

Nota

N₂O EMISSIONS FROM A CULTIVATED MOLLISOL: OPTIMAL TIME OF DAY FOR SAMPLING AND THE ROLE OF SOIL TEMPERATURE⁽¹⁾

Vanina Rosa Noemi Cosentino⁽²⁾, Patricia Lilia Fernandez⁽³⁾, Santiago Andrés Figueiro Aureggi⁽⁴⁾ & Miguel Angel Taboada⁽⁵⁾

SUMMARY

The correct use of closed field chambers to determine N₂O emissions requires defining the time of day that best represents the daily mean N₂O flux. A short-term field experiment was carried out on a Mollisol soil, on which annual crops were grown under no-till management in the Pampa Ondulada of Argentina. The N₂O emission rates were measured every 3 h for three consecutive days. Fluxes ranged from 62.58 to 145.99 µg N-N₂O m⁻² h⁻¹ (average of five field chambers) and were negatively related ($R^2 = 0.34$, $p < 0.01$) to topsoil temperature (14 - 20 °C). N₂O emission rates measured between 9:00 and 12:00 am presented a high relationship to daily mean N₂O flux ($R^2 = 0.87$, $p < 0.01$), showing that, in the study region, sampling in the mornings is preferable for GHG.

Index terms: soil N₂O fluxes, climate change, GHG sampling.

RESUMO: EMISSÕES DE N₂O DE UM CHERNOSSOLO CULTIVADO: O TEMPO IDEAL DO DIA PARA AMOSTRAGEM E PAPEL DA TEMPERATURA DO SOLO

O uso adequado de câmaras estáticas para determinar as emissões de N₂O no campo requer a definição da hora do dia que melhor representa a taxa de emissão média diária. Um experimento de campo de curta duração foi realizado em um Chernossolo do Pampa Ondulado

⁽¹⁾ This paper was part of a thesis. Received for publication in October 14, 2011 and approved in September, 25, 2012.

⁽²⁾ Doctorate student of the Post Graduation Program of Soil Science, Facultad de Agronomía de la Universidad de Buenos Aires. Avenida San Martín 4453, C1417DSE Buenos Aires, Argentina. E-mail: cvanina@agro.uba.ar

⁽³⁾ Teacher assistant of Facultad de Agronomía de la Universidad de Buenos Aires. Avenida San Martín, 4453. C1417DSE Buenos Aires, Argentina. E-mail: fpl@agro.uba.ar

⁽⁴⁾ Doctorate student of the Post Graduation Program of Soil Science, Facultad de Agronomía de la Universidad de Buenos Aires. E-mail: figueiro@agro.uba.ar

⁽⁵⁾ Professor of Facultad de Agronomía de la Universidad de Buenos Aires and director of the Soils Institute CIRN, INTA Castelar. E-mail: mtaboada@agro.uba.ar

da Argentina, cultivado com soja em sistema plantio direto. As taxas de emissão de N₂O foram medidas a cada 3 h durante três dias consecutivos. As taxas de emissão de N₂O variaram entre 62,58 e 145,99 mg m⁻² h⁻¹ de N-N₂O (média de cinco câmaras de campo) e foram negativamente relacionadas (R² = 0,34; p < 0,01) com a temperatura do solo (14 - 20 °C). As taxas de emissão de N₂O medidas entre 9 e 12 h foram positivamente relacionadas com a média diária (R² = 0,87; p < 0,01), mostrando que na região de estudo a melhor época para amostragem de GEE é pela manhã.

Termos de indexação: fluxo de N₂O no solo, mudança climática, amostragem de GEE.

INTRODUCTION

Nitrous oxide (N₂O) is the main greenhouse gas emitted by agricultural soils, with a global warming potential 310 times greater than carbon dioxide (Pérez-Ramírez, 2007). Its concentration in the atmosphere increased at a rate of 0.25 % per year between 1980 and 1998 (Houghton et al., 2001) and, according to Snyder et al. (2007), its concentration reached 319 ppb in 2005.

Closed chambers are widely used for measuring soil greenhouse gas fluxes. The most common of these procedures involves manual sampling of headspace gas from the chamber using syringes (Chen et al., 2000; Ball et al., 2002; Jantalia et al., 2008) or more advanced systems such as vacuum pumps or automated flux monitoring systems (Akiyama et al., 2000; Dobbie & Smith, 2001).

The method used to measure field N₂O emissions is relatively recent, and it has no universal standard or internationally accepted guidelines (Hutchinson & Livingston, 2002). The current global estimate of agricultural N₂O emissions has an uncertainty ranging from -60 to 170 % of the mean estimate (Venterea et al., 2009). Rochette & Eriksen-Hamel (2008) concluded that 50 - 60 % of the N₂O data measured using field chambers is unreliable, usually due to the use of inappropriate methods. This makes the minimization of experimental errors during field sampling a key concern to improve confidence levels of N₂O measurements (Schindlbacher et al., 2004; Venterea et al., 2009).

The high spatial variability of N₂O fluxes, related to differences in environmental variables (McClain et al., 2003) requires a high number of chamber replicates to evaluate N₂O fluxes at a reasonable precision, but compromises have to be made in order to limit the number of samples to manageable quantities. Soil N₂O daily emission calculations are usually based on the extrapolation of a single daily measurement during a short period to represent the mean flux of a 24 h period. If the time of day that best represents the mean daily N₂O flux is known, more accurate results can be expected.

In order to identify this time period, a short-term field experiment was conducted throughout three days with cultivated soils of the Argentine Pampas under no-till management. As soil temperature is a recognized key factor determining daily rates of N₂O

emissions (Denmead et al., 1979; Blackmer et al., 1982; Akiyama et al., 2000; di Marco et al., 2004; Jantalia et al., 2008) this variable was also considered in our experiment.

MATERIALS AND METHODS

The study was carried out on an agricultural field in the Province of Buenos Aires [34° 57' 29" S, 60° 13' 11" W], on a loamy Typic Argiudol (clay 190 g kg⁻¹, silt 400 g kg⁻¹) from the O'Higgins Series (INTA, 2010). Soil organic matter was determined by wet combustion (Walkley & Black, 1934) was 35.2 g kg⁻¹ and pH in water of the A horizon was 5.7. The field had been under no-till management for the previous 15 years. The crop sequence in the three years before our measurements was maize, wheat/soybean (double cropping) and full-season soybean. Samples were taken in autumn 2010 before the harvest of the full-season soybean.

After a rainfall of 30 mm, five closed chambers (surface = 1.333 cm², height = 12.5 cm) randomly spread across the soybean field, were inserted into the soil to a depth of 0.05 m. This size of field chambers was described as optimal by other authors (Rochette & Eriksen-Hamel, 2008) and was already used by Jantalia et al. (2008) and Alves et al. (2012). After closing the chambers, gas samples were taken after 0, 20 and 40 min, with a vacuum pump, and injected into previously evacuated 25 mL vials with a rubber stopper fixed to the vial with an aluminum flange. Once sampling was finished, the top of the chamber was removed. This process was repeated every 3 h for three consecutive days beginning at 9:00 am on the first day. The N₂O collected was always measured within seven days after sampling with a GC 6890 Agilent Technologies Network gas chromatograph. The daily average soil N₂O flux was calculated as the mean of the eight fluxes measured each day. Samples of the five chambers collected during three days provided 15 estimates of N₂O fluxes per sampling time.

N₂O flux (f) was calculated as:

$$f = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \times \frac{m}{V_m} \quad (1)$$

where $\Delta C/\Delta t$ is the change of N_2O concentration in the chamber during the incubation time Δt , V is the volume of the chamber (16.7 dm^3), A is the area of soil covered by the chamber (1.333 cm^2), V_m is the molar volume of N_2O and m is its molecular weight. Gas fluxes were calculated as the increase in concentration during the incubation period and expressed by the arithmetic mean and its standard deviation.

Soil temperature was measured with a thermometer inserted in the soil to a depth of 0.10 m and air temperature with a shaded thermometer at the soil surface. The concentration of $N-NO_3^-$ (0-0.20 m) was determined by colorimetric spectrophotometry (Markus et al., 1985). Soil bulk density (BD) was determined in 100-cm^3 cylinders (diameter 0.05 m) and gravimetric water content (GWC) by oven-drying at 105°C during 48 h. The volumetric water content (VWC) and total porosity (TP) were calculated using BD and GWC, assuming a particle density (D_p) of 2.65 Mg m^{-3} (equations 2 and 3):

$$TP = 1 - (BD / D_p) \quad (2)$$

$$VWC = GWC * BD \quad (3)$$

The percentage of water-filled pore space (%WFPS) was calculated with the TP and VWC values (Equation 4):

$$WFPS = TP - VWC \quad (4)$$

In order to determine the time of day that best represents the mean daily N_2O emission rate, regression analysis (InfoStat, 2002) was used to relate N_2O data with soil and air temperature.

RESULTS

Mean air temperature was 14.5°C , ranging from a minimum of 4.0°C to a maximum of 31.3°C , whereas the mean soil temperature was 16.8°C , with a minimum of 14.6°C and a maximum of 19.2°C . Percentage of water filled pore space (%WFPS) and NO_3^- content were kept constant during the three days of measurements, averaging $0.89 \text{ m}^3 \text{ m}^{-3}$ (89 %) and 73.4 mg kg^{-1} , respectively. The daily dynamics of soil and air temperature were similar in the three days of the study.

The soil temperature was slightly lower than 15°C on one occasion only. This temperature was the minimum value above which N_2O fluxes were observed (Keeney et al., 1979). However, this low temperature did not limit N_2O flux under the study conditions. The times of day when the mean daily N_2O emissions were represented best were at 9:00 and 12:00 am. The coefficients of determination obtained by the regression analysis between mean daily and hourly N_2O emission rates were highly significant in both cases (Table 1 and Figure 1). Other authors also found morning hours more suitable for gas sampling (Blackmer et al., 1982; Jantalia et al., 2008).

Table 1. Relation between mean daily and mean hourly N_2O emission rates

Sampling time	a	b	R ²
hour of day			
9:00	1.12***	-13.78	0.87***
12:00	1.13***	-23.73*	0.88***
15:00	0.48**	38.57**	0.35**
18:00	0.43**	36.50**	0.33**
21:00	0.82**	6.30	0.37**
24:00	1.31***	-28.24	0.75***
3:00	1.84***	-42.22	0.75***
6:00	0.86*	26.61	0.23*

$y = ax + b$. *, **, *** indicate significant adjustment of regression slopes and intercepts at $p = 0.1, 0.05$ and 0.01 , respectively.

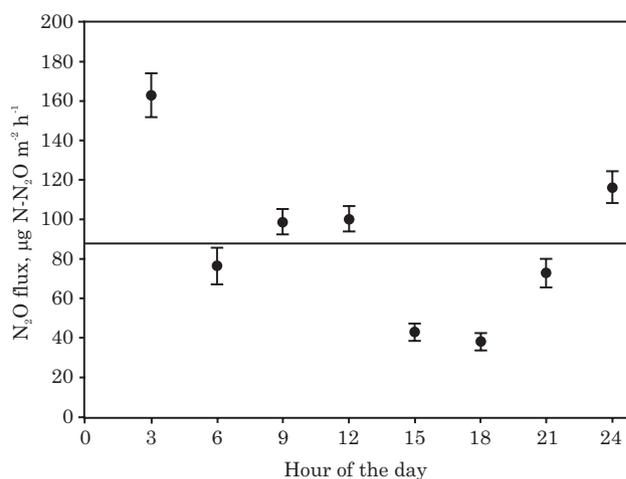


Figure 1. Dynamics of N_2O emission rates during the day. Bars indicate standard error of the means. The horizontal line corresponds to the daily average ($88.6 \mu\text{g N-N}_2\text{O m}^{-2} \text{ h}^{-1}$).

Interestingly, it was found that the dynamics of other soil N emissions (e.g. NO) were determined mainly by the season (Xunhua et al., 2003). Other daily patterns of N_2O flux were reported elsewhere (Denmead et al., 1979; Blackmer et al., 1982; Akiyama et al., 2000; di Marco et al., 2004). Most of these studies reported that N_2O emission rates were positively related to soil temperature (Denmead et al., 1979; Alves et al., 2012). The results obtained in this paper differ in this aspect.

N_2O emission rates were poorly related to air temperature (data not shown) and were negatively related to soil temperature ($R^2 = 0.34$). N_2O emission tended to increase as topsoil temperature decreased (Figure 2 and 3). We only found two cases that agreed with our results: Bailey (1976) observed an increase in N_2O production when topsoil temperature

decreased from 30 to 10 °C, while Avrahami & Bohannan (2009) reported similar results in soils with low or moderate amounts of fertilizer. N₂O emissions measured on these Mollisols can be ascribed to denitrification rather than nitrification, as WFPS was always greater than 70 % (Bateman & Baggs, 2005). However, the fact that N₂O emission rates decrease above 24 °C is not easy to explain. It can be speculated that during denitrification at higher temperatures, the rate of N₂ production is higher than that of N₂O (Maag & Vinther, 1996). Soil anaerobiosis could be enhanced by the occurrence of horizontal pores in the topsoil of the non-tilled soils studied.

The flux of trace gases between the soil and the atmosphere is the result of three basic processes: production, consumption and transport (Conrad, 1996). Another possible factor influencing soil N₂O emissions is the continuous no-till management of

these soils. Many of them have a low volume of structural pores (Taboada et al., 1998; Micucci & Taboada, 2006; Taboada et al., 2008). The formation of these pores has been attributed to the lack of mechanical disturbance as well as to the traffic of heavy farm machinery in no-till systems, resulting in shallow compaction in the form of laminar structures (Bonel et al., 2005; Sasal et al., 2006; Alvarez et al., 2009). This type of structure favors the appearance of horizontal pores, which also tend to be more tortuous and less connected (Bonel et al., 2005), thus promoting the development of anaerobiosis after heavy rain episodes.

Taking into account that diffusion capacity is related to impedance to gas diffusion, which depends on the shape and orientation of the soil pores (Fen et al., 2009), it can be also suggested that this pore arrangement, plus a WFPS percentage close to 90 %, could reduce the rate at which gases move from the soil to the atmosphere (Glinski & Stepniewski, 1985). This is consistent with results of Bartelt-Hunt & Smith (2002), who found that with a decrease in soil moisture content, and therefore an increase in the percentage of air-filled pores (30 to 39 %), the gas diffusion coefficient rises from 0.0133 to 0.0609 cm²s⁻¹. This decrease in gas transport rate from soil to air leads to an accumulation of N₂O molecules in the ground making them available for use by nitrous oxide reductase to produce N₂, causing a decrease in N₂O rate with increasing temperature in the soil studied here.

A similar observation was described by Focht (1974), who found that as the denitrification rate increased, the quantity of N₂O evolved decreased, due to the greater increase in N₂O reduction rate than in its formation rate. Their results also support and further develop the hypothesis proposed by Bailey & Beauchamp (1973) that account for the change in relative proportion of denitrification gases produced as temperature changes. These authors reported that at 15 °C, a partial inhibition of the final reduction step of denitrification occurred (N₂O → N₂) (Bailey, 1976).

Results indicate that to sample N₂O gases from a Mollisol, the morning hours (09:00 to 12:00 am) are more appropriate to minimize errors. Soil temperature appears to be the main factor negatively regulating the N₂O emission rate. This differs from results obtained by other authors (Denmead et al., 1979; Alves, 2011) and should be verified in the future.

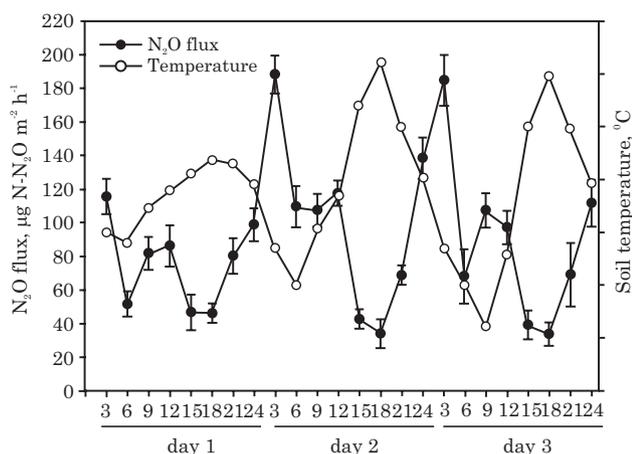


Figure 2. Soil N₂O emission rates and soil temperature at different times of the day. Bars indicate standard errors of the mean.

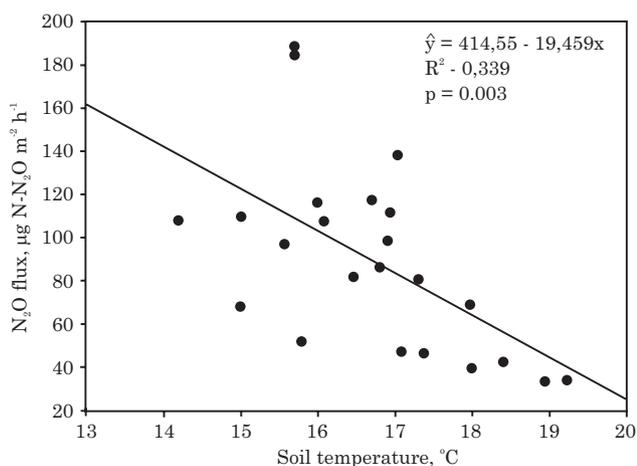


Figure 3. Soil N₂O emission rates from a Mollisol as a function of soil temperature.

ACKNOWLEDGEMENTS

We acknowledge the friendly collaboration of the Cartier family, owners of the farm where the study was carried out. The study was financed by grants from Foncyt-ANPCyT (PICTs N° 1991 and N° 32399),

CONICET (PIP n° 5971) and UBA (G 100-2008-2010). Vanina Cosentino was supported by a scholarship from ANPCyT (project PICT 32-399).

LITERATURE CITED

- AKIYAMA, H.; TSURUTA, H. & WATANABE, T. N₂O and NO emissions from soils after the application of different chemical fertilizers. *Chemosphere - Global Change Sci.*, 2:313-320, 2000.
- ALVAREZ, C.R.; TABOADA, M.A.; GUTIERREZ BOEM, F.H.; BONO, A.; FERNANDEZ, P.L. & PRYSTUPA, P. Topsoil properties as affected by tillage systems in the rolling pampa region of Argentina. *Soil Sci. Soc. Am. J.*, 73:1242-1250, 2009.
- ALVES, B.J.R., SMITH, K.A., FLORES, R.A., CARDOSO, A.S., OLIVEIRA, W.R.D., JANTALIA, C.P., URQUIAGA, S. & BODDEY, R.M. Selection of the most suitable sampling time for static chambers for the estimation of daily mean N₂O flux from soils. *Soil Biol. Biochem.*, 46:129-135, 2012.
- AVRAHAMI, S. & BOHANNAN, B.J.M. N₂O emission rates in a California meadow soil are influenced by fertilizer level, soil moisture and the community structure of ammonia-oxidizing bacteria. *Global Change Biol.*, 15:643-655, 2009.
- BAILEY, L.D. Effects of temperature and root on denitrification in a soil. *Can. J. Soil Sci.*, 56:79-87, 1976.
- BAILEY, L.D. & BEAUCHAMP, E.G. Effects of temperature on NO₃⁻ and NO₂⁻ reduction, nitrogenous gas production and redox potential in a saturated soil. *Can. J. Soil Sci.*, 53:213-218, 1973.
- BALL, B.C.; McTAGGART, I.P. & WATSON, C.A. Influence of organic ley-arable management and afforestation in sandy loam to clay loam soils on fluxes of N₂O and CH₄ in Scotland. *Agric. Ecosyst. Environ.*, 90:305-317, 2002.
- BARTELT-HUNT, S.L. & SMITH, J.A. Measurement of effective air diffusion coefficients for trichloroethene in undisturbed soil cores. *J. Contam. Hydrol.*, 56:193-208, 2002.
- BATEMAN, E.J. & BAGGS, E.M. Contributions of nitrification and denitrification to N₂O emissions from soils at different water-filled pore space. *Biol. Fert. Soils*, 41:379-388, 2005.
- BLACKMER, A.M.; ROBBINS, S.G. & BREMNER, J.M. Diurnal variability in rate of emission of nitrous oxide from soils. *Soil Sci. Soc. Am. J.*, 46:937-942, 1982.
- BONEL, B.A.; MORRÁS, H.J.M. & BISARO, V. Modificaciones de la microestructura y la materia orgánica en un Argiudol bajo distintas condiciones de cultivo y conservación. *Ci. Suelo*, 23:1-12, 2005.
- CHEN, G.X.; HUANG, B.; XU, H.; ZHANG, Y.; HUANG, G.H.; YU, K.W.; HOU, A.X.; DU, R.; HAN, S.J. & VANCLEEMPUT, O. Nitrous oxide emissions from terrestrial ecosystems in China. *Chemosphere - Global Change Sci.*, 2:373-378, 2000.
- CONRAD, R. Soil microorganisms as controllers of atmospheric trace gases (H₂, CO, CH₄, OCS, N₂O and NO). *Microbiol. Rev.*, 60:609-640, 1996.
- DENMEAD, O.T.; FRENEY, J.R. & SIMPSON, J.R. Studies of nitrous oxide emission from a grass sward. *Soil Sci. Soc. Am. J.*, 43:726-728, 1979.
- DI MARCO, C.; SKIBA, U.; WESTON, K.; HARGREAVES, K. & FOWLER, D. Field scale N₂O flux measurements from grassland using eddy covariance. *Water Air Soil Pollut.*, 4:143-149, 2004.
- DOBBIE, K.E. & SMITH, K.A. The effects of temperature, water-filled pore space and land use on N₂O emissions from an imperfectly drained gleysol. *Eur. J. Soil Sci.*, 52:667-673, 2001.
- FEN, C.S.; HUANG, Y. & CHEN, J.L. Experimental study of gas transport parameters in unsaturated silica flour. *Vadose Zone J.*, 8:373-382, 2009.
- FOCHT, D.D. The effect of temperature, pH and aeration on the production nitrous oxide and gaseous nitrogen a zero order kinetic model. *Soil Sci.*, 118:173-179, 1974.
- GLINSKI, J. & STEPNIIEWSKI, W. Soil aeration and its role for plants. Boca Raton, CRC Press, 1985. 138p.
- HOUGHTON, J.T.; DING, Y.; GRIGGS, D.J.; NOGUER, M.; van der LINDEN, P.J.; DAI, X.; MASKELL, K. & JOHNSON, C.A. Climate change 2001: The scientific basis. contribution of Working Group I to the third assessment report of the intergovernmental panel on climate change.. In: CAMBIO CLIMÁTICO 2001: Informe de síntesis. Cambridge, Cambridge University Press, 2001.
- HUTCHINSON, G.L. & LIVINGSTON, G.P. Soil-atmosphere gas exchange. In: DANE, J.D. & TOPP, C., eds. *Methods of soil analysis*. Madison, Soil Science Society of America, 2002. Part 4. p.1159-1182. (Book Series, 5)
- INFOSTAT. 2002. Software estadístico. Grupo InfoStat. Córdoba, Facultad de Ciencias Agropecuarias/Universidad Nacional de Córdoba, 2002. Argentina.
- INSTITUTO NACIONAL DE TECNOLOGIA AGROPECUARIA -INTA. Carta de Suelos de la Republica Argentina. Provincia de Buenos Aires. Hoja 3560-15-4. Chivilcoy. 2010. Disponible: <<http://www.inta.gov.ar/suelos/cartas/3560/Chivilcoy/index.htm>>
- JANTALIA, C.P.; DOS SANTOS, H.P.; URQUIAGA, S.; BODDEY, R.M. & ALVES, B.J.R. Fluxes of nitrous oxide from soil under different crop rotations and tillage systems in the South of Brazil. *Nutr. Cycl. Agroecosyst.*, 82:161-173, 2008.
- KEENEY, D.R.; FILLERY, I.R. & MARX, G.P. Effect of temperature on the gaseous nitrogen products of denitrification in a silt loam Soil. *Soil Sci. Soc. Am. J.*, 43:1124-1128, 1979.
- MAAG, M. & VINTHER, F.P. Nitrous oxide emission by nitrification and denitrification in different soil types and at different soil moisture contents and temperatures. *Appl. Soil Ecol.*, 4:5-14, 1996.

- McCLAIN, M.E., BOYER, E.W., DENT, C.L., GERGEL, S.E., GRIMM, N.B., GROFFMAN, P.M., HART, S.C.; HARVEY, J.W., JOHNSTON, C.A., MAYORGA, E., MCDOELL, W.H. & PINAY, G. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. *Ecosystems*, 6:301-312, 2003.
- MARKUS, D.K.; McKINNON, J.P. & BUCCAFURI, A.F. Automated analysis of nitrite, nitrate and ammonium nitrogen in soils. *Soil Sci. Soc. Am. J.*, 49:1208-1215, 1985.
- MICUCCI, F.G. & TABOADA, M.A. Soil physical properties and soybean (*Glycine max* Merrill) root abundance in conventionally- and zero-tilled soils in the humid Pampas of Argentina. *Soil Tillage Res.*, 86:152-162, 2006.
- PÉREZ-RAMÍREZ, J. Prospects of N₂O emission regulations in the European fertilizer industry. *Appl. Catalysis B: Environ.*, 70:31-35, 2007.
- ROCHETTE, P. & ERIKSEN-HAMEL, N.S. Chamber measurements of soil nitrous oxide flux: Are absolute values reliable? *Soil Sci. Soc. Am. J.*, 72:331-342, 2008.
- SASAL, M.C.; ANDRIULO, A.E. & TABOADA, M.A. Soil porosity characteristics and water movement under zero tillage in silty soils in Argentinian Pampas. *Soil Tillage Res.*, 87:9-18, 2006.
- SCHINDLBACHER, A.; ZECHMEISTER-BOLTENSTERN, S. & BUTTERBACH-BAHL, K. Effects of soil moisture and temperature on NO, NO₂, and N₂O emissions from European forest soils. *J. Geophys. Res.*, 109:D17302, 2004.
- SNYDER, C.S.; BRUULSEMA, T.W. & JENSEN, T.L. Greenhouse gas emissions from cropping systems and the influence of fertilizer management. A literature review. Norcross, GA: International Plant Nutrition Institute, 2007. 25p.
- TABOADA, M.A.; BARBOSA, O.A. & COSENTINO, D.J. Null creation of air-filled structural pores by soil cracking and shrinkage in silty loamy soils. *Soil Sci.*, 173:130-142, 2008.
- TABOADA, M.A.; MICUCCI, F.G.; COSENTINO, D.J. & LAVADO, R.S. Comparison of compaction induced by conventional and zero tillage in two soils of the Rolling Pampa of Argentina. *Soil Tillage Res.*, 49:57-63, 1998.
- VENTEREA, R.T.; SPOKAS, K.A. & BAKER, J.M. Accuracy and precision analysis of chamber-based nitrous oxide gas flux estimates. *Soil Sci. Soc. Am. J.*, 73:1087-1093, 2009.
- WALKLEY, A. & BLACK, I. An examination of the Degtjareff method and a proposed modification of the chromic matter and a proposed modification of the chromic acid titration method. *Soil Sci.*, 34:29-38, 1934.
- XUNHUA, Z.; YAO, H.; YUESI, W.; MINGXING, W.; JISHENG, J. & LAOTU, L. Effects of soil temperature on nitric oxide emission from a typical Chinese rice-wheat rotation during the non-waterlogged period. *Global Change Biol.*, 9:601-611, 2003.