HISTORICAL BALANCE OF NITROGEN, PHOSPHORUS, AND SULFUR OF THE ARGENTINE PAMPAS

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ABSTRACT

A surface balance for nitrogen (N), phosphorus (P), and sulfur (S) was performed for the Argentine Pampas during the 1870-2010 time interval, comprising the agricultural expansion period in the region. Nitrogen inputs accounted in the balance were atmospheric deposition, symbiotic fixation, and fertilization. Outputs included were grain harvest and livestock products. P and S balances included atmospheric deposition and fertilization as inputs and the same outputs than in the case of N balance. Annual and cumulative balances were calculated and also an annual output/input ratio. National information and official statistics were used to determine the nutrient outputs whereas atmospheric deposition, symbiotic fixation, and fertilizer inputs were estimated. Cumulative N input was of 202 Mt, atmospheric deposition (36%) and symbiotic fixation (58%) represented the main components. The output was of 76 Mt, with grain harvest as main factor (83%), thus resulting in a positive N balance of 126 Mt. This nutrient flow is equivalent to one quart of the soil N stock to 1 m depth. As previous studies showed that soil N stock did not changed between 1960-1980 and 2007-2008, period during which a positive N balance of 52 Mt was calculated, this resulted in a loss of 26 kg ha^{-1} yr^{-1} due to gas emissions and leaching in recent decades. Phosphorus input was 4.2 Mt, mainly explained by fertilization (67%), and the output was 12.2 Mt, generated mainly by grain harvest (76%), which determined a negative balance of -8.0 Mt. Sulfur input was 3.9 Mt, mainly determined by atmospheric deposition (81%) and the output was 5.6 Mt, mainly due to grain harvest (82%) resulting also in a negative balance of -1.7 Mt. These results indicate P and S losses from soil stocks. The N output/input ratio varied from 0.2 to 0.7 along the study period, while the P and S ratios have been higher than 1 since decades.

Key words. Nutrient balance, nutrient ouput/input ratio, Argentine Pampas Region.

BALANCE HISTÓRICO DE NITRÓGENO, FÓSFORO Y AZUFRE DE LA REGIÓN PAMPEANA

RESUMEN

Se realizó un balance de superfice de nitrógeno (N), fósforo (P) y azufre (S) para la Región Pampena desde 1870 a 2010, período en que se produjo la expansión agrícola en la región. Para N se computaron como entradas el aporte atmósferico, la fijación simbiótica y la fertilización. Las salidas fueron la exportación en grano y productos animales. Para P y S el balance incluyó como entradas el aporte atmosférico y la fertilización y como salidas las mismas que para N. El balance se calculó en forma anual y acumulada y también se calculó la relación salida/entrada anual. Las bases de datos fueron censos nacionales y estadísticas oficiales para estimar las salidas y se hicieron estimaciones de aporte atmosférico, fijación simbiótica y consumo de fertilizantes. La entrada de N fue de 202 Mt, siendo el aporte atmósferico (36%) y la fijación simbiótica (58%) los componentes principales. La salida fue de 76 Mt, con la exportación en grano como principal factor (83%); resultando en un balance positivo de 126 Mt. Este flujo equivale a un cuarto del stock de N de los suelos hasta 1 m. Otros estudios mostraron que no se produjeron cambios en los stock de N pampeano entre 1960-80 y 2007-2008, período durante el cual el balance de N fue de +52 Mt. En consecuencia, se estimaron pérdidas gaseosas o por lixiviación durante este lapso de 26 kg ha^{-1} año^{-1}. Para fósforo la entrada fue 4,2 Mt, con mayor peso del componente fertilizantes (67%) y la salida de 12,2 Mt, generado sobre todo por la cosecha de granos (76%), determinando un balance negativo de -8,0 Mt. La entrada de azufre fue de 3,9 Mt, principalmente generada por la atmósfera (81%) y la salida de 5,6 Mt, debido sobre todo a la exportación en grano (82%), con un balance negativo de -1,7 Mt. Estos resultados indican pérdida de P y S desde las reservas de los suelos. La relación salida/entrada de N pasó de 0,2 a 0,7 en el lapso estudiado, mientras que para P y S ha sido mayor a 1 desde hace décadas.

Palabras clave. Balance de nutrientes, relación salida/entrada de nutrientes, Región Pampeana Argentina.

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INTRODUCTION

The mass balance approach is a useful tool for understanding nutrient cycling (Galloway *et al.,* 2004), predicting future trends (Howarth *et al.,* 2002) and assessing potential environmental impacts (Eickhout *et al.,* 2006). According to the complexity of the model used, different types of balances can be proposed. Soil balances include main inputs and outputs to the soil, among the latter, nutrients in harvested products and losses due to gaseous emissions and leaching are incorporated (Oenema *et al.,* 2003). A simplified version is the surface balance in which losses are ignored (OECD, 2001). This method allows estimating nutrient surpluses that can be retained in the soils or passed on to the atmosphere or water bodies (OECD, 2001; Panten *et al.,* 2009; Sheldrikck *et al.,* 2002). The advantage of not considering some flows which are difficult to estimate, as the losses, is that uncertainty of the results decreases (Oenema *et al.,* 2003).

Positive nitrogen (N) balances for the year 1880 have been determined previously in the Argentine Pampas (Viglizzo *et al.,* 2001). Symbiotic fixation and fertilizers were computes as inputs, while grain and meat production were accounted as outputs. Depending on the Pampean sub-region, these balances went from positive to negative during mid (1940) and end (1980) of the XX Century, as agriculture expanded and yields increased. Phosphorus balances were continuously negative between 1880 and 1980, accounting only for fertilizers as inputs and grain and meat as outputs (Viglizzo *et al.,* 2001). However, at national scale, a positive soil N balance was calculated during 1960 and 2005 including atmospheric deposition, symbiotic fixation, fertilizers, and animal feed as inputs and grain harvest, meat, milk, erosion, and denitrification as outputs (Viglizzo *et al.,* 2011). A national negative soil phosphorus (P) balance was also determined computing fertilizers and animal feeds as inputs and grain harvest, meat, milk, erosion, runoff, and leaching as outputs (Viglizzo *et al.,* 2001). In these two latter studies, methodologies developed for other regions of the World were used for fluxes estimation and average parameters values taken from literature were applied for estimating symbiotic fixation and denitrification. More recently, for the 1960-2010 time interval, a positive N surface balance was estimated for the Pampas using local adjusted models (Álvarez *et al.,* 2014a). No sulfur (S) balances have been calculated that include the main nutrient inputs and outputs of local agro-ecosystems. Computing only fertilizer as input and grain harvest as output a negative regional sulfur balance has been estimated (Alvarez *et al.,* 2015). Our goal was to determine N, P and S balances in the Pampean region comprising the time period from agricultural introduction in the region up to present time, including nutrient flows that can be estimated using locally adjusted models. Possible nutrients fates are also discussed.

MATERIALS AND METHODS

Area of study

An area of 55 Mha comprised by 149 counties from Buenos Aires, Córdoba, Entre Ríos, La Pampa and Santa Fe provinces was accounted for (Fig. 1). In this area, almost all Pampean agricultural production is generated. The effective study area was of 50.4 Mha as cities, lakes, salt marshes, and rocky areas were discarded using satellite image classification (Berhon-garay *et al.,* 2013). The study area was then partitioned into cropped area in which grain crops and cropped forages were cultivated and natural systems, mainly occupied by grasslands and forest.

N input

Total N input was calculated as the sum of inputs from the atmosphere (humid and dry deposition), N fixation from pastures and soybean, and fertilizers. Minor leguminous crops as peanut (*Arachis hipogaea*), pea (*Pisum sativum*) and others were not taken into account. Animal feeds initially harvested as grains and then returned to agroecosystems were also

Figure 1. Map showing the study area in grey.
Figura 1. Mapa indicando el área de estudio en color gris.

accounted for (see output section). Based on local experiments previously analyzed (Álvarez *et al.*, 2001), atmospheric input was estimated at 13 kg N ha^{-1} yr^{-1} 100 cm^{-1} rainfall and adjusted as a function of average county rainfall data of meteorological records from ca. 1900 to 2000. Historical rainfall evolution was calculated using published records of about 30 meteorological stations distributed along the Pampas (Davis, 1914; Ministerio de Agricultura, 1943, SMN, 1962; 1972; 2014) estimating county averages by the inverse distance weighting method (De Paepe & Álvarez, 2013). National and provincial censuses and other information sources were used to determine leguminous pasture area (Anónimo, 1888; 1909; 1917; 1923; 1939; 1947; INDEC, 1964; 1969; 1974; 1988; 2002; Secanell, 2009). As in the census of the year 2002 the area devoted to each pasture type was described in detail, which was not available in the previously published censuses, it was assumed that this areal partition was constant along the analyzed period. Locally, it was determined that alfalfa (*Medicago sativa*) fixed 38 kg N t^{-1} aboveground biomass, taking into account both N fixed in aboveground organs and in roots (Álvarez *et al.*, 2014a). Alfalfa productivity at county scale was estimated with a climate model adjusted locally (Álvarez *et al.*, 2014a) and fixation was calculated combining biomass productivity and the indicated fixation factor. It was assumed that alfalfa accounts for 50% of total biomass in mixed pastures (Mortenson *et al.*, 2004) and therefore N fixation was corrected by half. Mixed pastures with clovers as leguminous components represented 34% of total mixed pastures (INDEC, 2002) but no local tools were available to determine their N fixation and therefore the same methods used for alfalfa were applied. No local evolution of the historical yield gain of alfalfa was available so we assumed a yield gain of 100% from 1920 to 2000, as reported for the alfalfa producing region of USA (Putman *et al.*, 2007). Our alfalfa productivity estimations, based on experiments performed in recent years, were decreased by a factor of 0.63% year^{-1} and past N fixation estimations adjusted on this basis. Natural grasslands fixation was considered to be null (Chaneton *et al.*, 1996). Soybean N fixation for the Pampas was estimated with de model proposed by Di Ciocco *et al.* (2011) according to which fixation averages 52 kg N t^{-1} dry grain (0% water) in above and belowground organs. The results calculated with this model were very similar to those estimated by the model of Collino *et al.* (2015), adjusted for the whole Argentina country, if it is assumed that 24% of the crop N is allocated to roots. Combining this model with soybean county yield information (MinAgri, 2014), N input to soils through this biological mechanism was estimated. Fertilizer input was estimated by compounding national fertilizer consumption (FAOSTAT, 2014), its partition among the main annual crops (FAO, 2004; González Sanjuán *et al.*, 2013; Heffer, 2009) and the county cultivated area per each crop (MinAgri, 2014). Approximately 90% of national fertilizer consumption is used in the Pampas and 80% for grain crops.

It was assumed that the rest was split among seeded pastures (10%) and intensive crops (10%). These latter crops predominate in the horticultural belts surrounding cities and were not considered in the analysis. Fertilizer inputs were estimated at county scale using pampean overall nutrients consumption and a partitioning index calculated using results from an official survey performed by RIAP (INTA) as indicated in De Paepe and Álvarez (2016).

N output

Nitrogen output was calculated as the sum of N outputs in grain harvest and livestock products. Grain harvest output was calculated based on grain production and its N concentration. Past production data were obtained from the above mentioned censuses and also official statistics were used for the 1960-2010 period (MinAgri, 2014). Up to ca. 1950 the main annual crops in the Pampas were wheat (*Triticum aestivum*), corn (*Zea mays*) and flax (*Linum usitatissimum*), the latter being replaced by sunflower (*Helianthus annuus*) and soybean (*Glycine max*) during the last decades. Grain N concentration of soybean, corn, wheat, and sunflower were the same used in Álvarez *et al.* (2014a). A content of 40 kg N t^{-1} dry grain (0% water) was used for flax (Morris, 2007). Minor crops like sorghum and barley were not taken into account because it was estimated that this crops produced an off set of N from agroecosystems lower than 2% in the total output estimation. As 25% of corn is usually used for livestock feeding (Eyhérabide *et al.*, 2009) and its N returns to soils through excreta, it was accounted for in the balance computations as N input. Because animal feed return was of ca. 1% of total N input, it was not disengaged in the analysis. Another ca. 20% of corn production is used for small animals feeding (Eyhérabide, 2009) but excreta does not return to soils in which extensive agriculture is performed. These excreta are applied to the intensive agriculture areas, usually located in the horticultural belts around cities. As these areas were not accounted for in our analysis the N flux was computed as an output.

Livestock output was the sum of N in the living bodies of cattle and sheep and wool. Livestock production was based on sheep until 1910 and cattle afterwards. Animal populations were obtained from national census and other sources (Antuña, 2010; MinAgri, 2010; Rossanigo *et al.*, 2009) and the annual sacrificed amount was calculated (MinAgri, 2010; Observatorio Bovino, 2013). An average cattle weight of 400 kg per animal was used (MinAgri, 2010), a 29% sacrifice fraction per year, 20% ruminal content and 3% of N in body tissues (Thompson *et al.*, 1983). Previously, it was estimated that from the milk production no more than 1% of total N output was exported (Álvarez *et al.*, 2014a) and therefore it was discarded from the analysis as no past information was available on milk production. Average sacrificed sheep weight estimated was of 40 kg and an annual sacrifice fraction of 24 % (MinAgri, 2010).

Wool production of 4.8 kg sheep^{-1} yr^{-1} was applied for calculations (MinAgri, 2010). A N body content of 2.5% was assumed (Greenwood *et al.*, 1998) and 14% in wool (Thomas *et al.*, 1951). For dry matter production calculations 14% of water content in grains, 16% in wool and 60% in body weight (Marcondes, 2013) were assumed.

P input

Phosphorus input was estimated as the sum of atmospheric deposition and fertilization. Dry and humid depositions were accounted for as the average of the annual measurements in three pampean sites with mean rainfall of ca. 1000 mm (Lavado, 1983; Michel *et al.*, 2010). Average input was 0.23 kg P ha^{-1} yr^{-1} (0.23 g P ha^{-1} yr^{-1} mm^{-1}). Temporal and spatial P input was adjusted to the county rainfall estimated as previously indicated. Fertilizer P input was calculated using the same data and criteria applied for N.

P output

Phosphorus output was computed as the sum of fluxes in harvested grains, animal bodies and wool and the same data and criteria as for N were used. Grain P content was estimated at 4 kg t^{-1} for wheat, 3 kg t^{-1} for corn, 4 kg t^{-1} for sunflower, 6 kg t^{-1} for soybean (Álvarez, 2013, IPNI 2013) and 6 kg t^{-1} for flax (Morris, 2007). As was described for N, minor crops like sorghum and barley were not considered because their P output was estimated to be less than 3% of total nutrient output (2006-2010). A P concentration of 8 kg t^{-1} of cattle body weight was applied (Georgievski, 1982; Marcondes, 2013). Milk production information was obtained from ONCA data base (2009). During the 2008-2009 period the milk production was of 4.7 Gl. Considering a content of 785 mg P l^{-1} (Sola-Larrañaga & Navarro-Blasco, 2009), the P output was equivalent to ca. 1% of total regional output. As no past information on milk production at county scale was available, this flow was not accounted for. A P content of 8.2 kg t^{-1} of living sheep weight was estimated and 0.2 kg t^{-1} in wool (Grace, 1983).

S input

Sulfur input was calculated as the sum of atmospheric deposition and fertilizer application. Atmospheric deposition varies in the Pampas between values near zero and 0.83 kg S ha^{-1} yr^{-1} without apparent association with climate variables (Lavado, 1983; Michel *et al.*, 2010). Using published data for three different sites in the Pampas (Lavado, 1983; Michel *et al.*, 2010), a mean deposition of 0.45 kg S ha^{-1} yr^{-1} was estimated using dry and humid depositions. To calculate fertilizer input the same proceedings and data were used as for N and P.

S output

Sulfur output was calculated as the export of harvested grains, animal bodies and wool. The same methods and data

as for N and P were used and corresponding concentration coefficients for S were applied. Sulfur contents of 1.7 kg t^{-1} for wheat, 1.4 kg t^{-1} for corn, 2.2 kg t^{-1} for sunflower, 3.2 kg t^{-1} for soybean (Álvarez, 2013; IPNI, 2013) and 1.8 kg t^{-1} for flax were applied (Madhusudhan, 2009). Sulfur content used for calculations of cattle bodies without rumen was of 1.5 kg t^{-1} (Hale *et al.*, 1984), for sheep of 1.7 kg t^{-1}; both calculated with data of Breytenbach (1999) and Greenwood *et al.* (1998); and 35 kg S t^{-1} in wool (Reis, 1967). Sulfur exported in milk production (ONCA 2009), with a concentration of 290 mg S l^{-1} (Masters & McCance, 1939), represented less than 1% of total output and therefore was not accounted for as past information on milk production was not available as occurred with the other nutrients.

Calculation

For all variables, county scale estimations were determined and aggregated for the entire study area. Spline estimations were performed to estimate harvested area, seeded forage area, grain production, yield, animal population and livestock production during the intermediate years between censuses. Cubic splines were used for the annual estimations of these variables using Tablecurve facilities (Systat Software, Inc.). Annual data were aggregated in periods of five years to avoid some extreme values. The surface balance was calculated as the difference between annual inputs and outputs from 1870 to 2010 for the whole study area. Cumulative balances were also calculated for the 140 year time period. Additionally, separated balances were estimated for the Pampas cropped area and for natural systems. The former devoted to grain crops and seeded forages accounting for 27.9 Mha as an average of the 2006-2010 period and the later devoted mainly to grasslands and a small fraction to forest, accounting for 22.5 Mha in the same period. For partitioning livestock production from cropped soils areas and natural areas it was estimated that 66% of animal products became from seeded forage crops based on receptivity data from Secanell (2009). Output/input ratios were calculated on a yearly basis. Time series of the nutrient balances and the output/input ratio were analyzed by piecewise regression (Toms & Lesperance, 2003) in order to separate periods with different trends and identifying possible break point times. Time series analysis was performed with SegReg (www.waterlog.info).

RESULTS AND DISCUSSION

Cultivated area under grain and forage crops increased in the Pampas from nearly zero around 1870 to an average of 27.9 Mha for the period 2006-2010 (Fig. 2A). As the common production system was rotation with grain crops and permanent pastures or annual forages (Hall *et al.,* 1992; Viglizzo *et al.*, 2001) these crops alternated on the same
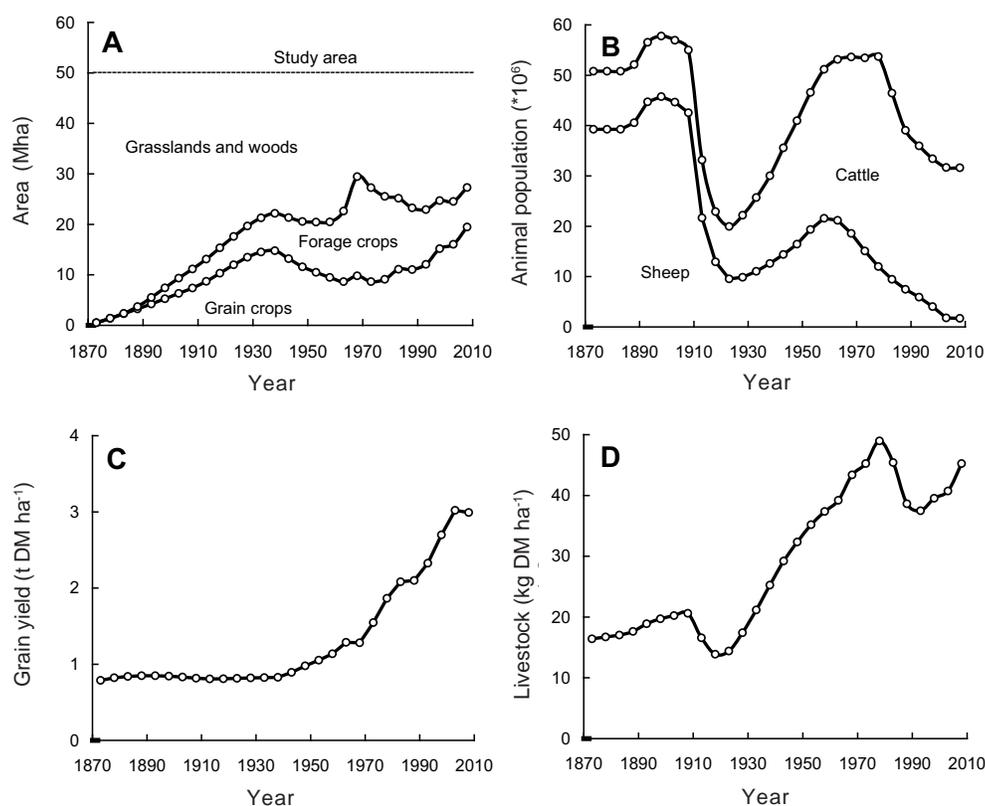
Figure 2. A: Evolution of the area under different land uses in the Pampas. B: Evolution of animal population. C: Average grain yield increase (0% water content) of the main pampean crops (wheat, corn, flax, sunflower and soybean). D: Average livestock yield increase (0% water) of the main pampean products (sheep bodies, wool and cattle bodies).

Figura 2. A: Evolución de la superficie bajo diferentes usos del suelo en la Región Pampeana. B: Evolución de la población de animales. C: Incremento promedio de rendimiento (0% de contendio de agua) de los principales cultivos pampeanos (trigo, maíz, lino, girasol y soja). D: Incremento del rendimiento de los principales productos pecuários (cuerpo de ovejas, lana y cuerpo de vacunos).

soils. Conversely, uncultivated soils, mainly devoted to natural grasslands and in a minor proportion to forest, were not rotated with crops. During the last five decades the ratio grassland area/forest area stabilized at ca. 5:1 (Álvarez *et al.*, 2014a). In the 2006-2010 period the uncultivated area averaged 22.5 Mha and much of the area corresponded to hydromorphic soils, that covered an area which rounded 20 Mha in the Pampas (Imbellone *et al.*, 2010a,b). Pampean livestock production was based on sheep production until the end of the XIX Century, and turned to cattle during the XX Century (Fig. 2B). Average grain yield in the region increased ca. 3-fold from 1950 to present (Fig. 2C). A similar increase of livestock yield was estimated computing the area under cropped forages, grasslands and forest (Fig. 2D). Because cattle are partially feed with straw when grazing postharvest crop area, the later figures may be ove-

restimated. However, the bias would not be greater than 12% (Secanell, 2009).

The evolution of N inputs showed that the relative importance of different N fluxes changed through time (Fig. 3A). Atmospheric deposition was the main input before agriculture development. After the widespread adoption of alfalfa in the Pampas (from 1900), N fixation became the main N input. Since 1970 nitrogen fixation by soybean replaced partially alfalfa input and recently N fertilizer contributed agroecosystems. The two latter inputs have become important only during the last 30 years. Cumulative N input during the 1870-2010 period was of 202 Mt (Table 1). The relative order of the various inputs was N fixation by pastures (48%), atmospheric deposition (36%), soybean N fixation (11%), and fertilization (5%). At present, analyzing

Table 1. Nitrogen, phosphrus and sulfur balance of pampean agroecosystems. Cumulative results for inputs, outputs and the balance (inputs-outputs) are presented in Mt for the 1870-2010 period. All agroecosystems correspond to the whole study area of 50.4 Mha. Cropped agrooecosystems (grain and forage crops) corresponds to an area of 27.9 Mha during the 2006-2010 period. Uncropped agroecosystems (grasslands and forest) corresponds to an area of 22.9 Mha for the same time period. The cumulative balance results were also calculated on an areal basis (kg ha^{-1}) and anualized (kg ha^{-1} year^{-1}).

Tabla 1. Balances de nitrógeno, fósforo y azufre de los agroecosistemas pampeanos. Se presentan los datos acumulados de entradas, salidas y balances (entradas-salidas) en Mt para el período 1870-2010. Todos los agroecosistemas corresponden al total del área de estudio de 50,4 Mha. Agroecosistemas cultivados (cultivos de granos y forrajeros) corresponden a un área de 27,9 Mha en el período 2006-2010. Agroecosistemas no cultivados (pastizales y montes) corresponden a un área de 22,9 Mha en el mismo período. Los balances acumulados se calcularon también sobre una base areal (kg ha^{-1}) y anualizados (kg ha^{-1} year^{-1}).

	Nitrogen			Phosphorus			Sulfur		
	All	Cropped	Uncropped	All	Cropped	Uncropped	All	Cropped	Uncropped
Atmosphere (Mt)	73.4	40.4	33.0	1.38	0.759	0.621	3.18	1.75	1.43
Pastures (Mt)	96.4	96.4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Soybean (Mt)	21.7	21.7	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fertilizer (Mt)	10.8	10.8	0.00	2.80	2.80	0.00	0.770	0.770	0.00
Total input (Mt)	202	169	33.0	4.18	3.56	0.62	3.95	2.52	1.43
Livestock (Mt)	13.1	8.65	4.32	2.90	1.91	0.96	1.06	0.70	0.35
Grain (Mt)	63.3	63.3	0.00	9.32	9.32	0.00	4.57	4.57	0.00
Total output (Mt)	76.4	71.9	4.32	12.2	11.2	0.96	5.6	5.27	0.35
Balance (Mt)	126	97.3	28.7	-8.04	-7.68	-0.34	-1.68	-2.75	1.08
Balance (kg ha^{-1})	2498	3488	1276	-160	-275	-14.9	-33.3	-98.6	48.1
Balance (kg ha^{-1} year^{-1})	17.8	24.9	9.11	-1.14	-1.96	-0.11	-0.24	-0.70	0.34

the 2006-2010 time interval, the relative importance of different N sources changed in relation to historical values. Soybean fixation is the main N input of the pampean agroecosystems being more important than pasture input because soybean displaced pastures from crop rotations in many areas. Around 40% of pasture area was turned to soybean crops during the 1970-2010 period (Álvarez *et al.*, 2014a). Symbiotic N fixation by grasslands and forest was not taken into account. Because of the very low presence of leguminous species, grassland input of N by fixation in the Pampas was estimated to be null previously (Chaneton *et al.*, 1996). In forest ecosystems some N fixing trees are found as *Casuarina* sp in planted forest or *Acacia* sp. in natural ones. Total forest area in the Pampas accounts for 10% of the surface since 1970 (Álvarez *et al.*, 2014a) with only a minimal occupation of N fixing trees. In a soil survey of the Pampas (Berhongaray *et al.*, 2013), 82 forest widespread over the region were sampled and tree species identified. In only 3% of the sites N fixing trees were recognized (unpublished data). Consequently, the N input by tree fixation seems to be very small. When partitioning the study area into cropped (grain and forage crops) and uncropped agroecosystems (grasslands and forest) atmospheric deposition contribution decreased in the first case and was the only source of N in the latter (Table 1).

Outputs of N were lower than the inputs during the whole study period (140 years) (Fig. 3B). Accumulated N output was of 76 Mt, ca. 2.5 times less than the N input (Table 1), originated mainly by grain harvest (82%) and much less by the livestock products (18%). Consequently, nearly all N output from the Pampas was accounted for by grain N from cropped agroecosystems. The N balance was positive along the whole study period (Fig. 3C) and the cumulative N balance of the Pampas was +126 Mt, being positive both in the cropped and the uncropped areas (Table 1). The annual surplus of N was 17.8 kg N ha^{-1} year^{-1} as a mean of the 140 years study period (Table 1). The output/input ratio of N rounded 0.2 during one Century, strongly increasing in the last decades and reaching a value of 0.7 (Fig. 3D), which can be attributed to the expansion of cultivation and high yields (Álvarez *et al.*, 2014a, MinAgri, 2014). Regression analysis showed that both the N balance and the output/input ratio can be split into two differing periods with a change in the earlier seventies. Positive N balance increased constantly and reached and equilibrium stage meanwhile the output/input ratio passed from a steady state condition to a significant rapid increase phase (Table 2).

Nitrogen output estimation uncertainty was low as its calculation was based on registered agricultural exported products and N concentrations that usually do not present
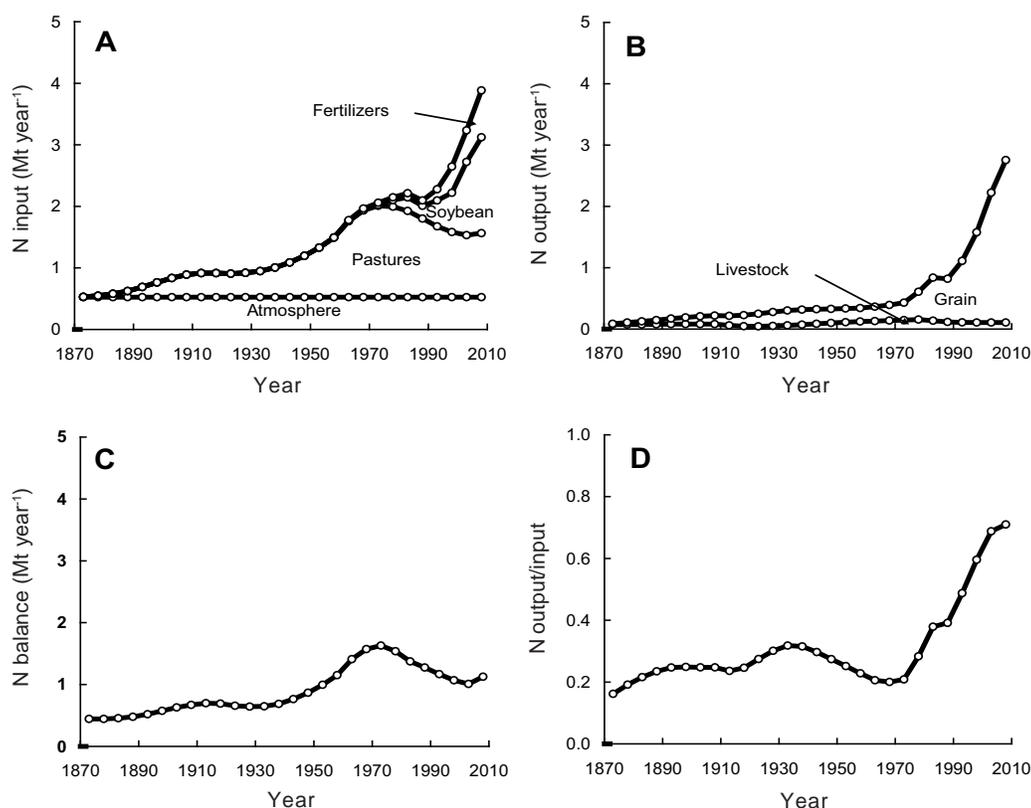
Figure 3. A: Nitrogen (N) input to the Pampean Region from different sources. B: N output of from the region. C: Nitrogen balance of the region (input-output). D: annual N output/input ratio.

Figura 3. A: Entrada de nitrógeno (N) a la Región Pampeana según su origen. B: Salida de N de la región. C: Balance de N (entrada-salida). D: Relación anualizada de la relación salida/entrada.

Table 2. Piecewise regression analysis of trends of the nutrien balances and the output/input ratios.

Tabla 2. Análisis de regresión no lineal de las tendencias de los balances de nutrientes y la relación salida/entrada.

Nutrient	Balance			Output/input		
	Model type	R^2	Break point year	Model type	R^2	Break point year
Nitrogen	Linear-plateau	0.78	1972	Plateau-linear	0.93	1976
Phosphorus	Linear	0.85	ns	Bilinear	0.54	1900
Sulfur	Plateau-linear	0.93	1959	Linear	0.78	ns

large variations. For example, coefficients of variation of grain N concentration rounded 10% using data from networks of field experiments with wheat (Romano *et al.*, 2015), corn (Álvarez *et al.*, 2011), and soybean (Di Ciocco *et al.*, 2011) performed in the Pampas. Nitrogen input estimations of fertilizers or soybean N fixation had also low uncertainty. These were based on consumption statistics

and a locally adjusted model for soybean fixation estimation (Di Ciocco *et al.*, 2011) that did not differ markedly from another two models: one adjusted at global scale (Salvagiotti *et al.*, 2008) and another fitted to data from experiments widespread over all Argentina (Collino *et al.*, 2015). The Pampean model was more conservative than the global model and with similar values than the

Argentinean model so it was chosen for the estimations. Uncertainty of the applied models and assumptions to estimate pasture N fixation was also low and was analyzed previously (Álvarez *et al.*, 2014a). However, in this case, it should be considered that the model for estimating contemporary alfalfa productivity was adjusted to estimate past data using a yield gain estimation not based on local information. But, assuming that genetic improvement and management allowed an alfalfa productivity increase 50% lower or higher than the one used in this study for calculation it would determine a sub- or an over-estimation of the pasture input not greater than 10% of the total output and it would not change the N balance significantly. The same can be added related to the atmospheric deposition estimation. This input estimation was based on a long-term experiment carried out in a humid site (Hein *et al.*, 1981) whose results served to model organic matter dynamics at regional scale in the Pampas assuming a linear relationship between N input and rainfall (Álvarez, 2001). This assumption remains to be confirmed in the future, even though this type of linear relationship has been described previously in other plain agricultural areas of the world (Parton *et al.*, 1993).

Enormous changes in N fluxes have been produced in the Pampas since 1870. Before this time the only relevant N input to the region was atmospheric deposition, from which soil N was mainly build up, as leguminous species were nearly absent from ecosystems (Chaneton *et al.*, 1996, Soriano *et al.*, 1992), and the output in livestock was minimal. The introduction of agriculture and cropped leguminous forages determined not only a huge increase of outputs in harvested grains but a parallel increase of inputs by N fixation. Cultivation leads to a 6-fold increase of N fluxes entering the ecosystems. At present anthropogenic N (N fixed by cropped species and fertilizers) accounts for 87% of the inputs, the major part due to N fixation. This contrasts with the global perspective. During a similar time periods to that in our analysis, N inputs in the continents doubled due to human activities, but the main input was fertilizer N (ca. 60-80%) with a minor contribution of biological N fixation (Galloway *et al.*, 2004; Vitousek *et al.*, 1997). For this reason pampean agriculture has been considered to be very efficient in N use for grain production, as the partial factor productivity of fertilizer N was much higher than in all other grain production regions of the World (Álvarez *et al.*, 2014a). Local grain production and soil N stock maintenance relays mainly on biological N fixation meanwhile in other regions it depends on fertilizers.

The surface N balance calculated for the Pampas and its different types of agroecosystems are positive, as happened in calculations at global scale for croplands in 1996 (Sheldrick *et al.*, 2002) and 2000 (Liu *et al.*, 2010). Average positive balances of +38 and +56 kg N ha^{-1} were estimated for years 1996 and 2000 respectively. Our data showed an historical positive surface N balance that stabilized in the last decades at +26 kg N ha^{-1} year^{-1}. Despite the positive surface balances calculated for global croplands, when computing the losses by gas emissions and leaching, soil balances were negative in -18 kg N ha^{-1} in 1996 and -11 kg N ha^{-1} in 2000 (Liu *et al.*, 2010; Sheldrick *et al.*, 2002). Consequently, global croplands are being depleted in N. Alike, pampean surface N balance was positive but it did not imply that the N stock of soils increased. Previously, a N stock comparison was performed in Pampean soils between 1960-1980 and 2007-2008 (Álvarez *et al.*, 2014b). This comparison showed that total N stock of the first 25 cm soil layer, in which 50% of the total N stock to 1 m depth was found, did not vary significantly between sampling times. During the comprised time interval of this latter study (ca. 1970-2010) the surface N balance was +51 Mt but the N was not retained by soils and was lost through volatilization, denitrification or leaching. Calculated average loss (the surface annual balance) was 26 kg N ha^{-1} yr^{-1} and this value was compatible with available data on N losses in agricultural soils locally reviewed (Álvarez *et al.*, 2012). During wheat and corn cycles the N amount that can be lost from fertilized soils to the environment ranged from a few grams up to 20-30 kg N ha^{-1}. These values were also compatible with global studies from croplands that reported losses commonly ranging from 16 to 60 kg N ha^{-1} year^{-1} (Eickhout *et al.*, 2006; Sleldrick *et al.*, 2002) depending on the region taken into account. The average N losses estimated for the whole Pampean region may have variations according to the initial total N content in each soil. Soils rich in N tended to reduce N stocks during 1970 and 2008 while N poor soils tended to increase their N stocks (Álvarez *et al.*, 2014b). A similar trend was also detected for organic carbon (Berhongaray *et al.*, 2013). Therefore, the present analysis is not applicable to particular sites and should only be considered as a Pampean generalization. Historically, mixed pasture-crop rotations were used so alfalfa-based pastu-res were cropped in the same soils than grain crops. Since the last 30 years in some pampean areas, as the central portion called Rolling Pampa (Hall *et al.*, 1992), a tendency to eliminate pastures and perform continuous agriculture has
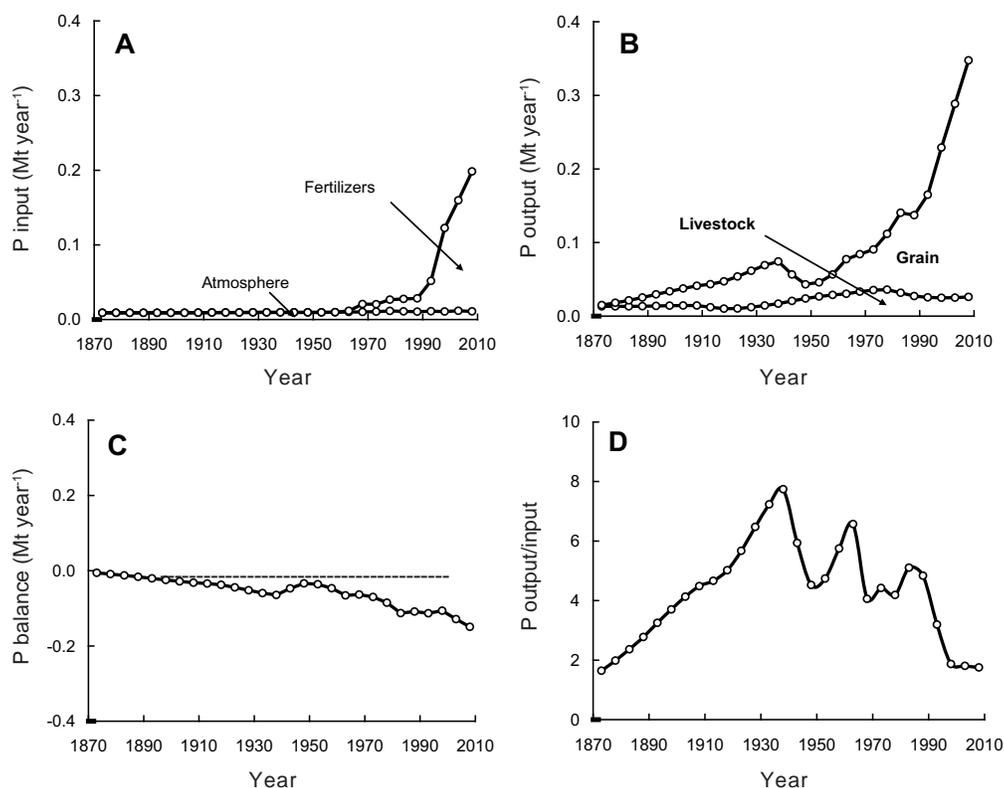
Figure 4. A: Phosphorus (P) input to the Pampean Region from different sources. B: Phosphorus output from the region. C: Phosphorus balance (input-output). D: annual P output/input ratio.

Figura 4. A: Entrada de fósforo (P) a la Región Pampeana según su origen. B: Salida de P de la región. C: Balance de P (entrada-salida). D: Relación anualizada de la relación salida/entrada.

been adopted. Under this scenario the surface N balance turns from positive to negative (Álvarez *et al.*, 2014a).

Phosphorus input into pampean agroecosystems increased sharply during the last four decades due to fertilizers use (Fig. 4A). At present, this later input is 20-fold greater than atmospheric input. Historically, cumu-lative P input to Pampean ecosystems was ca. 4.2 Mt. Around 67% of this total input was accounted for fertilizers and 33% for atmospheric deposition (Table 1). Taking into account different types of agroecosystems by separate, all the fertilizer input was received by cropped agroecosystems producing a huge increase of the P flux entering to the soils of this area in relation to natural systems (Table 1). The output of P also increased sharply during the last decades, mainly by grain harvest (Fig. 4B). The total output along the 140 years study was 12.2 Mt, mainly determined by grain harvest (75%) and a minor proportion was attributed to livestock products (25%) (Table 1). Consequently, nearly

all the output was originated in cropped agroecosystems (Table 1). A negative P balance was calculated along the whole study period (Fig. 4C) with a constant rate, as the trend of the balance could be very well modeled by a liner function (Table 2). As agriculture expanded the P balance turned to be more negative. For the 2006-2010 period the balance was -2.9 kg P ha^{-1} year^{-1}. The cumulative balance was ca. -8 Mt (Table 1). In average of the whole pampean region soils lost more than 1 kg P ha^{-1} year^{-1} but this average P loss was 20-fold greater when computing only cropped soils (Table 1). The annual loss from grasslands and forest was nearly null. In this case atmospheric deposition compensated livestock output. The P output/input ratio was larger than 1 during the entire analyzed period reaching values as high as 8 around 1930 (Fig. 4D). Piecewise regression identified a break point in the output/input trend in the year 1900 (Table 2). An increasing ratio was modeled to this year, decreasing
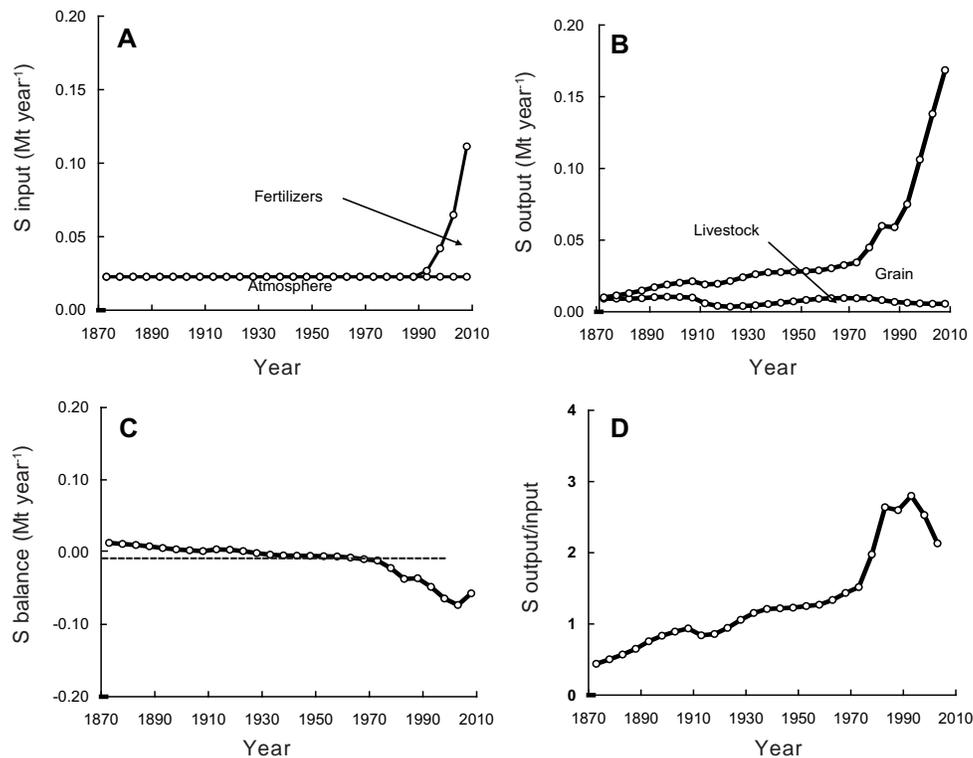
Figure 5. A: Sulfur (S) input to the Pampean Region. B: Output of S from the region. C: Sulfur balance of the region. D: annual S output/input ration of the region.

Figura 5. A: Entrada de azufre (S) a la Región Pampeana según su origen. B: Salida de S de la región. C: Balance de S (entrada-salida). D: Relación anualizada de la relación salida/entrada de S.

thereafter. As grain production increased, because of agricultural expansion, this ratio also increased. In recent decades it decreased due to fertilizer utilization.

Similar uncertainties can be expected in the P balance calculation as in the N balance. Outputs and fertilizer input were easily estimated. Conversely, the atmospheric deposition estimation was based on data from only three sites and the linear relationship with rainfall assumed in this study remains to be confirmed. As this input has a strong impact on the balance, results must be taken with care until more information becomes available. Contrary to our results, the global P surface balance in the year 1996 was of +5.4 kg P ha^{-1} (Sheldrick *et al.*, 2002). More recently a positive global balance was also calculated for soils under cultivation with annual crops and pastures due to fertilizer use (Bouwman *et al.*, 2013). At global scale, P use efficiency estimated as a function of the output/input ratio rounded 40% (Sheldrick *et al.*, 2002), ranging between 20% and 90% according to the country (OECD, 2008). This implies

that ca. 40% of the P applied as fertilizer at global scale was used by crops, the rest remained in the soils. The results of our study showed an opposite trend as the output/input ratio for P have been always higher than ca. 2, showing a strong soil P depletion rate by agriculture. As a consequence, the agricultural use in the Pampas determined losses of extractable P levels (Buschiazzo *et al.*, 2000; Galantini and Rossell, 1997) that at regional scale were estimated at 65% (Álvarez *et al.*, 2013). Also total soil P decreased but to a lesser extent, ca. 15% (Álvarez *et al.*, 2015).

Until the year 1990 the only S input to pampean agroecosystems was the atmospheric flux but, with the adoption of fertilization as a common agricultural practice, fertilizers became the main S entrance to the region (Fig. 5A). During the 2006-2010 period fertilizers accounted for an input 4-fold greater than the atmosphere. Cumulative S inputs along the study period summed ca. 4.0 Mt and atmospheric deposition represented the mayor part (81%) followed by fertilization (19%) (Table 1). Main output was

S in grain (Fig. 5B). Sulfur outputs in 140 years summed 5.6 Mt and harvested grains comprised the main output (82%) followed by animal products (18%) (Table 1). Almost all the output became from cropped soils (Table 1). The nutrient balance showed a different trend compared to those of N and P. It was positive 140 years ago and turned to negative during the last decades (Fig. 5C). Along the overall study period the balance was negative with a cumulative loss of ca. -1.7 Mt (Table 1). This loss was originated in cropped areas meanwhile natural systems are gaining S (Table 1). For the 2006-2010 period we estimated a loss of 1.3 kg S ha^{-1} year^{-1} in cropped soils. A plateau-lineal model could be fitted to the S balance results with a break point year in 1959. At that time the S balance turned to negative with an increasing annual loss. The S output/input ratio rose from values lower to 1 up to 2.8 along the analyzed period but it tended to decrease during the last years because of fertilizer application (Fig. 5D). At the present time the output of S is ca. 50% greater than the input (output/input = 1.5). Despite this trend, the piecewise regression identified only a linear trend with no significant changes along the 140 years studied (Table 2).

As for the other nutrients, S outputs uncertainty and the input uncertainty as fertilizers are low. Nevertheless, atmospheric deposition was measured only in 3 sites and only during one year in each case. The average atmospheric deposition used for estimations in the Pampas (0.45 kg S ha^{-1} yr^{-1}) was low as compared with other agricultural areas of the world, where values of 1 to 30 kg S ha^{-1} yr^{-1} have been reported (Franzen & Grant, 2008; Lovett, 1994). This can be attributed to the low regional industrialization, but more information is needed to confirm these values because of the relative importance of this input in the balance calculation as occurred with P. Around 95% of S integrated organic matter and the rest is present in the form of sulfates in the soil (McGrath *et al.,* 2003a, b). Average soil carbon (C) content in the Pampas is 100 t ha^{-1} in the 0-100 cm profile (Berhongaray *et al.*, 2013). If a C/S ratio of 100 is assumed (Dick *et al.*, 2008) a S stock of 1 t ha^{-1} can be estimated for an average Pampean soil. A loss of ca. 1.7 Mt of S at regional scale is equivalent to 3.5% of the average soil content. For the area under cropping use, a negative balance of -2.75 Mt was estimated. This loss is equivalent to 10% of the soil S stock of cultivated soils.

Nutrient fluxes in pampean agroecosystems had been strongly unbalanced during more than a century. The ratio N input/P input/S input for our 140 year study period was 35/1.8/1.0; meanwhile the ratio N output/P output/S output was 16.4/2.1/1. As a consequence, N fluxes disentangle from P and S fluxes. Nitrogen fluxes not only were much greater than P and S fluxes but also determined and opposite balance sign. Conversely, P fluxes doubled S fluxes but showed similar trends. What effects can have the nutrient fluxes unbalance on soil stoichiometry ratios and on plant productivity remains to be determined.

CONCLUSIONS

In the Pampean Region a positive N balance was calculated mainly determined by the strong input of biological N fixation to the agroecosystems. Cropped agroecosystems had an average gain during more than a century of agriculture of ca. 25 kg N ha^{-1} year^{-1}. During the last decades apparently this N did not accumulated in soils but lost to the environment depending on the pampean area considered. Phosphorus and S balance were negative indicating nutrient lost from the soils. The losses are increasing since the last 40 years in spite of the adoption of fertilization as a common practice.

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