

# Stover Quality and Soil Organic Carbon in Long-Term Nitrogen-Fertilized Maize

Ricardo J. M. Melchiori,\* Leonardo E. Novelli, Viviana C. Gregorutti, and Octavio P. Caviglia

## ABSTRACT

Nitrogen fertilization often increases maize (*Zea mays* L.) grain yield but reduces the C/N ratio of stover returned to the soil, which may affect the soil organic carbon (SOC) balance. This study evaluated the long-term effect of N fertilization on maize grain yield, stover quality in terms of its C/N ratio, and its effect on SOC. In addition, a simulation approach was used to account for the effect of stover quality on its mineralization and SOC balance. Maize grain yield, stover production and quality, and SOC stock were measured during a 6-yr period (2006–2012) in a long-term N fertilization experiment under continuous maize since 1994 in Paraná, Argentina. On average, grain yield ranged from 5.06 in 2011 to 9.10 Mg ha<sup>-1</sup> in 2009. The N effect on grain yield, significant in all seasons, was more important than the effect on C stover production. In contrast, stover C/N ratio showed a linear decrease as a function of N fertilization. Changes in the stover C/N ratio were inversely proportional to the difference between the N rate and the agronomical optimum nitrogen rate (AONR). Although N fertilization increased stover C inputs in 3 out of 6 yr, SOC stock remained unchanged. Simulation results indicate that the required stover amount to maintain the SOC stock increased as the C/N ratio decreased. Our results contribute to better understanding of the previous, controversial results of the N effect on SOC and provide useful insights to develop or improve simulation models for SOC dynamics.

**The increase of maize grain** and biomass yield as affected by N fertilization has been extensively investigated (e.g., Halvorson and Reule, 2006; Coulter and Nafziger, 2008; Jantalia and Halvorson, 2011; Sindelar et al., 2012). Maize is the second crop, in order of importance, in the northern Pampas region of Argentina (MAGyP, 2014), and its inclusion into crop sequences increases residue inputs which can improve soil C balance (Studdert and Echeverría, 2000; Alvarez 2005). Although extensive adoption of no-tillage, spanning more than 80% of the cultivated soil in Argentina, has contributed to minimize soil C losses (Díaz-Zorita et al., 2002; Alvarez 2005), the high proportion of soybean [*Glycine max* (L.) Merr.] as a single annual crop in approximately 70% of cropped area has raised many concerns regarding SOC balance (Novelli et al., 2011).

The use of fertilizer N in continuous maize has been shown to increase both maize grain yield and the amount of stover returned to the soil (Varvel et al., 2008; Halvorson and Johnson, 2009; Biau et al., 2013). However, the effects of fertilizer N rate and crop stover amount on soil C stocks still remains unclear (Blanco Canqui and Schlegel, 2013), with

contradictory findings in the literature. Khan et al. (2007) and Mulvaney et al. (2009) suggest that fertilizer N hastens mineralization rates based on the results of a declining trend in SOC in a long-term experiment. In contrast, other results showed that the N fertilization increased the SOC stock (Follett et al., 2013; Blanco-Canqui and Schlegel, 2013). On the other hand, it has been shown that C stock is not affected by N fertilization in continuous maize (Coulter et al., 2009).

The lack of effects of N fertilization on SOC stock may rely on the documented change in stover C/N ratio of maize returned to the soil (Russell et al., 2009; Jantalia and Halvorson, 2011; Biau et al., 2013). Likewise, Mulvaney et al. (2009), re-analyzing long-term experiments, showed that the N fertilization did not affect SOC level, and suggested that mineral N accelerates soil C degradation.

Although the reduction of C/N ratio when the increase in N rate has been documented (Russell et al., 2009; Jantalia and Halvorson, 2011; Biau et al., 2013), there are scarce studies considering the effects of N fertilization and changes in stover C/N ratio on SOC stocks. Recently, Sindelar et al. (2012) reported that the economical optimal N rate needed to maximize grain yield was higher than the rate of N to maximize stover production. Since N rate in maize is usually set to maximize yield, a low C/N ratio in stover may be anticipated as compared with suboptimal N rates. However, the impact of this strategy on SOC stocks may not be predicted using the knowledge available.

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**Abbreviations:** AONR, agronomical optimum nitrogen rate; BD, bulk density; HI, harvest index; RY, relative yield; SOC, soil organic carbon; Yp, yield plateau.

Therefore, we hypothesized that: (i) the change in stover C/N ratio depends on the difference between the N rate used and the N fertilization rate required to maximize grain yield, that is, N rates above the optimal one to maximize grain yield will promote a reduction in stover C/N ratio associated with the extra absorbed N not used to set additional grains, (ii) the increase in the stover inputs associated with N fertilization above the rate required to maximize grain yield do not increase SOC stock, due to hastened stover mineralization as a result of the decrease in the C/N ratio.

To test these hypotheses, we used two approaches based on: (i) the availability of data of a long-term fertilization experiment in continuous maize, which is useful to provide wide variability in stover inputs and quality required to our aims and, (ii) the use of a simulation model. Calibrated simulation models are complementary to test the hypothesis regarding management practices that require long experimental periods (Boote et al., 1996). Soil C stock evolution in N fertilized continuous maize may be evaluated throughout simulation models that take into account parameters related to stover and SOC mineralization and changes in C inputs and quality. Through a simple and locally validated simulation model such as the AMG (Andriulo et al., 1999), it is possible to consider C residue inputs and coefficients related to humification of crop residue and mineralization of SOC. Calibration of parameters in the AMG model using stover C input and SOC data may be useful for evaluating the effect of long-term N fertilization in continuous maize on SOC stock.

The main objective of this study was to determine long-term effects of N fertilization in continuous maize on stover inputs and its quality (C/N ratio) and the consequent effects on the total SOC stock. An additional aim includes the calibration of the AMG model and the long-term simulation of the effect of N rates on SOC stock.

## MATERIALS AND METHODS

### Site and Experiment Descriptions

The study was conducted on a long-term N fertilization experiment established in 1995 with continuous maize under no-tillage management from 2000 onward. The experiment was established in a field of INTA Paraná (31°50.9' S; 60°32.3' W), Entre Rios province (Argentina) with previous agriculture use under conventional tillage (moldboard plow and disk harrows) for more than 20 yr. Previous rotation included wheat (*Triticum aestivum* L.), soybean, and maize, as single annual crops. The soil was classified as Aquic Argiudoll (Soil Survey Staff, 2010), with a silty clay loam texture in the Ap horizon (4.5, 67.9 and 27.6% of sand, silt, and clay, respectively) (Plan Mapa de Suelos, 1998) and <1% of slope. The mean annual precipitation and air temperature for the site are 1027 mm and 18.3°C, respectively.

The experiment had fertilizer N rates in a randomized complete block design with three replications. The plots were 4.2 m wide and 20 m long. All the maize hybrids used were chosen from the most productive and adapted ones in the region according to regional comparative trials performed by INTA. Genotypes were single-cross hybrids with comparative relative maturities of 118 to 124 d. Sowing occurred on optimal dates, that is, September or October, according to soil water

availability using a commercial no-tillage pneumatic planter (Giorgi, Precisa 8000, Fuentes, Argentina) equipped with disc coupler. Plant density was 7.5 to 8.5 seed m<sup>-2</sup> in rows spaced 0.52 m apart.

Four selected fertilizer N rate treatments of the long-term experiment were used for this study: 0, 69, 138, and 276 kg N ha<sup>-1</sup>, hereafter N0, N69, N138 and N276, respectively. The N fertilizer was applied as urea that was hand broadcasted immediately before sowing in all treatments, although the N276 rate was split so that half was applied before sowing and half was sidedressed at the V6 maize developmental stage (Ritchie et al., 1989). Phosphorus fertilizer was applied annually at sowing at a rate of 100 kg ha<sup>-1</sup> as triple superphosphate (46% P<sub>2</sub>O<sub>5</sub>), even though the P availability was always above 20 mg kg<sup>-1</sup> P (0–0.2 m, Bray I). Weeds were controlled with preemergence and eventually postemergence herbicides. From 2006 onward, Bt hybrids were used to minimize potential insect damage and occasionally a specific insecticide was used.

### Plant Sampling and Analyses

Maize grain yield was determined by harvesting the two central rows of each plot. Hand harvest was made on 10 m<sup>2</sup> and ears were threshed in a static machine from 1995 to 2010, and thereafter using a small plot combine to harvest 20 m of two central rows. Grain moisture was determined on the threshed grains in each plot using a portable moisture tester (DICKEY-John, Auburn, IL). Grain yield was expressed at 14.5 g kg<sup>-1</sup> moisture.

Aboveground maize biomass was determined shortly after physiological maturity by hand harvesting 10 randomly selected plants per plot, which were cut at soil level. Plants were dried in a forced air oven at 65°C until constant weight. Ears were then removed and shelled manually. Cobs were weighed together with stalks, and leaves, and combined this is referred to as stover hereafter. Harvest index (HI) was calculated as the ratio between grain yield and total aboveground biomass. Stover was ground in a mill and sieved using a 1-mm screen.

Stover C and N concentration was determined by dry combustion using a LECO autoanalyzer model TRU SPEC (Leco Corp., St. Joseph, MI). Total organic C and N contents in stover were calculated as the product of stover biomass and C and N concentration. The stover C/N ratio was calculated from total C and N.

### Soil Sampling and Analyses

Soil samples were collected from the 0- to 0.05- and 0.05- to 0.10-m depths before sowing in years 2009, 2011, and 2013. Soil samples were composed with at least 20 soil cores of 2 cm diam., which were hand-driven and randomly taken within each plot, avoiding wheel track locations. Soil samples were air-dried, ground, and sieved through a 0.5-mm screen. Total C content was determined by dry combustion using a LECO autoanalyzer. Carbonate content was not determined on soil samples before analysis, since it has not been detected in Ap horizon of the soil described in the experimental area (Plan Mapa de Suelos, 1998). Therefore, total C content was assumed equivalent to SOC.

Bulk density (BD) in each plot, depth and sampling date was determined by the core method (Forsythe, 1975) using cores of 3 cm long and 5.4 cm in diameter. Bulk density was determined

between central rows, avoiding soil surface compaction in wheel track location. The SOC stock in the 0- to 0.1-m depth was evaluated in a fixed soil mass as the product of the thickness of the soil layer and the bulk density. Initial soil data were obtained in 1995 at the beginning of the experiment by randomly taken 40 cores per block to a depth of 0 to 0.1 m. Initial values were SOC = 1.94%; pH = 6.0, P (Bray I) = 38 mg P kg<sup>-1</sup>, and BD = 1.18 Mg m<sup>-3</sup>.

### Statistical Analyses

Statistical analyses were performed using INFOSTAT (Di Rienzo et al., 2011), including the ANOVA using mixed models. Years and replications were considered random, and fertilizer N rate as fixed effect. Means comparisons were performed using the Tukey test ( $\alpha = 0.05$ ). Data of grain yield, stover C, and stover C/N ratio were included in the ANOVA. Relationships between variables were studied using linear and nonlinear regression.

The relationship between fertilizer N rate and maize grain yield was described by a linear-plateau model for each year to determine AONR and yield plateau (Y<sub>p</sub>) using all replicates for each N rate ( $n = 12$ ). The Y<sub>p</sub> was considered as the maximum stable yield for each year (Waugh et al., 1973; Cerrato and Blackmer, 1990; Cerrato and Blackmer, 1991). Within each year, relative yield (RY) was calculated as the ratio between the maize grain yield of each replication and the Y<sub>p</sub>. Additionally, RY was used to determine the average critical level pooling all years.

The linear-plateau model was fit using an algorithm developed in a spreadsheet and optimized by Solver of Microsoft Office Excel (Windows Corporation, Redmond, WA). The algorithm minimized the sum of squares of error between estimated and observed data, and determined the significance of the model ( $P > F$ ) and regression coefficients.

The linear-plateau model is defined by Eq. [1] and Eq. [2]:

$$Y = a + bX \quad \text{if } x < \text{AONR} \quad [1]$$

$$Y = Y_p \quad \text{if } x > \text{AONR} \quad [2]$$

where  $Y$  is the response variable,  $X$  is N fertilization rate, and AONR is the agronomical optimum N rate, which is obtained in the intersection of the two linear models. Y<sub>p</sub> indicates a constant yield plateau, as a result  $Y_p = a + b \text{AONR}$ .

The use of linear-plateau models was only performed to determine an AONR which, in turn, was used to calculate the amount of N applied above or below of the fertilizer N rate required to maximize maize grain yield, and to relate this amount with changes in the stover C/N ratio.

### Soil Organic Carbon Simulation

To study the relationship between changes in the amount of stover C inputs as affected by N fertilization and SOC stock, an AMG simulation model was used (Andriulo et al., 1999). Briefly, AMG is a simple soil simulation model of annual time-step that considers three C compartments: m (C mass input of above-ground and belowground crop residue), Cs (stable soil organic C) and Ca (active initial soil organic C). The model uses two coefficients: the first represents the mineralization rate of active soil organic matter ( $k$ ) and the second represents the humification rate of crop residue input ( $k_1$ ). This model was developed and validated on long-term experiments in the rolling pampas of

Argentina (Andriulo et al., 1999; Milesi Delaye et al., 2013) and in the Northeast region of France (Mary and Wylleman, 2001).

Initial SOC data recorded at the beginning of the experiment in 1995 was used as the Co initial value (stock of SOC at 0.1-m depth = 22.42 Mg ha<sup>-1</sup>). The value of Cs was calculated as 60% of Co, according to Andriulo et al. (1999). The input data for the model were crop stover, HI, and organic C content in stover obtained annually in the experiment from 1995 to 2012. The parameter  $k_1$  was set to a value of 0.126, as suggested by Mary and Wylleman (2001) for no-tillage soils. The mineralization coefficient  $k$  was optimized minimizing the root mean square error between the observed and simulated values using SOLVER of Microsoft Office Excel (Windows Corporation, Redmond, WA).

## RESULTS

Rainfall in the maize season (September–February) ranged from 439 mm in year 2008 to 1097 mm in year 2009 (Table 1), with a mean of 809 mm. Apparent water balance, that is, the difference between rainfall and potential evapotranspiration, in the period around flowering ranged -259 to 170 mm. The years 2008 and 2011, had the most negative apparent water balance. Average mean air temperature during the 6 yr was 0.8°C higher than historical average (Table 1), with negligible differences in monthly values among years. In September in coincidence with sowing, and in October, in coincidence with early-season maize growth, mean air temperature ranged from 13.6 to 16.9°C and 17.1 to 20.9°C, respectively. In all years, rainfall after sowing and N fertilization were considered adequate to incorporating urea, and minimizing N losses.

### Nitrogen Fertilization Effects on Maize Production

There was a significant Year  $\times$  N interaction ( $P < 0.05$ ) for maize grain yield, stover C, and stover C/N ratio, but not for HI. Grain yield ranged from 2.07 to 4.75 Mg ha<sup>-1</sup> in the non-fertilized control treatment and from 7.99 to 13.21 Mg ha<sup>-1</sup> with the maximum fertilizer N rate (Table 2). On average, grain yield ranged from 5.06 in the year 2011 to 9.10 Mg ha<sup>-1</sup> in the year 2009. The N effect was significant for grain yield in all seasons ( $P < 0.05$ ), although the lowest response was recorded in 2008. The mean yield response to N was 3.71, 5.10, and 6.85 Mg ha<sup>-1</sup> for N69, N138, and N276, respectively.

Stover C ranged from 1.54 in the control treatment to 6.65 Mg ha<sup>-1</sup> with maximum N rate (Table 2). Fertilizer N rate affected stover C in years 2010 to 2012, and did not have a significant effect in the previous years. The mean stover C response to N, pooling all years, was 0.81, 1.14, and 1.86 Mg ha<sup>-1</sup> for N69, N138, and N276, respectively. In contrast to the grain yield response, the stover C response to N fertilization was lower; the mean increase in stover C due to N fertilization was 92 vs. 204% in grain yield. Harvest index was increased as a result of the N fertilization in all years, except 2006 and 2009. The mean HI across years was 0.33 in the control treatment and increased by 55% (HI = 0.52) in N276 (Table 2).

The mean C concentration was 42.4%, without significant differences due to N (not shown) and stable between years (CV = 2.3%). Stover N concentration showed a significant N  $\times$  Year interaction ( $P < 0.0001$ ). In 5 out of 6 yr, N fertilization affected the stover N concentration (not shown). The increase between the non-fertilized control and the maximum N rate in

Table 1. Monthly rainfall, potential evapotranspiration (ET<sub>0</sub>, Penman–Monteith), and mean air temperature during seven growing seasons at Paraná, Argentina. Historical average (1934–2005) for each variable are included for comparison.

Meteorological variables	Year	Month					
		September	October	November	December	January	February
Rainfall, mm	2006	3.0	95.3	130.9	375.2	121.5	123.5
	2008	32.9	94.0	106.0	25.4	34.7	154.6
	2009	101.1	73.6	91.5	253.8	222.4	354.8
	2010	64.6	57.8	27.6	61.7	148.6	78.8
	2011	8.4	161.3	129.5	53.2	46.5	232.7
	2012	80.5	235.5	94.9	256.9	34.3	81.6
	Historical	54.0	107.0	110.0	118.0	118.0	110.0
ET <sub>0</sub> , mm	2006	157.0	171.7	164.1	172.4	160.3	128.3
	2008	108.3	170.3	207.4	183.3	178.4	133.5
	2009	83.8	148.5	135.4	134.7	160.2	111.1
	2010	90.2	127.1	154.0	188.7	173.2	127.0
	2011	120.3	109.6	165.0	183.9	195.2	138.5
	2012	94.5	105.2	155.5	170.3	176.4	137.2
	Historical	98.0	131.0	158.0	180.0	180.0	139.0
Mean air temperature, °C	2006	15.8	20.9	21.6	24.6	24.6	24.1
	2008	15.7	19.0	23.1	24.7	25.0	24.3
	2009	13.6	18.8	23.2	22.8	25.3	24.5
	2010	15.4	17.1	21.0	24.7	25.9	23.7
	2011	16.9	17.6	22.9	23.9	26.4	25.1
	2012	16.7	19.1	22.9	24.2	25.0	23.5
	Historical	15.2	18.1	20.9	23.4	24.8	23.8

Table 2. Grain yield, stover C and stover C/N ratio as affected by different N fertilization rates in 6 yr of a long-term experiment of continuous maize conducted in Paraná, Argentina.

Variables	Fertilizer N rate† kg N ha <sup>-1</sup>	Year					
		2006	2008	2009	2010	2011	2012
Grain yield, Mg ha <sup>-1</sup>	0	4.76a	3.16a	4.47a	3.52a	2.07a	2.88a
	69	9.34b	8.34b	8.28b	7.54b	4.41b	5.09a
	138	8.86b	7.67ab	10.43bc	9.32b	6.66c	8.53b
	276	12.4c	7.99ab	13.21c	10.58b	7.11c	10.67b
	MSD	2.82	5.03	2.90	3.33	1.27	2.27
	P > F	***	*	***	**	***	***
Stover C, Mg ha <sup>-1</sup>	0	2.46a	5.71a	4.45a	1.54a	2.26a	2.00a
	69	3.62a	4.59a	5.11a	3.42b	3.92b	2.63ab
	138	2.88a	4.40a	6.65a	4.31b	3.09ab	3.91bc
	276	5.06a	4.96a	6.16a	4.90b	4.38b	4.16c
	MSD	3.00	3.30	3.37	1.54	1.63	1.47
	P > F	ns‡	ns	ns	**	*	**
Stover C/N ratio	0	102c	79c	89a	83b	86b	77c
	69	86bc	74bc	77a	82b	81b	67bc
	138	79b	67b	67a	63ab	78b	58b
	276	54a	35a	66a	47a	42a	39a
	MSD	22.71	9.88	25.06	22.03	20.28	18.11
	P > F	**	***	ns	**	**	**

\* Significant at 0.05.

\*\* Significant at 0.01.

\*\*\* Significant at 0.001.

† 0N, 69N, 138N, and 276N indicate nitrogen application rates (kg N ha<sup>-1</sup>). MSD indicates the minimum significant difference between N rates for each year according to the Tukey test ( $\alpha = 0.05$ ).

‡ ns, not significant.

Table 3. Agronomical optimum fertilizer nitrogen rate (AONR) and predicted yield at the AONR for grain yield in 6 yr of a long-term experiment of continuous maize conducted in Paraná, Argentina.

Year	AONR† kg N ha <sup>-1</sup>	Yield at AONR Mg ha <sup>-1</sup>	R <sup>2</sup>	P > F
2006	87	10.6	0.72	**
2008	66	8.0	0.69	**
2009	196	13.2	0.89	***
2010	159	10.6	0.82	***
2011	151	7.1	0.97	***
2012	196	10.7	0.94	***

\*\* Significant at 0.01.

\*\*\* Significant at 0.001.

† AONR was obtained by fitting linear-plateau models using the relationship between grain yield and N rate ( $n = 12$ ).

the stover N concentration ranged from 36 to 146%. Minimum values of stover N concentration in the non-fertilized control ranged from 0.44 to 0.54% and from 0.68 to 1.30% with the maximum N rate.

Stover C/N ratio was highly affected by N in all years except in 2009, where stover C/N ratio decreased only by 25% comparing N0 vs. N276. In contrast, in the other years the decrease in stover C/N ratio ranged from 46 to 55%. The mean stover C/N ratio was 86, 78, 69, and 47 for N0, N69, N138, and N276, respectively.

### Grain Yield Response, Critical Levels, and Carbon/Nitrogen Ratio

The agronomical optimum fertilizer N rate, obtained from the linear-plateau models, differed among years, (Table 3), ranging from 66 to 196 kg N ha<sup>-1</sup> whereas the yield at plateau ranged from 7.1 to 13.2 Mg ha<sup>-1</sup> (Table 3). In the year 2008, both the model fit and the AONR were lower than in the other years.

Stover did not show the same response to N in comparison to the grain yield. In the pooled data, RY showed a linear response to the N fertilizer applied up to a threshold of 150 kg N ha<sup>-1</sup>; above this level maize grain yield was unaffected (Fig. 1), whereas in the

Table 4. Soil organic C stock at 0- to 0.1-m depth of a long-term experiment of continuous maize conducted in Paraná, Argentina.

Fertilizer N rate kg N ha <sup>-1</sup>	SOC†		
	2009	2011	2013
0	24.8 ± 2.56‡	22.2 ± 1.10	23.7 ± 1.17
69	25.9 ± 2.37	24.3 ± 1.61	23.7 ± 1.60
138	26.4 ± 0.41	22.9 ± 0.73	22.8 ± 2.43
276	24.3 ± 3.87	23.9 ± 0.52	22.9 ± 2.29
P > F	0.65	0.10	0.81

† Soil organic C stock was calculated at an equivalent soil mass based on soil bulk density.

‡ Values besides SOC are standard deviation.

same range of N fertilizer rates, the stover C/N ratio decreased linearly by 0.14% per kg N ha<sup>-1</sup> applied ( $r^2 = 0.67$ ;  $P < 0.0001$ ). Pooling all the data, the estimated C/N ratio at AONR was 65.8, and at the maximum N rate it was 48.1, which represents a decrease of 27% when the N rate applied was 84% above AONR.

The AONR varied among years up to threefold (Table 3), and in a similar way the change in stover C/N ratio varied from -0.07 to -0.16 per kg N ha<sup>-1</sup> applied. When the N rate was below the AONR, the C/N ratio was increased in relation to the stover C/N ratio determined at the AONR; an opposite pattern was observed when the N applied was higher than the AONR (Fig. 2).

### Soil Organic Carbon Simulation

Soil organic C in the upper layer of the soil (0- to 0.10-m depth) at sowing in years 2009, 2011, and 2013 did not differ between years and N rates ( $P > 0.05$ ) (Table 4). The BD and SOC concentration also remained unchanged among years and treatments. The average BD was 1.39 Mg m<sup>-3</sup> and the average SOC concentration was 1.72%.

The optimization process using the AMG model resulted in a different coefficient of mineralization ( $k$ ) for each fertilization treatment (Fig. 3). Since the N rate affected both the amount and stover C/N ratio without evident changes in SOC, there

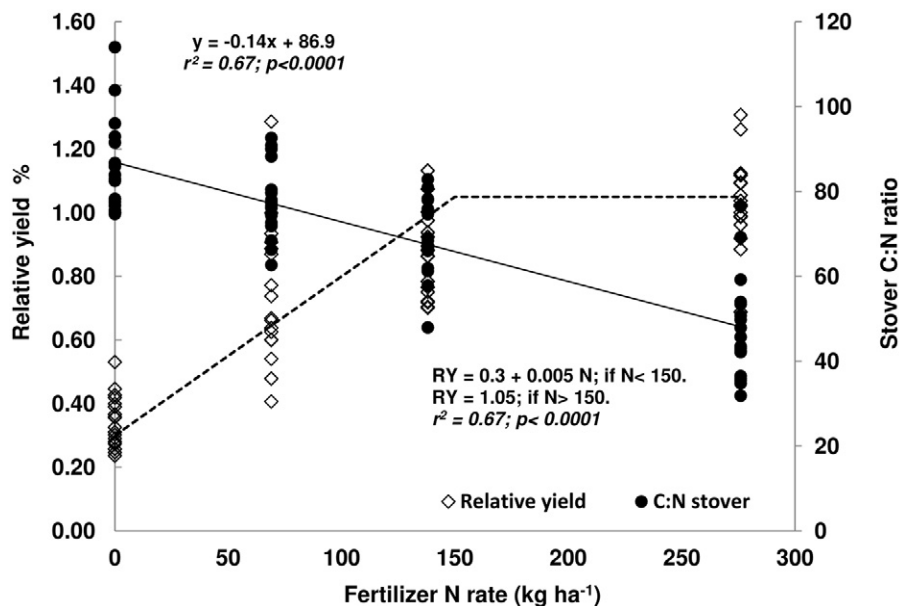


Fig. 1. Relative yield and maize stover C/N ratio as a function of fertilizer N rate. Data of a long-term experiment with continuous maize conducted from 2006 to 2012 in Paraná, Argentina. Dotted line: Linear-plateau model fit for relative yield. Continuous line: linear regression between stover C/N ratio and N fertilization rate.

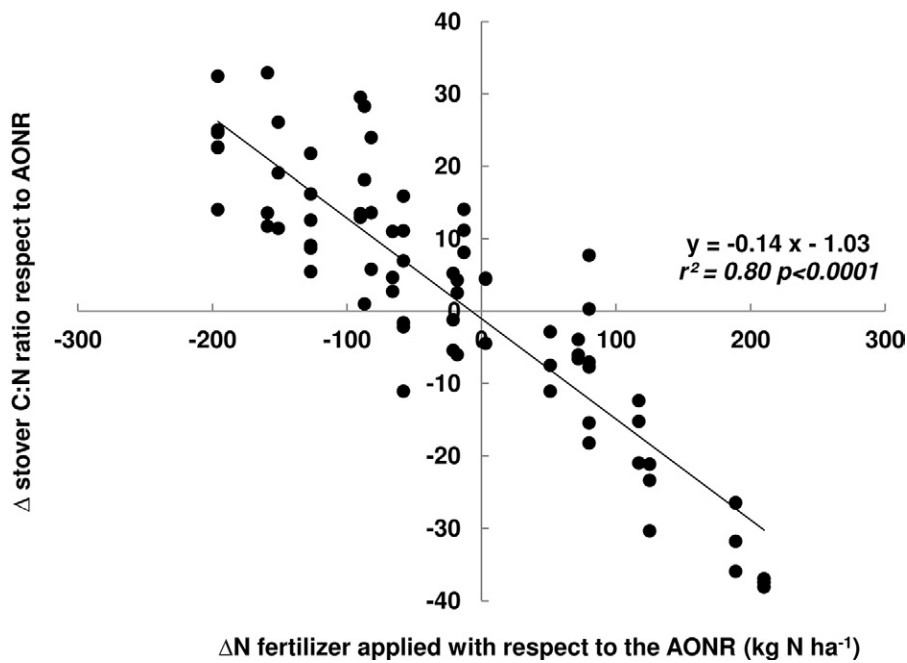


Fig. 2. Relationship between  $\Delta$ C/N ratio in maize stover and  $\Delta$ N fertilizer applied compared to the agronomical optimum fertilizer nitrogen rate (AONR). Data of a long-term experiment with continuous maize conducted from 2006 to 2012 in Paraná, Argentina. AONR was determined by linear-plateau models fit in each year.

was a close, negative relationship between the stover C/N ratio and the  $k$  values (Fig. 3). An increase of 3, 29, and 49% was determined in the  $k$  coefficient with respect to the controls in N69, N138, and N276, respectively, when the stover C/N ratio was reduced by the N effect up to 55% (Table 2).

The amount of C input required to maintain the SOC stock was higher when the inputs were increased by N fertilization (Fig. 3). The C input to maintain the SOC stock, that is, an annual change equal to 0, was 3.97, 4.47, 5.24, and 5.91  $\text{Mg ha}^{-1}$ , for treatments N0, N69, N138, and N276, respectively.

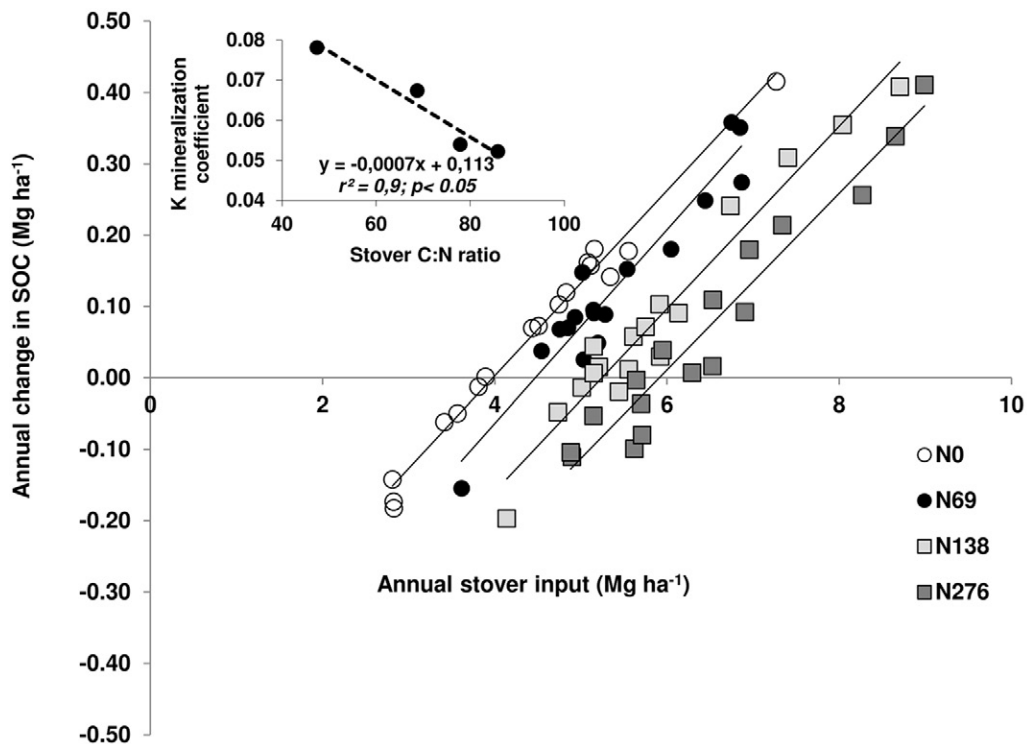


Fig. 3. Relationship between annual C stover inputs and annual change in soil organic carbon (SOC) stock. Data of a long-term experiment with continuous maize conducted from 2006 to 2012 in Paraná, Argentina. Annual change in SOC stock was estimated as input–outputs, which were simulated using modified AMG model ( $k$  adjusted to C/N stover ratio). N0:  $Y = -0.5381 + 0.1297x$ ,  $r^2 = 0.98$ ,  $P < 0.001$ ; N69:  $Y = -0.6353 + 0.1357x$ ,  $r^2 = 0.91$ ,  $P < 0.001$ ; N138:  $Y = -0.7001 + 0.1357x$ ,  $r^2 = 0.98$ ,  $P < 0.001$ ; N276:  $Y = -0.7629 + 0.1238x$ ,  $r^2 = 0.94$ ,  $P < 0.001$ ).

## DISCUSSION

Nitrogen fertilization increased maize grain yield up to AONR, while the stover C/N ratio showed a linear decrease (Fig. 1, Fig. 2) as the fertilizer N rate increased. The increase rate of stover production was lower than the increase rate of grain yield, because the N affected HI. Nitrogen fertilization linearly increases the crop growth rate (Uhart and Andrade, 1995), and nonlinearly the kernel number per plant when resources limitations are removed (Andrade et al., 1999), which explains the change in HI as affected by N fertilization. Similar results have been reported by Caviglia and Melchiori (2011).

When crop N uptake increases with N fertilization above the AONR, the demand for N for grain set is fulfilled; then, the N tissue content may increase probably due to a luxury uptake as suggested by Macy (1936) and Greenwood et al. (1990). This surplus of N applied above the AONR did not only increase grain yield but also reduced the stover C/N ratio, which may hasten stover degradation. Our results add new evidence to support the idea that the use of N rates above the AONR may generate negative environmental impacts associated with the increase in the availability of mineral N (Cassman et al., 2002). A high amount of mineral N availability is prone to loss by different pathways (runoff, leaching, denitrification, and volatilization). In addition, residual N may affect the dynamics of SOC between pools (Milesi Delaye et al., 2013) or cause a priming effect on SOC (Kuzakov et al., 2000).

Our results show that N fertilization did not affect the SOC in spite of the huge increase of C stover input (Table 4). The lack of change would be explained by three mechanisms: (i) hastened degradation of native SOC and the stover as a result of the addition of mineral N from fertilizer, (ii) a higher mineralization of stover as a result of a decrease in C/N ratio, or (iii) a combination of (i) and (ii).

It has been reported that N fertilization rate decreased SOC because it accelerates SOC mineralization (Khan et al., 2007) whereas, in contrast, Blanco Canqui and Schlegel (2013) and Follett et al. (2013) found that the N fertilization increased the SOC due to a higher biomass input. However, the reports referred above have not mentioned stover quality as being involved in their results. After 17 yr of N fertilization in continuous maize, our results showed that the SOC stock remained stable (Table 4), despite an important increase in the stover C input (Table 2), which are consistent with previous reports by Russell et al. (2009) and Jantalia and Halvorson (2011).

The higher C input in fertilized treatments did not increase the SOC because it could be more quickly degraded due to a decrease in C/N stover quality (Fig. 3) as has been previously suggested (Andriulo et al., 1999; Johnson et al., 2007; Milesi Delaye et al., 2013). The residues with high C/N ratio, typical of our non-fertilized treatments would be degraded slowly, in contrast with the residues with low C/N ratio (Stevenson, 1986).

Accordingly, the modeling of SOC evolution as a function of C inputs optimizing C mineralization coefficients showed a more accelerated rate of degradation when residues come from N fertilized maize with a low stover C/N ratio (see insert in Fig. 3). These results are in line with those reported by Russell et al. (2009). Higher C inputs are required to maintain a stable SOC stock if the residues of the crop have a lower C/N ratio which was evident when the N rate was above the AONR (Fig. 3).

The use of a simple soil C model allowed us test successfully the second hypothesis, which supports its further adoption to evaluate the potential impact of agronomical practices on soil C balance under changing scenarios. Moreover, the AMG model has been used to assess the effects of agriculture on SOC and soil organic N in grasslands of the Argentine Rolling Pampa over a long-term period (Milesi Delaye et al., 2013).

Overall, the documented impact of stover quality on SOC dynamics contributes to better understand the previous, controversial results of the effects of N fertilization on SOC. Furthermore, the suggested increase in stover mineralization as the C/N ratio decreased provides useful insights to develop or improve simulation models for SOC dynamics.

## CONCLUSIONS

The increase in maize grain yield due to N fertilization was more important than the increase in stover C production because the N fertilization increased HI. The stover C/N ratio showed a linear decrease as a function of N fertilization. The changes in the stover C/N ratio were inversely proportional to the difference between the N fertilization rate and AONR. Although N fertilization increased stover C inputs in our long-term experiment with continuous maize, the SOC stock in the uppermost soil layer remained unchanged. Simulation results showed that the higher C inputs of corn stover due to a higher rate of fertilization, with a concomitant reduction in stover C/N ratio, were more quickly degraded as a result of a higher mineralization coefficient.

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