Nutr Cycl Agroecosyst
https://doi.org/10.1007/s10705-017-9896-0

CrossMark

ORIGINAL ARTICLE

Land use affected nutrient mass with minor impact on stoichiometry ratios in Pampean soils

Roberto Alvarez · Analía Gimenez · María M. Caffaro · Federico Pagnanini · Verónica Recondo · Cecilia D. Molina · Gonzalo Berhongaray · María R. Mendoza · Denise A. Ramil · Facundo Facio · Josefina L. De Paepe · Haydee S. Steinbach · Rodolfo J. Cantet

Received: 1 September 2017 / Accepted: 20 November 2017

Abstract The effect of land use on soil nitrogen (N) and phosphorous (P) stocks and the stoichiometry ratios are not fully understood. We determined the impact of land use on total N and P stocks along with some of their fractions and carbon (C), N and P ratios in soils of the Pampas. The effect of human activities on N and P fluxes in agroecosystems was also assessed. We sampled 386 soils under contrasting land uses down to 1 m depth. Well drained uncultivated soils were used as control treatment, paired with forest, cropped and flooded soils. Significant effects of land use on N and P stocks were detected to 1 m depth. Cropping decreased soil total N and P contents, mineralizable N and extractable P by an average of 14, 21 and 63% respectively. Conversely, forest soils had larger total N stocks (17%), mineralization (10%) and extractable P (37%) than uncropped controls. Flooded lands had the lowest fertility. Nitrogen and P pools under cultivation decreased higher as soils had higher initial levels N and P. In some low fertility soils, cropping led to N and P increases. Stoichiometry ratios were minimally impacted by land use. The ratio of the cumulative P surface balance to the N surface balance for the last 140 years was + 0.01 kg P/kg N in uncropped control soils and − 0.08 kg P/kg N in cropped soils. Despite this difference, the soil N/P ratio was unaffected by land use indicating that processes at the profile level regulated it.

Keywords Land use · Total soil nitrogen · Total soil phosphorus · Nitrogen mineralization · Labile soil phosphorus · Stoichiometry ratios · Pampean region

R. Alvarez (✉) · A. Gimenez · M. M. Caffaro · F. Pagnanini · V. Recondo · C. D. Molina · M. R. Mendoza · D. A. Ramil · F. Facio · J. L. De Paepe · H. S. Steinbach · R. J. Cantet
Facultad de Agronomía, Universidad de Buenos Aires, Av. San Martín 4453 (1417), Buenos Aires, Argentina
e-mail: ralvarez@agro.uba.ar

R. Alvarez · M. M. Caffaro · C. D. Molina · G. Berhongaray · J. L. De Paepe · R. J. Cantet
Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina

Introduction

Organic matter affects soil productivity (De Paepe and Alvarez 2013) and it is a crucial component of the biogeochemical cycle of C and of some nutrients such as nitrogen (N) (Manlay et al. 2007). Many studies worldwide have been carried out to establish how climate, soil properties and land use impact C sequestration (Franzluebbers and Follett 2005; Jobbágy and Jackson 2000; Jones et al. 2005) but fewer efforts were invested to better understand how these factors impact on nitrogen and phosphorus (P) accumulation in soils and how external nutrient fluxes can regulate N and P stocks.

Published online: 23 November 2017

The model of McGill and Cole (1981) proposes that soil organic C and N changes are tightly associated, because C bounded N is mineralized when microorganisms degrade organic compounds in need of energy. Conversely, P is released from organic reservoirs only when needed, a nutrient whose dynamics is dissociated from that of C. There are several studies supporting the model which use data from hundreds to thousands of soils, and show that soil organic C is highly correlated to total soil N (total N). However, the correlation with total soil P (total P) is much lower (Cleveland and Liptzin 2007; Kirby et al. 2011; Steffens et al. 2008; Tian et al. 2010). Consequently, less stoichiometry C/N ratio variability is usually found when compared to C/P and N/P ratios (Bui and Henderson 2013; Kirby et al. 2011). Despite the expected association of organic C and total N, the C/N ratio may be strongly affected by soil order (Batjes 2000), vegetation type (Bui and Henderson 2013), climate (McCulley et al. 2009), depth (Vejre et al. 2003), and land use (Purton et al. 2015). Consequently, an independent evaluation of organic C and total N changes in soils related to land use change across climate and soil gradients is needed.

Total N stock usually decreases at surface layers when soils are cultivated under rainfed conditions (Gami et al. 2009; Li et al. 2014; Papini et al. 2011), although the effect of agriculture may be less pronounced in depth (Gami et al. 2009; Hass et al. 1957). Increases in total N stock due to cultivation have also been reported (David et al. 2009). The conversion of forests (Deng et al. 2014; Gami et al. 2009; Purton et al. 2015) and shrubs or grasslands (Li et al. 2014; Malo et al. 2005) to croplands resulted in a decrease in C/N ratio indicating a different C loss rate compared to total N. In addition, differences of soil organic matter composition have been reported among forest, shrubs and grasslands (Deng et al. 2014; Mudge et al. 2014; Schipper and Sparling 2011). The impact of land use on total N and the organic matter stoichiometry affects the ability of soils to mineralize N as evaluated by incubation tests (mineralized N). Total N is one of the main controls of mineralized N (Colman and Schimel 2013; Dessureault et al. 2015) and the reduction of this pool reduces mineralized N. The C/N ratio of some soil fractions negatively affects the mineralized N (Deng et al. 2014; Kader et al. 2010). As the C/N increases, the decomposition rate of the soil mineralizable N pool decreases. Consequently, the magnitude of the effects of land use on mineralized N would depend on how much it affects total N and the C/N ratio.

Differences in total P stock between soil types may be ascribed to their grade of evolution (Chen and Ma 2001; Cross and Schlesinger 1995), which also impact on the stoichiometry ratios (Chen et al. 2015; Turner and Laliberté 2015). As total P and the labile P fraction available to plants, usually called extractable P (extractable P), are correlated (Bai et al. 2013; Johnston et al. 2014), extractable P also differs between contrasting soil types. Land use, additionally, impacts total P and extractable P. Total P is lower in cultivated soils than under uncultivated conditions when fertilizers are not used (Li et al. 2016; Slazak et al. 2014) but higher levels of total P may be found in intensive fertilized agricultural soils (Liu et al. 2013; Rubaek et al. 2013). Extractable P suffers the same effects under cultivation (Crews and Brookes 2014; Negassa and Leinweber 2009) and the magnitude of these effects is relevant for assessing soil productivity and fertilizer requirement.

Human activities have altered the global N and P cycles. In agricultural soils, surface N and P balances moved from near neutrality in the year 1900 to + 138 Tg N year^{-1} and + 11 Tg P year^{-1} in the year 2000 (Bouwman et al. 2013). In the long-term, the imbalance between N and P may alter the N/P ratio of some plants that are not capable of regulating their composition, which in turn affects vegetation productivity and depresses C sequestration in soils (Peñuelas et al. 2013). It has not been determined whether the soil N/P ratio has been affected by the imbalance between N and P in agroecosystems.

The Argentinean Pampas is a vast plain that due to its extension and yield potential has been considered as one of the most suitable areas for grain crop production in the world (Satorre and Slafer 1999). The effect of land use on soil C has been assessed for the region (Berhongaray et al. 2013). It was observed that soil organic C increased up to 1 m depth in forest areas, when compared with an uncultivated grassland control. Conversely, cultivation led to a soil organic C decrease, which was significant only up to 50 cm depth. Land use impact on soil N and P has not been assessed at a regional scale but some experiments showed declines in different soil P fractions in the Pampas due to cultivation (Buschiazzo et al. 2000;

Galantini and Rossell 1997). Moreover, calculated regional surface balances were positive for N (Alvarez et al. 2014, 2016) and negative for P (Alvarez et al. 2016; Viglizzo et al. 2001) during the twentieth century as a consequence of agricultural practices. This imbalance between N and P fluxes makes Pampean agroecosystems an interesting research case to determine possible changes of the C/N/P ratios in soils due to human activities. Our objectives in the current research were: (1) to determine land use effect on total N and total P stocks in Pampean soils, and on some labile N and P fractions, and (2) to investigate if changes produced by land use on N and P balances impacted soil stoichiometry.

Materials and methods

Study area

The Pampas are located in Argentina between 28°S and 40°S and 57°W and 68°W while covering an area of ca. 50 Mha (Fig. 1). The natural vegetation is grassland with predominance of gramineous species, whereas some natural forests account for 7% of the area and planted trees, introduced about 150 years ago, occupied less than 1% of the total surface

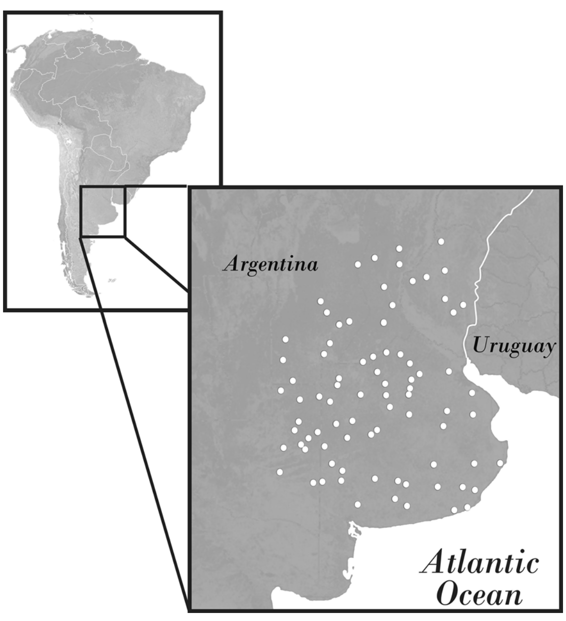

Fig. 1 Map of the Pampean region showing the location of sampled farms

(INDEC 2002). Mean annual temperature ranges from 14 °C in the South to 23 °C in the North with mean annual rainfall ranging from 500 mm in the West to 1200 mm in the East. The relief is flat or slightly rolling with Mollisols as the predominant soils formed on loess-like materials, but Alfisols and Entisols are also common (Alvarez and Lavado 1998). The eolian origin of sediments from Southwest to Northeast and the West–East rainfall gradient determine that soil texture and depth vary from sandy-shallow in the West to clayed-deep in the East, being illite the most common clay mineral (Alvarez and Lavado 1998; Berhongaray et al. 2013). Along the West and the South of the region, a petrocalcic horizon appears at many sites within the upper 1 m of the soil profile (Teruggi 1957). In areas with annual rainfall above 600 mm, rain-fed crops are cultivated on well-drained soils while hydromorphic lands are released for grazing (Hall et al. 1992; Alvarez and Lavado 1998). Agriculture was introduced in the Pampas around 1870 and expanded since then (Alvarez et al. 2016; Viglizzo et al. 2001). At present, some 60% of the Pampean area is under cropping with soybean [*Glycine max* (L.) Merr.], wheat (*Triticum aestivum* L.), corn (*Zea mays* L.) and sunflower (*Helianthus annuus* L.) as the main crops (MinAgro 2017). Grain crops are rotated with seeded pastures on high productive soils and low productive ones are maintained under permanent grasslands. A widespread adoption of fertilizer use occurred since 1990 but with low nutrient rates (Alvarez et al. 2015). Wheat was the most common crop in the past but was replaced by soybean that occupies about 60% of the cropped area at present time (MinAgro 2017).

Soil sampling

To obtain a regional coverage (Fig. 1), we analyzed data from 82 farms spread over the Pampas, during 2007–2008. Five common land uses were sampled at each farm: tree areas (Tree), areas that were never cropped under gramineous vegetation (Uncropped), agricultural plots with seeded pastures (Pasture), agricultural plots with grain crops (Crop), and flooded lands (Flooded). Sampled sites were georeferenced. Tree species present in forest areas were usually *Eucalyptus* sp., *Pinus* sp., *Prosopis* sp. and *Acacia* sp., with most of the trees having 30 years or older. For the Uncropped control treatment park grass surrounding the house was used in 60 farms, whereas natural grazing grasslands under very low animal stoking rate were used in 22 farms. All these sites were never cropped as far as the records indicated and represented adequately the Pampean soil environment without cultivation effects (Berhongaray et al. 2013). Pasture and Crop sites were cultivated sites that at the time of sampling were under the pasture or crop phase of a mixed rotation respectively. In nearly all Pasture sites the composition was a mixture of legume and grasses in at least the past 3 years. Crop sites were representative of common rotation × tillage system practices of the different Pampean sub-regions that had been under grain crop production continuously from 3 to 20 or more years at the time of sampling. Tree, Uncropped, Pasture and Crop sites were established on well drained soils (Mollisols, Vertisols and Entisols as determined using a digital database: INTA 2010). The Flooded treatment corresponded to never cropped lowlands used for grazing under predominant natural grass vegetation. Those soils were hydromorphic (Alphisols and Mollisols) suffering periodical flooding events.

A representative plot of 100 m^2 was delimited at each site and in four locations within the plot soil was sampled to 1 m depth in 0.25 m intervals with a corer. Samples were composited by depth. When petrocalcic horizons were present, soils were sampled to their upper limit (46 sites). In Tree sites the O horizon was removed and only the mineral soil was sampled to avoid possible interference of decomposing residue on soil stoichiometry, as nutrient ratios are very variable in residues (Kirby et al. 2011; Mcgroddy et al. 2004). As not all land uses were available in all farms, 386 sites were sampled generating a total of 1456 soil samples. The corer allowed for soil bulk density determination as the volume was known. Fresh samples were weighted; a sub-sample was used for water content determination after oven dried (105 °C), and the rest was air dried and ground through a 2 mm sieve discarding plant residues.

Analytical methods and climate data

Methods used for soil texture, organic and inorganic C content, pH and electrical conductivity determination were described in detail before (Berhongaray et al. 2013). Total N was determined by the Kjeldahl method quantifying ammonia by steam distillation (Bremner 1996). Mineralized N was evaluated by aerobic incubations of 25 g of soil in 400 ml flasks during 15 days at a water content equivalent to 50% of the soil water holding capacity and a temperature of 30 °C. This incubation method proved to give more consistent results than short anaerobic incubations in Pampean soils (Romano et al. 2017) and is a good predictor of field N mineralization both for fine-textured (Alvarez and Steinbach 2011) and coarse-textured (Romano et al. 2015) soils. Ammonium plus nitrate (mineral N) were determined by steam distillation before and at the end of the incubations (Mulvaney 1996). Total P was measured by the perchloric acid digestion method (Kuo 1996) determining phosphorus colorimetrically (Murphy and Riley 1962). Extractable P was assessed by the Bray-I method (Kuo 1996). This is the P availability diagnosis variable for crops in the Pampas (Rubio et al. 2015). The method may produce an incomplete extraction in calcareous soils (Ebeling et al. 2006; Randall and Grava 1971). To overcome this problem, when calcium carbonate equivalent surpasses 7%, the recommendation is to increase the extractant:soil ratio (Kuo 1996). For all our samples a common extractant:soil ratio of 7:1 was used, because in less than 4% of the samples the indicated threshold was surpassed but statistical analysis of treatment effects were additionally performed eliminating this 4% of data without noticeable changes, suggesting that our data set has no methodological constraints. Nitrogen and P concentrations were converted to stocks using bulk density data. Element ratios were calculated as mass ratios.

Mean annual rainfall and temperature of the sampled sites were estimated using records from 50 meteorological observatories of the Servicio Meteorológico Nacional for the period 1933–2006 by kriging interpolation using QGIS. The method allowed good estimation (R^2 > 0.90) of rainfall and temperature when tested against an independent data set of meteorological data from 20 stations belonging to Instituto Nacional de Tecnología Agropecuaria.

Modeling N and P profiles

The distribution of N and P pools in depth was modeled using the potential model (Bernoux et al. 1998) as follows:

$$M = A \times d^B \quad (1)$$

where M represents the cumulative pool mass (t ha^{-1} or kg ha^{-1}) to a depth d (m), A is the mass of the pool to 1 m, and B describes the curvature of the function. As the model is not linear in the parameters, it can be linearized by taking logarithms as follows:

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

This form of the potential model has been successfully used previously for describing soil organic C in depth with worldwide data (Jobbágy and Jackson 2000) and Pampean data (Berhongaray et al. 2013). Parameter B can be fitted using both untransformed and relative data. When $B = 1$, the model fits to a straight line and the pool mass is not stratified along the different soil layers. The smaller the B parameter, the more stratified is the nutrient pool. When $B > 1$, a greater accumulation of the pool is found in deeper soil layers than at the surface. The model was fitted for soils without petrocalcic horizon ($n = 340$). The modeling was performed by least squares minimization using the Levenberg–Marquardt algorithm with TableCurve 2D facilities (Systat Software, Inc.). The R^2 was calculated in each case and significance determined (F test, $P < 0.05$). The possibility of using the potential model for estimating nutrients pools in depth based on surface data was tested using as inputs the pool size from the upper soil layer (0–25 cm), and the average B parameter of the corresponding land use type.

Nitrogen and P surface balance

A surface nutrient balance was calculated for cropped (Pasture and Crop treatments) and uncropped (Uncropped control treatment) soils of the Pampas. The surface balance is a simplified version of the soil balance in which only inputs and outputs of the nutrient are computed and losses ignored (OECD 2001, 2008). Inputs accounted for are atmospheric deposition, fertilizers and manure and outputs take into account the harvested and livestock products. Not accounting for erosion, leaching, run-off, volatilization and denitrification when calculating balances, decreases model uncertainty as generally these losses are extremely difficult to estimate (Oenema et al. 2003). Nutrient surplus can be calculated with this methodology that may be retained in the soil, emitted to the atmosphere or leached to deeper soil layers. When the calculated balance is negative, it is indicative that nutrient is depleted in the soil (Oenema et al. 2003; Panten et al. 2009).

The N balance was computed with inputs from atmospheric deposition, N fixation by legume pastures and soybean, and fertilizer applications. Outputs were N exported in harvested grains and livestock products. The P balance computed as inputs atmospheric deposition and fertilizers and the output were the same as for N. Manure is not used for extensive agriculture in the Pampas. We employed a database that was elaborated using national censuses and other official statistics, data that has been described in detail before (Alvarez et al. 2016). The database comprised records on the evolution of seeded pastures surface, pasture composition, grain crop surface and yield and livestock production corresponding to the period 1870–2010, and these were obtained from different grazing resources (seeded pastures or grasslands). Atmospheric deposition of N (dry and wet) was estimated at 13 kg N ha^{-1} year^{-1} 100 cm^{-1} rainfall and adjusted as a function of average county rainfall (Alvarez et al. 2014). Nitrogen fixation by alfalfa based pastures was estimated using a locally developed factor of 38 kg N fixed t^{-1} biomass (aboveground + roots) (Alvarez et al. 2014). Present alfalfa productivity at a county scale was estimated also with a locally adjusted climate model (Alvarez et al. 2014), and fixation was calculated combining biomass productivity and the fixation factor. It was assumed for mixed pastures that alfalfa accounts for 50% of total biomass (Mortenson et al. 2004), and N fixation was corrected by half. One-third of mixed pastures were clover (*Trifolium* sp.) based pastures but as no methods were available to estimate its N fixation the same methodology used for alfalfa was applied. The evolution of alfalfa yield through time has not been recorded in the Pampas, therefore a 0.63% year^{-1} yield gain during the twentieth century was assumed for productivity adjustment in the past, based on data for the alfalfa producing region of USA (Putman et al. 2007). Natural grassland fixation was considered to be null (Chaneton et al. 1996). Nitrogen fixation by soybean was estimated with a model adjusted to local experiments and county yield data, according to which fixation in above and below ground biomass averages 52 kg N t^{-1} DM grain (Di

Ciocco et al. 2011). Nitrogen fertilizer input was calculated by computing national fertilizer consumption (FAOSTAT 2014) while estimating that 90% is applied to Pampean grain crops and pastures (Alvarez et al. 2015, 2016). Nitrogen output was calculated by multiplying harvested grain and livestock production with the corresponding nitrogen concentration (Alvarez et al. 2014, 2016). Grain production came entirely from cropped areas but 66% of livestock production was generated from seeded pastures in cropped areas and the remaining in grasslands (Alvarez et al. 2016). Phosphorus input from dry and humid depositions was estimated as 0.23 kg P ha^{-1} year^{-1} 100 cm^{-1} rainfall, and adjusted as a function of average county rainfall (Alvarez et al. 2016). Fertilizer P input was calculated using the same data and criteria applied for N. Phosphorus output was computed as the sum of fluxes in harvested grains and livestock products using adequate P concentration coefficients (Alvarez et al. 2016), while partitioning cultivated areas and grasslands.

County scale estimations were aggregated for the cultivated area, which during 2006–2010 averaged 27.9 Mha. Instead, the grassland area averaged 22.5 Mha. Data from censuses and the other official data sources (cited in Alvarez et al. 2016) were used for annual estimations of the variables of interest for the 1870–2010 period by cubic splines by means of TableCurve facilities (Systat Software, Inc.). Annual data were aggregated in periods of 5 years to avoid some extreme values. The average nutrient balances of the Pasture and Crop treatments were assumed to be equivalent to the average nutrient balance of the entire cultivated Pampean area as sampled sites were representative of the area. Conversely, for the Uncropped control treatment we calculated the weighted average of the surface balances of the grassland area ($n = 22$) and park grass sites ($n = 60$). In the latter case, the surface balance was estimated by taking into account only atmospheric N and P inputs, as no outputs by livestock production occurred.

Statistical analysis

Before fitting any model, all response variables were tested for normality using graphical and theoretical methods from Proc Univariate in SAS (SAS Institute Inc. 2016), specially the test by Shapiro and Wilk (1965), because the number of records in the current research was always less than 2000. As in most of these analyses the assumption of normality was untenable ($P > 0.05$), data were transformed to normality using mostly Box–Cox procedures as discussed by Peltier et al. (1998).

Transformed data were analyzed with three mixed models with random effects of farm and different sets of fixed effects, using Proc Mixed of SAS (SAS Institute Inc. 2016). To test for differences between land use effects at the same soil depth the following model was employed:

$$y_{ijk} = \alpha_i + \beta_{1i}x_{ijk} + \beta_{11i}x_{ijk}^2 + u_j + e_{ijk} \tag{3}$$

where y_{ijk} is the response variable, α_i $i = 1, \ldots, 5$, are fixed land use effects, x_{1i} is the jth soil depth $j = 0.125$, 0.375, 0.625 and 0.875 m; β_{1i} and β_{11i} are fixed linear and quadratic effects of the covariate soil depth k nested within land use effects i and farm j, respectively. The random variable u_j is the effect of farm j ($j = 1, \ldots, 82$) such that $u_j \sim i.i.d.\ N\ (0,\sigma_u^2)$. Finally, random error terms have $\mathrm{cov}(e_{ijk}, e_{ijk'}) = \sigma_e^2$ if $k = k'$ and to $\rho^{k \neq k'}\sigma_e^2$ if $k \neq k'$, the specification of an autoregressive process [AR(1)]. Attempts to fit a spatial covariance structure for error terms failed to converge, most probably because of the long distances between farms, whereas the AR(1) covariance structure gave a remarkable fit, i.e. for all response variables $\rho > 0.5$.

Tests for differences between soil depths within land use were calculated by the following model:

$$y_{ijk} = \alpha_i + \gamma_{ijk} + u_j + e_{ijk} \tag{4}$$

where the term that differs from model Eq. (3) is the fixed effect of the interaction between i-level of land use and k-level of soil depth, and the random terms follow normal distributions such as for model (3).

To test for variables aggregated to 1 m of soil and the estimated B parameters, the transformed observations (y_{ij}) followed the two-way random model:

$$y_{ij} = \alpha_i + u_j + e_{ij} \tag{5}$$

where land uses (α_i) were considered fixed effects, farm effects u_j were random such that $u_j \sim i.i.d.\ N\ (0, \sigma_u^2)$, and random error terms (e_{ij}) follow the distribution $e_{ij} \sim i.i.d.\ N\ (0, \sigma_e^2)$.

All tests were calculated by setting the appropriate linear contrasts (Searle 1971), and degrees of freedom were corrected by the procedure of Kenward and Roger (1997). Regression and correlation analysis were performed for searching associations between variables, and the F test was used with $P < 0.05$. Slopes and intercepts of predicted versus observed data were compared by the t test using IRENE ($P < 0.05$) (Fila et al. 2003). Root mean square error (RMSE) (Kobayashi and Salam 2000) were calculated for the evaluation of the regression models.

Results

Data set variability

Climate gradient along the sampled sites was quite broad, especially for rainfall. Even eliminating extreme values and accounting for 5 and 95% percentiles, rainfall from the most humid site was almost twice the precipitation from the driest one (Table 1). The variability of soil properties had a much wider range across sites and depth layers (Table 1). Organic carbon had a 20-fold variation, total N a 12-fold range and total P a fivefold range. This variability determined that C/N, C/P and N/P ratios varied 6-, 18-, and 11-fold respectively. Labile N and P fractions variation was even greater.

A strong association was observed between organic C and total N. Around 70% of total N variability could be explained by organic C across land uses and depths. As organic C content increased, extractable P, mineral N and mineralizable N also increased. This was the consequence that these variables were higher at soil surface, decreasing with depth in nearly all sampled sites and because more fertile sites (Tree and Uncropped sites) had greater values of the four variables at all soil layers. Total P and extractable P were positively correlated. Total N could explain 52% of mineralized N variability. Stoichiometry ratios were not highly correlated to climate and soil properties, but the C/P and N/P ratios were very closely correlated as they had the same denominator (spurious regression) (Table 2).

Land use effect on N and P pools

Land use had a significant effect on total N (Fig. 2). Compared to the Uncropped controls, soils under Tree increased their total N content up to 1 m depth. Cultivation resulted in a significant decrease in total N up to 0.75 m depth. Flooded soils had lower total N

Table 1 Variability of climate and soil properties across sites and depths (n = 1456)

Variable	Mean	SD	Percentiles	
			5%	95%
Temperature (°C)	16.1	1.33	14.0	18.6
Rainfall (mm)	874	120	657	1060
Bulk density (g cm^{-3})	1.24	0.18	0.91	1.50
Sand (g kg^{-1})	483	193	210	840
pH (in water 1:2.5)	6.58	0.95	5.30	8.50
Conductivity (dS m^{-1})	1.90	3.09	0.27	6.71
Organic C (g kg^{-1})	9.03	7.64	1.25	25.5
Carbonate C (g kg^{-1})	1.56	3.15	0.00	7.57
Extractable P (mg kg^{-1})	23.8	41.4	1.50	116
Total P (mg kg^{-1})	347	162	127	640
Total N (g kg^{-1})	1.06	0.893	0.230	2.85
Mineral N (mg kg^{-1})	17.9	16.3	3.30	48.7
Mineralized N (mg kg^{-1})	24.0	26.9	0.00	80.0
C/N (mass ratio)	8.80	5.26	3.06	17.1
C/P (mass ratio)	30.2	48.0	3.90	69.9
N/P (mass ratio)	3.38	4.72	0.700	7.71

Table 2 Pearson correlation coefficients between variables across sites and depths (n = 1456)

Variable	Temperature	Rainfall	pH	Conductivity	Sand	Organic C	Carbonate C	Extractable P	Total P	Total N	Mineral N	Mineralized N	C/N	C/P
Rainfall	**0.48**													
pH	**− 0.05**	**− 0.27**												
Conductivity	**− 0.03**	**− 0.09**	**0.37**											
Sand	**− 0.20**	**− 0.42**	**0.20**	− 0.02										
Organic C	**− 0.15**	**0.11**	**− 0.29**	− 0.05	**− 0.22**									
Carbonate C	**− 0.19**	**− 0.15**	**0.12**	0.03	**− 0.19**	**− 0.10**								
Extractable P	0.06	− 0.01	**− 0.26**	− 0.03	− 0.01	**0.42**	**− 0.07**							
Total P	**0.10**	**− 0.14**	**− 0.16**	0.03	− 0.04	**0.22**	**− 0.16**	**0.54**						
Total N	**− 0.08**	**0.12**	**− 0.38**	− 0.05	**− 0.30**	**0.84**	**− 0.10**	**0.42**	**0.31**					
Mineral N	**− 0.06**	− 0.04	**− 0.30**	0.01	**− 0.12**	**0.50**	**0.06**	**0.38**	**0.26**	**0.48**				
Mineralized N	**− 0.09**	**0.09**	**0.24**	**0.08**	**0.19**	**0.73**	0.04	**0.28**	**0.19**	**0.72**	**0.45**			
C/N	**− 0.13**	0.01	**0.16**	**0.09**	**0.13**	**0.24**	0.03	0.01	**0.12**	**− 0.15**	**− 0.05**	0.01		
C/P	0.01	**0.18**	− 0.05	− 0.03	− 0.06	**0.33**	0.06	**− 0.07**	**− 0.21**	**0.23**	**0.09**	**0.20**	**0.14**	
N/P	0.03	**0.20**	− 0.11	− 0.05	**− 0.09**	**0.29**	0.05	− 0.02	**− 0.29**	0.00	0.12	**0.23**	− 0.04	**0.96**

Significant coefficients are marked in bold ($P < 0.05$)

than the other treatments up to 1 m depth. Generally, there were no differences between Pasture and Crop treatments, except at some soil layers. The decrease in total N stock induced by cultivation averaged 14% in the whole sampled depth. Mineral N was not affected by cultivation, which increased under Tree compared to the Uncropped control (70%) and decreased in Flooded (Fig. 2). Mineralized N was similar in Tree and Uncropped, whereas it was lower in cultivated soils, and reached a minimum value in Flooded sites (Fig. 2). Significant cultivation effects on mineralized N were detected to 0.5 m depth. Cultivation resulted in an average decrease of 21% in mineralized N in the soil layer up to 1 m.

Total P was affected by cultivation; in Pasture and Crop treatments total P was significantly lower than in Uncropped to 0.75 m depth (Fig. 3). For the 0–1 m layer, total P decreased to an average of 14% due to cultivation. Flooding led to a decrease of total P stock. Extractable P was significantly affected by land use too (Fig. 3). Tree soil had greater extractable P than Uncropped controls in the upper 0–0.5 m layer but cultivation determined a significant drop of extractable P down to 0.75 m depth. Also, low extractable P levels were measured in Flooded soils. Taking into account the 0–1 m soil layer, the decrease by cultivation of extractable P averaged 63%.

The analysis of the land use effects on a farm by farm basis showed that, when the Uncropped controls had high levels of total N (Fig. 4a), mineralized N (Fig. 4c), total P (Fig. 4d), and extractable P (Fig. 4e), cultivation led to a substantially decrease of N and P stocks. Reduction of nutrients pools in the 0–1 m soil layer ranged from 48 to 89%, depending on the soil variable. These pools were less affected by cultivation in soils with low fertility, whereas in certain cases some increases were measured. Mineral N in cultivated soils did not show a consistent trend in variability relative to the Uncropped control stock (Fig. 4b).

Modeling N and P pools in depth

Nitrogen and P pools in depth were well modeled by the potential function (Table 3). The model could be fitted significantly to nearly all profiles with high performance. Total P showed a quite different stratification pattern when compared to the other

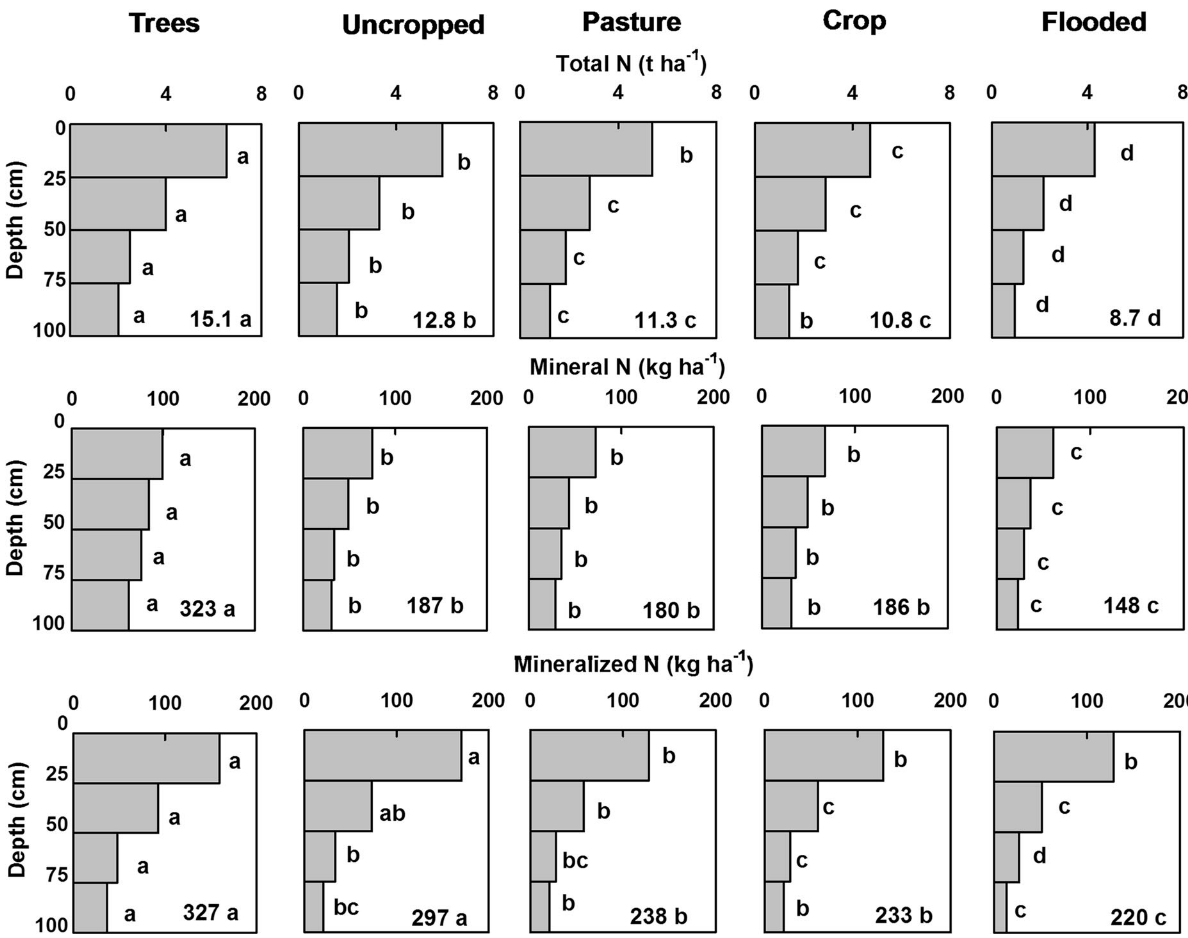

Fig. 2 Average pools of total N, mineral N and mineralizable N as a function of land use. The numbers at the bottom of the boxes indicate cumulative pools to 1 m depth. Different letters show significant differences ($P < 0.05$) between land uses for a soil layer

pools. With mean *B* parameters rounding to a value of 1, total P showed a non-stratified trend. Conversely, total N, mineral N, mineralized N and extractable P were highly stratified; specially mineralized N. Except for the mineral N pool, the *B* parameter was affected by land use, but this difference was generally small. In Flooded soils, total N and mineralizable N were more stratified than the Uncropped control and in the Tree soil the opposite was observed. Nitrogen pools in cultivated soils had similar stratification patterns with the Uncropped control. Extractable P was less stratified in Flooded than in the other treatments and no significant differences were detected between cultivated and uncultivated or Tree soils. The good fit of the potential model allowed using it for estimating N and P pools in depth when only data from the surface layer were available (Fig. 5). The best performance was attained when estimating extractable P. In this case, ordinate and slope of the observed against estimated values did not differ from 0 and 1 respectively (Fig. 5e). In the other cases, though ordinates and slopes of the regression lines were different from 0 to 1, root mean square errors ranged from 16 to 30% of the observed means.

Stoichiometry ratios and labile pools fractions

In most soil layers, land use had only a minimal impact on stoichiometry ratios (Fig. 6). The C/N ratio was higher in Flooded soils than in well drained ones in whole depth (0–1 m), but significant differences between Tree and Uncropped were not detected in general, and cultivation did not affect the ratio. No clear trends of the C/N ratio in depth were observed.

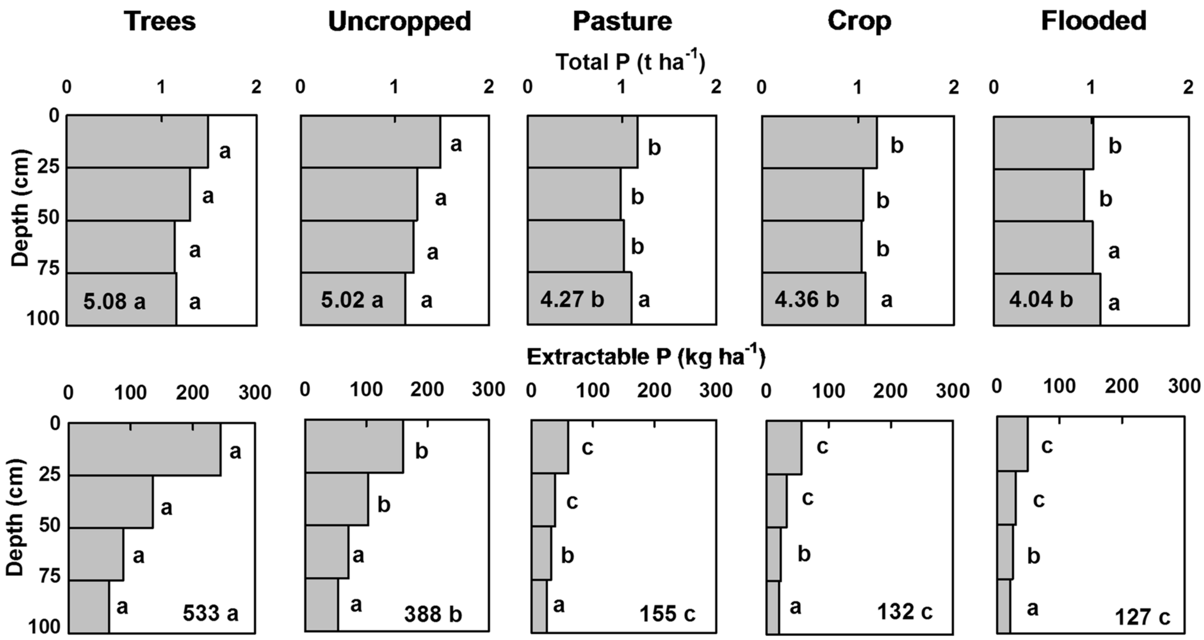

Fig. 3 Average pools of total P and extractable P as a function of land use. The numbers at the bottom of the boxes indicate cumulative pools to 1 m depth. Different letters show significant differences ($P < 0.05$) between land uses for a soil layer

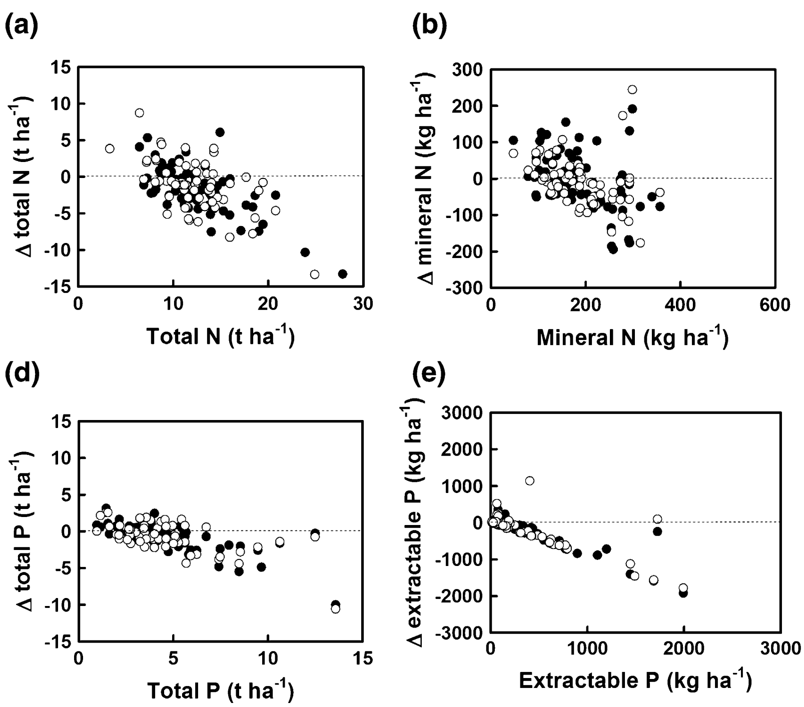

Fig. 4 Differences (Δ) of N and P pools (0–1 m) between cropped (pastures: empty drops, crops: full drops) and uncropped soils related to the pools in the uncropped soils (x axis) ($n = 146$)

A significant increase in C/N was detected between surface and subsurface soil layers from the Flooded treatment only. No significant differences were detected in the C/P ratio between land use treatments

Table 3 Performance of the potential function for modeling N and P stocks in soils without petrocalcic horizon

Variable	Statistics	Land use				
		Trees (73)	Uncropped (75)	Pasture (59)	Crop (72)	Flooded (61)
Total N	Significant fits (%)	100	100	100	100	100
	R^2 range	0.93–0.99	0.98–0.99	0.96–0.99	0.96–0.99	0.98–0.99
	Mean coef. *B*	0.591a	0.544bc	0.518c	0.585ab	0.505c
	Cases with $B > 1$	0	0	0	0	1
Mineral N	Significant fits (%)	100	100	100	100	100
	R^2 range	0.90–0.99	0.94–0.99	0.94–0.99	0.95–0.99	0.91–0.99
	Mean coef. *B*	0.786a	0.640a	0.663a	0.715a	0.665a
	Cases with $B > 1$	14	2	1	3	5
Mineralizable N	Significant fits (%)	100	100	100	100	100
	R^2 range	0.91–0.99	0.93–0.99	0.93–0.99	0.95–0.99	0.94–0.99
	Mean coef. *B*	0.547a	0.434b	0.444ab	0.457ab	0.401b
	Cases with $B > 1$	4	0	0	2	1
Total P	Significant fits (%)	97	97	100	100	100
	R^2 range	0.98–0.99	0.98–0.99	0.97–0.99	0.97–0.99	0.98–0.99
	Mean coef. *B*	0.885a	0.882a	0.933b	0.964bc	1.057c
	Cases with $B > 1$	16	17	18	28	37
Extractable P	Significant fits (%)	100	100	100	100	100
	R^2 range	0.98–0.99	0.96–0.99	0.98–0.99	0.98–0.99	0.98–0.99
	Mean coef. *B*	0.530a	0.552a	0.600ab	0.599ab	0.689b
	Cases with $B > 1$	0	1	0	0	7

Numbers in brackets indicate the amount of soils for each land use; total = 340

The percentage of significant ($P < 0.05$) fits is showed. Similar letters indicate no significant differences ($P < 0.05$) of the averages slopes of the potential function between land uses

at any sampled soil layer. When comparing this ratio for the whole 0–1 m layer some significant differences appeared but these differences were small, not exceeding 4% of the Uncropped control mean. The C/P ratio was strongly stratified with significant differences between the soil layers within a treatment for all treatments and depths. Generally, significant differences were not detected between land uses in the N/P ratio except for some soil depths without a clear trend. When testing the 0–1 m layer, only Flooded soils had a lower N/P ratio than the land use treatments from well drained soils. Similar to the C/P ratio, the N/P ratio was also well stratified with significant differences between soil layers within a treatment in all cases.

The mineralized N/total N ratio was significantly greater in Flooded soils and similar among Tree, Uncropped, Pasture and Crop treatments (Fig. 7). This ratio also decreased significantly in depth for all land uses, which suggests that organic reservoirs are more resistant to mineralization in the deeper soil layers. Cultivation resulted in a strong decrease of the extractable P/total P ratio (Fig. 7), which significantly decreased in depth in nearly all cases.

Nitrogen and P balances

The cumulative N and P balances presented quite opposite trends depending on the type of ecosystem considered (Fig. 8). The N balance was positive, both for the Uncropped control and the cultivated treatments. In the latter, the gain of N was much greater mainly because of the input of N by atmospheric fixation by legume pastures and soybean but also because of fertilizer input, which accounted for ca. 7% of the total input. Phosphorus balance was slightly positive in the Uncropped control, but highly negative in cultivated soils because fertilizer

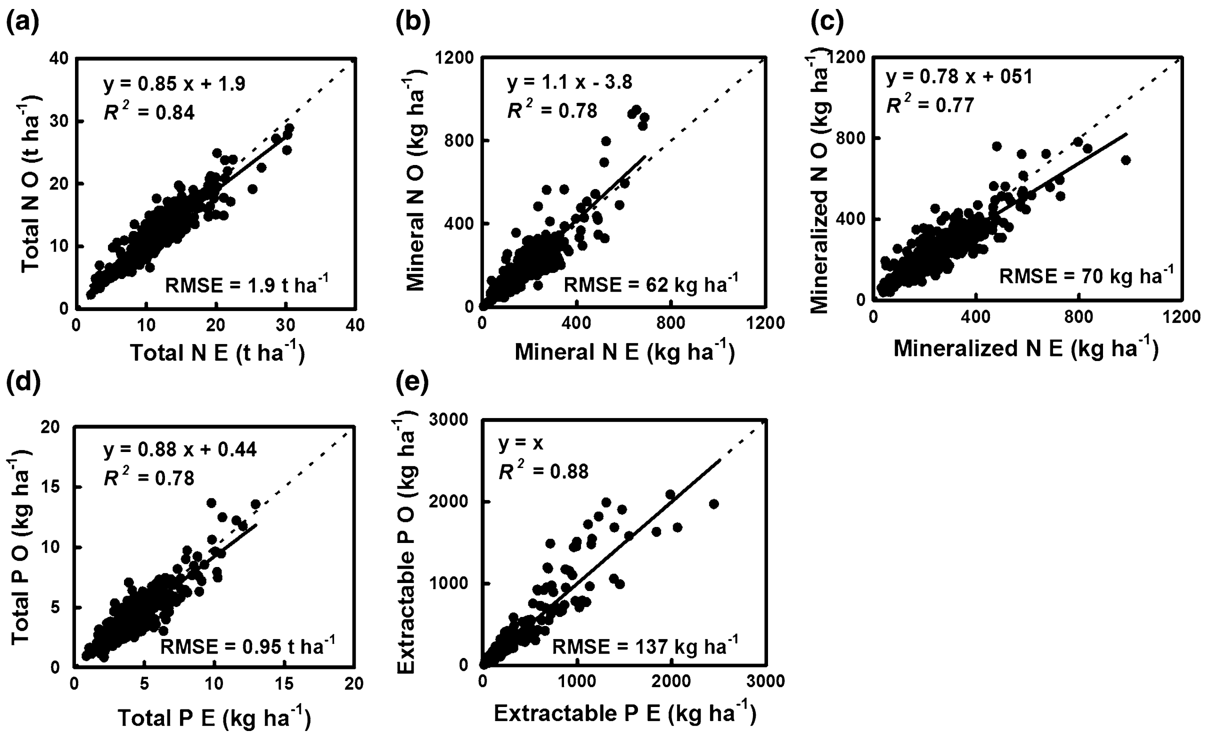

Fig. 5 Relationships between observed (O) and estimated (E) pools of N and P by the potential model to 1 m depth. Estimations were performed using measured pools in the 0–0.25 m layer as predicting variable and the average *B* parameter of each land use. Only soils without petrocalcic horizon were included ($n = 340$)

application was equivalent to only 25% of P outputs. The ratio P balance/N balance for the last 140 years was + 0.01 kg P/kg N in Uncropped and − 0.08 kg P/kg N in cultivated soils. This indicates that for 1 kg N of positive balance in the Uncropped treatment, 0.01 kg P was gained. Conversely, for every 1 kg N of positive balance in cultivated soils, we estimated a loss of 0.08 kg P. Despite this great difference in nutrients fluxes, the N/P ratio of soils did not vary significantly.

Discussion

Relationships between variables

The high correlation between organic C and total N across land uses and depths observed in Pampean soils had been reported with some other analyses of big datasets (Kirby et al. 2011; Tian et al. 2010), and had led to the possibility of estimating total N stock using soil C (Wu et al. 2009). The slope of the regression of organic C against total N in our dataset was 8.2, very close to the average C/N ratio. Fixed ammonium usually increases with soil clay content in depth producing a narrowing in the C/N in some soils (Young and Aldag 1982). In our sampled sites the exponential model could be fitted to organic C profiles with very good fits using a mean *B* parameter of 0.56 (Berhongaray et al. 2013). This value is very close to the mean *B* parameter of 0.55 for total N across land uses. The similar stratification pattern of C and N led to an overall mean C/N ratio of 8.8 that was not affected by soil depth except in Flooded soils. This suggests a low contribution of fixed nitrogen to total N in the soils of the region, especially in well drained soils. As the total N content of the samples increased, mineralized N and mineral N also increased because total N is the main control of mineralization (Colman and Schimel 2013; Dessureault et al. 2015; Smit and Velthof 2010) and higher soil mineralization capacity lead to greater mineral N level.

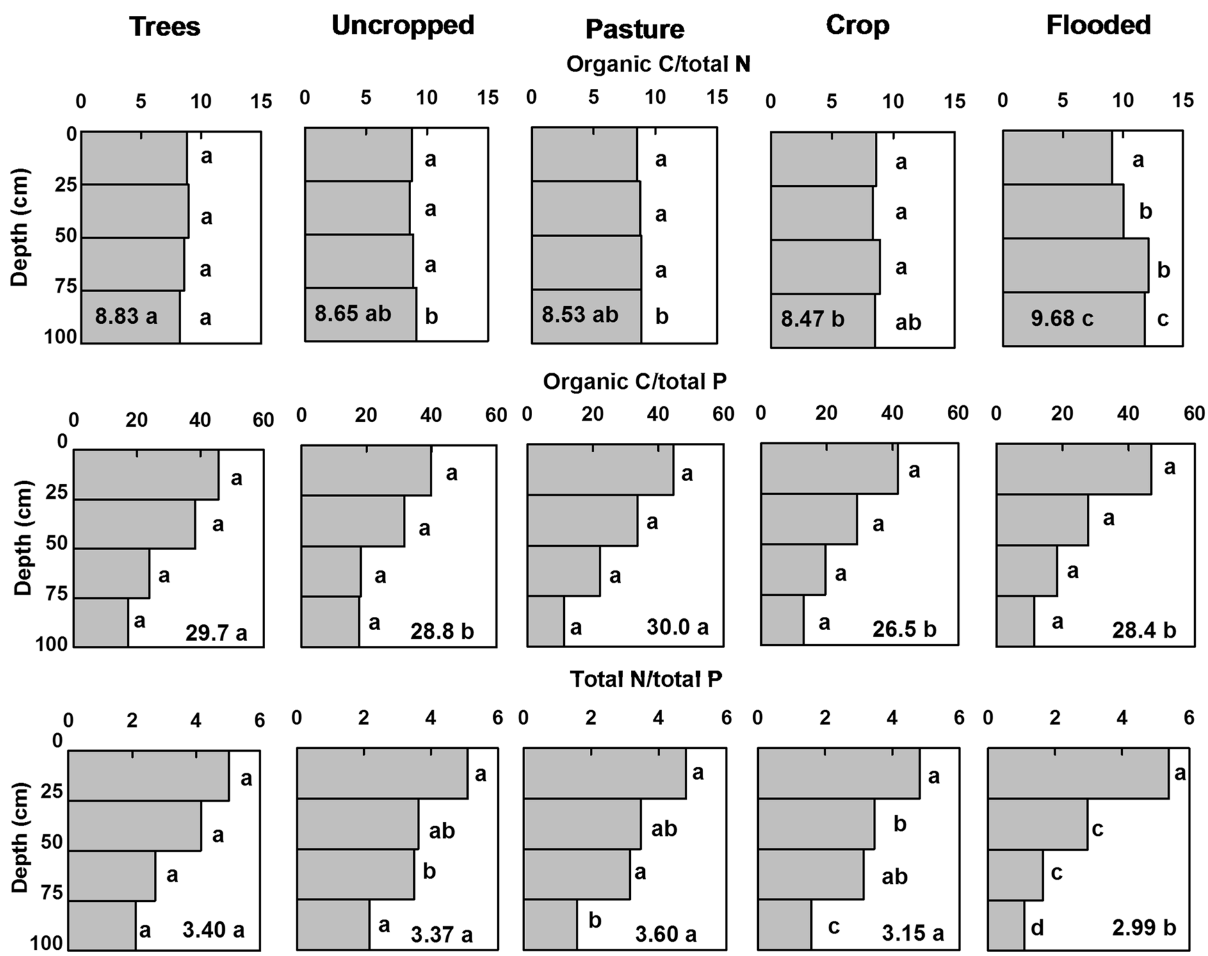

Fig. 6 Average elements ratios (calculated as mass ratios) as a function of land use. The numbers at the bottom of the boxes indicate mean ratios to 1 m depth. Different letters show significant differences ($P < 0.05$) between land uses for a soil layer

The relation between total P (which is not stratified in the profile) and organic C (which is stratified) was weak. We detected a significant correlation between organic C and extractable P when grouping all samples across land uses and depths. This can be attributed to the fact that Trees and Uncropped soils had high C and extractable P levels making the relationship significant, contrasting with cultivated soils in which both variable levels were low. When only cultivated soils were considered, no significant association was detected between C and extractable P contents.

Land use effects on nutrient pools

Total N was 18% greater under Trees than in the Uncropped control within the 0–1 m depth. Usually, more organic C is found in soils from forests than from grasslands (Guo and Gifford 2002) which can be related to the greater net primary productivity and C inputs (Dixon et al. 1994). In the Pampas, forest soils had 30% more organic C than grassland soils (Berhongaray et al. 2013) and this might make it easier to retain N in soil by organic matter accumulation. It has been estimated that total N stocks in Pampean soils came mainly from past rainfall inputs before recent leguminous introduction and fertilizer adoption (Chaneton et al. 1996). Leguminous species are nearly absent in natural Pampean grasslands but many forests have N fixing trees (Soriano 1991). Additionally, in the region some forested areas are used as shelters for cows (Jobbágy and Jackson 2007), which may produce an extra N input from the excreta. All these factors lead to greater total N

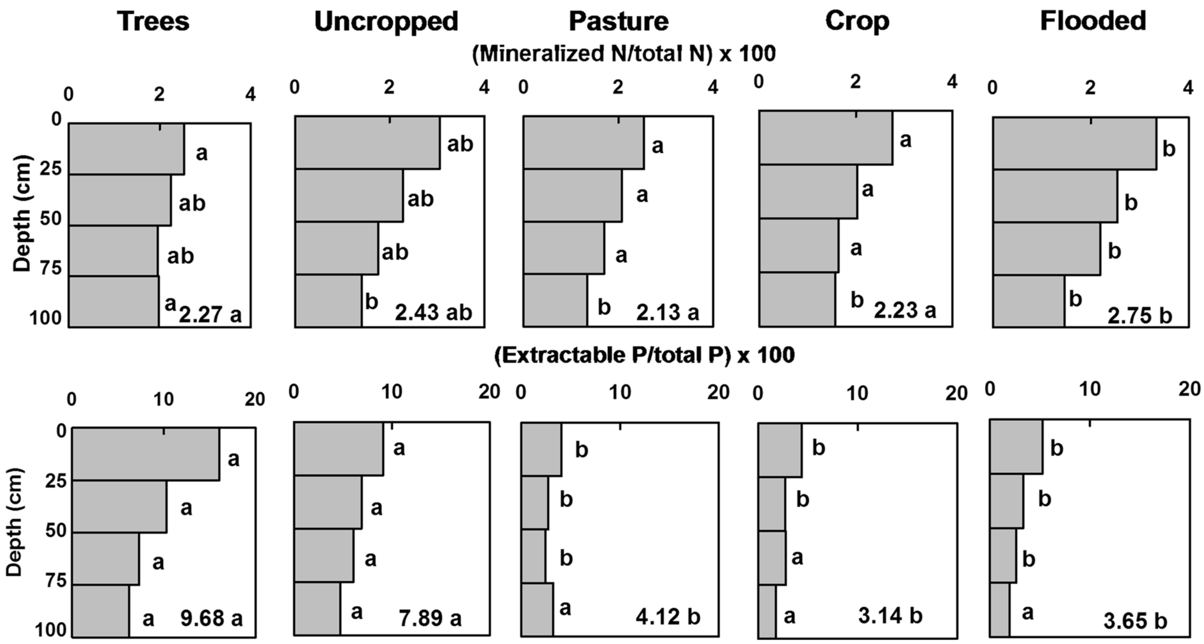

Fig. 7 Average ratios (calculated as percentage) between mineralized N and total N or extractable P and total P as a function of land use. The numbers at the bottom of the boxes indicate mean ratios to 1 m depth. Different letters show significant differences ($P < 0.05$) between land uses for a soil layer

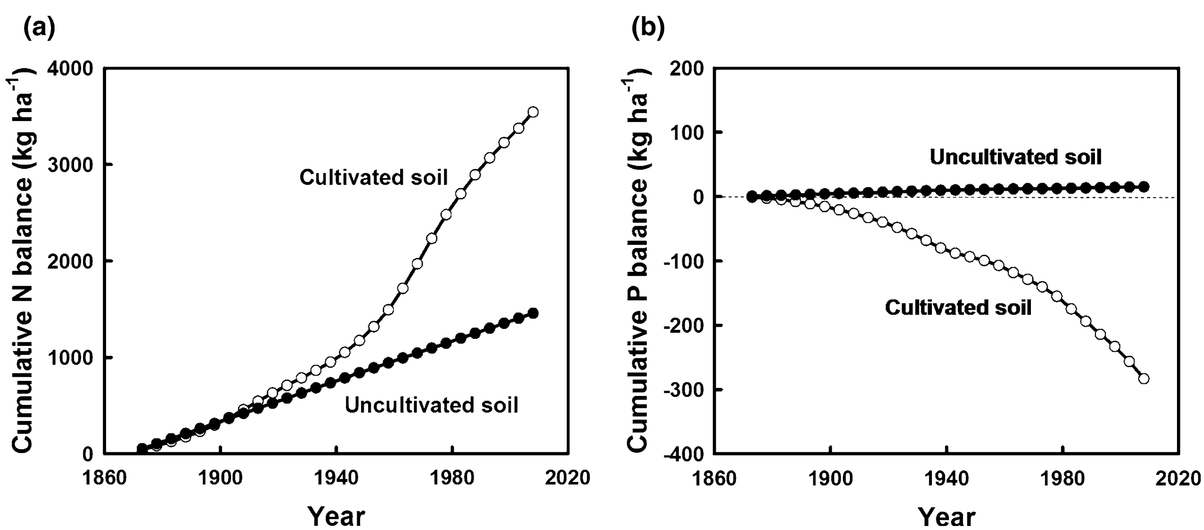

Fig. 8 Cumulative surface N and P balance of the Pampas. Each point represents a 5 year average. Uncultivated soils correspond to the Uncropped (control) treatment. Cultivated soils correspond to Pasture and Crop treatments

contents in forest areas of the Pampas than in grasslands.

Cultivation reduced total N to 1 m depth by 14% compared to the Uncropped control, which was of similar magnitude to organic C losses (Berhongaray et al. 2013). The reduction of total N in the Pampas is lower than commonly reported values of 40–50% losses at surface soil when grasslands are replaced by agriculture (Hass et al. 1957; Lobe et al. 2011; Qiao et al. 2015). Cultivation began in the Pampas around 140 years ago under mixed systems, in which half of the time the soils were under grassland or pasture management (Alvarez et al. 2016; Viglizzo et al. 2001), such that the average total N loss was small. However, total N decreases were heterogeneous among soils. Fertile soils lost more total N than low fertile ones and in some of these latter cases total N increases were measured as response to cultivation. A similar result was reported in Mollisols from USA (Hobbs and Thompson 1971). These results may be ascribed to changes in productivity and C and N retention in soils when natural ecosystems are cultivated. In the Pampas, cultivation of rich organic matter and fertile soils lead to negative C balances, meanwhile in low organic matter soils, positive C balances are easier to attain (Alvarez et al. 2011). In fertile soils, production of crop residue is lower than that from natural vegetation, but in unfertile ones cultivation led to greater C inputs than previous vegetation possible due to fertilizer application.

In cultivated soils, rotation phase did not have a significant impact on total N to 1 m depth. In the upper 0–0.25 m layer greater total N stock was detected during the pasture phase of rotation. Conversely, at the bottom 0.75–1 m total N was greater in soils under the crop phase of the rotation, compensating the former difference. The general lack of difference between rotation phases in total N stock was also observed for organic C in the same sampled sites (Berhongaray et al. 2013). In the Pampas, a small number of years of sown pastures have a minor effect on total soil organic matter content, mainly increasing the labile fraction (Studdert et al. 1997). Net primary productivity is around 35% lower in Flooded soils of the Pampas than in well drained ones (Paruelo et al. 2010). Also, denitrification losses may be higher as this N flux increases when soil pores are water filled (De Klein and Van Logtestijn 1996). This results in lower organic matter content and total N stock in Flooded soils than in the Uncropped or cultivated treatments.

Mineralized N followed total N trends despite an average decrease by cultivation that was slightly greater than total N drop. It was established many years ago that cultivation of grassland soils leads to a decrease of the mineralization potential in surface soil layers (Hass et al. 1957). In the Pampas, significant effects of land use on mineralized N were detected even to 1 m depth. As soil depth increased, the labile N fraction (mineralized N/total N) decreased but land use impact on this fraction was generally not detected, especially between treatments established on well drained soils. Total N variability accounted for 52% of mineralized N variability and the inclusion of depth in a multiple regression analysis allowed only a small increase ($R^2 = 0.56$) of the coefficient of determination. Other soil or climate variables did not improve the fit (results not presented).

Our results indicated a significant impact of cultivation on total P and extractable P content in Pampean soils in surface and deep soil layers down to 0.75 m depth. The loss was especially deep for extractable P content. Phosphorus losses by cultivation were the result of the very low fertilizer consumption in the region and its resulting negative P balance. Land use effects on soil P have been reported in other important grain producing regions of the world mainly at surface soil (Negassa and Leinweber 2009; Rennesson et al. 2013; Sharpley and Smith 1983), but some other studies showed that soil P may have also been impacted in deeper soil layers (Crews and Brookes 2014; Genxu et al. 2004). Generally, decreases of soil P by cultivation are reported but increases may be observed in sites heavily fertilized. Some Pampean experiments, in which only P dynamics at soil surface was investigated, showed similar trends (Alvarez and Steinbach 2017). Soils with high natural fertility lost more total P due to cultivation, meanwhile soils having naturally low total P level could sustain agriculture. This seems to be the consequence of great P harvesting due to greater productivity in fertile soils compared to unfertile ones and more negative P balances. The strong trend of extractable P decrease in high fertile soils but no change in poor P ones can be explained by the following observation. Low extractable P levels in soils can be sustained by recycling processes between P pools when P release by the stable pools needed to maintain extractable P level is low. Conversely, in high extractable P soils, stable pools can not release enough P and extractable P drops under cultivation unless soils are fertilized (Alvarez and Steinbach 2017; Johnston et al. 2014).

Trees had no effect on total P but resulted in an increase of extractable P to 0.5 m depth when compared to Uncropped control soils. This increase can be attributed to the different rooting systems architecture. Tree roots are deeper than grassland roots (Jackson et al. 1996) and can take nutrients from deep soil layers carrying them to surface layers. Additionally, as indicated above, forested areas in the Pampas are frequently used as shelter for cows and therefore P can concentrate at surface because of excreta. As extractable P accounts for a low fraction of total P (10% or less), this difference did not impact the total amount of P. It is unclear why P pools were low under Flooded conditions. Lowland soils accumulate P received from upland positions (Reddy et al. 2005), but this flux seems not to be of significance in the Pampas.

Stratification patterns

Different stratification patterns were observed for the nutrient pools. Averaging the *B* parameter across land uses and calculating the mean stratification ratio (SR) 0–0.2 m/0–1 m with the potential model, it was observed that total N and extractable P showed similar trends with SR ca. 0.40. Mineral N (SR = 0.32) and total P (SR = 0.22) were much less stratified, whereas mineralized N (SR = 0.48) was the most stratified pool. It has been proposed that nutrient stratification is a function of crop demand, and that nutrients that are most limiting for plants are concentrated at soil surface (Jobbágy and Jackson 2001). In the Pampas, total N and extractable P had a similar SR than in other world regions (SR = 0.40–0.50; Jobbágy and Jackson 2001). Mineral N seems less stratified than total N due to nitrate—N mobility in the profile, while total P, which was not stratified at all, was the sum of organic and inorganic components. Organic P would concentrate at surface soil layers but inorganic forms would predominate in deep ones, both pools compensating each other. Despite the close correlation usually found between total N and mineralized N, other research showed that mineralized N is more stratified than total N (Dodd et al. 2000; Murphy et al. 1998) as in Pampean soils. This can be attributed to the decrease of labile organic matter fractions in depth (Murphy et al. 1998; Yang et al. 2009). Independent of the stratification pattern, once the *B* parameter was fitted for each pool and land use, the potential model could be used for nutrient pool estimation in depth using surface data in all cases.

Stoichiometry ratios and nutrient balances

In well drained soils stoichiometry ratios barely changed, and if it did changes were generally not significant between land uses. Some clear differences were observed only in Flooded soils, when compared with other treatments. The C/N ratio was greater and the N/P ratio lower in Flooded soils than in well drained soils. We attributed these differences to higher denitrification loses under waterlogged conditions in Flodded soils that narrowed both ratios. Depth trends of the C/N ratio were not detected in well drained soils. Some regional studies reported decreases of the C/N ratio when virgin soils were cultivated (Hass et al. 1957; Sleutel et al. 2010; Tian et al. 2010) and as depth increased (Malo et al. 2005; Tian et al. 2010), but these trends were not observed in our dataset. The C/P and N/P ratios of Pampean soils decreased in depth due to the reduction of soil organic matter content but were generally not affected by land use. The depth decrease of both ratios is a common phenomenon (Li et al. 2016; Tian et al. 2010) but land use effect on stoichiometry ratios may be contradictory (Cleveland and Liptzin 2007; Slazak et al. 2014). When calculating the C/N/P ratio (molar basis) for our data set, a mean value of 61/6/1 was obtained for the 0–1 m depth across land uses. This value is similar to the average C/N/P ratio of Chinese soils (Tian et al. 2010) and lower than the ratio calculated for forest and grassland soils worldwide at the surface layer (186/13/1) (Cleveland and Liptzin 2007). The similarity between Pampean and Chinese soils may be attributed, possibly, to the loessic origin of many soils in both regions. Conversely, differences with other soil types remain to be clarified.

Nitrogen and P balances were not calculated for Tree and Flooded treatments because inputs in excreta for the former and run-off for the latter could not be estimated. The surface P balance was a suitable tool for predicting total P changes in soil but the surface N balance showed quite opposite trends to total N changes. The N cycle in soil is much complicated that the P cycle and losses must be addressed for a sound estimation of possible total N trends.

Notwithstanding the great nutrient balance differences between the Uncropped control and the adjacent cultivated soils, the average N/P ratio was unaffected in Pampean soils. This showed that processes at the profile level controlled the stoichiometry ratio instead of nutrient external fluxes. Apparently, the average N/P ratio remained unchanged due to N retention or losses from the soil, depending on the amount of total P present. Losses of N in Pampean agroecosystems have been estimated to approximately 25 kg N ha^{-1} $year^{-1}$ as gaseous forms and lixiviation (Alvarez et al. 2016). This value is a regional mean that may be greater or lower depending on the site. As the average C/N ratio was also not impacted by land use, carbon sequestration would be controlled by total P content of the soil as well.

Conclusions

Pampean soils lost 14% of the N and P stocks after 140 years of cultivation. Labile N and P fractions were more impacted by land use than total N and P which may impact crop productivity. These decreases of the N and P stocks were significant to 1 m depth in most cases and very fertile soils were more significantly affected by cultivation than low fertility ones. Forestation led to an increase in soil fertility. Stoichiometry ratios were minimally affected by land use despite its strong impact on N and P fluxes which in turn altered nutrient balances. Pampean soils possibly regulate N losses as a function of the total P present. More work is needed to understand the site effect on nutrient stocks and stoichiometry ratios as both varied greatly between sites.

Acknowledgements This study was supported by the Universidad de Buenos Aires (UBACYT 2011-2014, 20020100617; UBACYT 2014-2017, 20020130100484BA), the Consejo Nacional de Investigaciones Científicas y Técnicas (PID 084, 2016-2019) and the Agencia de Promoción Científica (PICT FONCyT 2009-2012, 37164). SAS Institute Inc. is acknowledged for the support with the use of its software due to an agreement with Facultad de Agronomía, Universidad de Buenos Aires.

References

Alvarez R, Lavado RS (1998) Climate, organic matter and clay content relationships in the Pampa and Chaco soils, Argentina. Geoderma 83:127–141

Alvarez R, Steinbach HS (2011) Modeling apparent nitrogen mineralization under field conditions using regressions an artificial neural networks. Agron J 103:1159–1168

Alvarez R, Steinbach HS (2017) Modeling soil test phosphorus changes under fertilized and unfertilized managements using artificial neural networks. Agron J. https://doi.org/10.2134/agronj2017.01.0014

Alvarez R, Steinbach HS, Bono A (2011) An artificial neural network approach for predicting soil carbon budget in agroecosystems. Soil Sci Soc Am J 75:965–975

Alvarez R, Steinbach HS, De Paepe JL (2014) A regional audit of nitrogen fluxes in Pampean agroecosystems. Agric Ecosyst Environ 184:1–8

Alvarez CR, Steinbach HS, De Paepe JL (2015) Fertilizer use in Pampean agroecosystems: impact on productivity and nutrient balance. In: Sinha S, Pant KK, Bajrai S, Govil JN (eds) Chemical engineering series (ISBN 1-62699-041-7), fertilizer technology, vol 2: biofertilizers (ISBN 1-62699-047-9), vol 15. Studdium Press LLC, Houston, pp 352–368

Alvarez R, Steinbach HS, De Paepe JL (2016) Historical balance of nitrogen, phosphorus, and sulfur of the Argentine Pampas. Ciencia del Suelo 34:231–244

Bai Z, Li H, Yang X, Zhou B, Shi X, Wang B, Li D, Shen J, Chen Q, Qin W, Oenema O, Zhang F (2013) The critical soil P levels for crop yield, soil fertility and environmental safety in different soil types. Plant Soil 372:27–37

Batjes NH (2000) Effects of mapped variation in soil conditions on estimates of soil carbon and nitrogen stocks for South America. Geoderma 97:135–144

Berhongaray G, Alvarez R, De Paepe JL, Caride C, Cantet RJC (2013) Land use effects on soil carbon in the Argentine Pampas. Geoderma 192:97–110

Bernoux M, Arrouays D, Cerri CC, Bourennane H (1998) Modeling vertical distribution of carbon in Oxisols of the western Brazilian Amazon (Rondonia). Soil Sci 163:941–951

Bouwman L, Goldewijk KK, Van der Hoek KW, Beusen AHW, Van Vuuren DP, Willems J, Rufino MC, Stehfest E (2013) Exploring global changes in nitrogen and phosphorus cycles in agriculture induced by livestock production over the 1900–2050 period. PNAS 110:20882–20887

Bremner JM (1996) Nitrogen-total. In: Sparks DL (ed) Methods of soil analysis. Part 3. Chemical methods, Soil Science Society of America Book Series, vol 5. Soil Science Society of America, Inc., Madison, pp 1085–1121

Bui EN, Henderson BL (2013) C:N: P stoichiometry in Australian soils with respect to vegetation and environmental factors. Plant Soil 373:553–568

Buschiazzo DE, Hevia GG, Urioste AM, Hepper EN (2000) Cultivation effects on phosphate forms and sorption in loess-soils of Argentina. Soil Sci 165:427–436

Chaneton EJ, Lemcoff JH, Lavado RS (1996) Nitrogen and phosphorus cycling in grazed and ungrazed plots in a temperature subhumid grassland in Argentina. J Appl Ecol 33:291–302

Chen M, Ma LQ (2001) Taxonomic and geographic distribution of total phosphorus in Florida surface soils. Soil Sci Soc Am J 65:1539–1547

Chen CR, Hou EQ, Condron LM, Bacon G, Esfandbod M, Olley J, Turner BL (2015) Soil phosphorus fractionation and nutrient dynamics along the Cooloola coastal dune chronosecuence, southern Queensland, Australia. Geoderma 257–258:4–13

Cleveland CC, Liptzin D (2007) C:N: P stoichiometry in soil: is there a "Redfield ratio" for the microbial biomass? Biogeochemistry 85:235–252

Colman BP, Schimel JP (2013) Drivers of microbial respiration and net N mineralization at the continental scale. Soil Biol Biochem 60:65–76

Crews TE, Brookes PC (2014) Changes in soil phosphorus forms through time in perennial versus annual agroecosystems. Agric Ecosyst Environ 184:168–181

Cross AF, Schlesinger WH (1995) A literature review and evaluation of the Hedkey fractionation: applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. Geoderma 64:197–214

David MB, Mclaac G, Darmody RG, Omonode RA (2009) Long-term changes in Mollisol organic carbon and nitrogen. J Environ Qual 38:200–211

De Klein CAM, Van Logtestijn RSP (1996) Denitrification in grassland soils in The Netherlands in relation to irrigation, N-application rate, soil water content and soil temperature. Soil Biol Biochem 28:231–237

De Paepe JL, Alvarez R (2013) Developments of a soil productivity index using an artificial neural network approach. Agron J 105:1803–1813

Deng Q, Cheng X, Yang Y, Zhang Q, Luo Y (2014) Carbon-nitrogen interactions during afforestation in central China. Soil Biol Biochem 69:119–122

Dessureault J, Zebarth BJ, Burton DL, Georgallas A (2015) Predicting soil nitrogen supply from soil properties. Can J Soil Sci 95:63–75

Di Ciocco C, Penón E, Coviella C, López S, Díaz-Zorita M, Momo M, Alvarez R (2011) Nitrogen fixation by soybean in the Pampas: relationship between yield and soil nitrogen balance. Agrochimica 40:305–313

Dixon RK, Brown S, Houghton RA, Solomon AM, Trexler MC, Wisniewski J (1994) Carbon pools and flux of global ecosystem. Science 263:185–190

Dodd MB, Lauenroth WK, Burke IC (2000) Nitrogen availability through a coarse-textured soil profile in the shortgrass steppe. Soil Sci Soc Am J 64:391–398

Ebeling A, Bundy L, Kittell A, Ebeling D (2006) Evaluation of the Bray P1 soil test on Eastern red soils in Wisconsin. In: Proceedings of the 2006 Wisconsin fertilizer, aglime & pest management conferences, vol 45, pp 296–306

FAOSTAT (2014) http://faostat.fao.org/. Accessed 21 June 2014

Fila G, Bellocchi G, Acutis M, Donatelli M (2003) IRENE: a software to evaluate model performance. Eur J Agron 18:369–372

Franzluebbers AJ, Follett RF (2005) Greenhouse gas contributions and mitigation potential in agricultural regions of North America: introduction. Soil Tillage Res 83:1–8

Galantini JA, Rossell RA (1997) Organic fractions, N, P and S changes in an Argentine semiarid Haplustoll under different crop sequences. Soil Tillage Res 42:221–228

Gami SK, Lauren JG, Duxbury JM (2009) Influence of soil texture and cultivation on carbon and nitrogen levels in soils of the eastern Indo-Gangetic Plains. Geoderma 153:304–311

Genxu W, Haiyan M, Ju Q, Juan C (2004) Impact of land use changes on soil carbon, nitrogen and phosphorus and water pollution in an arid region of northwest China. Soil Use Manag 20:32–39

Guo LB, Gifford M (2002) Soil carbon stocks and land use change: a meta-analysis. Glob Change Biol 8:345–360

Hall AJ, Rebella C, Guersa C, Culot J (1992) Field-crop system of the Pampas. In: Pearson CJ (ed) Field crop ecosystems. Elsevier, Amsterdam

Hass HJ, Evans CE, Miles EF (1957) Nitrogen and carbon changes in great plains soils as influenced by cropping and soil treatments. United States Department of Agriculture Tech. Bull., vol 1164, 111 pp

Hobbs JA, Thompson CA (1971) Effect of cultivation on the nitrogen and organic carbon contents of a Kansas Argiustoll (Chernozem). Agron J 63:66–68

INDEC (2002) Censo nacional de población, hogares y viviendas. http://www.indec.gov.ar/agropecuario/cna.asp. Accessed 10 Jan 2012

INTA (2010) http://geointa.inta.gov.ar. Accessed 11 Mar 2012

Jackson RB, Canadell J, Ehleringer JR, Mooney HA, Sala OE, Schulze ED (1996) A global analysis of root distributions for terrestrial biomes. Oecologia 108:389–411

Jobbágy EG, Jackson RB (2000) The vertical distribution of soil organic carbon and its relation to climate and vegetation. Ecol Appl 10:423–436

Jobbágy EG, Jackson RB (2001) The distribution of soil nutrients with depth: global patterns and the imprint of plants. Biogeochemistry 53:51–77

Jobbágy EG, Jackson RB (2007) Groundwater and soil chemicals changes under phreatophytic tree plantation. J Geophys Res 112:1–15

Johnston AE, Poulton PR, Fixen PE, Curtin D (2014) Phosphorus: its efficient use in agriculture. Adv Agron 123:177–288

Jones RJA, Hiederer R, Rusco E, Montanarella L (2005) Estimating organic carbon in the soils of Europe for policy support. Eur J Soil Sci 56:655–671

Kader MA, Sleutel S, Begum SA, D'Haene K, Jegajeevagan K, De Neve S (2010) Soil organic matter fractionation as a tool for predicting nitrogen mineralization in silty arable soils. Soil Use Manag 26:494–507

Kenward MG, Roger JH (1997) Small sample inference for fixed effects from restricted maximum likelihood. Biometrics 5:983–997

Kirby CA, Kirkegaard JA, Richardson AE, Wade LJ, Blanchard C, Batten G (2011) Stable soil organic matter: a comparison of C:N:P:S ratios in Australian and other world soils. Geoderma 163:197–208

Kobayashi K, Salam MU (2000) Comparing simulated and measured values using mean square deviation and its components. Agron J 92:345–352

Kuo S (1996) Chapter 32: Phosphorus. In: Sparks DL (ed) Methods of soil analysis. Soil Science Society of America Book Series, Part 3—Chemical methods, vol 5. Soil Science Society of America, Inc., Madison, p 869–919

Li M, Zhou X, Zhang Q, Cheng X (2014) Consequences of afforestation for soil nitrogen dynamics in central China. Agric Ecosyst Environ 183:40–46

Li C, Zhao L, Sun P, Zhao F, Kang D, Yang G, Han X, Feng Y, Ren G (2016) Deep soil C, N and P stocks and stoichiometry in response to land use patterns in the Loess Hilly Region of China. PLoS ONE 11(7):e0159075. http://doi.org/10.1016/j.agee.2013.10.018

Liu Z, Shao M, Wang Y (2013) Spatial patterns of soil total nitrogen and soil total phosphorus across the entire Loess Plateau region of China. Geoderma 197–198:67–78

Lobe I, Sandhage-Hofmann A, Brodowski S, du Preez CC, Amelung W (2011) Aggregate dynamics and associated soil organic matter contents as influenced by prolonged arable cropping in the South African Highveld. Geoderma 162:251–259

Malo DD, Schumacher TE, Doolittle JJ (2005) Long-term cultivation impacts on selected soil properties in the northern Great Plains. Soil Tillage Res 81:277–281

Manlay RJ, Feller C, Swift MJ (2007) Historical evolution of soil organic matter concepts and their relationships with the fertility and sustainability of cropping systems. Agric Ecosyst Environ 119:17–233

McCulley RL, Burke IC, Lauenroth WK (2009) Conservation of nitrogen increases with precipitation across a major grassland gradient in the Central Great Plains of North America. Oecologia 159:571–581

McGill WB, Cole CV (1981) Comparative aspects of cycling of organic C, N, S and P through soil organic matter. Geoderma 26:267–286

Mcgroddy ME, Daufresne T, Hedin LO (2004) Scaling of C:N: P stoichiometry in forest worldwide: implications of terrestrial Redfield-type ratios. Ecology 85:2390–2401

MinAgro (Ministerio de Agroindustria) (2017) http://www.agroindustria.gob.ar. Accessed 06 June 2017

Mortenson MC, Schuman GE, Ingram LJ (2004) Carbon sequestration in rangelands interseeded wuth yellow-flowering alfalfa (*Medicago sativa* ssp. Falcate). Environ Manage 33:475–481

Mudge PL, Schipper LA, Baisden WT, Ghani A, Lewis RW (2014) Changes in soil C, N and $\delta^{15}N$ along three forest-pasture chronosequences in New Zealand. Soil Res 52:27–37

Mulvaney RL (1996) Nitrogen-inorganic forms. In: Sparks DL (ed) Methods of soil analysis. Part 3—chemical methods. Soil Science Society of America, Madison, pp 1123–1184

Murphy J, Riley JP (1962) A modified single solution method for the determination of phosphate in natural waters. Anal Chim Acta 27:31–36

Murphy DV, Sparling GP, Fillery RP (1998) Stratification of microbial biomass C and N and gross N mineralization with soil depth in two contrasting Western Australian agricultural soils. Aust J Soil Res 36:45–55

Negassa W, Leinweber P (2009) How does the Hedley sequential phosphorus fractionation reflect impacts of land use and management on soil phosphorus: a review. J Plant Nutr Soil Sci 172:305–325

OECD (2001) OECD national soil surface nitrogen balances. www.oecd.org/arg/env/indicators.htm. Accessed 20 Nov 2014

OECD (2008) Environmental performance of agriculture in OECD countries since 1990, p 208. www.oecd.org/publishing/corrigenda. Accessed 20 Nov 2014

Oenema O, Kros H, Vries W (2003) Approaches and uncertainties in nutrients budgets: implications for nutrient management and environmental policies. Eur J Agron 20:3–16

Panten K, Rogasik J, Godlinski F, Funder U, Greef J, Schung E (2009) Gross soil surface nutrient balances: the OECD approach implemented under German conditions. Agric For Res 59:19–28

Papini R, Valboa G, Favili F, L'Abate G (2011) Influence of land use on organic carbon pool and chemical properties of Vertic Cambisols in central and southern Italy. Agric Ecosyst Environ 140:68–79

Paruelo JM, 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. Rangel Ecol Manag 63:94–108

Peltier MR, Wilcox CJ, Sharp DC (1998) Technical note: application of the Box–Cox data transformation to animal science experiments. J Anim Sci 76:847–849

Peñuelas J, Poulter B, Sardans J, Ciais P, van der Velde M, Bopp L, Boucher O, Godderis P, Hinsinger P, Llusia J, Nardin E, Vicca S, Obersteiner M, Janssens IA (2013) Human-induced nitrogen-phosphorus imbalances alter natural and managed ecosystems across the globe. Nat Commun 4:2934. https://doi.org/10.1038/ncomms3934

Purton K, Pennock D, Leinweber P, Walley F (2015) Will changes in climate and land use affect soil organic matter composition? Evidence from an ecotonal climosequence. Geoderma 253–254:48–60

Putman DH, Summers CG, Orloff SO (2007) Alfalfa production systems in California, vol 8287. University of California, Oakland, p 18

Qiao N, Xu X, Cao G, Ouyang H, Kuzyakov Y (2015) Land use change decreases soil carbon stocks in Tibetan grasslands. Plant Soil 395:231–241

Randall GW, Grava J (1971) Effect of soil: Bray °N 1 ratios on the amount of phosphorus extracted from calcareous Minnesota soils. Soil Sci Soc Am J 35:112–114

Reddy KR, Wetzel RG, Kadlec RH (2005). Biogeochemistry of phosphorus in wetlands. In: Sims JT, Sharpley AN (eds) Phosphorus: agriculture and the environment. Agronomy Monograph 46, American Society of Agronomy, Madison, pp 263–316

Rennesson M, Dufey J, Legrain X, Genot V, Bock L, Colinet G (2013) Relationships between the P status of surface and deep horizons of agricultural soils under various cropping systems and for different soil types: a case study in Belgium. Soil Use Manag 29:103–113

Romano N, Alvarez R, Bono A, Steinbach HS (2015) Comparison of nitrogen fertilizer demand for wheat production between humid and semi-arid portions of the Argentinean Pampas using a mass balance approach. Arch Agron Soil Sci 61:1409–1422

Romano N, Alvarez R, Bono A (2017) Modeling nitrogen mineralization at surface and deep layers of sandy soils. Arch Agron Soil Sci 63:870–882

Rubaek GH, Kristensen K, Olesen SE, Ostergaard HS, Heckrath G (2013) Phosphorus accumulation and spatial distribution in agricultural soils. Geoderma 209–210:241–250

Rubio G, Alvarez R, Steinbach HS (2015) Fósforo del suelo en agrosistemas, Chapter 5. In: Alvarez R (ed) Fertilidad de suelos y fertilización en la Región Pampeana. Editorial Facultad de Agronomía, Universidad de Buenos Aires, Buenos aires, pp 147–164

SAS Institute Inc. (2016) SAS/STAT® 14.2 user's guide. SAS Institute Inc., Cary

Satorre E, Slafer G (1999) Wheat production systems of the Pampas. In: Press ETH (ed) Wheat: ecology and physiology of yield determination. Food Products Press Inc, New York, pp 333–348

Schipper LA, Sparling GP (2011) Accumulation of soil C and change in C: N ratio after establishment of pastures on reverted scrubland in New Zealand. Biogeochemistry 104:49–58

Searle SR (1971) Linear models. Wiley, New York

Shapiro SS, Wilk MB (1965) An analysis of variance test for normality (for complete samples). Biometrika 52:591–611

Sharpley AN, Smith SJ (1983) Distribution of phosphorus forms in virgin and cultivated soils and potential erosion losses. Soil Sci Soc Am J 47:581–586

Slazak A, Matos ES, Nii-Annang S, Hüttl R (2014) Phosphorus pools in soil after land conversion from silvopasture to arable and grassland use. J Plant Nutr Soil Sci 177:159–167

Sleutel S, Kader MA, Begum SA, De Neve S (2010) Soil-organic-matter stability in sandy cropland soils is related to land-use history. J Plant Nutr Soil Sci 173:19–29

Smit A, Velthof GL (2010) Comparison of indices for the prediction of nitrogen mineralization after destruction of managed grassland. Plant Soil 331:139–150

Soriano A (1991) Río de la Plata Grasslands. In: Coupland RT (ed) Ecosystems of the world. 8A. Natural grassland. Elsevier, Amsterdam, pp 367–407

Steffens M, Kölbl A, Totsche KU, Kögel-Knaber I (2008) Grazing effects on soil chemical and physical properties in a semiarid steppe of Inner Mongolia (P.R. China). Geoderma 143:63–72

Studdert GA, Echeverría HE, Casanovas EM (1997) Crop-pasture rotation for sustaining the quality and productivity of a Typic Argiudoll. Soil Sci Soc Am J 61:1466–1472

Teruggi ME (1957) The nature and origin of argentine loess. J Sediment Petrol 27:322–332

Tian H, Chen G, Zhang C, Melillo JM, Hall CAS (2010) Patterns and variation of C:N:P ratios in China's soils: a sintesis of observational data. Biogeochemistry 98:139–151

Turner BL, Laliberté E (2015) Soil development and nutrient availability along a 2 million-year coastal dune chronosequence under species-rich Mediterranean scrubland in southwestern Australia. Ecosystems 18:287–309

Vejre H, Callesen I, Vesterdal L, Raulund-Rasmussen K (2003) Carbon and nitrogen in Danish forest soils-contents and distribution determined by soil order. Soil Sci Soc Am J 67:335–343

Viglizzo EF, Lértora F, Pordomingo AJ, Bernados JN, Roberto ZE, Del Valle H (2001) Ecological lessons and applications from one century of low external-input farming in the Pampas of Argentina. Agric Ecosyst Environ 83:65–81

Wu C, Wu J, Luo Y, Zhang L, DeGloria SD (2009) Spatial estimation of soil total nitrogen using cokriging with predicted soil organic matter content. Soil Sci Soc Am J 73:1676–1681

Yang Y, Guo J, Chen G, Yin YY, Gao R, Lin C (2009) Effects of forest conversion on soil labile organic carbon fractions and aggregate stability in subtropical China. Plant Soil 323:153–162

Young JL, Aldag RW (1982) Inorganic forms of nitrogen in soil. In: Stevenson FJ (ed) Nitrogen in agricultural soils. Agronomy, vol 22. American Society of Agronomy Inc Publisher, Madison, pp 43–66