INFLUENCE OF SOIL CHARACTERISTICS AND NITROGEN AMENDMENTS ON NITROUS OXIDE EMISSIONS IN A CORN PRODUCTION SYSTEM

Influencia de las Características del Suelo y las Mejoras con Nitrógeno sobre las Emisiones de Óxido Nitroso en un Sistema de Producción de Maíz

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SUMMARY

One of the greenhouse gases emitted in important amounts in Mexico is nitrous oxide. An appreciable part of its emissions is linked to the use of nitrogen (N) fertilizer in agricultural activities. The main objective of this work is to obtain emission factors (EF) for this gas in corn production systems fertilized using synthetic or organic sources of nitrogen (ammonium nitrate and cow manure, respectively). Three plots were selected, each with different fertilizing conditions, for the quantification of N_2O emission fluxes during the rainy season in corn cultivation. The plots were identified as JCFN, fertilized with 100 kg N ha^{-1} yr^{-1} using ammonium nitrate; plot JCAS, fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}; plot JCAN, references with no fertilizer. The N_2O emission fluxes measured from the JCFN plot during the total sampling period were between 7.3 and 153.2 µg N_2O-N m^{-2} h^{-1}, approximately four times those fluxes found during the same sampling period in the plots JCAS and JCAN. The results of the JCFN plot are comparable with similar studies in Europe where emissions varied between 1.5 and 63 g N_2O-N ha^{-1} d^{-1} (6.25 to 262.45 µg N_2O-N m^{-2} h^{-1}).

Index words*: soil properties, ammonium nitrate.*

RESUMEN

Uno de los gases con efecto invernadero que se emite en cantidades importantes en México es el óxido nitroso; una parte apreciable de sus emisiones está vinculada con el uso de fertilizantes nitrogenados en actividades agrícolas. Este trabajo tiene como objetivo principal la obtención de factores de emisión (FE) para este gas, en sistemas de producción de maíz, usando fuentes de nitrógeno sintéticas o naturales (nitrato de amonio y excreta de ganado vacuno, respectivamente). Se seleccionaron tres parcelas de un mismo sitio con condiciones de fertilización diferentes para la cuantificación de emisiones de óxido nitroso durante la temporada de lluvias en terrenos cultivados con maíz. Las parcelas se identificaron como JCFN, fertilizada con 100 kg N ha^{-1} año^{-1}, utilizando nitrato de amonio; JCAS, fertilizado con excretas secas de ganado bovino en una dosis de 5.5 kg m^{-2} año^{-1}; y JCAN, que se tomó como referencia sin ningún tipo de fertilizante. En las parcelas JCFN las emisiones de óxido nitroso, a lo largo del período de muestreo, estuvieron en el intervalo de 7.3 a 153.2 µg N_2O-N m^{-2} h^{-1}. Estos flujos fueron aproximadamente cuatro veces los valores encontrados, durante el mismo período, en las parcelas JCAS y JCAN. Los resultados de las parcelas JCFN son comparables con los de estudios de suelos similares de Europa, donde las emisiones variaron entre 1.5 y 63 g N_2O-N ha^{-1} d^{-1} (6.25 a 262.45 µg N_2O-N m^{-2} h^{-1}).

Palabras clave: *propiedades del suelo, nitrato de amonio.*

INTRODUCTION

Agricultural soils contribute significantly to nitrous oxide emissions, and thus to global climate change, but it depends, along with other factors, on climate, soil, and fertilizer used. Many countries, including Mexico, have signed a compromise to evaluate and to monitor greenhouse gas emissions linked to several activities. The update of the National Inventory of Greenhouse Gas Emissions shows that nitrous oxide accounted for 3% of the total emissions derived from agriculture

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(INE-SEMARNAT, 2001). This implies that nitrogen losses from agriculture represent an economic loss and an environmental impact.

It is accepted that the emission of nitrous oxide from soils is a result of the processing of the nitrogen contained in the nutrients by soil microorganisms where the principal process pathways are nitrification and denitrification. During denitrification of nitrate (NO_3^-) and nitrification of ammonium (NH_4^+), N_2O is released and so fertilizers or manure affect the availability of nitrate and/or ammonium in the soil.

Nitrogen oxide emissions from fertilized agricultural soils are considered a complex process. Factors involved are soil water content, oxygen concentration, soil texture, porosity, pH, C/N ratio, type and quantity of applied fertilizer, soil temperature, irrigation, type of cultivation, etc.

The intake of nitrous oxide to the soil has been observed, but it has not been explained convincingly. Sanhueza *et al*. (1990), Schiller and Hastie (1996), and Teira-Estmages *et al*. (1998) have reported negative nitrous oxide fluxes. Donoso *et al.* (1993) have measured negative fluxes of N_2O during the spring, in humid soils covered with green grass in Michigan and in cultivation fields in Iowa, USA. They found an inverse correlation between the consumption of nitrous oxide and the soil temperature (from 25 to 43 ºC), since the bacteria that consume and produce it, respond differently to the change of temperature.

In the nitrification and denitrification, nitrous oxide, nitric oxide and molecular nitrogen are emitted; also soil microorganisms can consume these gases; Wolf and Russow (2000) found that under water-saturated conditions the dominant process is the denitrification, but nitrification also occurred to some extent. Under this condition N_2O and N_2 emissions were observed but nitric oxide (NO) was not detected.

Speir *et al*. (1999), using the short-lived radioisotope ^{13}N, found that N_2O is produced via denitrification in very low-fertility ecosystems. Flessa *et al*. (1995) did not find extensive dependence between the N_2O emissions and soil temperature, soil water content and available NO_3^-. Veldkamp *et al.* (1998) observed a great dependence between NO and N_2O emissions and soil water content, which is related to the adequate supply of oxygen for nitrification and denitrification. They conclude that trace gas fluxes can be highly dependent on weather conditions at the time of sampling. In a previous publication, Veldkamp and Keller (1997) conclude that the most important factor on NO_x emissions from soils is related to the tillage level.

Interaction of tillage level with fertilization practice has been observed. Maximum N_2O emissions were measured in corn fields with no-tilled systems and the emissions were greater when fertilizers were added (MacKenzie *et al.*, 1998). This may be due to higher soil compaction which favors anaerobic conditions and denitrification. On the other hand, tillage favors aerobic conditions and nitrification. Adding fertilizers increases the available nitrogen to be processed on either way. The authors suggest, as a way to diminish N_2O emissions, to rotate crops (corn and forages), and to reduce fertilizer application and tillage intensity.

Teira-Estmages *et al*. (1998) have published one of the most conclusive works concerning the relationship of the physical, chemical and biological soil properties, weather conditions and complex interactions among these factors. They attribute high variations in N_2O and N_2 fluxes due to the diverse combinations of these factors controlling gas fluxes. They concluded that the denitrification rates generally augment with increasing soil moisture content. They reported 10 to 20 times increased N_2O losses when the soil was subjected to anaerobic-aerobic cycles. With a low soil C/N ratio, N can be mineralized creating favorable conditions for the generation of nitrous oxide. Denitrification had a positive correlation with pH, with an optimum in the range of 7.0 to 8.0, and below 6.0 the denitrification can be strongly inhibited. The N_2/N_2O ratio strongly increases with soil pH. Regarding the temperature they found that nitrification is enhanced between 25 and 35 ºC, whereas denitrification is favored between 30 and 67 ºC.

One of the works published on nitrous oxide emissions in soils amended with organic materials is that of Mogge *et al.* (1999). They found that the overall loss of nitrous oxide represents 5.7% of the annual N-input (mineral nitrogen fertilizer plus organic nitrogen fertilizer); this percentage might reach values of 10% of the applied fertilizer nitrogen and increase with soil moisture and the content of organic C available as electron donor. In this work nitrous oxide emissions were negatively correlated with pH throughout the entire study, $r^2 = 0.31$ ($P < 0.001$, n = 22).

The general objective of the present work was to measure nitrous oxide fluxes from corn fields after fertilizer application during the raining season using chamber techniques. Field information on nitrous oxide emission factors (EF) obtained from this work could be used for the next preparation of the National Inventory of Greenhouse Gases.

MATERIALS AND METHODS

The experimental site was located at La Joya (a rural area) near Cuernavaca, Mexico (18° 53' 39.6" N and 99° 07' 43.9" W at 1411 meters above sea level) and cultivated with corn.

Three treatments with different sources of nitrogen were applied in adjacent plots. One of the treatments consisted of a total of 100 kg ha^{-1} annual N fertilizer applied as ammonium nitrate in two events to the JCFN plot: the first one (half of the total ammonium nitrate) on June 29 (Julian day 180) and the second event on July 5 (Julian day 186). An other N source was organic matter (cow manure) applied at a rate of 5.5 kg m^{-2} yr^{-1} to the second plot, JCAS (20 m^{2}), on July 5, (Julian day186). And the third plot was a control plot, with no fertilizer added (JCAN). The content of total nitrogen and hydrogen in the cow manure was 1.55 and 12.58%, respectively.

Fertilizer inputs are not constant over agricultural lands; they can vary by country and from field to field; Matthews (1994) reports application rates of 47, 101, 151, 164, and 578 kg N ha^{-1} yr^{-1}. Stevens *et al.* (1997), measuring the contribution of nitrification and denitrification to the flux of nitrous oxide from soil, used an application rate of 100 kg N ha^{-1} yr^{-1}. Specifically, Williams *et al*. (1992) considered an average US fertilizer application rate, for all corn cultivation, of 121 kg N ha^{-1}.

The Instituto Nacional de Investigaciones Forestales, Agrícolas y Pecuarias (INIFAP), a governmental research institution, has data on the use of N fertilizer for corn production in the Morelos State that are in the range of 120 to 150 kg N ha^{-1} by cycle, which are similar to those reported in the literature.

The overall sampling period was from May to December 1999. Sampling dates were irregular as indicated in Figure 1.

The gas and soil sampling period started on May 13, (Julian day 133) in the JCAS plot before being fertilized and, in the JCFN plot, almost one month before starting the rainy season, founding in each parcel a water content of 1.2 and 3.9%, respectively. A total of 251 gaseous N samples were collected in the three plots. A stainless steel chamber (diameter 26.0 cm, height 20.0 cm, and 10.6 L in volume) was used for the sampling. It consists of two separable parts; the base was inserted at approximately 2.0 cm depth in the soil at least one week before beginning the series of measurements during the complete sampling cycle and an upper part that was sealed to the base. Gas samples from the chamber were taken with a 10 mL syringe (Hamilton 1010 SL), transferred to sealed vials and stored until being analyzed. The samples were taken at the beginning of the sampling daily period and at 15 min intervals. Statistical analysis for the data were run as t-tests ($P < 0.05$) (Montgomery, 1991) using the SigmaStat software package (SigmaStat for Windows v. 3.0, SPSS Science software).

A total of 37 soil samples of the upper 2.0 - 5.0 cm layer were taken from the surrounding area in order to

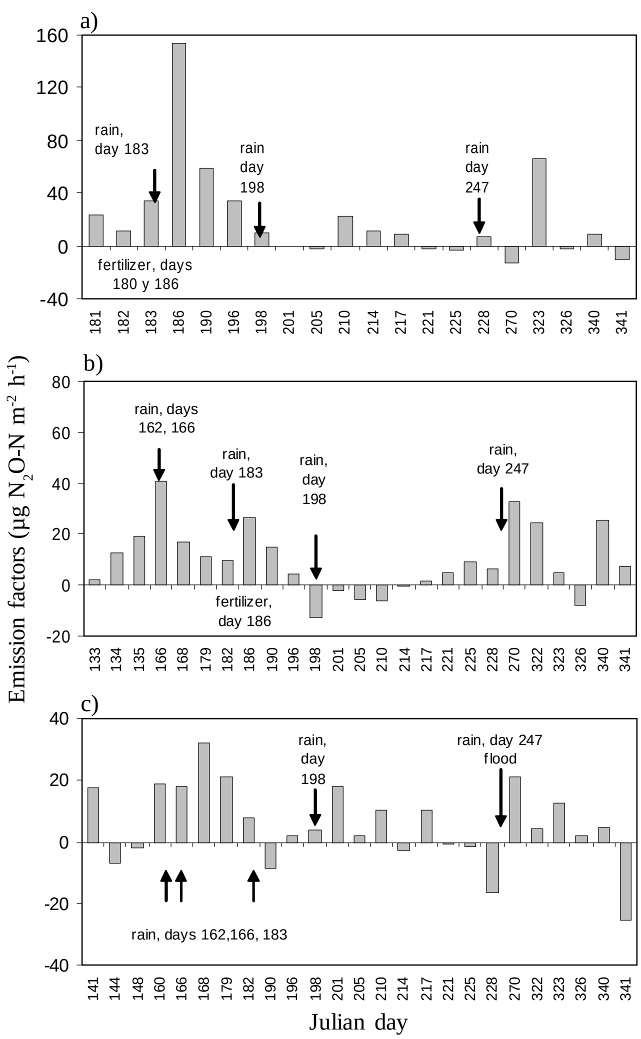

Figure 1. N$_2$O flux rates for the three plots. a) JCFN (fertilized with 100 kg N ha^{-1} yr^{-1} using ammonium nitrate), b) JCAS (fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}), c) JCAN (references with no fertilizer).

know the site variation in density, organic matter, phosphorous, potassium, nitrates, pH, electric conductivity, and moisture content. In each one of the plots, the soil temperature at 3 cm depth was measured using an ASTM thermometer. We normally sampled daily between 09:00 h and 17:00 h local time. There was frequently a linear increase in the N_2O concentration throughout the sampling period. Table 1 shows soil characteristics and texture type for the three plots.

Samples were analyzed by electron capture gas chromatography within no more than 10 days after collection. The analysis procedure was the same as used by several researchers (Seiler and Conrad, 1981; Conrad *et al.*, 1983; Levine *et al.*, 1996; Schiller and Hastie, 1996; Veldkamp and Keller, 1997; MacKenzie *et al.*, 1998; Teira-Estmages *et al.*, 1998).

Calibration curves were made using an appropriate system for the preparation of internal standards of nitrous oxide (99%) in nitrogen, using relationships of partial pressures measured with a calibrated pressure transducer (Data Instruments, Model SA). The precision of analysis expressed as the coefficient of variation (CV) for 10 replicate standard injections was 3.0% and the system presented a minimum detection limit of 81.65 $\mu g\ L^{-1}$. We extensively tested this very well established sampling set-up and analysis procedure finding high repeatability, with a CV of 4.8%.

The concentration of N_2O of each sealed vial (20.0 mL) was determined transferring 2.0 mL aliquots to a gas chromatograph (GC Tracor 540) equipped with an electron capture detector, a column of Porapak QS and a gas carrier of 5% CH_4 in argon. We used three aliquots to obtain data in triplicate and use the mean of these values. Hourly, area-based N_2O fluxes were calculated from the time-linear rate of concentration increase in headspace during chamber deployment. These data were time-integrated using the trapezoidal rule to calculate the area-based N_2O-N emission over the entire observational period for each experiment (Longoria-Ramirez *et al.*, 2003).

RESULTS AND DISCUSSION

Table 1 shows some soil characteristics as mean values for the complete sampling period. Some of these values fluctuated, mainly those related to the rain frequency and intensity or to the application of fertilizers in the JCAS and JCFN sites. The density ranged from 1.75 to 1.88 Mg m^{-3}; there were no significant differences among sites, the soil pH ranged from 7.07 at JCFN and JCAN to 7.23 at JCAS; JCFN had the highest N-NO_3 content (301 mg kg^{-1}), and JCAN the lowest (49 mg kg^{-1}). The average values of organic matter and water content showed no significant differences between the three sites (P < 0.01). Figures 2, 3, and 4 show the variations in the content of organic matter, N-NO_3^-, and water-filled pore space (WFPS), respectively, during the sampling period. The statistical analysis of soil properties (Table 1) was evaluated by ANOVA at a 99% level of confidence by the Fisher's F test (Least Significant Difference) using the SigmaStat software package (Version 3.0).

Table 1. Soil characteristics obtained for the plots JCAS (fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}), JCFN (fertilized with 100 kg N ha^{-1} yr^{-1} using ammonium nitrate), and JCAN (references with no fertilizer).

Characteristics	JCAS	JCFN	JCAN
Texture type	Clay loam	Clay loam	Clay loam
Density (Mg m^{-3})**	1.75 ± 0.01 a	1.88 ± 0.02 a	1.75 ± 0.01 a
Water content (%)*	17.16 ± 2.17 a	20.95 ± 1.98 a	15.75 ± 2.18 a
pH **	7.23 ± 0.04 a	7.07 ± 0.11 b	7.07 ± 0.2 b
Organic matter (%)*	1.71 ± 0.17 a	1.45 ± 0.17 a	1.64 ± 0.15 a
N-NO_3^- (mg kg^{-1})***	58.88 ± 20.06 a	300.9 ± 205.14 b	49.52 ± 12.41 a
Potassium (mg kg^{-1})***	1.47 ± 0.04 a	1.52 ± 0.03 a	1.66 ± 0.02 a
Field capacity (%)	30.96	30.96	30.96
Wilting point (%)	16.8	16.8	16.8
Electric conductivity (dS m^{-1})***	1.08 ± 0.17 a	1.7 ± 2.02 b	0.6 ± 0.02 c

Values are means ± SE (*: n = 25, **: n = 14 y ***: n = 12). Different letter by row indicates significant differences according to Fisher´s test (P < 0.01).

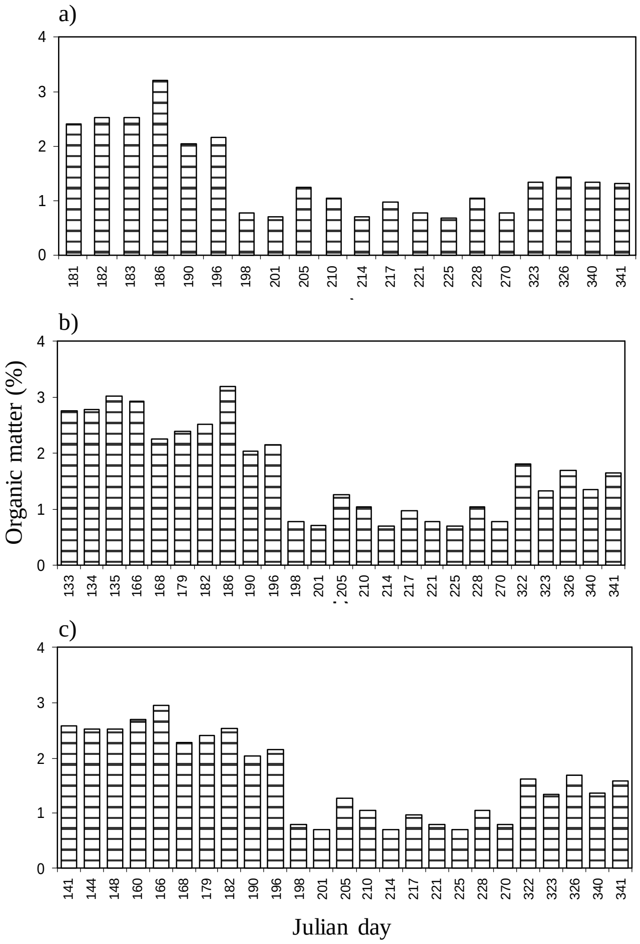

Figure 2. Organic matter content during the sampling period for the three plots. a) JCFN (fertilized with 100 kg N ha^{-1} yr^{-1} using ammonium nitrate), b) JCAS (fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}), and c) JCAN (references with no fertilizer).

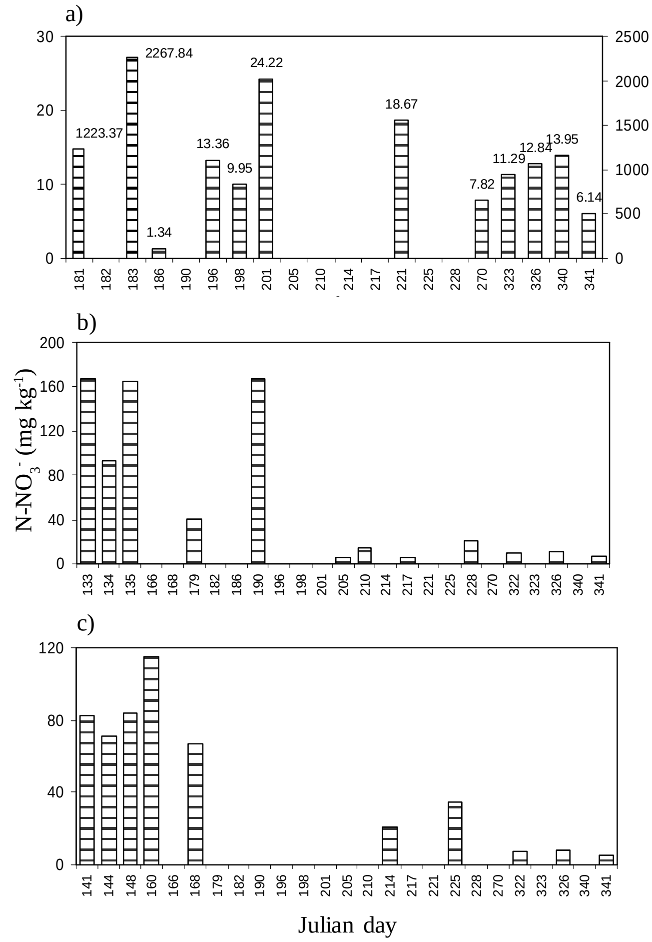

Figure 3. N-NO$_3^-$ content during the sampling period for the three plots. a) JCFN (fertilized with 100 kg N ha^{-1} yr^{-1} using ammonium nitrate), b) JCAS (fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}), and c) JCAN (references with no fertilizer).

Field studies

Moisture content averages were not different among plots, but the plot JCFN presented a moisture content of 17.4% when fertilized; this content increased as much as 33% in the following five days; nitrous oxide emissions incremented too (from Julian day 181 to 199).

The rainy season was very irregular, concerning the rain events and its respective amount or intensity. Half of the total annual precipitation occurred in 27 days, in August and the first half of September. During this time interval the site was not accessible and it was not possible to continue the sampling schedule.

Nitrous oxide emissions were the highest at JCFN plot and ranged from 7.3 to 153.2 µg N_2O-N m^{-2} h^{-1} (Figure 1). Nitrous oxide emissions at JCAS and JCAN plots were not different ranging from 1.9-40.9 µg N_2O-N m^{-2} h^{-1} and from 2.0-31.9 µg N_2O-N m^{-2} h^{-1}, respectively. Table 2 shows the Kruskal-Wallis test to compare nitrous oxide emissions between the three plots.

These fluxes showed high and significant correlations ($P < 0.05$) with soil pH with 0.79 and 0.78 r^2 values for

Table 2. Kruskal-Wallis test for N_2O-N (µg m^{-2} h^{-1}) emissions.

Plot	N	Median	Std. dev.
JCFN	13	9.51	40.63
JCAS	19	5.39	11.04
JCAN	17	3.95	8.66

H = 5.172 with 2 degrees of freedom (P = 0.075).
JCFN = fertilized with 100 kg N ha^{-1} yr^{-1} using ammonium nitrate; JCAS = fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}; JCAN = references with no fertilizer.

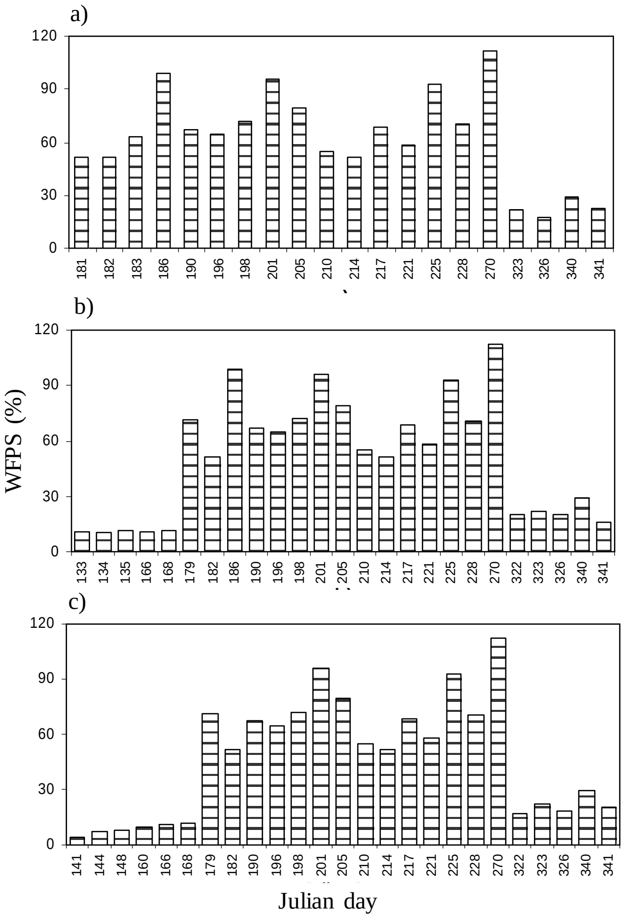

Figure 4. WFPS (Water-Filled Pore Space) during the sampling period for the three plots. a) JCFN (fertilized with 100 kg ha^{-1} yr^{-1} N using ammonium nitrate), b) JCAS (fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}), and c) JCAN (references with no fertilizer).

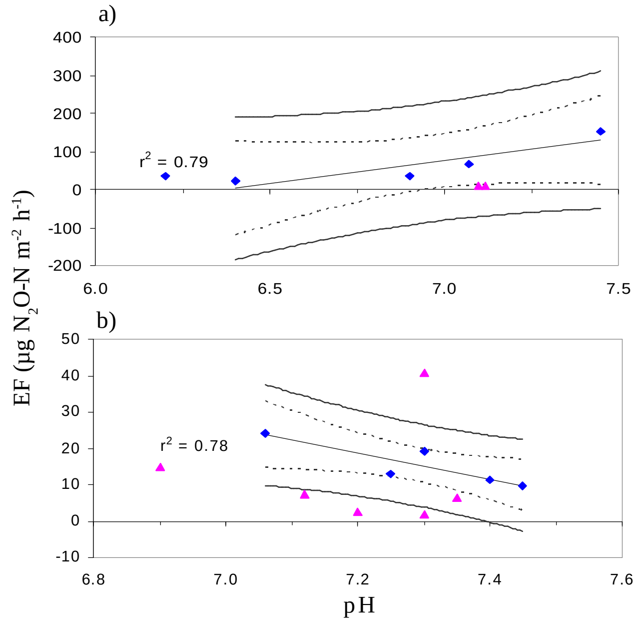

Figure 5. Correlation observed between pH and the emission rate during the measurement period for a) JCFN plot and b) JCAS (*P* < 0.05) plot. Triangles in the plots indicate "outliers".

JCFN and JCAS, respectively. Some "outliers" were detected and are indicated with triangles in Figure 5.

Teira-Estmages *et al.* (1998) quantified N_2O emissions from three arable soils at sites sown with maize in Catalonia (northeast Spain). The ranges of measured emission fluxes were quite different among the three sites, as were the texture type of the sites. The site with clay loam soil, as our site of study, had an emission range from 1.5 to 63 g N_2O-N ha^{-1} d^{-1} (6.25 to 262.45 µg N_2O-N m^{-2} h^{-1}) which is similar to our result in the fertilized plot with ammonium nitrate (7.3 to 153.2 µg N_2O-N m^{-2} h^{-1}). It is remarkable that for both works the main sampling period was during the summer season, when the weather could be similar.

Figure 6 shows the relationship between the values of WFPS and fluxes of N_2O. These variables showed a significant correlation ($P < 0.05$) up to 50% WFPS: r^2 = 0.60, 0.63, and 0.61 for the JCFN, JCAS, and JCAN parcels, respectively, while at lower water content a significant correlation of fluxes and WFPS could not be found. This is in agreement with the observations of Rudaz *et al.* (1999), who found that the magnitude of the fluxes of N_2O and N_2 were not directly correlated with soil temperature, but augmented with increasing soil water content.

Fluxes of N_2O from all the plots showed a good relationship with soil temperature (Figure 7) with r^2 values of 0.52, 0.40, and 0.64 for the JCFN ($n = 7$; $P < 0.05$), JCAS ($n = 13$; $P < 0.05$), and JCAN ($n = 11$; $P < 0.05$) plots, respectively. These correlation coefficients could be considered similar to those reported by Yamulki *et al.* (1997) of 0.49, 0.79, and 0.46 ($n = 11$, $P < 0.014$) for soils with pH of 3.9, 5.9, and 7.6, respectively.

Organic matter content also has some influence on N_2O emissions, as expected (Mogge *et al.*, 1999; Paavolainen *et al.*, 2000). Figure 8 shows the fluxes of N_2O plotted against the content of organic matter. The highest correlation found was of $r^2 = 0.39$ in the plot JCFN, although the correlation improved ($r^2 = 0.77$) when 23% of the measurements were eliminated as "outliers". The same case occurred (for outliers) for the JCAS and JCAN plots. The "outliers" were removed to improve correlations.

Some soil characteristics are used as indicators of the N_2O production and emission. Table 3 shows

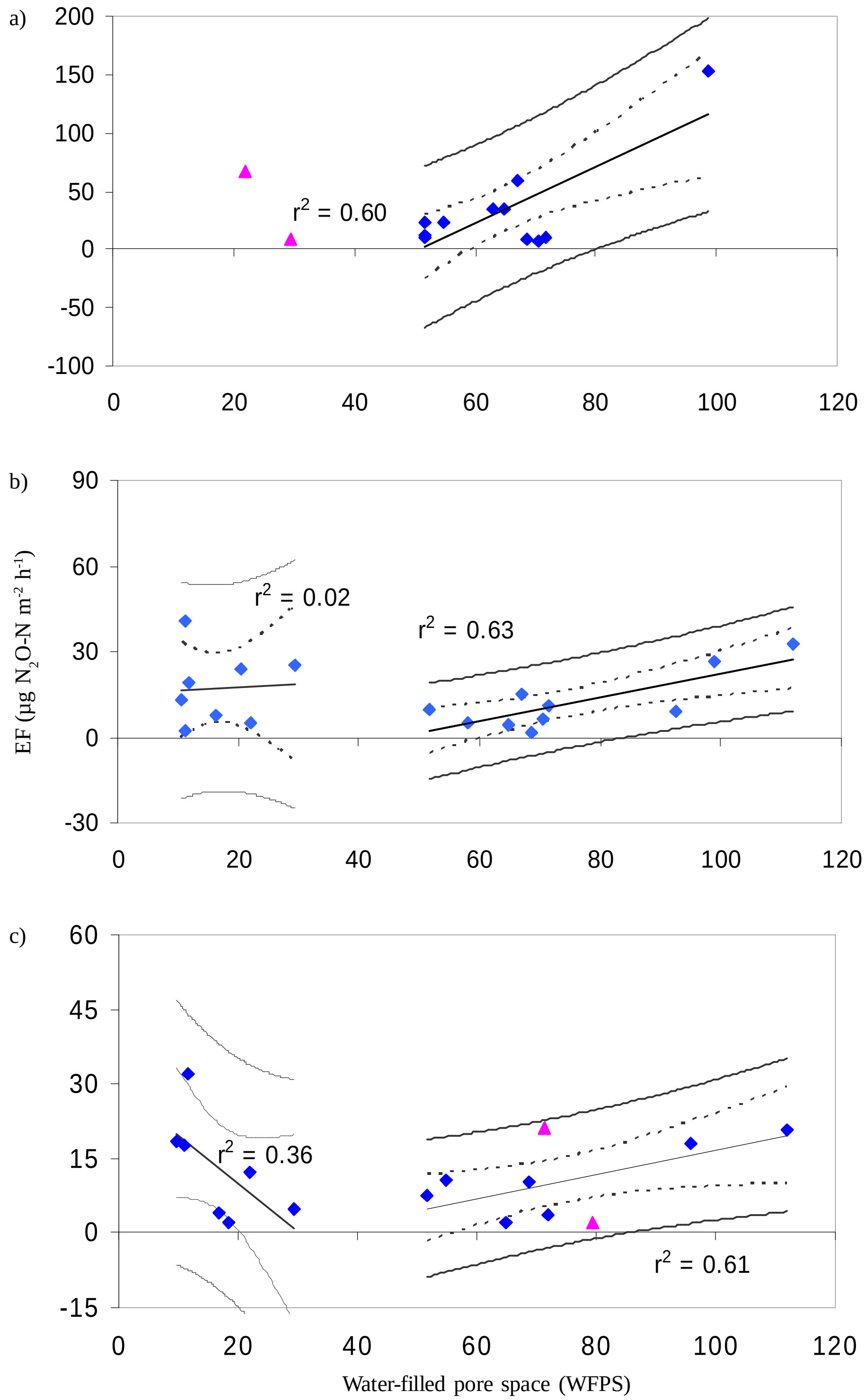

Figure 6. Relationship between nitrous oxide fluxes and WFPS, (*P* < 0.05). a) JCFN (fertilized with 100 kg ha^{-1} yr^{-1} N using ammonium nitrate), b) JCAS (fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}), and c) JCAN (references with no fertilizer). Triangles in the plots indicate "outliers".

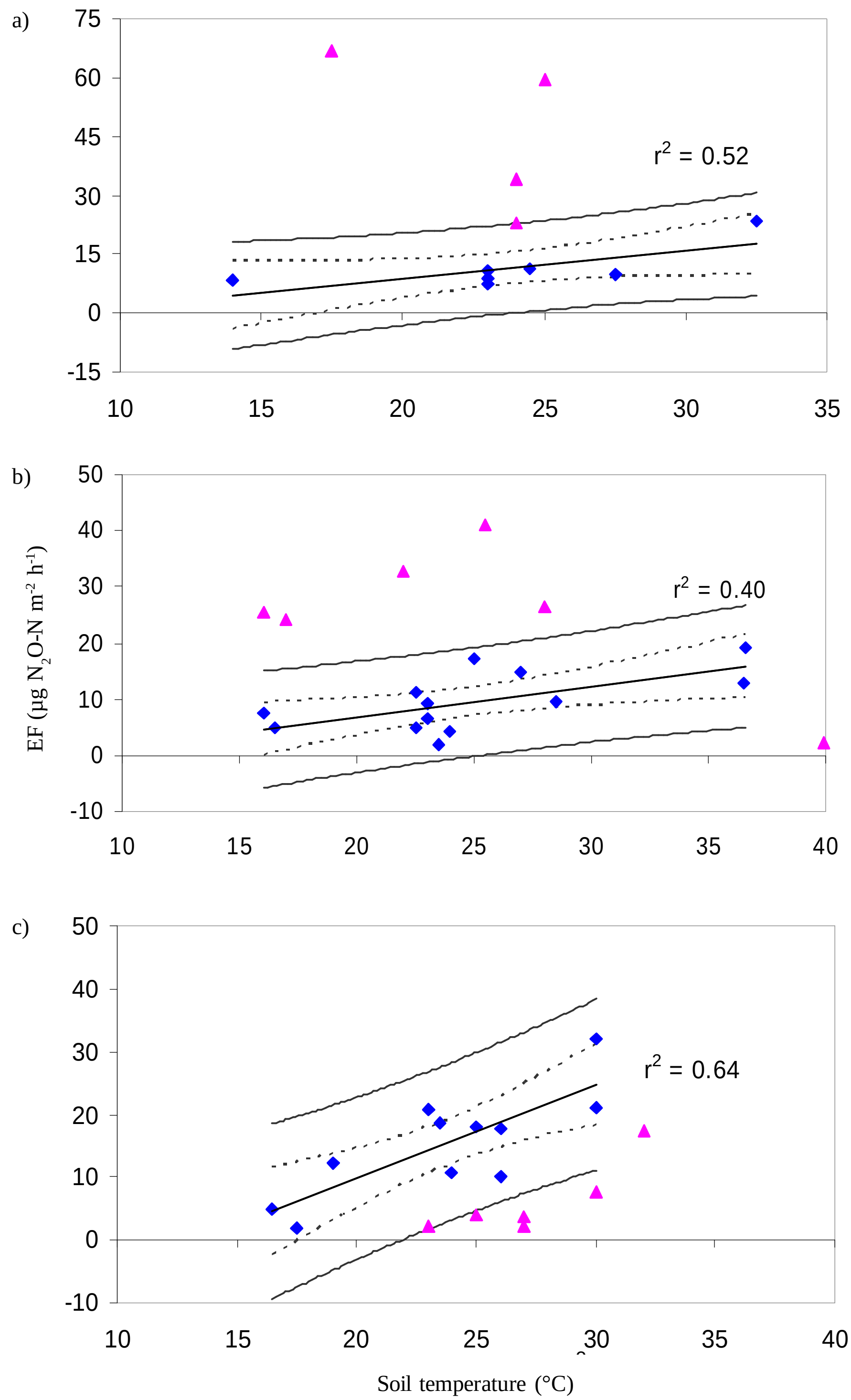

Figure 7. Linear regression between N_2O flux and soil temperature, ºC, (P < 0.05). a) JCFN (fertilized with 100 kg ha^{-1} yr^{-1} N using ammonium nitrate), b) JCAS (fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}), and c) JCAN (references with no fertilizer). Triangles indicate "outliers".

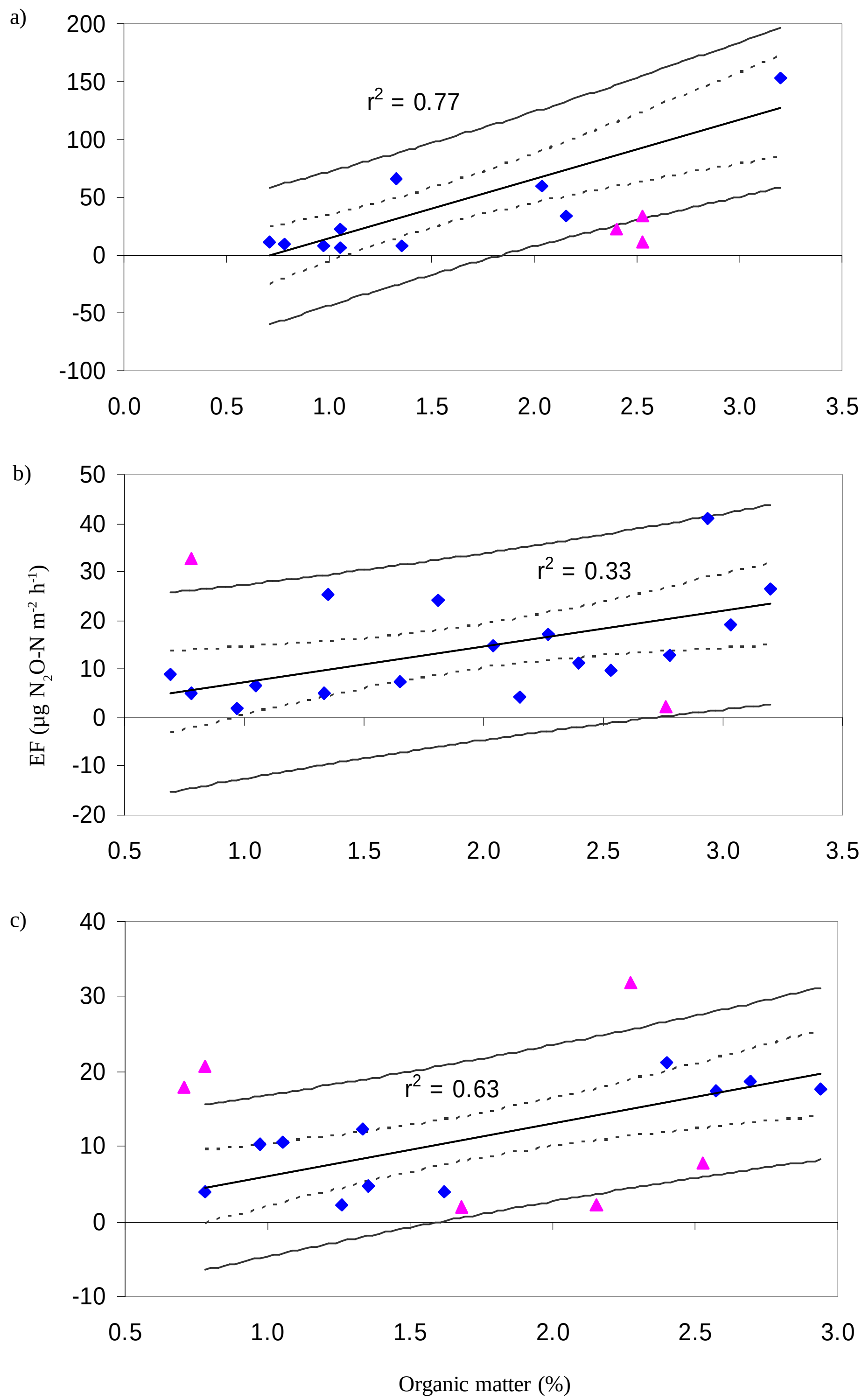

Figure 8. Correlation coefficient between N_2O flux and organic matter contents, P < 0.05. a) JCFN (fertilized with 100 kg ha^{-1} yr^{-1} N using ammonium nitrate), b) JCAS (fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}), and c) JCAN (references with no fertilizer). Triangles in the plots indicate "outliers".

Table 3. Linear models for the N_2O emission factors (EF) estimation as a function of organic matter and temperature.

Plot†	Equation	R
JCFN	EF = -29.37 + 34.55 * Organic matter	0.69
JCAS	EF = -2.88 + 7.35 * Organic matter	0.47
JCAN	EF = -18.53 + 0.97 * Soil temperature	0.35

JCFN = fertilized with 100 kg N ha^{-1} yr^{-1} using ammonium nitrate; JCAS = fertilized with dry cow manure at a rate of 5.5 kg m^{-2} yr^{-1}; JCAN = references with no fertilizer.

the equations that allow considering the behavior of the emission factors for the three plots.

CONCLUSIONS

- Plots fertilized with livestock manure or ammonium nitrate showed differences in nitrous oxide emissions. Plots with an organic source of nitrogen produced 4 to 5 times less gaseous N_2O and were similar to those of the control plot, without fertilizer.
- There is a net flux of nitrous oxide to the atmosphere from the agricultural land sown with maize, even if the sites are not fertilized.
- Considering that our measured emissions of nitrous oxide are in agreement with those obtained from arable soils of similar texture and sown with maize in Europe, the nitrous oxide emission factors (EF) obtained from this work could be used, as a first good approximation, to prepare the National Inventory of Greenhouse Gases, rather than use "default emission factors" from the Intergovernmental Panel on Climate Change (IPCC) Guidelines. However, more field work is needed to obtain EF for other situations in Mexico, to consider diversity in climate, soils, crops, and agricultural practices.

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