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Abstract

Among the main greenhouse gases (CO$_2$, CH$_4$ and N$_2$O), N$_2$O has the highest global warming potential. N$_2$O emission is mainly connected to agricultural activities, increasing as nitrogen concentrations increase in the soil with nitrogen fertilizer application. We evaluated N$_2$O emissions due to application of increasing doses of ammonium nitrate and urea in two sugarcane fields in the mid-southern region of Brazil: Piracicaba (São Paulo state) and Goianésia (Goiás state). In Piracicaba, N$_2$O emissions exponentially increased with increasing N doses and were similar for urea and ammonium nitrate up to a dose of 107.9 kg ha^{-1} of N. From there on, emissions exponentially increased for ammonium nitrate, whereas for urea they stabilized. In Goianésia, N$_2$O emissions were lower, although the behavior was similar to that at the Piracicaba site. Ammonium nitrate emissions increased linearly with N dose and urea emissions were adjusted to a quadratic equation with a maximum amount of 113.9 kg N ha^{-1}. This first effort to measure fertilizer induced emissions in Brazilian sugarcane production not only helps to elucidate the behavior of N$_2$O emissions promoted by different N sources frequently used in Brazilian sugarcane fields but also can be useful for future Brazilian ethanol carbon footprint studies.

Keywords: greenhouse gases, ammonium nitrate, urea, global warming, ethanol

1. Introduction

The N$_2$O atmospheric concentration increased from 270 parts per billion (ppb) in the preindustrial period to approximately 319 ppb in 2005, and agriculture is considered the main cause for this (IPCC 2007). Approximately 70% of annual anthropogenic N$_2$O emissions in the world come from animal and crop production (Mosier 2001). N$_2$O emissions are of great importance due to its high global warming potential: 298 times greater than CO$_2$, considering 114 years lifetime and 100 years of time horizon (Forster *et al* 2007). Brazilian N$_2$O emissions in 2005 were around 221.2 Mt CO$_2$ eq (11% of national emissions) and agricultural soils were responsible for 87.20% of this (Cerri *et al* 2009).

Nitrogen gaseous emissions (N$_2$O, NO and N$_2$) from soils are a consequence of several processes (Bockman and Olfs 1998, Stevens and Laughlin 1998, Conrad 1996), but most of the N$_2$O is produced by nitrification and denitrification reactions. Emissions depend on the balance

Table 1. Physical and chemical characteristics of the two oxisols in the studied areas. (Sand, silt and clay determined by the Bouyoucos method. Ca^{2+}, Mg^{2+}, P and K^+ determined by ion exchange resin (Raij and Quaggio 1983). Al^{3+} determined by titration with KCl, 1 mol l^{-1}. H+Al determined by the SMP buffer method.)

Soil layer (cm)	Sand (g kg^{-1})	Silt (g kg^{-1})	Clay (g kg^{-1})	pH water	C[a] (g kg^{-1})	Ca^{2+} (mmol$_c$ dm^{-3})	Mg^{2+} (mmol$_c$ dm^{-3})	K^+ (mmol$_c$ dm^{-3})	Al^{3+} (mmol$_c$ dm^{-3})	H+Al (mmol$_c$ dm^{-3})	P (mg kg^{-1})
						Piracicaba					
0–10	442	49	509	5.1	15.7	38	22	1.1	1	35	10
10–20	433	32	535	4.7	13.9	21	12	0.6	7	49	7
						Goianésia					
0–10	194	240	566	5.4	24.6	36	91	3.5	1	36	5
10–20	187	253	560	5.3	21.2	39	92	2.5	2	39	3

[a] Carbon determined by Walkley–Black method (wet combustion) in Piracicaba and by dry combustion in Goianésia.

among production, consumption and diffusion of nitrogen gases to the atmosphere (Firestone and Davidson 1989). As N_2O production by nitrification or denitrification depends on the N available in the soil (Akiyama *et al* 2000), nitrogen fertilizer application is an important driver of N_2O emissions (Brentrup *et al* 2000, Bergstrom *et al* 2001, Passianoto *et al* 2003, Chen *et al* 2008).

Brazil is the largest sugarcane producer in the world, with 8368 million hectares planted and a harvest of 571 439.3 million tons of sugarcane in the 2011/2012 crop (CONAB 2012). Brazilian sugarcane production is concentrated in two distinct regions: northeastern and mid-southern. The second one is responsible for around 90% of the national production. Approximately 50% of Brazilian sugarcane production was directed towards ethanol production (CONAB 2012), that is used as biofuel by vehicles. According to the International Fertilizer Industry Association (IFA), in 2007/2008 Brazilian sugarcane used 22.3% of nitrogen fertilizers consumed in the country and 0.6% of the world consumption (Heffer 2009). According to the Brazilian National Supply Company (CONAB), around 92.4% of the recent sugarcane area expansion took place in the mid-southern region (43.3% in São Paulo state and 10.9% in Goiás state) (CONAB 2008).

Given the importance of Brazilian sugarcane ethanol to substitute for fossil fuels, it is important to evaluate greenhouse gas (GHG) emissions associated with its production process, including those deriving from the sugarcane agrosystem. Macedo *et al* (2008) estimated ethanol GHG emissions in Brazil as 436 kg CO_2 eq m^{-3} and affirmed that this value was mainly affected by cane productivity, N-fertilizer use and ethanol yield. Taking in account data from Macedo *et al* (2008) and CONAB (2012), Brazilian GHG emissions in sugarcane areas would be 1.19 kg CO_2 eq ha^{-1}. GHG emissions related to sugarcane production are associated with land use change; fertilization, fertigation and irrigation; residue management (including preharvest burning); tillage operations and diesel use (Figueiredo and La Scala Jr 2011, Lisboa *et al* 2011). Excluding land use change, since in Brazil sugarcane areas are not established directly after the native vegetation conversion, N fertilization is the major contributor to the GHG emissions of the ethanol–sugarcane system (Lisboa *et al* 2011). However, these authors, in a GHG balance for bioethanol from sugarcane, affirmed that there is

a large uncertainty on the information due to lack of available data, and highlighted the need for GHG quantification after liming and N–P–K fertilization.

We hypothesized that there are differences in N_2O emissions according to sources and rates of N fertilizers applied to the soil. The objective of this research was to evaluate N_2O emissions according to different urea and ammonium nitrate application rates in sugarcane crop areas in Brazil's mid-southern region. This will provide useful information for Brazilian GHG inventories because information about N_2O emissions induced by N fertilizers for sugarcane in Brazil is not currently available. Moreover, our results can directly contribute to international institutions and organizations such as the IPCC, GHG Protocol, GBEP, Bonsucro etc related to biofuel assessments.

2. Materials and methods

Two experiments were conducted in Brazil's mid-southern region. The first one was done in Piracicaba (22°43′ S, 47°38′ W) in São Paulo state (site 1), and the second one was conducted in Goianésia (15°19′ S, 49°07′ W) in Goiás state (site 2). Characteristics of the soils in the two experimental sites are in table 1. In Piracicaba, the area was cultivated with sugarcane for more than 60 years and the cane was in the second ratoon during the experiment. Harvesting was done without fire, and there was 15 Mg ha^{-1} dry matter of straw on the soil surface.

The Piracicaba climate is tropical moist (Cwa, Köeppen), with rainy summers and dry winters. The annual average temperature is 21.5 °C, and precipitation is about 1270 mm. The influence of nitrogen fertilizers on N_2O emissions was evaluated by comparing emissions in areas without fertilizer application and in areas that received different doses of nitrogen from two sources (urea and ammonium nitrate). Treatments tested were C (control; with no application of nitrogen fertilizer), four rates of urea (60 (U60), 90 (U90), 120 (U120), and 180 (U180) kg N ha^{-1} year^{-1}), and four rates of ammonium nitrate (60 (AN60), 90 (AN90), 120 (AN120), and 180 (AN180) kg N ha^{-1} year^{-1}). For all treatments, we made a single fertilizer application at the beginning of the experimental period.

At site 1, plots of each treatment were formed by four sugarcane rows, each 10 m long. Fertilizers were applied to the soil in the same way as done in commercially cultivated areas, i.e. on the surface at approximately 10 cm from the sugarcane ratoon. N_2O emissions were measured with static chambers (Steudler *et al* 1996) (volume about 10 liters), composed of two parts: a 28 cm diameter metal base partially buried in soil (approximately 5 cm deep) and a polyvinyl chloride (PVC) lid with a small opening where gas samples were collected. The upper end of the metal base had a rim (approximately 2.8 cm high) where the lid was supported at collection time and where water was placed to ensure perfect sealing between the lid and the base.

Four bases were installed in the two central lines of each plot, representing four replicates of each treatment. The bases were installed one day before the fertilizer applications and stayed in the same place until the end of the experiment. In each evaluation gas samples was collected from each chamber at three times: immediately after closing the chamber and 10 and 30 min after that. Samples were collected in 20 ml plastic syringes coupled to a three-way connector to avoid the loss of gas. After this, the lids were removed and the metal bases remained uncovered until the next collection. Immediately after the collection, syringes were sent to the laboratory for determinations of N_2O concentrations in a gas chromatograph with a detector temperature of $310\,°C$ and column oven temperature of about $350\,°C$. N_2O concentration over time, chamber volume, chamber area, soil temperature and atmospheric pressure were used for calculation of N_2O flux expressed as μg N–N_2O m^{-2} h^{-1}. In Piracicaba, measurements were made from 21 October to 9 December 2009 (50 days). In the first 10 days, daily samplings were conducted. After this, collections were carried out every two days. Moreover, immediately after rain events the measurements were made daily.

The second experiment was conducted in Goianésia (site 2), from 23 January to 8 February 2010. The Goianésia climate is tropical (Aw, Köeppen) with dry winters; annual temperature varies between $22\,°C$ and $25\,°C$ and precipitation is about 2473 mm. Sugarcane has been cultivated in the area for more than 20 years, harvesting has been done without fire and plants were in the fifth ratoon during the experiment. Treatments tested at site 2 were C, three rates of urea (U60, U120 and U180) and three rates of ammonium nitrate (AN60, AN120 and AN180). Each treatment was applied separately in a 1 m long row, on the soil surface at approximately 10 cm from the sugarcane ratoon. Chambers used in this experiment were the same as described above and were installed in the middle of the fertilizer application row. Four chambers were used per treatment (replicates) and gas samples were collected as the same way as described above. The samples were immediately transferred from syringes to pre-evacuated vials closed with a rubber stopper, sent to the laboratory in Piracicaba and analyzed as the same way as for site 1.

Statistical analyses of the two sites were done individually using the SAS 9.0 program. During the experiments, daily means of N_2O fluxes for each treatment were compared by mean test (Tukey, $\alpha < 0.05$), using the *glm* procedure. Total amounts of N_2O emitted during the 50 days study at Piracicaba and during the 16 days study at Goianésia were estimated by integration of N_2O daily fluxes from each plot. With accumulated emissions, we calculated the proportion of the added N that is emitted as N_2O.

Cumulative N_2O emissions in each N source were subjected to regression analyses. At site 1 the following exponential equation was used: $y = ae^{bx}$, where y represents N_2O emission during the evaluated period (mg N–N_2O m^{-2}), x is the amount of fertilizer applied (kg ha^{-1}), a represents the intercept of axis y and b determines the shape of the curve. The exponential equation was adjusted through the *glm* procedure of the SAS 9.0 program to the linear form of the following model: $\ln(y) = b_0 + b_1x$. From the parameters obtained with this equation we calculated the terms needed for the exponential equation, considering that a corresponds to e^{b0} and b of the exponential equation is equivalent to b_1 of the linear equation (Sit and Poulin-Costello 1994).

For site 2, accumulated N_2O emissions were adjusted to a linear model for ammonium nitrate ($y = ax + b$) and to a second degree polynomial (quadratic equation) for urea ($y = ax^2 + bx + c$), where y is the cumulated N_2O emission (mg N–N_2O m^{-2}) during the experiment and x is the N rate (kg ha^{-1}).

3. Results

Precipitation during the experiment and N_2O fluxes for each treatment at site 1 are presented in figure 1. For site 2, data of soil moisture and N_2O fluxes are presented (figure 2). Considering precipitation and soil moisture are related, we consider that the influence of precipitation on N_2O fertilizer induced emissions was more evident at site 1 (Piracicaba), probably because the period of study was longer than at site 2 (Goianésia) and precipitation was lower than at site 1. When emissions began to decline in Piracicaba (after the 20th day) rainfall increased N_2O emissions. In Goianésia, as the experiment was shorter, fertilizer effects were more important than rainfall events.

In site 1, nitrogen sources increased N_2O emissions in different ways. Higher N_2O fluxes occurred for ammonium nitrate (maximal flux of 6543.71 μg N–N_2O m^{-2} h^{-1} on the tenth day in AN180) when compared to treatments with urea (maximal flux of 2528.69 μg N–N_2O m^{-2} h^{-1} on the 20th day in U120) (figures 1(a), (b)).

N_2O fluxes at site 1 increased with N rates for both fertilizers (figure 1). On all evaluation days, AN60 and AN90 fluxes were not different from unfertilized plots (Tukey, $\alpha < 0.05$). On the first day after N application, AN120 and AN180 fluxes were similar and higher than those for other treatments (Tukey, $\alpha < 0.05$). On the sixth day of measurements, AN180 flux became higher than AN120 flux and remained so until the 30th day. As AN180 increased, AN120 fluxes became similar to those of the other treatments. Approximately 30 days after the fertilizer application, fluxes of all treatments were enhanced by rainfall events. After that, AN180 N_2O fluxes still surpassed emissions of the other treatments. On
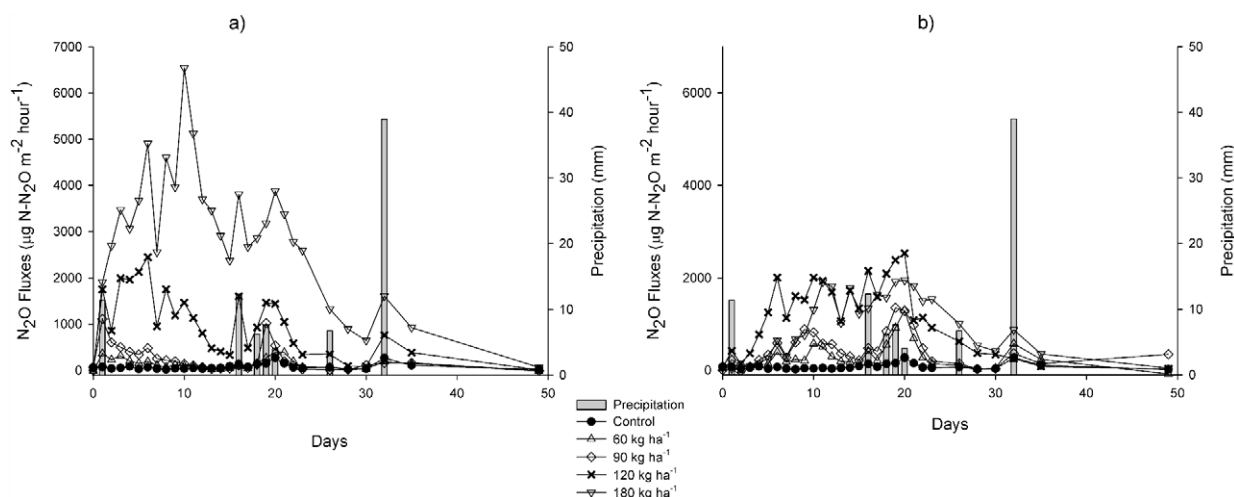
Figure 1. N$_2$O fluxes (lines) according to different doses of ammonium nitrate (a) and urea (b) applied to soil and precipitation (mm) (bars) during the experimental period in sugarcane farmland in Piracicaba ($n = 4$).
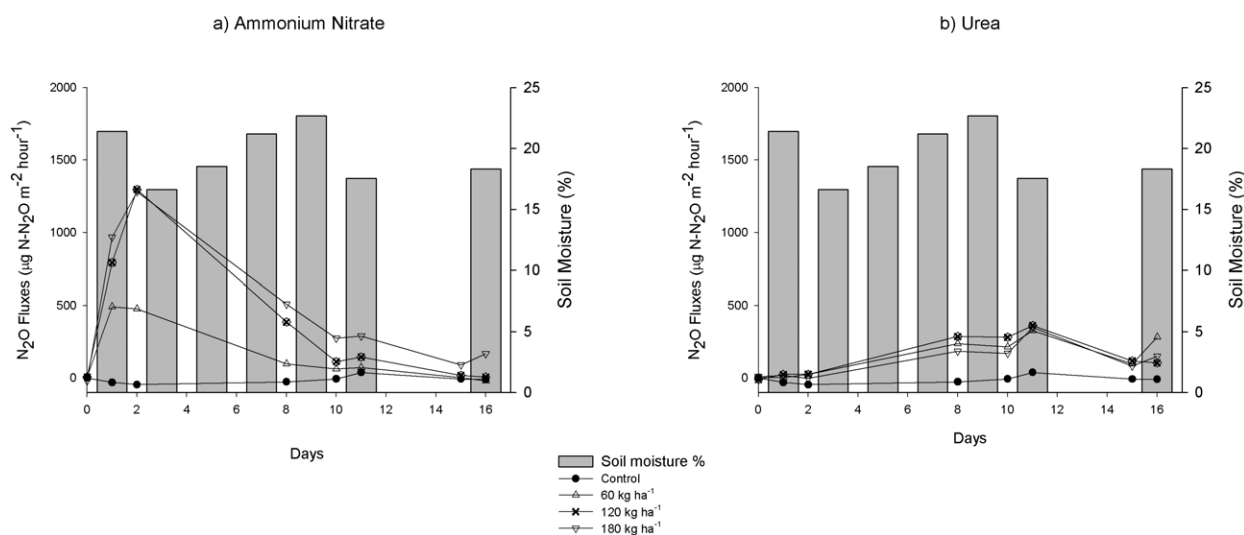

Figure 2. N$_2$O fluxes (lines) according to different doses of ammonium nitrate (a) and urea (b) applied to soil and soil moisture (%) (bars) during the experimental period in sugarcane farmland in Goianésia ($n = 4$).

the last day of measurements, all ammonium nitrate fluxes became similar (figure 1(a)).

For urea treatments at site 1 (figure 1(b)), differences between treatments occurred after the fourth day of measurements, when U120 flux was similar to U90 and higher than those for other treatments. U60 and U90 fluxes were similar to control along the 50 days of evaluation (Tukey, $\alpha < 0.05$). U120 fluxes were higher than U180 fluxes until the seventh day, but became similar from then on (Tukey, $\alpha < 0.05$). Approximately 20 days after fertilizer application, N$_2$O fluxes started to decrease and U120 fluxes were similar to the higher fluxes of U180 and to the lower fluxes of U60 and U90. After the 30th day of measurements, fluxes of all treatments were enhanced by rainfall events.

Exponential models for cumulated emissions at site 1 had determination coefficients of 0.82 ($p < 0.05$) and 0.66 ($p < 0.05$) for ammonium nitrate and urea respectively (figure 3a). U180 emission in this study was similar to that of U120, suggesting there is a plateau in urea emissions, while for

ammonium nitrate increasing the dose from 120 kg ha^{-1} to 180 kg ha^{-1} increased the N$_2$O emissions by 35%. Despite the stabilization observed in urea induced emissions, we adjusted cumulated emission of this N source to an exponential equation because in this case a second degree equation would show a minor determination coefficient.

At site 1, the proportion of added N lost as N$_2$O varied between 0.80 and 12.94% for ammonium nitrate and from 2.84 to 6.67% for urea (table 2). For ammonium nitrate, increasing the N rate increased the proportion of N lost, while for urea the proportion of N lost was not the highest when the highest N rate was applied. This behavior is similar to that observed for total emissions (figure 3).

N$_2$O emissions in the second experiment (Goianésia) had similar behaviors to those observed at site 1 although flux magnitudes were lower (figures 2(a), (b)). Negative N$_2$O fluxes on control plots were observed through most of the sampling period, so our estimate of mean fluxes for control plots was negative (-10.74 ± 8.99 μg N–N$_2$O m^{-2} h^{-1}).
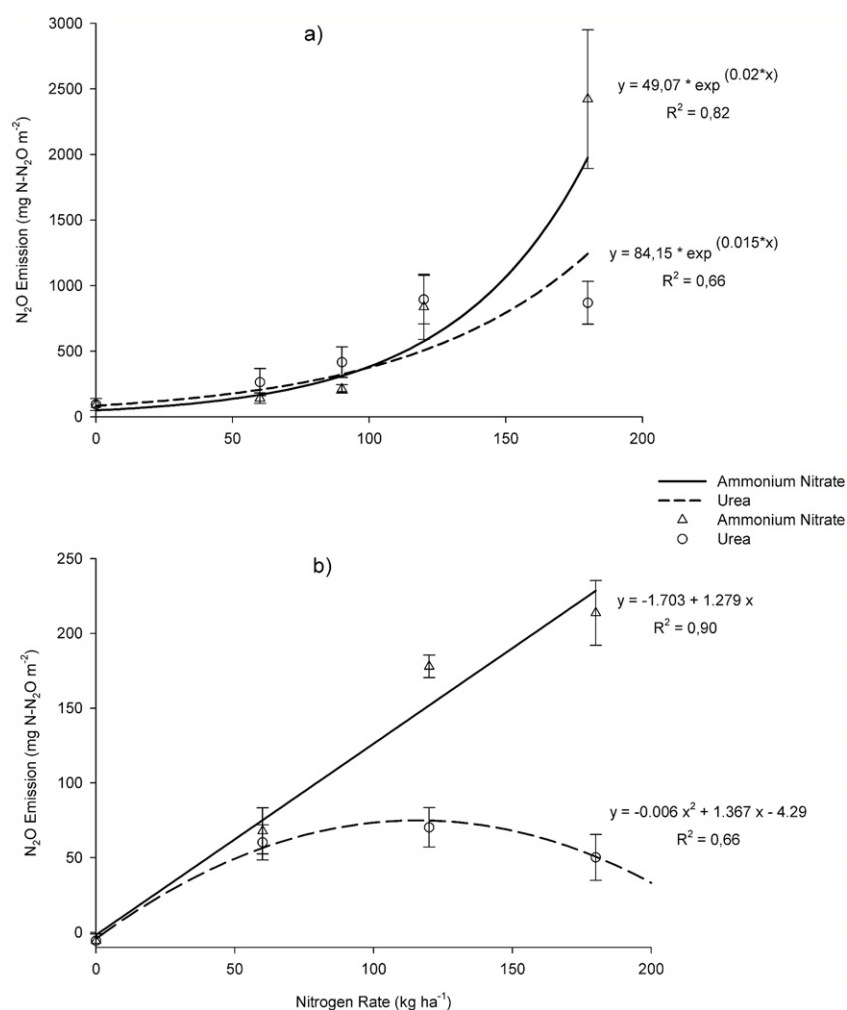
Figure 3. N_2O emissions related to N doses applied to the soil as ammonium nitrate and urea in sugarcane farmland areas in Piracicaba (50 day experiment) (a) and Goianésia (16 day experiment) (b). Vertical bars represent standard mean error ($n = 4$).

Table 2. Cumulated N_2O emission and proportion of added N lost as N_2O associated with different ammonium nitrate and urea doses applied to the sugarcane farmland areas in Piracicaba and Goianésia. (Values represent mean $\pm$ mean standard error ($n = 4$).)

N Rate (kg ha^{-1})	Emission (mg N–N_2O m^{-2})		Emission (kg N–N_2O ha^{-1})		Emission treatment—control[a]		Proportion of N emitted as N_2O[a]	
	Ammonium nitrate	Urea	Ammonium nitrate	Urea	Ammonium nitrate	Urea	Ammonium nitrate	Urea
				Piracicaba				
60	141.37 ± 39.55	263.75 ± 104.47	1.41 ± 0.39	2.64 ± 1.04	0.48 ± 0.60	1.71 ± 1.14	0.80 ± 1.00	2.85 ± 1.90
90	213.22 ± 32.16	416.03 ± 115.85	2.13 ± 0.32	4.16 ± 1.16	1.20 ± 0.56	3.23 ± 1.25	1.33 ± 0.62	3.59 ± 1.39
120	837.82 ± 248.95	893.80 ± 185.45	8.38 ± 2.49	8.94 ± 1.85	7.45 ± 2.53	8.01 ± 1.91	6.21 ± 2.11	6.67 ± 1.59
180	2421.84 ± 528.16	868.77 ± 163.19	24.22 ± 5.28	8.69 ± 1.63	23.29 ± 5.30	7.76 ± 1.69	12.95 ± 2.95	4.31 ± 0.94
Control	93.21 ± 45.84		0.93 ± 0.46					
				Goianésia				
60	67.85 ± 15.42	60.15 ± 11.76	0.68 ± 0.15	0.60 ± 0.12	0.73 ± 0.16	0.66 ± 0.13	1.22 ± 0.27	1.10 ± 0.22
120	177.88 ± 7.53	70.25 ± 13.24	1.78 ± 0.08	0.70 ± 0.13	1.83 ± 0.09	0.76 ± 0.14	1.53 ± 0.07	0.63 ± 0.12
180	213.68 ± 21.68	50.19 ± 15.33	2.14 ± 0.22	0.50 ± 0.15	2.19 ± 0.22	0.56 ± 0.16	1.22 ± 0.12	0.31 ± 0.09
Control	-5.56 ± 4.53		-0.06 ± 0.05					

[a] Mean standard errors calculated considering error propagation.

Ammonium nitrate induced emissions could be observed on the first day after fertilizer application. N_2O fluxes from AN60 were similar to control on all the evaluated days

(Tukey, $\alpha < 0.05$). AN120 and AN180 had greater fluxes than AN60 in the first 8 days of experiment and then they were similar. The highest flux in the ammonium nitrate

treatments was observed in AN120 on the second day after fertilizer application (1296.89 ± 285.49 μg N–N$_2$O m^{-2} h^{-1}). However, AN180 and AN120 presented similar fluxes until the 11th day and AN180 fluxes were higher on days 15 and 16.

The highest flux for the urea treatments occurred for U120 on the 8th day (362.34 ± 41.22 μg N–N$_2$O m^{-2} h^{-1}). N$_2$O fluxes induced by urea application could be seen just after the 8th day, when U120 presented flux similar to that of U180 and U60 but higher than control plots.

Ammonium nitrate induced a pulse in N$_2$O fluxes more rapidly than urea, as differences between control plots and treatments could be seen on the 1st day after the N application on soil for ammonium nitrate and just on the 8th day for urea. Moreover, ammonium nitrate fluxes at site 2 began to decrease between the 3rd and 10th days, while for urea they increased until the 10th day (figure 2).

At site 2, increasing ammonium nitrate input by 1 kg ha^{-1} enhanced N$_2$O cumulated emissions by almost 1.3 mg N–N$_2$O m^{-2} (0.013 kg N–N$_2$O ha^{-1}) (figure 3(b)). Urea emissions were adjusted to a second degree polynomial (quadratic equation; $p < 0.05$), the maximum emission corresponding to 73.6 mg N–N$_2$O m^{-2} and occurring when 113.9 kg ha^{-1} of N of urea was applied.

The proportion of added N that was emitted to the atmosphere as N$_2$O was similar in all ammonium nitrate treatments (table 2). When the N source was urea, the proportion of lost N was higher when low doses were used. This was a consequence of accumulated N$_2$O emission behavior, with has a point of maximum emission from which N$_2$O emissions decrease with increasing N dose.

4. Discussion

Generally, the highest N$_2$O fluxes occurred in the first or second week after application of N fertilizers to the soil (Liu *et al* 2005, 2006, Schils *et al* 2008). According to Zhang and Han (2008), the effect of fertilization disappears approximately two months after the application of N. In site 1, N$_2$O fluxes for urea and ammonium nitrate started to decrease approximately 20 days after the fertilizer application. Probably the presence of sugarcane stubble on the soil surface contributes to maintain the soil moisture, enabling anaerobic conditions in some microsites and, consequently, allowing elevated N$_2$O emissions for more than one week. Additionally, precipitation events occurring at site 1 may have extended the fertilizer N-induced emissions. At site 2, the influence of rainfall events was less important, probably because the evaluation period was restricted to 16 days after fertilizer application. Based on results from the experiment carried out at site 1, we considered that, although limited in time duration, the evaluation period in the Goiánesia experiment was adequate to generate a comprehensive behavior of N$_2$O emissions for the two N tested sources.

In both experiments, N$_2$O fluxes enhanced by ammonium nitrate were observed at the beginning of the experiment, while for urea this took several days to occur (figures 1

and 2). At site 1, urea induced emissions occurred on the fourth day after the fertilizer application (figure 1(b)). At site 2, emissions of control, U60, U120 and U180 were similar during the first three days of evaluation (figure 2(b)). This delay time might be attributed to a reduced availability of N at the beginning of the experimental periods, since the N in urea has to be hydrolyzed before being available for nitrification and denitrification processes.

Carvalho *et al* (2006) evaluated N$_2$O emissions in the first five days after urea application (60 kg ha^{-1} of N) in a corn field in the Brazilian Cerrado, and they found N$_2$O concentrations below the chromatography detection level. According to them, urea does not affect N$_2$O emissions. However, according to figures 1 and 2, the restricted evaluation period after the fertilizer application considered by these authors and the lower urea dose tested may not have been sufficient to observe urea effects on soil N$_2$O fluxes. In figure 2(b), U60 presented fluxes similar to control during the whole evaluation period.

The exponential model adjusted to N$_2$O emissions from site 1 (figure 3(a)) was also used by Ma *et al* (2010). Urea cumulated emissions in Piracicaba suggested there was stabilization in N$_2$O emissions due to the N dose of this fertilizer. In corn crop areas in Canada, Ma *et al* (2010) did not notice the occurrence of a threshold in urea induced N$_2$O emissions. In figure 3(a) this stabilization occurs between 120 and 180 kg N ha^{-1}, but it is not possible to identify exactly when it happens. Doing the same experiment in another area (site 2) has permitted us to better understand the behavior of urea induced N$_2$O emissions. Although the magnitude of emissions in Goiánesia was lower than those in Piracicaba, we can affirm that the urea stimulates N$_2$O emissions, but emissions are reduced when elevated rates are used. Nitrogen addition has a negative effect on microbial biomass (Treseder 2008) and on soil microbial respiration (Ramirez *et al* 2010), and hence it can have a negative effect on soil N$_2$O fluxes that are mediated by microorganisms. Although we did not evaluate the microorganism activity or biomass, our results suggest that rates of urea application greater than 114 kg N ha^{-1} would potentially cause harmful effects under soil transforming N microorganisms.

While at site 1 ammonium nitrate emissions were adjusted to an exponential equation, at site 2 a better determination coefficient was obtained in the linear equation. This difference may be attributed to the reduced evaluation time (50 days at site 1 and 16 days at site 2) and also to the fewer available data (treatments AN90 and U90 were not used in the second experiment).

According to equations in figure 3, at site 1 (Piracicaba) urea and ammonium nitrate had the same N$_2$O emissions at a dose of approximately 107.9 kg ha^{-1} of N and then emissions were higher for ammonium nitrate (figure 3(a)). In Piracicaba differences between urea and ammonium nitrate occurred only for the 180 kg ha^{-1} dose, while at site 2 (Goiánesia) differences between N sources occurred for 120 and 180 kg N ha^{-1}. Despite this, emissions had similar behaviors in the two experiments. In Canada, 100 kg N ha^{-1} of urea, ammonium sulfate and calcium nitrate resulted in similar N$_2$O emissions (Bergstrom *et al* 2001).

N$_2$O emissions presented a high standard mean error (table 2). Buchkina *et al* (2010) also reported high variability in N$_2$O accumulated fluxes in areas receiving applications of different nitrogen fertilizers. Jones *et al* (2011) reported a coefficient of variation of 139% for N$_2$O emissions after fertilization events. A high variability in N$_2$O emissions occurs independently from the N$_2$O origin being nitrification or denitrification. The heterogeneity in N$_2$O emissions may be explained by a variation in nitrification potential, which, in turn, is associated with differences in distribution of nitrifying microorganism populations (Davidson *et al* 1996). These considerations may also be applied to denitrifying communities.

In this work N$_2$O fluxes were measured using static chambers. Rochette and Eriksen-Hamel (2008) emphasized that several precautions should be taken into account to avoid biased flux estimates when chambers are used, which is a major limitation of the method. Micrometeorological techniques can also be used to estimate N$_2$O fluxes with high time and spatial resolution (the area evaluated can range from 0.01 to 1 km^2) (Jones *et al* 2011). However these techniques require high expertise and uniform source surface and are expensive (Jones *et al* 2011). Moreover, comparisons between static chamber and micrometeorological techniques for measurements of N$_2$O fluxes have shown no significant differences between these two approaches (Jones *et al* 2011, Denmead *et al* 2010, Christensen *et al* 1996). Despite the static chamber disadvantages, such as high labor requirement, large number of replicates to overcome spatial variability, the possibility of the chamber to alter gases fluxes, and other bias in fluxes, the method is useful to establish the effects of variables on N$_2$O fluxes within a given study (Rochette and Eriksen-Hamel 2008, Smith *et al* 1995). Our results could not be so reliable as to be directly used in national greenhouse gas inventories, but they may be useful for them, because there are no data available for sugarcane emissions induced by N fertilizers in Brazil, as stated by Lisboa *et al* (2011). Additionally, our static chamber measurements allowed us to understand the pattern of N$_2$O emissions according to N sources and doses in sugarcane fields, achieving the objectives of this research.

The influence of rainfall events on N$_2$O emissions in all treatments suggested that these events increase soil moisture and microbial processes involved in N$_2$O production and emission. N$_2$O is produced by nitrifying microorganisms under aerobic or semi-anaerobic conditions (Stevens *et al* 1997) and by denitrifying microorganisms under anaerobic conditions (Bremner 1997, Khalil *et al* 2004). Buchkina *et al* (2010), Metay *et al* (2007) and Smith and Owens (2010) have associated N$_2$O emission with application of fertilizers under humid weather conditions and to rain events. Therefore, the rain one day after the application of fertilizers probably contributed to higher N$_2$O fluxes at site 1. In addition, this may have favored urea transport to the inner soil, probably reducing the N loss through volatilization, allowing a greater amount of N available to nitrification and denitrification processes Havlin *et al* (2005).

In Southern Brazil, Jantalia *et al* (2008) observed no relationships between N$_2$O emissions and the number of soil pores filled with water. Nevertheless, Allen *et al* (2010) also verified significant correlations between soil N$_2$O emissions and water field pore space in soil and Gomes *et al* (2009) observed the highest N$_2$O fluxes were connected to rain events in Brazil's South Region, confirming our results. Similar results were obtained in sugarcane fields in Australia (Weier 1999) and in cornfields in Canada (Ma *et al* 2010).

In GHG inventories, the amount of N fertilizer lost as N$_2$O is estimated through an emission factor proposed by the IPCC (International Panel on Climate Change). This emission factor considers that N$_2$O emissions are equivalent to 1% of the amount of N applied as fertilizer. Only a few studies are available with direct N$_2$O emissions in sugarcane fields and most of them were done in Australia. Nevertheless, Lisboa *et al* (2011) reported an emission factor of 3.87 ± 1.16% for N fertilizer induced emissions from a sugarcane field in Brazil. In site 1, the proportion of N lost as N$_2$O ranged from 0.80 to 12.95% (table 2). The proportion of N emitted as N$_2$O for AN180 is almost twice that for AN120. Ma *et al* (2010) observed similar emission factors for 30 and 90 kg ha^{-1} of urea, whereas they practically double for the 150 kg ha^{-1} dose. Increasing the N application rate on maize land had increased the N$_2$O emission and also the emission factor, independently of the N source (calcium ammonium nitrate, injected cattle slurry or injected pig slurry) (Velthof and Mosquera 2011). In our second experiment (Goianésia), N$_2$O emissions varied from 1.22 to 1.53% of added N for ammonium nitrate treatments and from 0.31 to 1.10% for urea. Other studies conducted in Southern Brazil found N$_2$O emission factors below the value proposed by IPCC (Jantalia *et al* 2008, Gomes *et al* 2009).

The emission factor proposed by IPCC is also associated with a wide range (0.3%–3%). This is common, as related by Li *et al* (2001) and Clayton *et al* (1997), who presented N$_2$O emission factors ranging from 0.25 to 4% and from 0.2 to 2.2%, respectively. Mosier *et al* (2004), considering 35 studies conducted in farming systems in temperate climate, presented emission factors ranging from 0.1 to 7.3%. In Australia Denmead *et al* (2010) observed emission factors of 2.8% in a sandy loam soil and of 21% in a clay loam soil (acid sulfate soil) both cultivated with sugarcane. It is necessary to consider that the behavior of different fertilizers also depends on soil type and crop (Clayton *et al* 1997), soil structure, soil water content and temperature (Smith *et al* 1995), and these variable factors are not considered in the emission factor proposed by IPCC.

Although the proportions of N emitted as N$_2$O were different in Piracicaba and Goianésia, these values showed the same behavior of cumulated emissions during the evaluation periods. The proportion of N emitted as N$_2$O in Goianésia is similar to emission factors proposed by IPCC. However, to establish the present carbon footprint of Brazilian ethanol, it is necessary to monitor all of the ethanol production stages, from planting the sugarcane until the disposal of residues produced during the industrial process. Despite the wide data range and the differences in the magnitude of N$_2$O emissions, the present study is the first initiative to contribute to evaluating N$_2$O emissions derived from nitrogen fertilizer application in

soils in sugarcane farming in Brazil. Moreover, our results elucidated the behavior of N$_2$O emissions promoted by different N sources frequently used in Brazilian sugarcane fields.

5. Conclusions

Adding ammonium nitrate or urea as N source in sugarcane fields induced a pulse in N$_2$O emissions. However, ammonium nitrate promotes more intense and faster N$_2$O emissions than urea. Ammonium nitrate induced emissions can be noted the day after the fertilizer application on soil, while urea induced emissions took some days to occur.

Our results confirm that N$_2$O induced emissions by N fertilizers are dependent on the N rate and the responses are different according to the N source. Emissions induced by ammonium nitrate increase as the N dose applied to soil increases. However, urea emissions present a maximum point that occurs at an approximate dose of 114 kg N ha^{-1}.

The wide range in proportion of N emitted as N$_2$O observed here confirmed the difficulty of using a pre-established value of emission factor. Moreover, our results demonstrated that not only the rate of N fertilizer applied to soil influenced the proportion of N lost as N$_2$O.

Acknowledgments

References

Akiyama H, Tsuruta H and Watanabe T 2000 N$_2$O and NO emissions from soils after the application of different chemical fertilizers *Chemosphere—Glob. Change Sci.* **2** 313–20

Allen D E, Kingston G, Rennenberg H, Dalal R C and Schmidt S 2010 Effect of nitrogen fertilizer management and waterlogging on nitrous oxide emission from subtropical sugarcane soils *Agric. Ecosyst. Environ.* **136** 209–17

Bergstrom D W, Tenuta M and Beauchamp E G 2001 Nitrous oxide production and flux from soil under sod following application of different nitrogen fertilizers *Commun. Soil Sci. Plant Anal.* **32** 553–70

Bockman O C and Olfs H W 1998 Fertilizers, agronomy and N$_2$O *Nutr. Cycl. Agroecosyst.* **52** 165–70

Bremner J M 1997 Sources of nitrous oxide in soils *Nutr. Cycl. Agroecosyst.* **49** 7–16

Brentrup F, Küsters J, Lammel J and Kuhlmann H 2000 Methods to estimate on-field nitrogen emissions from crop production as an input to LCA studies in the agricultural sector *Int. J. Life Cycle Assess.* **5** 349–57

Buchkina N P, Balashov E V, Rizhiya E Y and Smith K A 2010 Nitrous oxide emissions from a light-textured arable soil of North-Western Russia: effects of crops, fertilizers, manures and climate parameters *Nutr. Cycl. Agroecosyst.* **87** 429–42

Carvalho A M, Bustamante M M C, Kozovits A R, Miranda L N, Vivaldi L J and Sousa D M 2006 Emissão de óxidos de nitrogênio associada à aplicação de uréia sob plantio convencional e direto *Pesqu. Agropecu. Bras.* **41** 679–85

Cerri C C, Maia S M F, Galdos M V, Cerri C E P, Feigl B J and Bernoux M 2009 Brazilian greenhouse gas emissions: the importance of agriculture and livestock *Sci. Agric.* **66** 831–43

Chen S T, Huang Y and Zou J W 2008 Relationship between nitrous oxide emission and winter wheat production *Biol. Fertil. Soils* **44** 985–9

Christensen S *et al* 1996 Nitrous oxide emissions from an agricultural field: comparison between measurements by flux chamber and micrometerological techniques *Atmos. Environ.* **30** 4183–90

Clayton H, McTaggart I P, Parker J, Swan L and Smith K A 1997 Nitrous oxide emissions from fertilised grassland: a 2-year study of the effects of N fertiliser form and environmental conditions *Biol. Fertil. Soils* **25** 252–60

Companhia Nacional De Abastecimento (CONAB—Ministério da Agricultura, Pecuária e Abastecimento) 2008 *Perfil do Setor de Açúcar e Álcool no Brasil* (Brasília: CONAB) (available at www.conab.gov.br/conabweb/download/safra/perfil.pdf, accessed 19 October 2012)

Companhia Nacional De Abastecimento (CONAB—Ministério da Agricultura, Pecuária e Abastecimento) 2012 *Acompanhamento da Safra Brasileira: Cana-de-Açúcar, Safra 2012/2013, Primeiro Levantamento, Abril/2012* (Brasília: CONAB) (available at www.conab.gov.br/OlalaCMS/uploads/arquivos/12_04_10_09_19_04_boletim_de_cana.pdf, accessed 16 July 2012)

Conrad R 1996 Soil microorganisms as controllers of atmospheric trace gases (H$_2$, CO, CH$_4$, OCS, N$_2$O and NO) *Microbiol. Rev.* **60** 609–40

Davidson E A, Matson P A and Brooks P D 1996 Nitrous oxide emission controls and inorganic nitrogen dynamics in fertilized tropical agricultural soils *Soil Sci. Soc. Am. J.* **60** 1145–52

Denmead O T, Macdonald B C T, Bryant G, Naylor T, Wilson S, Griffith D W T, Wang W J, Salter B, White I and Moody P W 2010 Emissions of methane and nitrous oxide from Australian sugarcane soils *Agric. For. Meteorol.* **150** 748–56

Figueiredo E B and La Scala N Jr 2011 Greenhouse gas balance due to the conversion of sugarcane areas from burned to green harvest in Brazil *Agric. Ecosyst. Environ.* **141** 77–85

Firestone M K and Davidson E A 1989 Microbial basis of NO and N$_2$O production and consumption in soils *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere* ed M O Andrae and D S Schimel (New York: Wiley) pp 7–21

Forster P *et al* 2007 Changes in atmospheric constituents and in radiative forcing *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* ed S Solomon, D Qin, M Manning, Z Chen, M Marquis, K B Averyt, M Tignor and H L Miller (New York: Cambridge University Press) pp 129–234

Gomes J, Bayer C, Costa F D, Piccolo M D, Zanatta J A, Vieira F C B and Six J 2009 Soil nitrous oxide emissions in long-term cover crops-based rotations under subtropical climate *Soil Tillage Res.* **106** 36–44

Havlin J L, Beaton J D, Tisdale S L and Nelson W L 2005 *Soil Fertility and Fertilizers: An Introduction to Nutrient Management* (Upper Saddle River, NJ: Pearson Prentice Hall)

Heffer P 2009 *Assessment of Fertilizer Use by Crop at the Global Level 2006/07–2007/08* (Paris: International Fertilizer Industry Association—IFA) (available at http://sustainablecropnutrition.net/ifacontent/download/7204/113684/version/8/file/AgCom.09.28+-+FUBC+assessment+at+the+global+level+(2006+%2B+2007).pdf, accessed 2 August 2010)

IPCC (Intergovernmental Panel on Climate Change) 2007 *Climate Change: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* ed Core Writing Team, R K Pachauri and A Reisinger (Geneva: IPCC)

Jantalia C P, Dos Santos H P, Urquiaga S, Boddey R M and Alves B J R 2008 Fluxes of nitrous oxide from soil under different crop rotations and tillage systems in the South of Brazil *Nutr. Cycl. Agroecosyst.* **82** 161–73

Jones S K, Famulari D, Di Marco C F, Nemitz E, Skiba U M, Rees R M and Sutton M A 2011 Nitrous oxide emissions from managed grassland: a comparison of eddy covariance and static chamber measurements *Atmos. Meas. Tech. Discuss.* **4** 1079–112

Khalil K, Mary B and Renault P 2004 Nitrous oxide production by nitrification and denitrification in soil aggregates as affected by O_2 concentration *Soil Biol. Biochem.* **36** 687–99

Li C S, Zhuang Y H, Cao M Q, Crill P, Dai Z H, Frolking S, Moore B, Salas W, Song W Z and Wang X K 2001 Comparing a process-based agro-ecosystem model to the IPCC methodology for developing a national inventory of N_2O emissions from arable lands in China *Nutr. Cycl. Agroecosyst.* **60** 159–75

Lisboa C C, Butterbach-Bahl K, Mauder M and Kiese R 2011 Bioethanol production from sugarcane and emissions of greenhouse gases—known and unknowns *GCB Bioenergy* **3** 277–92

Liu X J, Mosier A R, Halvorson A D and Zhang F S 2005 Tillage and nitrogen application effects on nitrous and nitric oxide emissions from irrigated corn fields *Plant Soil* **276** 235–49

Liu X J, Mosier A R, Halvorson A D and Zhang F S 2006 The impact of nitrogen placement and tillage on NO, N_2O, CH_4 and CO_2 fluxes from a clay loam soil *Plant Soil* **280** 177–88

Ma B L, Wu T Y, Tremblay N, Deen W, Morrison M J, McLaughlin N B, Gregorich E G and Stewart G 2010 Nitrous oxide fluxes from corn fields: on-farm assessment of the amount and timing of nitrogen fertilizer *Glob. Change Biol.* **16** 156–70

Macedo I C, Seabra J E A and Silva J 2008 Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: the 2005/2006 averages and a prediction for 2020 *Biomass Bioenergy* **32** 582–95

Metay A, Oliver R, Scopel E, Douzet J M, Alves Moreira J A, Maraux F, Feigl B J and Feller C 2007 N_2O and CH_4 emissions from soils under conventional and no-till management practices in Goiania (Cerrados, Brazil) *Geoderma* **141** 78–88

Mosier A R 2001 Exchange of gaseous nitrogen compounds between agricultural systems and the atmosphere *Plant Soil* **228** 17–27

Mosier A, Wassmann R, Verchot L, King J and Palm C 2004 Methane and nitrogen oxide fluxes in tropical agricultural soils: sources, sinks and mechanisms *Environ. Dev. Sustainabil.* **6** 11–49

Passianoto C C, Ahrens T, Feigl B J, Steudler P A, Do Carmo J B and Melillo J M 2003 Emissions of CO_2, N_2O, and NO in conventional and no-till management practices in Rondonia, Brazil *Biol. Fertil. Soils* **38** 200–8

Raij B and Quaggio J A 1983 *Boletim Técnico 81: Métodos de análise de solo para fins de fertilidade* (Campinas: Instituto Agronômico) p 31

Ramirez K S, Craine J M and Fierer N 2010 Nitrogen fertilization inhibits soil microbial respiration regardless of the form of nitrogen applied *Soil Biol. Biochem.* **42** 2336–8

Rochette P and Eriksen-Hamel 2008 Chamber measurements of soil nitrous oxide flux: are absolute values reliable? *Soil Sci. Soc. Am. J.* **72** 331–42

Schils R L M, Van Groenigen J W, Velthof G L and Kuikman P J 2008 Nitrous oxide emissions from multiple combined applications of fertiliser and cattle slurry to grassland *Plant Soil* **310** 89–101

Sit V and Poulin-Costello M 1994 Catalogue of curves for curve fitting *Biometrics Informations Handbook* vol 4 (Victoria: B C Ministry of Forests)

Smith K A, Clayton H, Mctaggart I P, Thomson P E, Arah J R M and Scott A 1995 The measurement of nitrous-oxide emissions from soil by using chambers *Phil. Trans. R. Soc.* A **351** 327–37

Smith D R and Owens P R 2010 Impact of time to first rainfall event on greenhouse gas emissions following manure applications *Commun. Soil Sci. Plant Anal.* **41** 1604–14

Steudler P A, Melillo J M, Feigl B J, Neill C, Piccolo M C and Cerri C C 1996 Consequence of forest-to-pasture conversion on CH_4 fluxes in the Brazilian Amazon Basin *J. Geophys. Res.—Atmos.* **101** 18547–54

Stevens R J and Laughlin R J 1998 Measurement of nitrous oxide and di-nitrogen emissions from agricultural soils *Nutr. Cycl. Agroecosyst.* **52** 131–9

Stevens R J, Laughlin R J, Burns L C, Arah J R M and Hood R C 1997 Measuring the contributions of nitrification and denitrification to the flux of nitrous oxide from soil *Soil Biol. Biochem.* **29** 139–51

Treseder K K 2008 Nitrogen additions and microbial biomass: a meta-analysis of ecosystem studies *Ecol. Lett.* **11** 1111–20

Velthof G L and Mosquera J 2011 The impact of slurry application technique on nitrous oxide emission from agricultural soils *Agric. Ecosyst. Environ.* **140** 298–308

Weier K L 1999 N_2O and CH_4 emission and CH_4 consumption in a sugarcane soil after variation in nitrogen and water application *Soil Biol. Biochem.* **31** 1931–41

Zhang J and Han X 2008 N_2O emission from the semi-arid ecosystem under mineral fertilizer (urea and superphosphate) and increased precipitation in northern China *Atmos. Environ.* **42** 291–302