adequately estimated by empirical modeling with regression and neural network models. Both techniques have equal performance with RMSE equivalent to 13% of the mean. Conversely, comparison of regression and neural networks for SOC prediction in other regions displayed a better fit of the latter method (Somaratne et al., 2005). The magnitude of the area from which predictions are made and its range of variability impact model fit. For small regions better adjustments may be obtained (Meersmans et al., 2009) than when modeling results for large areas or at a global scale (Grey et al., 2009), but our models did a good job for the entire Pampean Region. Better fits than those obtained in the current study were previously reported for SOC estimation in the Pampas using regression techniques (Alvarez, 2005; Alvarez and Lavado, 1998), but the models adjusted in those studies used integrated data for areas of around 1.5 Mha. Integration of data at regional scales allowed improving the fit by averaging outliers, with greater improvement as the area increases (Bakker et al., 2005). Those previous models were not able to

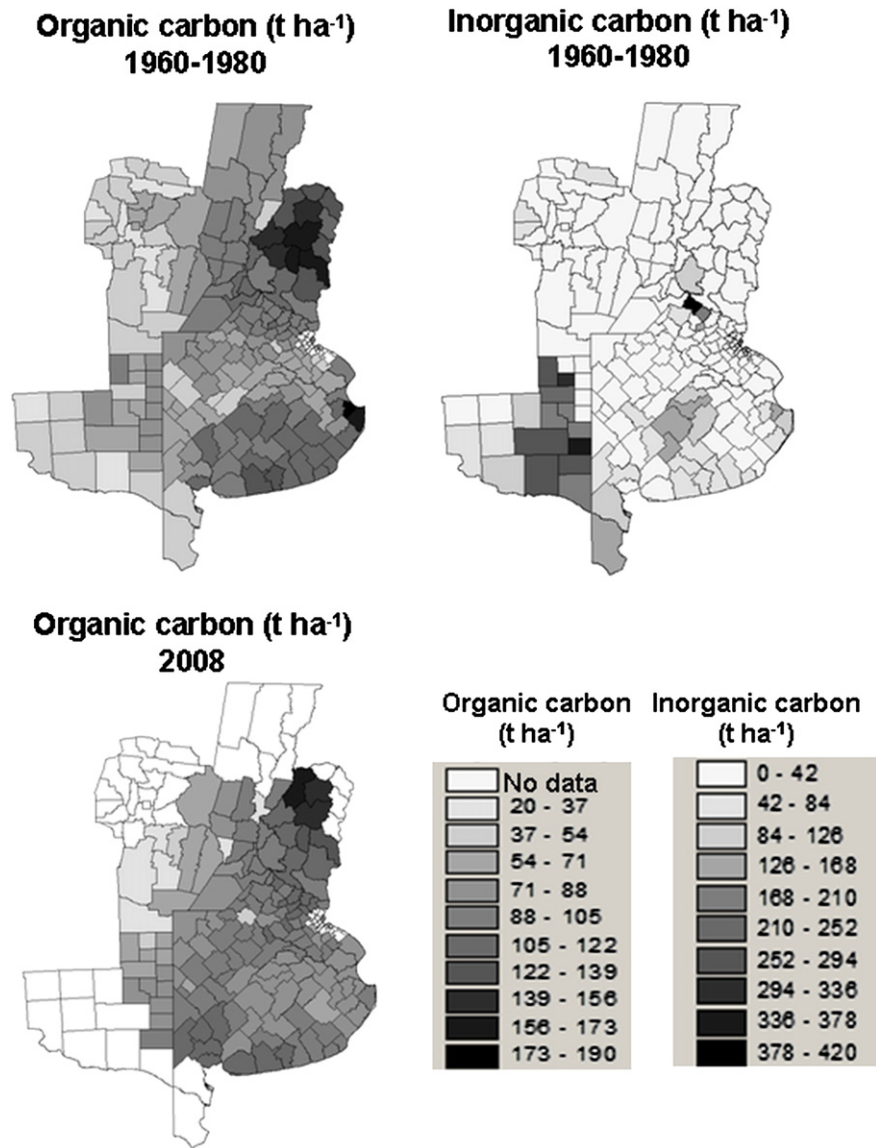


Fig. 7. Carbon stock in pampean soils as surveyed by INTA (1960–1980) and in 2007–2008, estimated using the neural network model developed and results from satellite image classification.

estimate SOC at site level or to discriminate between vegetation types or land uses.

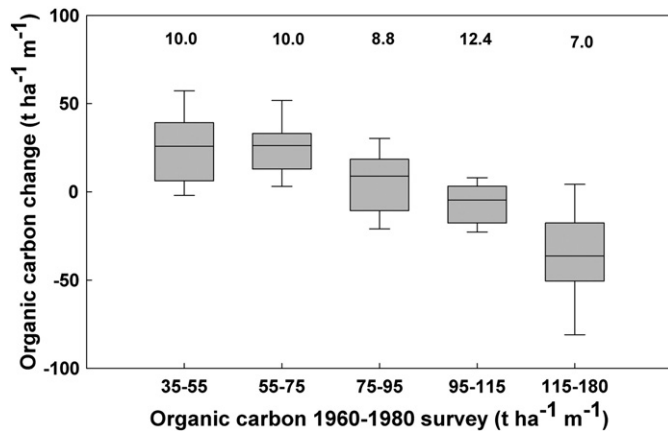


Fig. 8. Box plot (5, 25, 50, 75 and 95% percentiles) of the soil organic carbon content change up to 1 m depth at county scale between 2007–2008 and 1960–1980, as a function of SOC in 1960–1980. Numbers over the bars indicate the area corresponding to each SOC range (Mha).

The effect of land use on SOC was estimated assuming that flooded land surface and forested areas remained unchanged during the last 150 years, a period during which agriculture was introduced and expanded in the region replacing natural grasslands. If the area cropped nowadays was initially grasslands, we estimate a net flux of 326 Mt of carbon to the atmosphere for the surveyed portion of the Pampas. This value is equivalent to 9 years of regional fossil fuel consumption (CIA World Factbook, 2008).

The overall change in the pampean SOC stock seemed to be produced before 1960–1980, as estimates of SOC at this time and nowadays are similar. The intensification of agricultural use of soils, linked to the introduction of soybean in rotations, apparently has no negative impact on sequestered carbon stock in the Pampas. Nevertheless, our comparison of SOC levels at two different periods must be taken with care because different methodologies were applied in each case. The use of datasets from soil surveys not performed for SOC evaluation, which lacks management information (Frogbrook et al., 2009), uncertainties in bulk density (Bell and Worrall, 2009), and estimations performed at great scales (Gojdt, et al., 2009) are important error sources. These reasons may explain the greater uncertainty of SOC stock estimation calculated using the 1960–1980 soil survey than the 2007–2008 survey. The former was not focused

on SOC stock estimation and land use was not assessed. In the 2007–2008 period soil sampling was stratified by land use and soil depth, decreasing uncertainty. Nevertheless, uncertainty in both cases was low in relation to other studies (Ogle et al., 2003). This may be attributed to the great number of categories aggregated. Aggregation in an inventory produces a decrease of the overall uncertainty in comparison to single category uncertainty (IPCC, 2006).

The estimations performed in the present study contrasts with a previous one using the IPCC methodology. In the latter research losses of soil carbon were estimated during the last 50 years in pampean soils (Viglizzo et al., 2010). We tested the accuracy of the IPCC method for SOC estimation at our sampled sites. Using the average *B* parameter fitted, SOC in the 0–30 cm soil layer was estimated and confronted to IPCC values for unaltered and cropped conditions ($n = 230$). Poor results were obtained (regression of observed vs. predicted values $R^2 = 0.26$, $a \gg 0$, $b \ll 1$) indicating that this methodology is unsuitable for pampean soils.

Recent studies have reported different patterns in the change of SOC at cropped areas of the World during the last decades. While many European soils are losing SOC (Jones et al., 2009), in USA some soils reached equilibrium ca. 50 years ago (David et al., 2009), and net gains have been detected in eastern China (Sun et al., 2009). Increases of net primary productivity in natural and managed ecosystems have been described as a consequence of climate change and technology (Twine and Kucharik, 2009). These increases lead to greater carbon inputs to the soils and may produced SOC gains. In the Pampas, increases of carbon inputs to the soil have been estimated during the past 30 years in cropped soils, despite the inclusion of soybean in rotations (Alvarez et al., 2011). This process was the consequence of yield increases of wheat and corn crops, associated to greater straw and root production. Greater carbon inputs seem to equilibrate losses and allow carbon gains in soils with low SOC but not in rich ones. Soil carbon budgets performed in field experiments in the Pampas have shown that under cropping soils with high SOC content lose carbon (Alvarez et al., 1998). Meanwhile, soils with poor SOC have lower losses, or are near steady state (Bono et al., 2008). Additionally, rainfall increases have been registered mainly in the semiarid portion of the Pampas during the last 40 years (Magrin et al., 2005) which can also lead to higher productivity on coarse-low SOC soils.

Similar results were obtained with SIC data from the 2007–2008 sampling and data of soil surveys from the period 1960–1980. On average, 35–40% of total soil carbon is present as SIC in pampean soils ranging between 0 and 30% in the humid portion of the Pampas and between 0 and 85% in the semiarid one. Results like those observed here have been reported for other regions of the World (Li et al., 2007). Petrocalcic horizons were scarcely found under humid environments but they were common under arid conditions. In the dry West part of the region, in some soils up to 99% of SIC was estimated to be contained in petrocalcic horizons. Our estimations of SIC in cases where petrocalcic horizons were present in soils must be taken with care because their thickness was not determined at each site. Despite this constraint, similar results were obtained when analyzing data of SIC taking into account the carbon content on petrocalcic horizons or not. Significant impacts of vegetation or land use were not detected. Agriculture did not affect SIC of soils. This result could be the consequence of the short cropping history and low fertilizer rates used in the Pampas.

5. Conclusion

This study determined the effect of land use on SOC and SIC stocks its profile distribution in the Pampas. The main conclusions are: 1) Land use impacted SOC stock but not its stratification pattern in depth. Cultivation determined a reduction of 16% of SOC to 50 cm depth. From 50 to 100 cm depth a 9% decrease of SOC was detected

though not significant. 2) Total regional SOC stock (48.2 Mha) was estimated as 4.22 ± 0.14 Gt to 1 m depth, without changes during the last decades. Since 1960–80 to the present, areas with SOC content greater than 95 t ha^{-1} tended to lose carbon. Below this threshold increases were estimated. 3) SIC accounted for one third of total soil carbon stock. Land use had no effect on both its amount and distribution in depth.

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References

- Alvarez, R., 2001. Estimation of carbon losses by cultivation from soils of the Argentine Pampa using the Century model. *Soil Use and Management* 17, 62–66.
- Alvarez, R., 2005. Carbon stocks in pampean soils: a simple regression model for estimation of carbon storage under non degraded scenarios. *Communications in Soil Science and Plant Analysis* 36, 1583–1589.
- Alvarez, R., 2009. Predicting average regional yield and production of wheat in the Argentine Pampas by an artificial network approach. *European Journal of Agronomy* 30, 70–77.
- Alvarez, R., Lavado, R.S., 1998. Climatic control of the organic matter of the Pampas and Chaco soils. *Geoderma* 83, 127–141.
- Alvarez, R., Steinbach, H.S., 2010. Efecto del uso agrícola sobre el nivel de materia orgánica. Fertilidad de suelos. Caracterización y manejo en la Región Pampeana. Editorial Facultad de Agronomía-Universidad de Buenos Aires, Argentina, p. 181202.
- Alvarez, R., Santanoglia, O.J., Garcia, R., 1995. Soil respiration and carbon inputs from crops in a wheat–soybean rotation under different tillage systems. *Soil Use and Management* 11, 45–50.
- Alvarez, R., Russo, M., Prystupa, P., Sheiner, J., Blotta, L., 1998. Soil carbon pools under conventional and no-tillage systems in the Argentine Rolling Pampa. *Agronomy Journal* 90, 138–143.
- Alvarez, R., Steinbach, H.S., Bono, A., 2011. An artificial neural network approach for predicting soil carbon budget in agroecosystems. *Soil Science Society of America Journal* 75, 965–975.
- Amato, M., 1983. Determination of ^{12}C and ^{14}C in plant and soil. *Soil Biology and Biochemistry* 15, 611–612.
- Bakker, M.M., Govers, G., Ewert, F., Rounsewell, M., Jones, R., 2005. Variability in regional wheat yield as a function of climate, soil and economic variables: assessing the risk of confounding. *Agriculture, Ecosystems & Environment* 110, 195–209.
- Bell, M.J., Worrall, F., 2009. Estimating a region's soil organic carbon baseline: the undervalued role of land-management. *Geoderma* 152, 74–84.
- Bernoux, M., Arrouays, D., Cerri, C.C., Bourennane, H., 1998. Modeling vertical distribution of carbon in Oxisols of the western Brazilian Amazon (Rondonia). *Soil Science* 163, 941–951.
- Bishop, T.F.A., McBratney, A.B., Laslett, G.M., 1999. Modelling soil attribute depth function with equal-area quadratic smoothing splines. *Geoderma* 91, 27–45.
- Bono, A., Alvarez, R., Buschiazzi, D.E., Cantet, R., 2008. Tillage effects on soil carbon balance in a semiarid agroecosystem. *Soil Science Society of America Journal* 72, 1140–1149.
- Brouwer, R.K., 2004. A hybrid neural network for input that is both categorical and quantitative. *International Journal of Intelligent Systems* 19, 979–1001.
- Burke, I.C., Yonker, C.M., Parton, W.J., Cole, C.V., Flach, K., Schimel, D.S., 1989. Texture, climate, and cultivation effects on soil organic matter content in U.S. grasslands soils. *Soil Science Society of America Journal* 53, 800–805.
- Carter, M.R., 1990. Relative measures of soil bulk density to characterize compaction in tillage studies on fine sandy loams. *Canadian Journal of Soil Research* 70, 425–433.
- Casanovas, E.M., Echeverría, H.E., Studdert, G.A., 1995. Materia orgánica del suelo bajo rotaciones de cultivos. I Contenido total y de distintas fracciones. *Ciencia del Suelo* 13, 16–20.
- CIA World Factbook, 2008. available in: www.cia.gov/2008.
- Congalton, R., 1991. A review of assessing the accuracy of classifications of remotely sensed data. *Remote Sensing of Environment* 37, 35–46.
- Conover, W.J., 1999. *Practical Nonparametric Statistics*. John Wiley & Sons Inc., New York, p. 488.
- David, M.B., McIsaac, G.F., Darmody, R.G., Omonde, R.A., 2009. Long-term changes in Mollisol organic carbon and nitrogen. *Journal of Environmental Quality* 38, 200–211.
- Davidson, E.A., Ackerman, I.L., 1993. Changes on soil carbon inventories following cultivation of previously untilled soils. *Biogeochemistry* 20, 161–193.
- Dixon, R.K., Brown, S., Houghton, R.A., Solomon, A.M., Trexler, M.C., Wisniewski, J., 1994. Carbon pools and flux of global ecosystem. *Science* 263, 185–190.
- FAO, 2004. Fertilizer use by crop in Argentina. Rome, Italy, p. 88.
- FAO, 2006. LocClim. Local Climate Estimator Version 1.10. FAO/SDRN. Rome; Italy. www.fao.org/sd/locclim/srv/locclim.home2006.
- Fila, G., Bellocchi, G., Acutis, M., Donatelli, M., 2003. IRENE: a software to evaluate model performance. *European Journal of Agronomy* 18, 369–372.
- Frogbrook, Z.L., Bell, J., Bradley, R.I., Evans, C., Lark, R.M., Reynolds, B., Smith, P., Towers, W., 2009. Quantifying terrestrial carbon stocks: examining the spatial variation in

- two upland areas of UK and a comparison to mapped estimates of soil carbon. *Soil Use and Management* 25, 320–332.
- Galantini, J., 2005. Calidad y dinámica de las fracciones orgánicas en sistemas naturales y cultivados. *Proceedings Jornadas Materia Orgánica y Sustancias Húmicas*. Argentina, p. 6.
- Gee, G.W., Bauder, J.W., 1996. Particle-size analysis. Part 3—Physical and Mineralogical Methods. Madison; Wisconsin; USA: *Methods of Soil Analysis*. Soil Sci. Soc. Am. Book Series, 5, pp. 383–412.
- Gevey, M., Dimopoulos, I., Lek, S., 2003. Review and comparison of methods to study the contribution of variables in artificial neural network models. *Ecological Modelling* 160, 249–264.
- Goidts, E., van Wesemael, B., Crucifix, M., 2009. Magnitude and sources of uncertainties in soil organic carbon (SOC) stock assessment at various scales. *European Journal of Soil Science* 60, 723–739.
- Grant, R.F., Izaurralde, R.C., Chanasyk, D.S., 1995. Soil temperature under different surface managements: testing a simulation model. *Agricultural and Forest Meteorology* 73, 89–113.
- Grey, J.M., Humphreys, G.S., Deckers, J.A., 2009. Relationships in soil distribution as revealed by a global soil database. *Geoderma* 150, 309–323.
- Guerschman, J.P., Paruelo, J.M., Di Bella, C.M., Giallorenzi, M.C., Pacino, F., 2003. Land cover classification in the Argentine Pampas using multi-temporal LANDSAT TM data. *International Journal of Remote Sensing* 24, 3381–3402.
- Guo, L.B., Gifford, M., 2002. Soil carbon stocks and land use change: a meta analysis. *Global Change Biology* 8, 345–360.
- Hall, A.J., Rebella, C.M., Ghera, S.M., Culot, J.P., 1992. Field crop systems of the Pampas. In: Pearson, C.J. (Ed.), *Field crop ecosystems of the World*, 18. Elsevier, Amsterdam, pp. 413–450.
- Hassink, J., 1997. The capacity of soils to preserve organic C and N by their association with clay and silt particles. *Plant and Soil* 191, 77–87.
- Heim, A., Wehrli, L., Eugster, W., Schmidt, M.W.J., 2009. Effects of sampling design on the probability to detect soil carbon stock changes at the Swiss CarboEurope site Lägeren. *Geoderma* 149, 347–354.
- Houghton, R.A., Hobbie, J.E., Melillo, J.M., Moore, B., Peterson, B.J., Shaver, G.R., Woodwell, G.M., 1983. Changes in the carbon content of terrestrial biota and soils between 1860 and 1980: a net flux release of CO₂ to the atmosphere. *Ecological Monographs* 53, 235–262.
- INDEC, 2002. Censo Nacional de Población, Hogares y Viviendas available at [http://www.indec.gov.ar/agropecuaria/cna.asp2002\(10/12/1910\)](http://www.indec.gov.ar/agropecuaria/cna.asp2002(10/12/1910)).
- INTA, 1980. Inventario integrado de los recursos naturales de la Provincia de La Pampa. Instituto Nacional de Tecnología Agropecuaria, Buenos Aires, Argentina, p. 493.
- INTA, 1981. Mapa de suelos de la Provincia de Santa Fe, Parte I. Instituto Nacional de Tecnología Agropecuaria, Buenos Aires, Argentina, p. 245.
- INTA, 1983. Mapa de suelos de la Provincia de Santa Fe, Parte II. Instituto Nacional de Tecnología Agropecuaria, Buenos Aires, Argentina, p. 216.
- INTA, 1984. Plan mapa de suelos de la Provincia de Entre Ríos. Convenio INTA-Gobierno de Entre Ríos. Suelos y erosión de la provincia de Entre Ríos. Paraná, Entre Ríos, INTA-EEA, p. 1408.
- INTA, 1989. Mapa de suelos de la Provincia de Buenos Aires. Instituto Nacional de Tecnología Agropecuaria, Buenos Aires, Argentina, p. 525.
- INTA, 2003. Agencia Córdoba Ambiente. Recursos naturales de la Provincia de Córdoba, p. 512.
- INTA, 2010. available at: <http://geointa.inta.gov.ar2010>.
- IPCC, 2006. IPCC guidelines for National Greenhouse Gas Inventories. In: Eggleston, H.S., Miwa, K., Ngara, T., Tanabe, K. (Eds.), Chapter 3: Uncertainties. General Guidance and reporting, vol. 1. IGES, Japan, 66 pg.
- Jackson, R.B., Canadell, J., Ehleringer, J.R., Mooney, H.A., Sala, O.E., Schulze, E.D., 1996. A global analysis of root distributions for terrestrial biomes. *Oecologia* 108, 389–411.
- Jobbágy, E.G., Jackson, R.B., 2000. The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecological Applications* 10, 423–436.
- Jobbágy, E.G., Jackson, R.B., 2001. The distribution of soil nutrients with depth: global patterns and the imprint of plants. *Biogeochemistry* 53, 51–77.
- Jobbágy, E.G., Jackson, R.B., 2007. Groundwater and soil chemicals changes under phreatophytic tree plantation. *Journal of Geophysical Research* 112, 1–15.
- Jones, R.J.A., Stolbovoy, V., Rusco, E., Gentile, A.R., Gardi, C., Marechal, B., Montanarella, L., 2009. Climate change in Europe. 2. Impact on soil. A review. *Agronomy* 29, 423–432.
- Kleinbaum, D.G., Kupper, L.L., 1979. *Applied Regression Analysis and Other Multivariable Methods*. Duxbury Press, Massachusetts; USA, p. 555.
- Kobayashi, K., Salam, M.U., 2000. Comparing simulated and measured values using mean square deviation and its components. *Agronomy Journal* 92, 345–352.
- Lauenroth, W.K., Burke, I.C., Paruelo, J.M., 2000. Patterns of production and precipitation-use efficiency of winter wheat and native grasslands in the Central Great Plains of the United States. *Ecosystems* 3, 334–351.
- Li, Z.P., Han, F.X., Su, Y., Zhang, T.L., Sun, B., Monts, D.L., Plodinec, M.J., 2007. Assessment of soil organic and carbonate carbon storage in China. *Geoderma* 138, 119–126.
- Liang, B.C., Campbell, C.A., McConkey, B.G., Padbury, G., Collas, P., 2005. An empirical model for estimating carbon sequestration on the Canadian prairies. *Canadian Journal of Soil Science* 85, 549–556.
- Lillesand, T.M., Kiefer, R.W., 1994. *Remote Sensing and Image Interpretation*. John Wiley & Sons, New York.
- Littell, R.C., Henry, P.R., Ammerman, C.B., 1998. Statistical analysis of repeated measures data using SAS procedures. *Journal of Animal Science* 76, 1216–1231.
- Loeppert, R.H., Suarez, D.L., 1996. Carbonate and gypsum. In: *Methods of Soil Analysis*. Part 3—Chemical Methods. Madison; Wisconsin; USA: Soil Sci. Soc. Am. Book Series, 5, pp. 437–474.
- Magrin, G.O., Travasso, M.I., Rodríguez, G.R., 2005. Changes in climate and crop production during the 20TH century in Argentina. *Climatic Change* 72, 229–249.
- Mahibbur, R.M., Govindarajulu, Z., 1997. A modification of the test of Shapiro and Wilks for normality. *Journal of Applied Statistics* 24, 219–235.
- Meersmans, J., De Ridder, F., Canters, F., De Baets, S., Van Molle, M., 2008. A multiple regression approach to assess the spatial distribution of soil organic carbon (SOC) at regional scale (Flanders; Belgium). *Geoderma* 143, 1–13.
- Meersmans, J., Van Wesemael, B., De Ridder, F., Van Molle, M., 2009. Modelling the three-dimensional spatial distribution of soil organic carbon (SOC) at regional scale (Flanders, Belgium). *Geoderma* 152, 43–52.
- Miao, Y., Mulla, D.J., Robert, P.C., 2006. Identifying important factors influencing corn yield and grain quality variability using artificial neural networks. *Precision Agriculture* 7, 117–135.
- MinAgri, 2010. Series y estadísticas agrícolas disponible en: www.minagri.gov.ar2010.
- Minasny, B., McBratney, A.B., Mendonça-Santos, M.L., Odeh, I.O.A., Guyon, B., 2006. Prediction and digital mapping of soil carbon storage in the Lower Namoi Valley. *Australian Journal of Soil Research* 44, 233–244.
- Mishra, U., Lal, R., Slater, B., Calhoun, F., Liu, D., Van Meirvenne, M., 2009. Predicting soil organic carbon stock using profile depth distribution functions and ordinary kriging. *Soil Science Society of America Journal* 73, 614–621.
- Moreno, F., Murillo, J.M., Pelegrín, F., Girón, I.F., 2006. Long-term impact of conservation tillage on stratification ratio of soil organic carbon and loss of total and active CaCO₃. *Soil and Tillage Research* 85, 86–93.
- Nelson, L., Sommers, L.E., 1996. Total carbon, organic carbon, and organic matter. In: Sparks, D.L. (Ed.), *Methods of Soil Analysis*. Part 3 - Chemical Methods: Soil Science of America. Madison, Wisconsin, USA, pp. 961–1010.
- Neter, J., Wasserman, W., Kutner, M.H., 1990. *Applied Linear Statistical Models*. Irwin, Illinois; USA, p. 1172.
- Nordt, L.C., Hallmark, C.T., Wilding, L.P., Boutton, T.W., 1998. Quantifying pedogenic carbonate accumulation using stable carbon isotopes. *Geoderma* 82, 115–136.
- Ogle, S.M., Breidt, F.J., Eve, M.D., Paustian, K., 2003. Uncertainty in estimating land use and management impacts on soil organic carbon storage for US agricultural lands between 1982 and 1997. *Global Change Biology* 9, 1521–1542.
- Özesmi, S.L., Tan, C.O., Özesmi, U., 2006. Methodological issues in building, training, and testing artificial neural networks in ecological applications. *Ecological Modelling* 195, 83–93.
- Park, S.J., Vlek, P.L.G., 2002. Environmental correlation of three-dimensional soil spatial variability: a comparison of three adaptive techniques. *Geoderma* 109, 117–140.
- Paruelo, J.M., Piñeiro, G., Baldi, G., Baeza, S., Lezama, F., Altesor, A., Oesterheld, M., 2010. Carbon stocks and fluxes in rangelands of the Río de la Plata basin. *Rangeland Ecology & Management* 63, 94–108.
- Pazos, M.S., Mestelan, S.A., 2002. Variability of depth to toska in Udolls and soil classification. Buenos Aires Province, Argentina. *Soil Science Society of America Journal* 66, 1256–1264.
- Peltier, M.R., Wilcox, C.J., Sharp, D.C., 1998. Technical note: application of the Box–Cox data transformation to animal science experiment. *Journal of Animal Science* 76, 847–849.
- Post, W.M., Emanuel, W.R., Zinke, P.J., Stangenberger, A.G., 1982. Soil carbon pools and world life zones. *Nature* 298, 156–159.
- Poultou, P.R., Pye, E., Hargreaves, P.R., Jenkinson, D.S., 2003. Accumulation of carbon and nitrogen by old arable land reverting to woodland. *Global Change Biology* 9, 942–955.
- Rawls, W.J., 1983. Estimating soil bulk density from particle size analysis and organic matter content. *Soil Science* 135, 123–125.
- Rhoades, J.D., 1996. Salinity: electrical conductivity and total dissolved solids. *Methods of Soil Analysis*, Part 3, Chemical Methods, Chapter 14. : Soil Sci. Soc. Am. Book Series, 5. Soil Science Society of America Inc., Madison, USA, pp. 417–435.
- Richard, G., Boizard, H., Roger-Estrade, J., Boiffin, J., Guérif, J., 1999. Field study of soil compaction due to traffic in Northern France: pore space and morphological analysis of the compacted zones. *Soil and Tillage Research* 51, 151–160.
- Richter, M., Massen, G., Mizuno, I., 1973. Total organic carbon and oxidizable organic carbon by the Walkley–Black procedure in some soils of the Argentine Pampa. *Agrochemical* 17, 462–473.
- Rogers, L.L., Dowla, F.U., 1994. Optimization of groundwater remediation using artificial neural networks with parallel solute transport modeling. *Water Research* 30, 457–481.
- SAGyP-INTA (National Institute for Agricultural Technology - Department of Agriculture, Livestock and Fisheries), 1990. *Soil Atlas of Argentina*. SAGyP INTA, Buenos Aires, Argentina.
- Satorre, E.H., Slafer, G.A., 1999. Wheat production systems of the Pampas. In: Satorre, E.M., Slafer, G.A. (Eds.), *Wheat. Ecology and physiology of yield determination*. The Haworth Press Inc., New York, pp. 333–348.
- Schulp, C.J.E., Nabuurs, G.J., Verburg, P.H., 2008. Future carbon sequestration in Europe—effects of land use change. *Agriculture, Ecosystems & Environment* 127, 251–264.
- Searle, S.R., 1971. *Linear Models*. Wiley, New York.
- Shen, J., Li, R., Zhang, F., Rengel, Z., Tang, C., 2003. Orthogonal polynomial models to describe yield response of rice to nitrogen and phosphorus at different levels of soil fertility. *Nutrient Cycling in Agroecosystems* 65, 243–252.
- Slobodian, N., Van Rees, K., Pennock, D., 2002. Cultivation-induced effects on below-ground biomass and organic carbon. *Soil Science Society of America Journal* 66, 924–930.
- Soil Taxonomy, 1975. A basic system of soil classification for making and interpreting soil surveys. United States Department of Agriculture, 572 pp.
- Somaratne, S., Seneviratne, G., Coomaraswamy, U., 2005. Prediction of soil organic carbon across different land-use patterns: a neural network approach. *Soil Science Society of America Journal* 69, 1580–1589.

- Soriano, A., 1991. Río de la Plata Grasslands. In: Coupland, R.T. (Ed.), *Ecosystems of the world*. 8A. Natural Grassland. Elsevier, Amsterdam, pp. 367–407.
- Sun, W., Huang, Y., Zhang, W., Yu, Y., 2009. Estimating topsoil SOC sequestration in croplands of eastern china from 1980–2000. *Australian Journal of Soil Research* 47, 261–272.
- Teruggi, M.E., 1957. The nature and origin of argentine loess. *Journal of Sedimentary Research* 27, 322–332.
- Tisdale, S., Nelson, W.L., Beaton, J.D., Haulin, J.L., 1993. *Soil Fertility and Fertilizers*. Mcmillan Publishing Company, New York, USA. 631 pp.
- Tou, J.T., Gonzalez, R.C., 1974. *Pattern recognition principles*. Addison-Wesley Publishing Company, Reading Massachusetts.
- Twine, T.E., Kucharik, C.J., 2009. Climate impacts on net primary productivity trends in natural and managed ecosystems of the central and eastern United States. *Agricultural and Forest Meteorology* 149, 2143–2161.
- Viglizzo, E.F., Létora, F., Pordomingo, A.J., Bernardos, J.N., Roberto, Z.E., Del Valle, H., 2001. Ecological lessons and applications from one century of low external-input farming in the pampas of Argentina. *Agriculture, Ecosystems & Environment* 83, 64–81.
- Viglizzo, E.F., Frank, F.C., Carreño, L.V., Jobbágy, E.G., Pereyra, H., Clatt, J., Pincén, D., Ricard, F., 2010. Ecological and environmental footprint of 50 years of agricultural expansion in Argentina. *Global Change Biology* 17, 959–973.
- Wu, H., Guo, Z., Gao, Q., Peng, C., 2009. Distribution of soil inorganic carbon storage and its changes due to agricultural land use activity in China. *Agriculture, Ecosystems and Environment* 129, 413–421.
- Xiong, R., Meullenet, J.F., 2006. A PLS dummy variable approach to assess the impact of jar attributes on linking. *Food Quality* 17, 188–198.
- Yang, Y., Mohammat, A., Feng, J., Zhou, R., Fang, J., 2007. Storage, patterns and environmental controls of soil organic carbon in China. *Biogeochemistry* 84, 121–141.