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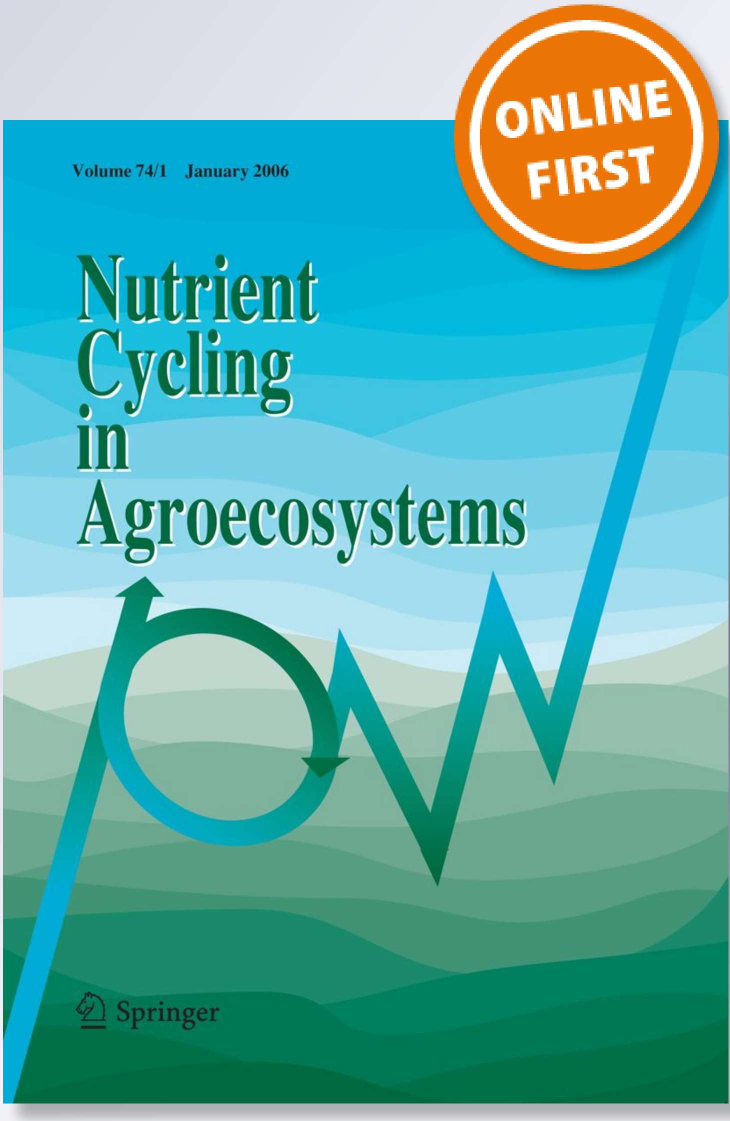

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ORIGINAL ARTICLE

Fate of the nitrogen from fertilizers in field-grown maize

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Abstract The nitrogen (N) from fertilizers has different fate, some of which affect the environment or the human health, e.g. nitrates in groundwater. We determined the fate (plant organs, soil organic matter, remaining nitrates and volatilization) of the N applied to field-grown direct drilling maize. An experiment was carried out in a Typic Argiudoll at Chivilcoy, Argentina (35°02′S, 60°06′W). Treatments were: control; 70; 140 and 250 kg N ha^{-1}. Microplots were fertilized with urea tagged with ^{15}N (1.5 % abundance). Plant biomass and N concentration were determined at flowering and at physiological maturity. Soil organic N (0–30 cm) and nitrates and ammoniacal N concentrations (0–300 cm) at harvest, and ammonia volatilization were determined. ^{15}N was determined in all samples. The crop was the main sink, recovering an average of 56 % of the N from the fertilizer. Both the soil organic fraction and ammonia volatilization were the second N sink. The N remaining as residual nitrates averaged 8.6 % and the leached nitrates were only 0.8 % of the fertilizer applied. Most N leached after maize cropping could be accredited to mineralization of organic N. Organic matter could then be a temporary sink, which reduces N leaching from a single fertilization but releases nitrates the following years.

Keywords Maize · Nitrates · Tagged nitrogen · Nitrate leaching · Organic fractions · Volatilization

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Introduction

The nitrogen (N) cycling in an agroecosystem includes inputs like biological fixation and the additions from fertilizers, and the recycling of the nutrient due to agriculture and livestock production activities, including manure, organic matter and crop residue mineralization (Archer and Thompson 1993; Keeney and Follet 1991). Urban activities and industrial production are other sources of N. The N added or cycling in agrosystems has different fate, some of which affect the environment or human health, for example by contaminating the groundwater with nitrates, which is a generalized worldwide problem (Delgado and Follet 2010). Nitrates are normal substances in human metabolism but can cause different health problems when their concentration in drinking water exceeds a certain threshold (Madison and Brunett 1985). Although both the limits and the problems of this issue are under scrutiny (Addiscott and Benjamin 2004), the contamination of waters with nitrates has

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become an increasing concern. Nitrates accumulation in water is due to nitrate leaching from the soils. This process is defined as the nitrate movement below the soil volume explored by roots and where they can not take the nutrient (Knox and Moody 1991).

Nitrate leaching losses depend on the occurrence of high contents of nitrates in the soil and a water volume able to carry them through the soil depth (Vagstad et al. 1997). When the fertilization dose is excessive or when a crop is not able to develop its productive potential, due to any stress, a high level of nitrates usually remains in the soil after harvest. Those nitrates are prone to be leached (Macdonald et al. 1997; Rimski-Korsakov et al. 2004). The quantity of N lost via leaching can be very high. Bjorneberg et al. (1996) found losses of N from maize receiving 200 kg N ha^{-1}, in a range equivalent to 5–54 % of applied N. Not all lost N came from the fertilizer. For example, using the isotope technique, Jayasundara et al. (2007) found that from the 100 % of the leached N, 11 % was originated in the fertilizer and 89 % came from the soil. This means for that maize fertilized with 150 kg N ha^{-1}, only 2.5 % of the N applied as fertilizer was lost by leaching. The remaining N lost came from the nitrates present in the soil from previous fertilizations or microbial mineralization of the soil organic matter and crop residues.

There are several other sinks for the N added or cycling in agrosystems. Crop absorption, the objective of fertilization, is just one of them but not always the most important. Nitrogen recovery from fertilizers depends on the crop, environmental conditions and cropping technology. To quantify the fate of plant nutrients in different soil/plant compartments, labeled tracers have been used (Carter and Rennie 1987; Stevens et al. 2005). The ^{15}N isotope gives a direct method to quantify the nutrients coming from the fertilizer that are located in different plant organs (Schindler and Knighton 1999). This technique has been widely used to study the fate of fertilizers and there are several studies addressing the issue of the plant recovery of N from fertilizers. However, studies involving the fate of fertilizer nitrogen in all possible compartments are less common. It is also uncommon to discriminate the N recovery in all aerial organs or roots. Several authors (Reddy and Reddy 1993; Schindler and Knighton 1999; Stevens et al. 2005) have found average recoveries of N in maize ranging from 28 to 57 %. Within this figure, grains are usually the main sink of the fertilizer N, since they accumulate an average of 24 % of the N applied. The lowest recovery percentages have been found when some stress (like drought or high temperatures) occurs and crops can not reach their productive potential (Ma et al. 1995; Macdonald et al. 1997; Stevens et al. 2005).

Soil microbial biomass and soil organic matter are two other relevant sinks of N. The N retained or immobilized in soil microbial biomass, crop residues and soil organic matter shows a cycling rate which ranges from days to years (Álvarez et al. 2007; Davidson et al. 1990). Portela et al. (2006) and Reddy and Reddy (1993) have found N recoveries from 10 to 30 % of the fertilizer N in the organic fraction. Other significant fates of the N from the soil are gaseous losses: ammonia volatilization and denitrification. Volatilization losses usually range between 3 and 30 % of the N applied (Álvarez et al. 2007; Palma et al. 1998; Wang et al. 2004). An extreme loss by volatilization in the order of 48 % has been recorded (Cai et al. 2002). The main factors controlling N volatilization from fertilizers are the fertilizer type and rate, and the application form. Losses of N oxides from the soil via the denitrification process have been reported to be between 2 and 12 % (Liang and MacKenzie 1997; Nishio et al. 2002). There are other sinks for N usually considered minor (Davidson et al. 1990; Vitousek and Matson 1984). These include N fixation or N losses in water runoff. The former was considered very stable in the area studied and was not affected by changes in the ammoniacal N concentration in the soils after fertilization (Rubio and Lavado 1994) and the latter was not considered because of the flatness of the area (INTA 1980) and the tillage system (direct drilling) (Peterson and Power 1991).

The Pampas region of Argentina, located in the south cone of south America (33–35°S, 62–64°W), is one of the largest grasslands in the world, analogous to the tallgrass prairie of North America. The region is now a large plain of fertile lands suitable for agriculture and livestock husbandry. At present, cash-cropping predominates and the main field crop is soybean followed by wheat and maize. Around 85–95 % of the maize is fertilized and the national N rate averages 50–60 kg N ha^{-1}. Our objective was to determine the fate of the fertilizer N applied to field-grown maize. Most sinks were recorded using labeled N: plant compartments (grains, aerial organs and roots), soil organic matter, nitrate leaching, ammoniacal N content in the soil and gaseous losses (ammonia volatilization).

Materials and methods

The experiment was carried out in a farm located near the town of Chivilcoy (35° 02′S, 60° 06′W) in the Province of Buenos Aires, Argentina. The soil was an O′Higgins Series Typic Argiudoll. The soils of the area were developed from loessic sediments and are deep with sandy-loam to loam texture (INTA 1980). The main characteristics of the top soil, determined using standard techniques (Sparks et al. 1996), were: clay 20.0 %; silt 42.0 %; sand 38.0 %; pH in water 5.9; organic carbon (Walkley and Black) 1.45 %; total nitrogen (Kjeldhal) 0.16 %; and available phosphorus (Bray and Kurtz) 23.6 mg kg^{-1}. The farmer followed a typical crop sequence of the area: wheat/soybean double crop annually, followed by maize the following year. No tillage was used for cropping during the 8 years previous to the experiment. During the experiment, the crop did not suffer water stress: rainfall was 616 mm. Rainfall was measured in the same farm using standard pluviometers and following current procedures. Crop evapotranspiration was 513 mm, determined as by Penman method (Penman, 1948).

Maize (Cargill Titanium F1) was seeded on October 15th 2001; the row distance was 0.70 m and plant density was 71,000 plants ha^{-1}. Mono ammonia phosphate (18 kg P ha^{-1}) was surface broadcast in all plots before seeding. The treatments were doses of N based on N applied as urea: (a) control (N0); (b) 70 kg N ha^{-1} (N70); (c) 140 kg N ha^{-1} (N140); and (d) 250 kg N ha^{-1} (N250). Plots were 6.5 m (9 rows) × 5 m length. A complete randomized block design with four repetitions was established. We mimicked the procedure used for some farmers, urea was applied in bands at 10 cm from the maize row and semi-incorporated (at around 2–3 cm depth) at six-leaf stage (Ritchie and Hanway 1982). A microplot (3 rows and 1.50 m length) was installed in the middle of each plot (Fig. 1). Microplots were fertilized with urea tagged with ^{15}N (1.5 % abundance) following the same doses as those applied in the main plot. The urea used came from grinding and mixing commercial urea and tagged urea with ^{15}N 5 % abundance. Each microplot was then surrounded by an outside boundary plot and they were not contained. In each microplot there were three rows of plants fertilized with ^{15}N and to avoid the border effects with the larger area receiving unlabelled urea the maize middle row was sampled (Fig. 1).

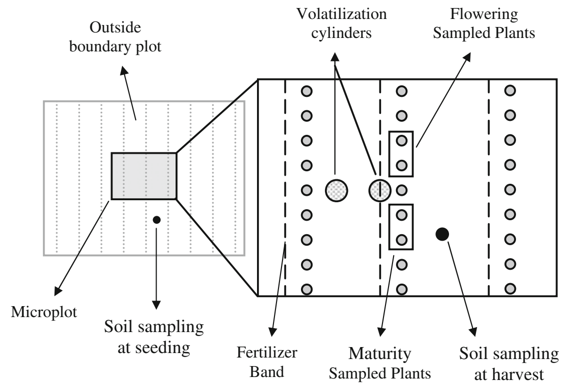

Fig. 1 Diagram showing a plot boundaries and the microplot location, and within them the fertilized band, the place of the cylinders for volatilization determination, the sampling plants, the sampling soil site and the rows of maize

Plant material (aerial-stems + leaves- and root-biomass) was collected at flowering (82 days after seeding-DAS) and at physiological maturity (143 DAS). Two plants were harvested in each sampling. In the last sampling, cobs, husks and grains were also collected. Root sampling was carried out up to 0.50 m depth, assuming that more than 90 % of maize underground biomass is located at that depth (Andrade et al. 1996). Dry weights for the different plant organs were obtained after heating in an oven at 60 °C to constant weight. Total N by Kjeldahl (Bremner and Mulvaney 1982) and the proportion of ^{15}N, using optical emission spectrometry (Fiedler and Proksch 1975), were determined in all plant samples.

Soil samples at 0.33 m intervals up to 3.0 m depth were taken in each plot at seeding and harvest time using a percussion soil sampler. The diameter of the auger was 5 cm. Samples were taken in the middle point among rows, some 25 cm from the fertilized band (Fig. 1). A total of 144 soil samples were obtained. Nitrates and ammoniacal N concentration were determined in all samples, by extraction with 2 M KCl and distillation with MgO and Devarda alloy (Keeney and Nelson 1982). The proportion of NO_3-^{15}N was also determined. To transform N concentration into N quantity in soil, bulk density of

1.2 g cm^{-3} for 0–60 cm deep and 1.3 g cm^{-3} for 60–300 cm deep were considered. Organic N by the Kjeldahl method (Bremner and Mulvaney 1982) and the ^{15}N percentage, using the above-mentioned technique, were determined at harvest in top soil samples only. To calculate the N derived from the fertilizer and located in the organic fraction, the NO_3-^{15}N value was deducted from the total ^{15}N. Our own previous data (Rimski-Korsakov et al. 2009) and data from other authors (Álvarez et al. 2008), using the same ^{15}N enrichment in ther fertilizer and determining it in the soil organic pool using the same equipment, were satisfactory, which indicate that our results are enough accurate for our purposes.

The ammonia losses via volatilization were determined using the Nommik method (Nommik 1973). The position of the cylinders to measure ammonia volatilization is shown in Fig. 1. We weighted the area covered by each cylinder and attributed to the cylinder over the fertilization band 21.4 % of the whole surface and 78.6 % for the cylinder located among the rows. Ammonium N was determined by microdistillation (Sparks et al. 1996) and NH_3-^{15}N using optic emission spectrometry (Fiedler and Proksch 1975).

The effects of the treatments were statistically analyzed using ANOVA. The least significant difference (LSD) was used to differentiate means.

Calculations of the fate of the fertilizer

The percentage of N derived from the fertilizer (NdfF) in each compartment was calculated using Eq. 1. The natural abundance of ^{15}N for the commercial urea used to the dilute the tagged urea, was estimated as 0.366 % (IAEA 2001). For the other compartments (plant, soil and volatilization extracts) of the fertilized treatments, the natural abundance of ^{15}N in the equivalent N0 treatment compartment was used.

$$\text{NdfF}\,(\%) = \big(\%\,^{15}\text{N abundance in the plant, soil organic N, NO}_3-\text{N, or volatilization extracts} - \%\text{ of natural abundance of }^{15}\text{N}\big)/\big(\%\,^{15}\text{N in the fertilizer} - \%\text{ of natural abundance of }^{15}\text{N}\big)\times 100 \quad (1)$$

The recovery of fertilizer in each compartment was estimated following Eq. 2.

$$\text{Fertilizer recovery}\,(\%) = \text{NdfF}/\text{N}_{\text{fertilizer}} \times 100 \quad (2)$$

where NdfF (%), N derived from the fertilizer in the plant, soil organic N, NO_3-N, or volatilization extracts (kg N ha^{-1}); $N_{fertilizer}$, nitrogen applied by fertilization (kg N ha^{-1}).

The total recovery of the fertilizer applied was calculated using Eq. 3.

$$\text{N}_{\text{fertilizer}}\,(100\%) = \text{NdfF}_{\text{plant}}\,(\%) + \text{NdfF}_{\text{volatilized}}\,(\%) + \text{NdfF}_{\text{nitrate}}\,(\%) + \text{NdfF}_{\text{organic}} + \text{NdfF}_{\text{unaccounted}}\,(\%) \quad (3)$$

where $N_{fertilizer}$, N applied by fertilization (100 %); $NdfF_{plant}$, N from the fertilizer taken by the whole plant at physiological maturity (%). $NdfF_{volatilized}$, N from the fertilizer detected in volatilization extracts (%). $NdfF_{nitrate}$, N from the fertilizer remaining as nitrates in the soil (%). $NdfF_{organic}$, N from the fertilizer remaining in the soil as organic N (%). $NdfF_{unaccounted}$, N from the fertilizer not detected in any of the compartments studied (%).

Results

The maize biomass production at flowering (82 DAS) did not show significant differences between treatments (data not shown). An increase in N concentration as urea doses increased was found in the aerial compartment. Conversely, the N concentration in root biomass showed no significant differences between treatments. The concentration of the N from the soil did not change in the aerial or root biomass but the N absorption by plants from the fertilizer varied. Some differences were found at harvest (data not shown). Table 1 shows dry matter production, total absorbed N, N derived from the soil and N derived from the fertilizer in aerial biomass components (stems + leaves + husks), roots and grains, at physiological maturity (143 DAS). Most compartments were significantly affected by fertilization. The treatments with larger N doses (N140 and N250) led to significantly greater total biomass production (24,068 and 25,896-kg dry matter (DM) ha^{-1}, respectively) than treatments N0 and N70 (18,877 and 19,071-kg DM ha^{-1}, respectively). The greater grain production was found in treatment N250. The three fertilization treatments exhibited significant greater cobs biomass than the control. The root biomass showed no significant differences between

Table 1 Dry matter (*DM*) production at harvest, total N absorbed (production × N concentration), N derived from the soil (*NdfS*) and N derived from fertilizer (*NdfF*), in aerial biomass (stems + leaves + husks), roots, cobs and grains

	Dry matter (kg DM ha^{-1})	Total N (kg N ha^{-1})	NdfS (kg N ha^{-1})	NdfF (kg N ha^{-1})
Aerial biomass				
N0	8,058 (b)	42.33 (b)	42.33 (a)	–
N70	7,254 (b)	45.00 (b)	34.01 (a)	10.99 (c)
N140	10,098 (a)	77.52 (a)	51.73 (a)	25.74 (b)
N250	10,772 (a)	85.45 (a)	48.20 (a)	37.25 (a)
Root biomass				
N0	1,550 (a)	20.80 (a)	20.80 (a)	–
N70	1,394 (a)	24.19 (a)	21.57 (a)	2.616 (b)
N140	1,242 (a)	22.74 (a)	19.30 (a)	3.440 (b)
N250	1,629 (a)	29.70 (a)	21.32 (a)	8.379 (a)
Cobs				
N0	1,590 (b)	4.496 (b)	4.496 (a)	–
N70	1,778 (ab)	7.184 (a)	7.074 (a)	0.110 (c)
N140	2,092 (a)	8.391 (a)	7.874 (a)	0.517 (b)
N250	2,153 (a)	8.498 (a)	7.380 (a)	1.117 (a)
Grains				
N0	7,679 (c)	73.75 (c)	73.75 (a)	–
N70	8,646 (bc)	101.8 (bc)	74.19 (a)	27.57 (b)
N140	10,635 (ab)	137.7 (ab)	87.88 (a)	49.85 (ab)
N250	11,342 (a)	149.9 (a)	79.14 (a)	70.81 (a)

Different letters means significant differences among treatments ($p < 0.05$)

treatments. The total aerial biomass/root biomass ratio at harvest varied from 12.1 to 18.9, and the harvest index varied from 0.40 to 0.45. Nitrogen concentration was generally lower in the control treatment (data not shown). The whole maize plant showed greater N accumulation in treatments N140 and N250 as compared with N0 and N70 (Table 1). Fertilization increased the N accumulated in all plant organs with the exception of roots, which did not show significant differences between treatments. The N coming from the soil showed no differences between treatments in any of the plant organs. Conversely, the N recovered from the fertilizer showed significant differences between treatments, in all the organs studied. In general, the N coming from the fertilizer in plants increased as the N dose increased (Table 1).

Figure 2 show the N located in the soil organic matter after harvest. Total N content in the top soil (0.30 m) was, in average, 0.164 %, and did not show

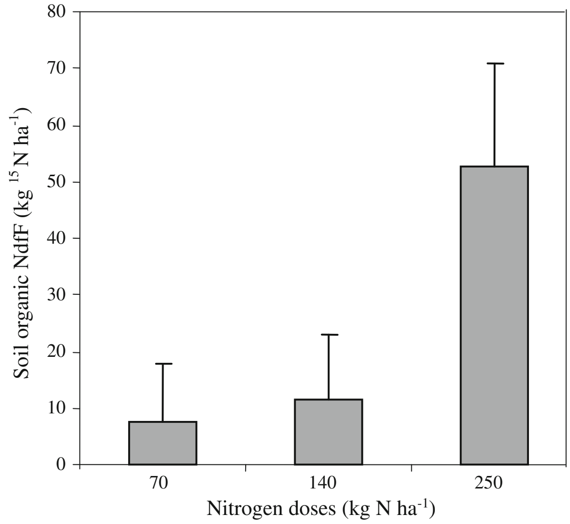

Fig. 2 Nitrogen derived from the fertilizer at harvest, located in the soil organic matter at 0–30 cm depth (kg N ha^{-1}). *Bars* standard error

significant differences between treatments. However, some significant differences were found in the N content in the soil organic fraction coming from the fertilizer (^{15}N). A close relationship was established between the N derived from the fertilizer in the organic matter and the fertilizer dose ($R^2 = 0.98$; $p = 0.02$). Treatment N250 showed a significantly larger N content from the fertilizer (52.8 kg ^{15}N ha^{-1}), in the organic fraction.

Ammonia volatilization either from the soil or the fertilizer showed significant differences between treatments, from the start to the end of the experiment. Total losses by volatilization were significantly greater as the N dose applied increased (Table 2). Significant differences between treatments were found in the NH_3-^{15}N volatilized. The losses were 24.6, 20.3 and 15.4 % of the N applied in treatments N70, N140 and N250, respectively. The ammonia volatilized from the soil also showed significant differences between treatments: the larger fertilizer doses corresponded with the larger ammonia volatilization from the soil.

The content of native nitrates in the whole soil profile (0–300 cm depth) at seeding was not significantly different than that at harvest, amounting to 104 and 107 kg NO_3-N ha^{-1}, respectively. The total content of nitrates native to the soil and total content of nitrates native to the soil plus the nitrates coming from the fertilizer at the end of the experiment did not

Table 2 Ammonia losses via volatilization: derived from the soil (*NdfS*), derived from the fertilizer (*NdfF*) and total losses (*NdfS + NdfF*)

	NH_3-N (kg NH_3-N ha^{-1})	NdfS (kg NH_3-N ha^{-1})	NdfF (kg NH_3-N ha^{-1})
0–2 DAF			
N0	0.599 (c)*	0.599 (a)	–
N70	0.646 (bc)*	0.351 (ab)	0.294 (b)*
N140	3.327 (a)*	0.183 (b)	3.144 (a)*
N250	2.515 (ab)*	0.188 (b)	2.327 (a)*
2–9 DAF			
N0	0.610 (c)	0.610 (c)	–
N70	17.097 (b)	1.743 (bc)	15.355 (b)
N140	23.376 (a)	3.632 (a)	19.744 (a)
N250	25.019 (a)	2.962 (ab)	22.057 (a)
9–30 DAF			
N0	0.634 (b)*	0.634 (a)*	–
N70	2.074 (b)*	0.689 (a)*	1.385 (b)*
N140	6.260 (a)*	1.330 (a)*	4.930 (a)*
N250	14.047 (a)*	2.760 (a)*	11.287 (a)*
30–99 DAF			
N0	0.467 (c)	0.467 (b)	–
N70	0.705 (c)	0.513 (b)	0.192 (c)
N140	1.318 (b)	0.678 (b)	0.640 (b)
N250	5.029 (a)	2.224 (a)	2.805 (a)
Total accumulated			
N0	2.311 (c)*	2.311 (b)*	–
N70	20.522 (b)*	3.296 (b)*	17.226 (c)*
N140	34.280 (a)*	5.823 (a)*	28.457 (b)*
N250	46.611 (a)*	8.135 (a)*	38.476 (a)*

The shown data are the losses between measurement dates and the total accumulated during the whole measurement time

DAF days after fertilization

* Logarithmic transformed data to obtain equal variances in the statistic. Different letters means significant differences among treatments ($p < 0.05$)

show significant differences between treatments at any depth (Fig. 3). The nitrates native to the soil exceeded the nitrates from the fertilizer in all the treatments except in the top soil (0–33 cm depth) in treatments N140 and N250 and at 100–133 cm depth in treatment N250. Conversely, the content of nitrates from the fertilizer showed significant differences between treatments: 4.58, 15.31 and 27.21 kg NO_3-^{15}N ha^{-1} in the whole soil profile (0–300 cm) for treatments N70, N140 and N250, respectively. In our experiment there was an effect of fertilization on the quantity of soil residual nitrates. Treatments N140 and N250 contained more residual nitrates coming from fertilizer than N70 treatment, but the formers did not differ among them (Fig. 4). The nitrates derived from the fertilizer accumulated in the top soil (0–33 cm depth) were 1.67, 14.14 and 20.77 kg NO_3-^{15}N ha^{-1} for treatments N70, N140 and N250, respectively. The nitrates from the fertilizer found from 150 to 300 cm depth did not show significant differences between treatments. These "leached" nitrates amounted in average to 1.13 kg NO_3-^{15}N ha^{-1}, which means a loss of 0.84 % of the N applied via fertilization. The ammoniacal N content in the soil was not discriminated by its origin (soil or fertilizer). At seeding it was not significantly different from that at harvest: 161 and 187 kg NH_4-N ha^{-1} respectively. Also, ammoniacal N did not present significant differences between treatments in any of the depths studied (data not shown).

The sinks of N from the fertilizer and their changes according to the fertilizer doses applied are shown in Fig. 5. The fertilizer recovery in all the compartments studied (plant, organic matter, volatilized and remaining as nitrates, either residual or leached) averaged 97.98 %. The recovery was greater as fertilizer dose was lower, being the unaccounted N 11.4 kg N ha^{-1} in treatment N250.

Discussion

At flowering, maize plants accumulated an average of 60 % of the total N accumulated at harvest, with no differences between treatments (data not shown). These values are similar to those found by several authors (Coque and Gallais 2007; Cregan and Van Berkum 1984; Pommel et al. 2006). The N from the soils accumulated in plant tissues from seeding to flowering was in average 56 % of the total N of this origin accumulated at harvest. Meanwhile, an average of 71 % of the N from the fertilizer was absorbed from seeding to flowering in the whole plant. This indicates that the effect of fertilization is still important in advanced stages of the crop.

The increases in N availability in the soil increased the N accumulation in plants: N concentration in grains varied from 0.95 to 1.31 %. Due to N

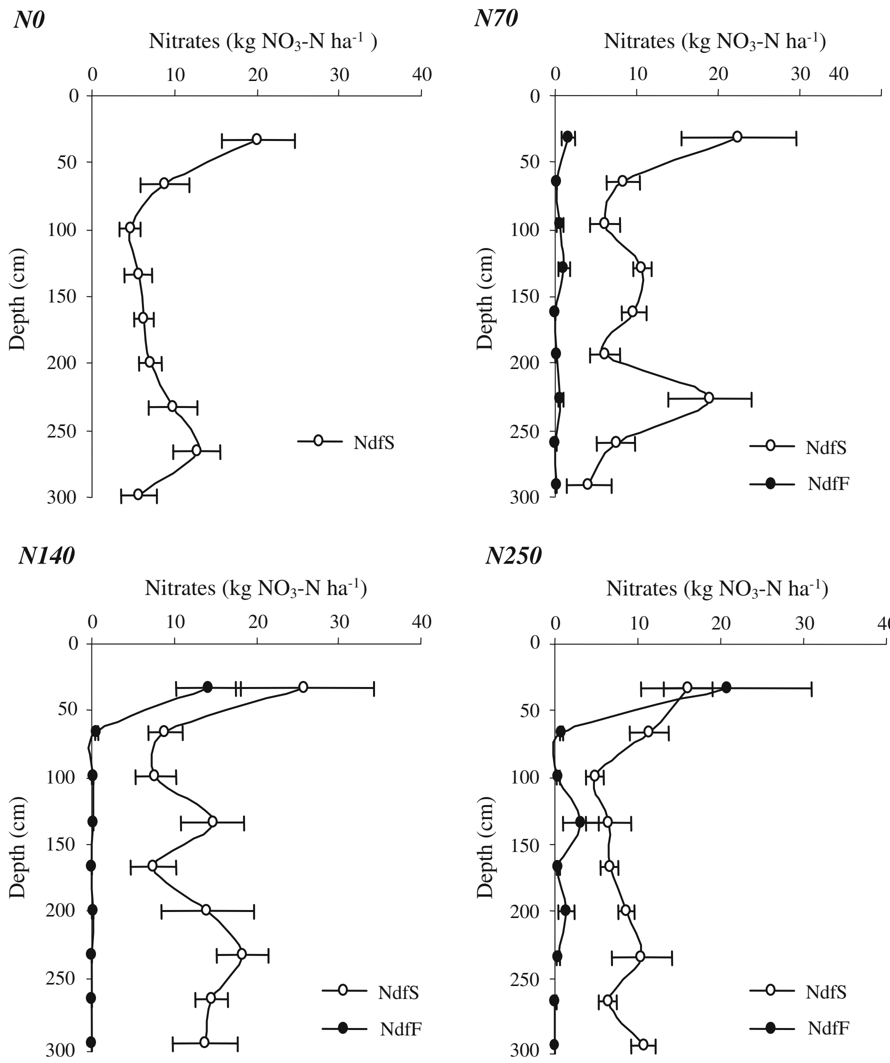

Fig. 3 Content of nitrates native to the soil and nitrates coming from the fertilizer, from 0 to 300 cm depth (kg N-NO_3 ha^{-1}). NdfS: N derived from the soil, NdfF: N derived from the fertilizer. *Bars* standard error

remobilization toward reproductive organs, the N concentration in stems + leaves decreased in average from 1.31 % at flowering to 0.67 % at harvest. The apparent N movement from stems + leaves to grains in the present study was 45 kg N ha^{-1}, in average, similar to that found by Pommel et al. (2006) in non-stressed maize. To determine N limitations in maize grain production, Cerrato and Blackmer (1990) proposed the N accumulated in the grain/maize yield ratio. This limit was locally validated by Uhart and Andrade (1995) around 12 g N kg^{-1} grain. The ratios found in the present research were 9.5, 11.6, 12.9 and 13.1 in treatments N0, N70, N140 and N250, respectively. Treatments N0 and N70 showed ratios lower than the established limit, in agreement with their lower yields.

The absorption of N from the soil by the whole plant was larger, in relative terms, than the N absorbed from the fertilizer, representing from 54 to 78 % of the total N absorbed. This is in agreement with the results of Schindler and Knighton (1999). This fact emphasizes the importance of organic matter (including crop residues) mineralization as a source of N for crops (Álvarez and Steinbach 2010). The relative proportion of the N coming from the soil decreased as the fertilizer dose increased. In fact, the N from the soil did not differ significantly between treatments but the N from the fertilizer taken by plants increased as the N dose increased. Those results differ from those found by Stevens et al. (2005). These authors found increases in N from the soil parallel to increases in the absorption of N from the fertilizer. This is the so-

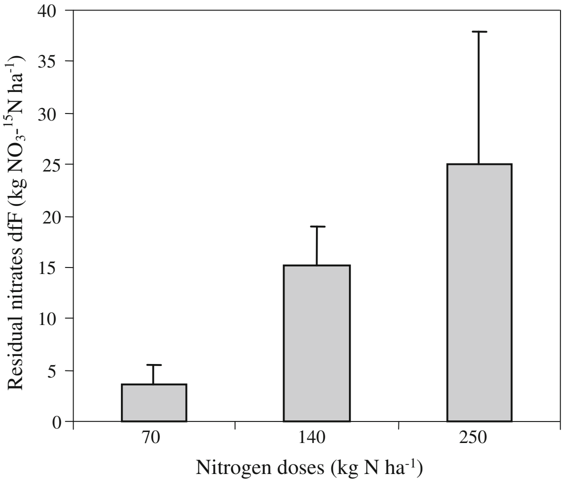

Fig. 4 Residual nitrates (0–150 cm) coming from the fertilizer, at maize harvest. *Bars* standard error

called "priming effect" (Kuzyakov et al. 2000; Westerman and Kurtz 1973), which means increases in N mineralization as the N fertilizer dose increases. In the present case, no evidences of "priming effect" were found. On the other hand, the N from the soil was relatively less important from seeding to flowering than from flowering to harvest. This can be caused by the initial greater availability of the N from the fertilizer. After flowering, when the N from the fertilizer became increasingly exhaust, the supply of N from the soil increased, due to the larger mineralization rates due to the larger temperatures at this time (Álvarez et al. 2007). Using ^{15}N, Daniel et al. (1986) also found that the N from the fertilizer was very important during the vegetative stages.

The N from the fertilizer recovered by the whole plant was 56 % in average, varying from 48 to 62 %. These percentages are larger than those found by Schindler and Knighton (1999), Stevens et al. (2005) and Tolessa et al. (2007), among others, using tagged fertilizers. These authors recovered from 28 to 45 % of the N applied. The fact that our experiment showed no water limitations or pest attacks may account for the results found. In accordance with Nissen and Wander (2003), our greater relative recoveries were found with the lowest dose of N applied, either in the whole plant or when each plant organ was considered separately. The recovery of N from the fertilizer by the grains was 39.4, 35.6 and 28.3 % as the N dose increased. This means that an average of 65 % of the N applied with the fertilizer was not exported within the grains but remained in the soil/plant system or was lost in different ways. Schindler and Knighton (1999) found similar recoveries in maize grains. The N recovery by stems + leaves + husks was 15.7, 18.4 and 14.9 %, for treatments N70, N140 and N250, respectively. Roots and cobs recovered percentages of N of 3.23 and 2.27 %, respectively were found.

The soil organic fraction has also been found as an important sink to N from fertilizers, in the area studied (Portela et al. 2006; Sainz Rozas et al. 2004). This fraction is more stable that the inorganic fraction and must suffer gradual mineralization to release nitrates (Reddy and Reddy 1993). It is supposed this fate is an important N conservation sink in soils until the crop can use it. However, it must be taken into account that the N retained in this organic fraction enters the more

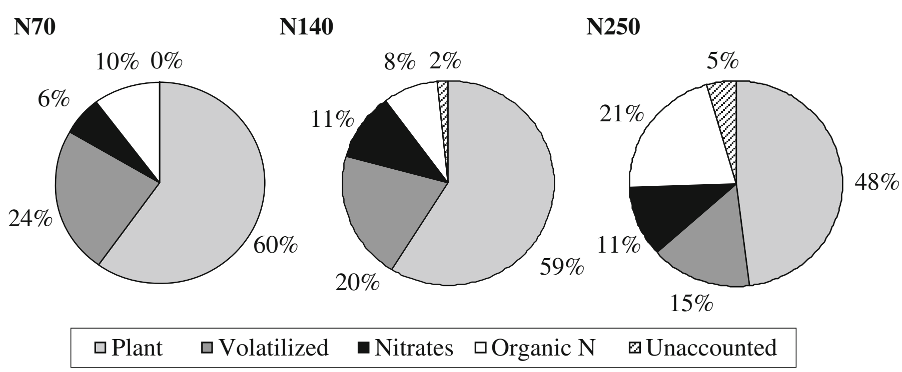

Fig. 5 Sinks of the N coming from the fertilizer in each treatment, relative to the N applied via fertilization. Plant: N accumulated by the whole plant at harvest; volatilized: ammonia-N volatilized from fertilization to crop harvest; nitrates: nitrates-N from 0 to 300 cm depth, at maize harvest; organic N: ^{15}N measured in the soil organic pool, 0–30 cm depth; unaccounted: fraction of the applied N, non-recovered

labile fractions (Álvarez and Álvarez 2000). That is why the buffer effect could be time-limited, particularly when soils are subjected to conditions of high mineralization rates.

Ammonia volatilization data were similar to those observed in maize in the area but within the highest values recorded in the Pampas (Álvarez et al. 2007; Palma et al. 1998; Sainz Rozas et al. 2004). This can be accredited to the high air and soil temperatures at the fertilization times. Usually most losses of ammonia occur mainly during the first days after fertilization (Cai et al. 2002; Wang et al. 2004). The ammonia losses in the fertilization treatments within 10 days after the application of the fertilizer amounted to 86, 77 and 59 % of total ammonia loss in treatments N70, N140 and N250, respectively. Those initial losses could be caused by increases in soil pH and a peak of NH_4^+ concentration in the soil solution (Cai et al. 2002). The high soil basal volatilization rate in the fertilization treatments could also be caused by an increase in soil pH (Ferguson et al. 1984) or by an isotopic exchange between ^{15}N and ^{14}N (Jenkinson et al. 1985). Anyway, the N loss from the soil via ammonia volatilization was a relatively minor fraction, around 26–18 % of the total ammonia volatilized.

Fertilization in the present experiment affected only the residual nitrates (0–150 cm depth), which are not considered lost from the soil/plat system, because they can be taken for the next crop or by growing vegetation during fallow such as cover crop or weeds (Peterson and Power 1991). Nitrates located below 150 cm depth were, in average, 1.13 kg NO_3-^{15}N ha^{-1}. They, conversely, are considered already leached because their recovery by roots is very low or null (Follett et al. 1994). This shows that the N from the fertilizer applied at seeding of maize means a minimum leaching of nitrates during the crop cycle. A single fertilizer application represents, in average, a loss of 0.84 % of the N applied. This percentage is even lower than that found by Nissen and Wander (2003), who found an average of 2.3 % of the N applied from fertilizers. The nitrates leached from the soil did not differ between treatments but their values were significant: 45.3 kg NO_3-N ha^{-1} in average of all treatments. Those nitrates could come from the organic matter and crop residues mineralization, either from previous or present cropping cycle as well as nitrates remaining from previous fertilizations. Nitrate leaching is an important loss from the soil/plant system, but it does not respond to a single event, as a fertilizer application, but to several sources.

The ammoniacal N in soils was high in all treatments and most times even greater that nitrate N. This is not an uncommon result found in the area (Pidello et al. 1995; Portela et al. 2006) and can be attributed to different reasons: high levels of non-exchangeable ammonium, related to the soil high content of illites, the effect of previous fertilizations and the no tillage management of the soil (Blevins et al. 1996; Portela et al. 2006). Ammoniacal N showed a close relationship with nitrates N ($R^2 = 0.88$; $p = 0.0001$). From the results obtained, it seems that this N fraction was not an important sink for the N from the fertilizer.

Finally, Fig. 5 shows that the crop was the main sink for the N from the fertilizer, followed by the soil organic fraction and ammonia volatilization. With the lower N doses (treatments N70 and N140), ammonia volatilization was a more important fate than the organic pool. Conversely, in treatment N250, the organic pool was a more important sink than ammonia volatilization (21 vs. 15 %, respectively). For the conditions of the experimental area, the fertilizer dose of 140 kg N ha^{-1} appeared to be a turning point. Elevated N doses did not increase grain production but the N uptake from fertilizer efficiency decreased and the concentration of nitrates from the fertilizer increased in the soil. The organic matter sink increased exponentially at the larger fertilizer doses and appeared to act as the buffer of the system and also ammonia volatilization was not saturated. Even taking into account the different precision levels of the different analytical methods used for the N fractions measured, the high N recovery in the compartments studied indicate that other non-quantified sinks, such as denitrification, were of low magnitude.

Concluding remarks

The crop was the main sink for the N from the fertilizer, recovering an average of 56 % of the N applied. The other sinks for the N from the fertilizer were the soil organic fraction and ammonia volatilization. The amount of N in the organic matter sink increased exponentially as the fertilizer dose increased. This would indicate that when the plant can not maintain its capacity to accumulate N from the fertilizer, the organic sink appears to be of larger importance, and could act as the buffer of the system. Also, ammonia volatilization was a sink that was apparently not saturated, as it increased linearly with the dose applied.

The N applied by fertilization and remaining as residual nitrates averaged 8.6 % and the leached nitrates represented only 0.8 % of the N applied with the fertilizer. This clearly shows that the significant N leaching values measured when maize is cropped could be accredited to other origin such as mineralization of the soil organic matter or residues from previous crops or remains of previous fertilizations. According to these results, the organic matter would be a temporary sink, which reduces N leaching from a single N application but releases nitrates the following years. In the long term, the organic matter sink would be irrelevant to avoid N leaching from high fertilizer doses.

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