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ORIGINAL ARTICLE

# NO, $N_2O$ and $CO_2$ soil emissions from Venezuelan corn fields under tillage and no-tillage agriculture

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**Abstract** The largest share of Latin American and Caribbean (LAC) anthropogenic greenhouse gases is derived from land use changes as well as forestry and agriculture, representing up to 67 % of the relative contribution from all sources. However, in spite of the rapid expansion of LAC tropical agriculture, little is known about its impact on atmospheric trace gases emissions, such as nitrogen oxides ($NO_x$), nitrous oxide ($N_2O$) and carbon dioxide ($CO_2$), which are produced in soils by microbial processes and also accelerated in tropical climates. This information is crucial for assessing mitigation strategies linked to agricultural practices to satisfy food demands for the region's future. We measured NO, $N_2O$ and $CO_2$ soil emissions along with soil variables from corn fields under tillage (T) and no-tillage (NT) agriculture at two of the largest cereal-producing regions in Venezuela during the crop-growing season. We found statistically significant positive correlations between the logarithms of nitrogen gas emissions and soil inorganic nitrogen concentrations, soil water and clay contents. Average emissions of NO and $CO_2$ were larger in T than NT sites, while $N_2O$ fluxes showed the opposite. $CO_2$ emissions from T were 1.6 as much as those found in NT, whereas $N_2O$ was 0.5 of that found in NT. These results imply that NT practices more effectively mitigate climate change from these monoculture systems mainly because of $CO_2$ emission reduction. We suggest then that agricultural mitigation actions for tropical monoculture systems should aim for the enhancement of NT management practices along with N fertilization rate reduction to compensate for the larger $N_2O$ emissions.

**Keywords** Land management · Nitrogen oxide emissions · Soil respiration · Tropical crop soils

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## Introduction

Human activities have roughly doubled the production rate of reactive nitrogen (N) in comparison to the preindustrial rate, and it is expected to continue increasing to satisfy the food demands of the future human population (IPCC 2013). Perturbations of the N cycle affect atmospheric chemistry through the production of three key N-containing trace gases: nitrous oxide ($N_2O$), ammonia ($NH_3$) and nitrogen oxides [$NO_x$ = nitric oxide (NO) + nitrogen dioxide ($NO_2$)]. Nitrous oxide is the fourth largest single contributor to

positive radiative forcing, while $NH_3$ emission to the atmosphere contributes to aerosol formation. $NO_x$ has a short atmospheric lifetime and directly influences the formation of tropospheric ozone, the third largest single contributor to positive radiative forcing (IPCC 2013).

Agricultural as well as crop production for food is one of the main reasons for perturbation of the N cycle (Smil 1999; Bouwman et al. 2002; Christensen et al. 2006; de Carvalho et al. 2006; Cavigelli et al. 2012). Soil management practices under intensive agriculture (i.e., N fertilization, tillage, irrigation, pesticide application and crop varieties) strongly influence the soil-atmosphere exchange of the most important long-lived greenhouse gases (GHGs) (Smil 1999; Robertson et al. 2000; Boeckx and Van Cleemput 2001; Follett 2001; Mosier 2001; Galloway et al. 2004; Akbolat et al. 2009). Emissions of $N_2O$ from agricultural systems (1.7–4.8 Tg $N_2O$–N $year^{-1}$) comprise the largest single source (Bouwman et al. 1995; Boeckx and Van Cleemput 2001; IPCC 2007; Baggs 2011; Ciais et al. 2013), while agricultural systems are also a significant source of $NO_x$ (4 Tg N $year^{-1}$), representing 9 % of the total sources (Ciais et al. 2013). The cumulative net $CO_2$ emissions from land use changes between 1750 and 2011 are estimated at approximately $180 \pm 80$ Pg C and represent the largest terrestrial source of this greenhouse gas to the atmosphere (Ciais et al. 2013).

Globally, application of N fertilizer to crop soils results in 0.3–3 % of N being lost as $N_2O$ (IPCC 2006) and from 0.5 to 0.7 % as NO (Veldkamp and Keller 1997; Bouwman et al. 2002). However, most of the information used to establish these default values comes from temperate regions, which might not be representative of tropical crop soils (Veldkamp et al. 1998). In fact, a recent review of available data reported higher N losses from tropical crop soils, 0.01–24.2 % and 0.57–5.7 % of N applied as $N_2O$ and NO, respectively (Marquina et al. 2013 and references therein). Recent inverse modeling approaches (Hirsh et al. 2006; Huang et al. 2008) also indicate that terrestrial $N_2O$ sources in the tropics (Equator to 30°N) are larger by a factor of 20–64 % than previously estimated (Prinn et al. 1990; Bouwman et al. 1995). Like $N_2O$, potential global emissions of NO rank in decreasing order from agricultural fields > savannas > forests > other natural systems, with tropical ecosystems being the largest potential emitters of NO (Yan et al. 2005). Additionally, the release of carbon (C) via changes in land use and management (from the period 1850 to 2000) has resulted in 156 Pg C being released to the atmosphere, with tropical regions responsible for ~60 % of this (Houghton 2003). Climatic conditions within tropical regions promote microbial activity (e.g., soil temperature and moisture) and impact upon the production and emission of these trace gases (Bakwin et al. 1990; Davidson et al. 2000; Breur and Butterbach-Bahl 2005).

In Venezuela, there have been a number of studies on the emission of nitrogen oxides (NO and $N_2O$) from natural and cropped soils (Hao et al. 1988; Johansson et al. 1988; Johansson and Sanhueza 1988; Sanhueza et al. 1990, 1994, 1996; Cárdenas et al. 1993; Donoso et al. 1993; Rondón et al. 1993; Pérez et al. 2007). However, long-term studies of croplands under local management practices are lacking. These studies are of particular importance at the national level because approximately 26 % of the Venezuelan savannas are under agricultural management (López-Hernández et al. 2005). A considerable area has been deforested, at a rate of 500,000 ha $year^{-1}$, and the rate of deforestation is expected to grow (M.P.P.A.T. 2005; Baldizán and Chacón 2007).

In Latin America and the Caribbean (LAC), the N cycle has been transformed significantly in the past 50 years (Austin et al. 2013), and conversion of natural ecosystems to agricultural uses is expanding rapidly, particularly in tropical regions (Bustamante et al. 2014). The largest share of anthropogenic GHG emissions in LAC are derived from land use changes and forestry and agriculture, representing up to 67 % of the relative contribution from all sources. These trace gases from tropical and temperate agroecosystems are controlled by the complexity of interactions among land management, N-fertilizer application, residue management and crop type (Parkin and Kaspar 2006). Therefore, systematic measurements of the impact on trace gas emissions from tropical LAC agricultural soils are needed for assessing mitigation strategies linked to agricultural practices to satisfy food demands for the region's future. These measurements will increase the available data, improve global estimates of trace gas emissions and contribute to proposing mitigation strategies for intensive agriculture. For this, we measured fluxes of $N_2O$, NO and $CO_2$ from corn fields of two of the largest cereal-

producing regions in Venezuela, along with other soil variables, in order to identify the effect of local management practices on these trace gas emissions. This study presents a large database for tropical agricultural soils that generally is not available in those few published papers from this region.

## Methodology

### Sampling sites

Studies were conducted at the Fundo Tierra Nueva farm located in Guárico State (9°23′33″N, 66°38′30″W) and at the Nardini farm located in Portuguesa State (9°6′45″N, 69°2′12″W) in 2005, 2006 and 2007, respectively. These regions have two well-defined climatic periods: a dry season (November–April) and rainy season (May–October). Ninety percent of the precipitation occurs during the rainy season with mean annual values ranging between 760 and 1,400 mm for Guárico State and 1,400 and 1,800 mm for Portuguesa State. For both regions, air temperature ranges from 23 to 33 °C (INAMEH 2009). These states are two of the largest cereal-producing regions in Venezuela: 35 and 24 % of national corn (*Zea mays* L.) production for Guárico and Portuguesa, respectively (M.P.P.A.T. 2007), and monoculture is the most common agricultural practice. Regional cultivation practices include tillage (T, 30 %) and no-tillage (NT, 70 %) (Piñango et al. 2001) with some regional differences in residue management before planting.

### Soil management

For T management, farmers plow soils by means of a roto tiller to incorporate crop residues in the first 30 cm of depth, while for NT two procedures are followed: (1) Tierra Nueva farm (Guárico State): 2 days before planting, crop residues are treated with the herbicide Glyphosate [*N*-(phosphonomethyl)glycine] and insecticides Deltakill (Deltametherin) and Lannate-L (methomyl) and (2) Nardini farm (Portuguesa State): crop residues are burned 3 months before planting. Table 1 shows the soil management, fertilization and seeding of the sampling sites in each region. The corn fields ($\sim$1 km$^2$) had received the same land management for at least the previous 7 years. Guárico State agriculture is mainly one crop rotation per year [maize or sorghum (*Sorhum* spp.)], and after harvesting residues are used for animal feed. Portuguesa State soils have 3–4 crop rotations per year [maize, sorghum, sunflower (*Helianthus annuus*), and sesame (*Sesamum indicum* L.)]. For both sites, we chose adjacent sampling sites for T and NT measurements in order to have the same meteorological conditions.

**Table 1** Sampling period, fertilizer type and amount applied on the corn fields

| | Guárico-2005 | Guárico-2006 | Portuguesa-2007 |
|---|---|---|---|
| Sampling period | 31 May–8 July | 31 May–29 July | 14 May–11 July |
| Corn field agricultural practices | No-tillage (NT-05) | No-tillage (NT-06) | No-tillage (NT-07) |
| | | Tillage (T-06) | Tillage (T-07) |
| First fertilization and seeding | 2 June | T-06: 1 June | 23 May |
| | | NT-06: 2 June | |
| Fertilizer type | NPK | NPK/MgO, S | NPK/S |
| | (12:24:12) | T-06:(13:18:16/3,3) | (10:20:20/4) |
| | | NT-06:(12:25:12/3,3) | |
| kgN ha$^{-1}$ | 54 | T-06:65 | 30 |
| | | NT-06:56 | |
| Second fertilization | 3 July | 8–9 July | 13 and 21 June |
| Fertilizer type | $NH_4NO_3$ | $NH_4NO_3$ | Urea |
| kgN ha$^{-1}$ | 46 | 58 | 92 (46 each) |
| Total fertilizer, kgN ha$^{-1}$ | 100 | 114–123 | 122 |

### Field measurements

Measurements were made in corn fields under T and NT management at both sites during the crop-growing season (May–July of each year). In Guárico State, two corn fields under NT during 2005 (NT-05) and 2006 (NT-06) and one under T in 2006 (T-06) were measured. In Portuguesa State, two corn fields were measured in 2007: T (T-07) and NT (NT-07).

We selected a sampling area within each site, approximately 150 m away from the access road. Each sampling area consisted of eight PVC rings

(10 cm height × 26 cm diameter) placed randomly (in furrows and beds) and inserted at ~2 cm depth after fertilization and seeding of T and NT sites. Daily measurements of NO, $N_2O$ and $CO_2$ emissions as well as soil water content were made over a 2-month period. Soil samples (0–10 cm) were collected every 2 days to measure soil nitrate and ammonium concentrations and pH; some of these soil samples were also used to measure total C (TC) and total N (TN). A weather station (Campbell Scientific) was placed in a clear area near the corn fields in order to monitor precipitation, air temperature, wind direction and speed and solar irradiance during the field campaign. Table 2 shows the measured soil properties of each sampling area.

*Gaseous soil emissions*

Nitrous oxide soil emissions were measured using the closed chamber technique (PVC base and chamber) (Vitousek et al. 1989). Gas samples were taken using 20-ml silicone or glass syringes provided with stopcocks at 1, 10, 20 and 30 min after chamber closure. Five chambers per site were measured daily. Concentrations of $N_2O$ were determined using a Shimadzu GC-8A gas chromatograph equipped with an electron capture detector at 375 °C, with a Porapak Q (2 m) column and $N_2$ UHP as carrier gas. Two $N_2O$ standard calibration gases (320 and 800 ppbv manufactured by Scott-Marrin, Inc.; cylinder nos. LL111578 and LL58856, respectively) were used. Emissions of $N_2O$ (expressed as ng N $cm^{-2}$ $h^{-1}$) were calculated

**Table 2** Soil properties of T and NT corn fields in each campaign (0–5 cm of depth)

| | Guárico State | | | Portuguesa State | |
|---|---|---|---|---|---|
| | 2005 | 2006 | | 2007 | |
| | NT | T | NT | T | NT |
| Sand (%) | 18 | 24 | 28 | 34 | 25 |
| Clay (%) | 45 | 50 | 48 | 11 | 17 |
| Slit (%) | 37 | 26 | 24 | 55 | 58 |
| Textural class | Clay | | | Silt loam | |
| Soil classification | Vertisols | | | Inceptisols | |
| Bulk density[a] (g $cm^{-3}$) | 1.5 ± 0.1 (3) | 1.19 ± 0.05 (3) | 1.45 ± 0.05 (3) | 1.4 ± 0.1 (3) | 1.51 ± 0.05 (3) |
| $[NO_3^-]$[a] (μg N $g^{-1}$) | 39 ± 49 (65) | 28 ± 38 (79) | 32 ± 56 (68) | 21 ± 22 (111) | 13 ± 12 (111) |
| $[NH_4^+]$[a] (μg N $g^{-1}$) | 41 ± 91 (65) | 48 ± 153 (79) | 62 ± 169 (68) | 2 ± 13 (111) | 21 ± 92 (111) |
| Total N[a] (%) | 0.24 ± 0.05 (40) | 0.23 ± 0.05 (25) | 0.25 ± 0.06 (20) | 0.17 ± 0.01 (22) | 0.18 ± 0.01 (26) |
| Total C[a] (%) | 2.7 ± 0.5 (40) | 2.8 ± 0.5 (25) | 2.8 ± 0.7 (20) | 2.1 ± 0.1 (22) | 2.1 ± 0.2 (26) |
| C/N[a] | 11 ± 1 (40) | 12 ± 1 (25) | 11 ± 1 (20) | 12.0 ± 0.4 (22) | 11.4 ± 0.6 (26) |
| pH ($H_2O$)[a] | NA[b] | 5.8 ± 0.4 (239) | 6 ± 1 (233) | 7.8 ± 0.5 (134) | 7.7 ± 0.4 (134) |
| Soil temp.[a] (°C) | 29 ± 2 (498) | 28 ± 2 (344) | 28 ± 1 (334) | 29 ± 3 (198) | 29 ± 2 (202) |
| Gravimetric soil moisture[a] (%) | 28 ± 6 (110) | 18 ± 2 (244) | 18 ± 2 (232) | 12 ± 3 (7,278) | 16 ± 4 (7,268) |
| Water-filled pore space[a] (%) | 97 ± 6 (110) | 39 ± 2 (244) | 58 ± 3 (232) | 36 ± 5 (7,278) | 56 ± 6 (7,268) |

*NT* no tillage, *T* tillage land management

[a] Mean ± SD (*n*),

[b] NA = nonavailable

using the rate of $N_2O$ concentration increase after chamber closure.

Nitric oxide and carbon dioxide emissions were measured using a dynamic chamber technique (PVC base and chamber) (Keller and Reiners 1994). Eight chambers per site were measured daily. We analyzed NO mixing ratios in the chambers by means of a chemiluminescence $NO_x$ Analyzer (model LMA-3D) manufactured by Scintrex, Inc., which was calibrated daily (before use) by means of a dilution system (flow box) with a NO standard calibration gas of 990 ppb (Scott Specially Gases, PA 18949-0310). We measured $CO_2$ with a nondispersive infrared (NDIR) analyzer (LICOR-820) that was connected in series to the LMA-3D. The NDIR analyzer used a reference channel where there was no $CO_2$ absorption (filter with a center wavelength at 3.95 μm), and we selected the operation range of 0–2,000 ppm for calibration. This portable equipment allowed continuous measurements (minimum response time is 0.2 s). Data were recorded in datalogger model DAS 1245 (Datastick Systems, Inc.) and stored in a handheld computer (Palm OS 3.5, Zire 72 model) by means of commercial software (Connection Datastick DAS-1245, version 3.06). Gas fluxes were calculated using the rate of NO and $CO_2$ concentration increase after chamber closure. Emissions were expressed as NO-N (ng N $cm^{-2}$ $h^{-1}$) and $CO_2$-C (μg C $cm^{-2}$ $h^{-1}$).

*Soil measurements*

Soil samples between 0 and 100 cm of depth ($n = 3$ for each depth) were taken to determine bulk density (core method, Blake and Hartge 1994) and soil texture (hydrometer method, Gee and Bauder 1994).

For Guárico State (2005 and 2006 campaigns), gravimetric soil water content ($\theta g$) was determined by taking soil samples (3 per plot) between 0 and 2 cm depth near each PVC base. Soil aliquots (10 g duplicate samples) were oven dried at 105 °C for 48 h and stored in desiccators until reaching a constant weight. For Portuguesa State sampling in 2007, soil water content was measured volumetrically ($\theta v$) using soil moisture sensor ECH$_2$O Decagon Devices, model EC-5. Sensors were placed at a depth of 2 cm inside each PVC base (8 for each plot) and measured the variation in soil water content every 10 min.

Water-filled pore space (WFPS) was calculated according to Saxton et al. (1986) from the upper 0–2 cm layer using Eq. 1, where $\theta g$ and $\theta v$ are the average water content values of each plot during the sampling period calculated gravimetrically and volumetrically, respectively; BD is the mean bulk density value, and PD is the particle density assumed as 2.61 g per dry soil gram (g $dsg^{-1}$) (Davidson and Schimel 1995).

$$\%\text{WFPS} = \left(\frac{\theta g \times \text{BD}}{1 - \left(\frac{\text{BD}}{\text{PD}}\right)}\right) \times 100 = \left(\frac{\theta v}{1 - \left(\frac{\text{BD}}{\text{PD}}\right)}\right) \times 100 \quad (1)$$

Soil samples between 0 and 10 cm depth (3 for each plot) were taken every other day to measure the concentrations of inorganic N as nitrate ($NO_3^-$) and ammonium ($NH_4^+$), pH and TC and TN. Soil N was extracted with 2 M KCl (10 g soil in 100 ml KCl) on a shaker for 1 h. Samples were then centrifuged (30 min at 3,000 rpm) and filtered (Whatman 42). Inorganic N concentrations were analyzed colorimetrically on a continuous flow analyzer (Autoanalyzer II, Technicon Instrument Corp.): nitrate by the cadmium reduction and the Griess-Ilosvay method and ammonium by the indophenol blue method (Sparks et al. 1996a). Soil pH was measured with a calibrated digital pH meter (Thermo Orion, model 420) using 10 g of soil per 10 ml of deionized water and shaken for 20 min. It stood for 5 min before measurement (Sparks et al. 1996c). For TC and TN, soil samples without roots or vegetation remnants were homogenized, dried at 60 °C for 48 h, sieved (2 mm) and ground before being measured using an elemental analyzer (FISON, model 1108) (Sparks et al. 1996b, d).

*Enzyme characterization*

Dehydrogenase was measured according to Casida et al. (1964). For this, 1 g of soil (wet weight) was dissolved in 0.25 ml of 2,3,5-triphenyltetrazolium chloride (TTC) and 0.5 ml of distilled water and then incubated at 37 °C for 24 h in darkness. Using methanol as solvent, dissolved dehydrogenase was measured spectrophotometrically at 485 nm. For each determination, a control solution was made following the same procedures but without substrate addition. Dehydrogenase activity was expressed as micrograms of triphenilformazan per dry soil gram (μg TPF $dsg^{-1}$).

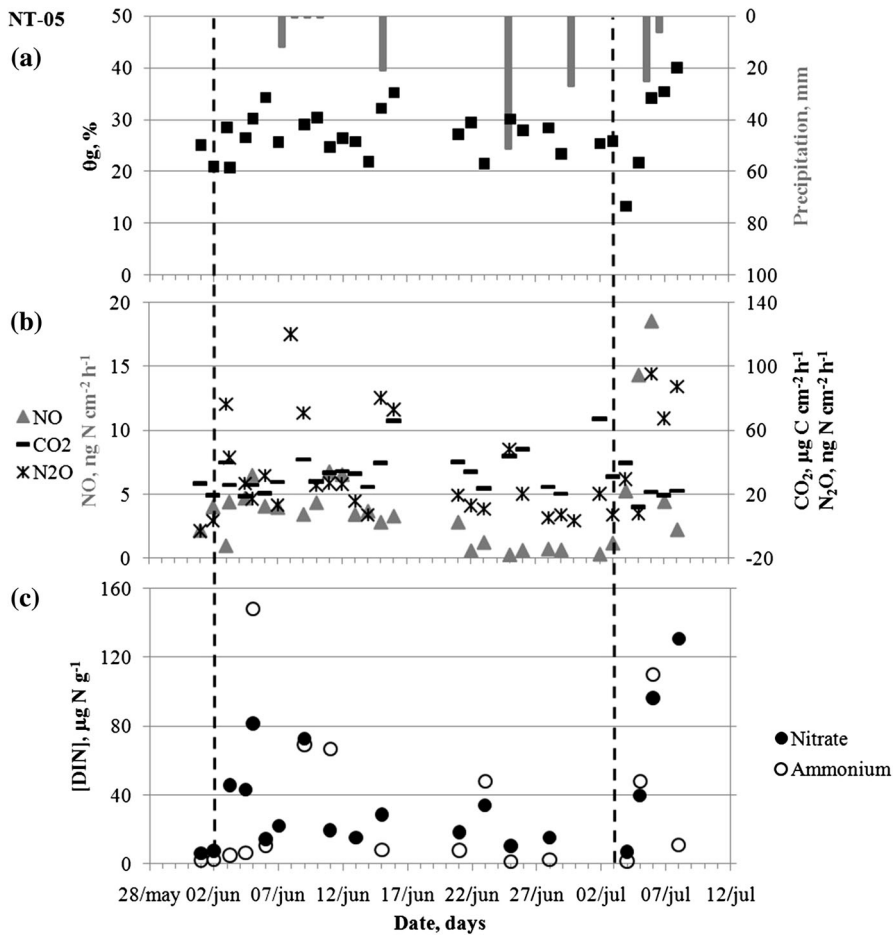


**Fig. 1** **a** Soil gravimetric water content and precipitation events, **b** daily median values of NO, $N_2O$ and $CO_2$ soil emissions, and **c** daily mean values of nitrate and ammonium soil concentrations during the sampling time of the NT-05 corn field. *Dashed black lines* indicate fertilization events

Statistical analysis

Kolmogorov-Smirnov tests were performed to verify normal distribution of the data. Correlations between trace gas fluxes (or their logarithm) and other variables (soil water content, nutrient soil concentrations, pH, soil temperature and precipitation, among others) were determined using SPSS Statistic 17 by means of Pearson and Spearman coefficients. Trace gas emission data were analyzed using a one-way ANOVA in order to determine statistical differences between sites.

## Results

Trace gas soil emissions

At all sites, fluxes of $N_2O$ were higher than NO fluxes under both T and NT management with $N_2O$/NO ratios between 2 and 9 (Figs. 1, 2, 3; Table 3). T treatment caused NO and $CO_2$ soil emissions to be significantly larger ($p < 0.05$) at T sites (T-06 and T-07) than NT sites (NT-05, NT-06 and NT-07), but the opposite was found for $N_2O$ fluxes (Figs. 1, 2, 3; Table 3). Temporal variation of gas fluxes occurred at all sites. In general, NO fluxes were higher after the second fertilization, while the highest $N_2O$ fluxes (or peaks) usually occurred after fertilization and/or after successive rainfall events (Figs. 1, 2, 3). In contrast to NO and $N_2O$ emissions, only $CO_2$ fluxes from the T-06 site were significantly larger ($p < 0.05$) than those from the other sites (Figs. 1, 2, 3; Table 3).

Mean NO, $N_2O$ and $CO_2$ emissions from Guárico corn fields (2005 and 2006) were significantly larger ($p < 0.05$) than those from the Portuguesa corn fields in 2007 (Table 3). The correlation between the logarithm of NO (log(NO)), $CO_2$ (log ($CO_2$)), $N_2O$ (log($N_2O$) fluxes and the other measured soil variables

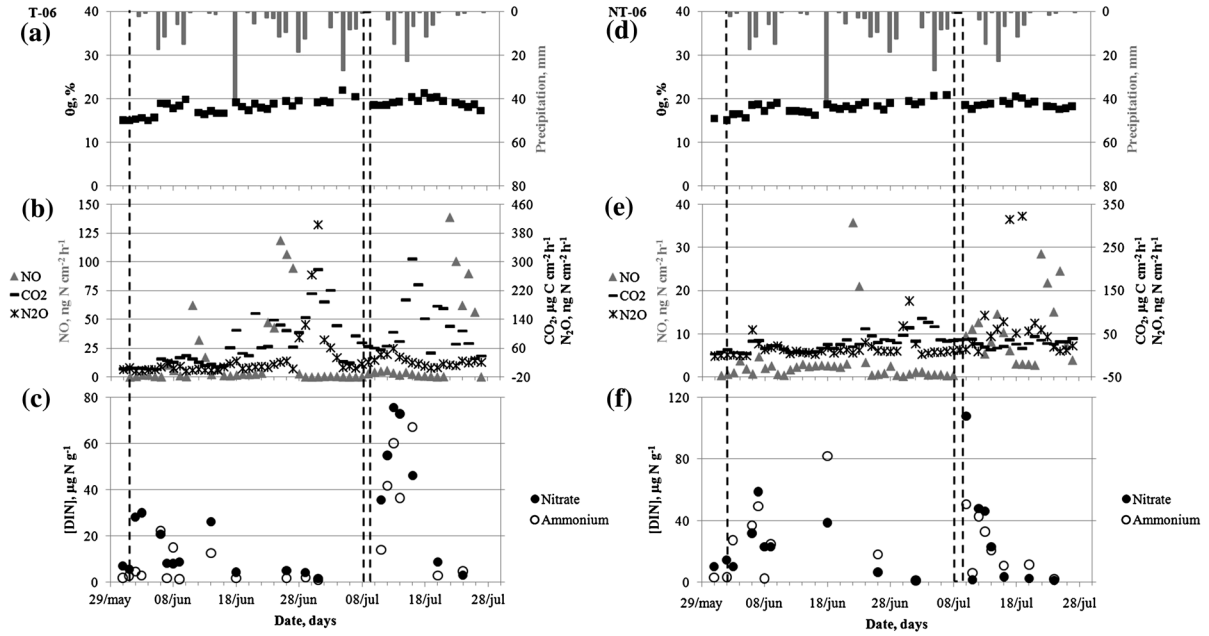


**Fig. 2** **a**, **d** Soil gravimetric water content and precipitation events, **b**, **e** daily median values of NO, $N_2O$ and $CO_2$ soil emissions, and **c**, **f** daily mean values of nitrate and ammonium soil concentrations during the sampling time of T-06 (**a–c**) and NT-06 (**d–f**) corn fields. *Dashed black lines* indicate fertilization events

was calculated, with both significant positive and negative correlations (Table 4).

## Soil measurements

In general, NT crops had higher gravimetric soil moisture than T (Figs. 1, 2, 3; Table 2), probably because of larger soil compaction. Gravimetric soil moisture contents at all sites were positively correlated with soil inorganic N concentrations, precipitation and clay content, but negatively correlated with soil pH, sand and silt contents (Table 4).

T did not affect soil inorganic N or TC and TN concentrations. For Guárico crops (NT-05, T-06 and NT-06) $NO_3^-$ and $NH_4^+$ soil concentrations were similar (Figs. 1, 2). In Portuguesa crops, T-07 site soil had larger concentrations of $NO_3^-$ than $NH_4^+$ (Fig. 3c), whereas the opposite was found for the NT-07 site (Fig. 3f). Larger $NO_3^-$ and $NH_4^+$ soil concentrations were found for all Guárico crops in comparison to Portuguesa crops (Table 2). No differences in TC, TN and C/N ratios were found among all sites (Table 2). Soil inorganic N was correlated with log(NO), log($N_2O$), soil moisture, WFPS, soil pH and clay, sand and silt contents (Table 4).

## Dehydrogenase enzyme activity

In 2006 in Guárico State, the average dehydrogenase activity value at 0–5 cm depth was significantly larger ($p < 0.05$) at the NT-06 site ($245 \pm 20$ µg TPF $dsg^{-1}$, $n = 108$) than at the T-06 site ($95 \pm 6$ µg TPF $dsg^{-1}$, $n = 108$). In contrast, at the Portuguesa sites in 2007 there were no differences between T and NT treatments. When averaged across the regions, Guárico crop soils had more ($p < 0.05$) dehydrogenase enzyme activity ($170 \pm 11$ µg TPF $dsg^{-1}$) compared with the Portuguesa crop soils ($108 \pm 5$ µg TPF $dsg^{-1}$).

# Discussion

Studies in tropical cultivated soils have shown an NO and $N_2O$ soil emission increase as a consequence of N-fertilizer application, T and crop type (Stehfest and Bouwman 2006; Snyder et al. 2009; Marquina et al. 2013 and references therein). Similarly, soil respiration and C storage are affected by land management, which in turn influences soil $CO_2$ emissions (Sanhueza and Santana 1994; Passianoto et al. 2004; Mosier et al.

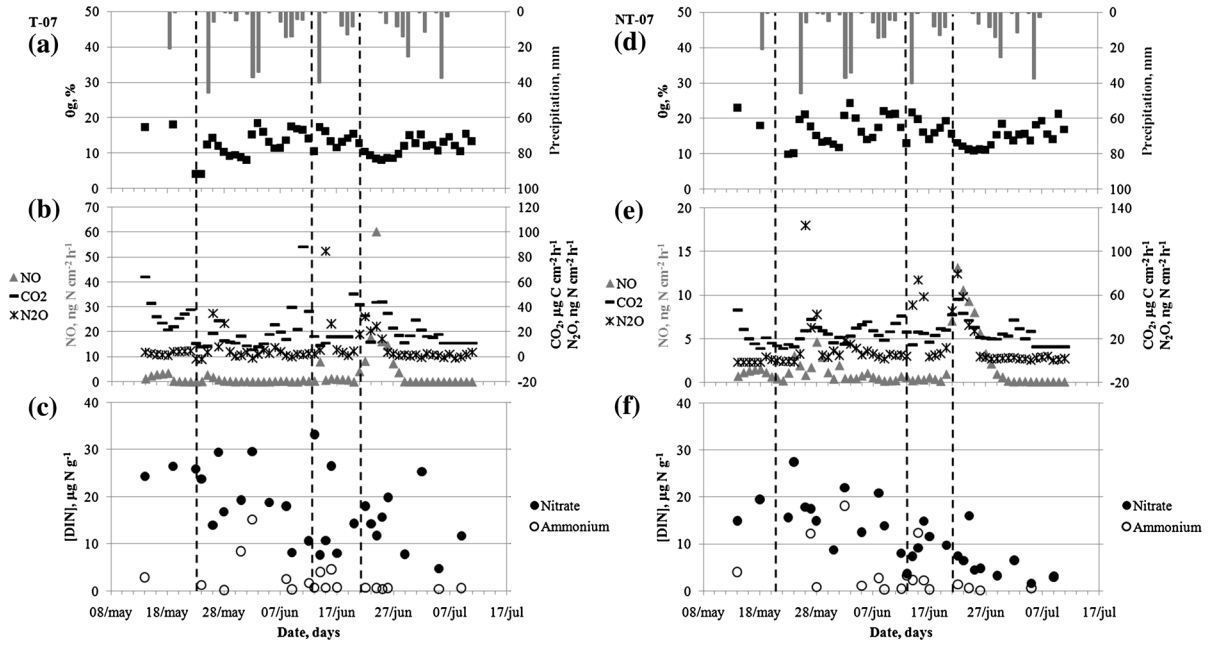


**Fig. 3** **a**, **d** Soil gravimetric water content and precipitation events, **b**, **e** daily median values of NO, $N_2O$ and $CO_2$ soil emissions, and **c**, **f** daily mean values of nitrate and ammonium soil concentrations during the sampling time of the T-07 (**a**–**c**) and NT-07 (**d**–**f**) corn fields. *Dashed black lines* indicate fertilization events

2005, 2006; Baggs et al. 2006; Liu et al. 2006; IPCC 2013). Rates of total soil and plant respiration and soil microbial activity can be ascertained from soil $CO_2$ fluxes. We found $CO_2$ fluxes are positively correlated with both NO and $N_2O$ fluxes (Table 4), which is consistent with the influence of microbial activity on trace gas emissions (Kiese and Butterbach-Bahl 2002; Garcia-Montiel et al. 2004; Ishizuka et al. 2005; Neill et al. 2005; Baggs et al. 2006).

The increase in these trace gas emissions is mainly derived from soil decomposers, nitrifying and denitrifying bacterial activity. This microbial activity is influenced by soil variables such as N and C contents, moisture, pH, temperature, texture and land management, which in turn affect the magnitude of NO, $N_2O$ and $CO_2$ emissions from crop soils. Nevertheless, field conditions often override the individual effect of any soil variable on trace gas emissions (Gödde and Conrad 2000), which makes identifying the main variables responsible for the emissions harder. In this current study, land management, N fertilization, soil moisture and texture were identified as the main variables that regulate the trace gases emitted.

## Influence of land management and fertilization on trace gas soil emissions

Similar to other studies, we found larger NO fluxes and lower $N_2O$/NO ratios under T than from NT soils (Table 3) (Sanhueza et al. 1994; Passianoto et al. 2004; Pinto et al. 2004; Liu et al. 2005, 2006; Pérez et al. 2007) and larger $N_2O$ fluxes and $N_2O$/NO ratios from NT than from tilled soils (Table 3) (Grageda-Cabrera et al. 2004; Liu et al. 2006; Rochette 2008; Jian-She et al. 2011). The Liu et al. (2006) study was done in a continuous corn rotation in northeastern Colorado (with 224 kgN $ha^{-1}$ applied as liquid urea-ammonium nitrate). Although their N application was twice as much as in the current study, lower fluxes were obtained, probably because of the climatic conditions (semiarid vs. tropical region) and also N-fertilizer placement (deep injected vs. superficial). These results suggest that T promotes soil-atmosphere NO exchange, possibly because of the larger porosity in comparison to NT soils (confirmed by soil bulk density values; Table 2) and a higher resulting oxygen availability that enhances organic matter decomposition and NO production by means of aerobic microbial

**Table 3** Mean average and range of NO, $N_2O$ and $CO_2$ emissions from the evaluated corn field soils

| Region | Management | NO (ng N $cm^{-2}$ $h^{-1}$) | $N_2O$ (ng N $cm^{-2}$ $h^{-1}$) | $CO_2$ (μg C $cm^{-2}$ $h^{-1}$) | $N_2O$/NO* |
|---|---|---|---|---|---|
| Guárico State | NT-05 | 7 ± 16 (499) | 43 ± 57 (206) | 33 ± 20 (491) | 6 |
| | | [0.1–75][a] | [−51–371][a] | [0.7–107][a] | |
| | T-06 | 19 ± 41 (337) | 31 ± 79 (238) | 89 ± 108 (350) | 2 |
| | | [0.1–189][b] | [−30–687][a] | [0.7–682][b] | |
| | NT-06 | 6 ± 10 (343) | 52 ± 135 (228) | 33 ± 43 (346) | 9 |
| | | [0.03–61][a] | [−18–1,480][b] | [1.3–548][a] | |
| Portuguesa State | T-07 | 3 ± 10 (213) | 8 ± 20 (199) | 29 ± 29 (217) | 3 |
| | | [0.02–78][c] | [-36–172][c] | [3.1–162][a] | |
| | NT-07 | 3 ± 6 (221) | 21 ± 42 (203) | 43 ± 86 (216) | 7 |
| | | [0.02–51][c] | [−8–302][d] | [4.1–849][a] | |
| Average | NT | 6 ± 13 (1,063) | 39 ± 91 (637) | 35 ± 48 (1,053) | 7 |
| | | [0.02–75][A] | [−51–1,480][A] | [0.7–849][A] | |
| | T | 13 ± 34 (550) | 21 ± 61 (437) | 66 ± 91 (567) | 2 |
| | | [0.02–189][B] | [−36–687][B] | [0.7–682][B] | |

Mean ± SD (n), [range]. In the same column, different lower case superscripts indicate significant differences between sampling sites; significant differences between land managements are indicated with different capital superscripts

*NT* no-tillage land management, *T* tillage land management

* Mean values

reactions (Firestone and Davidson 1989; Wrage et al. 2001). The larger WFPS values and soil bulk densities found in NT than T sites (Table 2) support Liu et al.'s (2005) idea that two possible mechanisms for the largest NO emissions from T in comparison to NT soils are related to: (1) more NO consumption induced by a denitrification reaction due to more water content in NT soils and (2) compaction and high soil moisture in NT-limited NO diffusion. Also, soil compaction in NT soils promoted anaerobic conditions (more water retention and low oxygen availability, Linn and Doran 1984), which favor $N_2O$ production via denitrification or nitrate ammonification microbial reactions (Firestone and Davidson 1989; Baggs 2011). In fact, $N_2O$ production by denitrification is mainly from the hot spot of microbial activity, and management influence (T vs. NT), residue incorporation and compaction can influence the size and distribution of these hot spots (Ball 2013). Even if soil T promotes gas diffusion, it is necessary to consider the production sites of these gases. Ball (2013) proposes that the largest $N_2O$ emissions from NT are due to production sources of $N_2O$ closer to the soil surface.

Other tropical agroecosystem studies have shown no difference between N trace gases from T and NT soils (Sanhueza et al. 1994; Passianoto et al. 2004; Pinto et al. 2004; Liu et al. 2005, 2006; Pérez et al. 2007). These and our results suggest that a complex interaction of processes governing N oxide emissions (production sites, diffusion, microbial activity) produces a contrasting effect of land management on NO and $N_2O$ emissions. We therefore suggest that for national and regional N trace gas flux estimates, other variables additional to soil management need to be considered; particular attention should be given to fertilizer application (composition, rate and timing), clay and water contents (see section below).

Soil T enhanced $CO_2$ fluxes from the Guárico soils in comparison to those from NT crops, which is consistent with findings in other temperate and tropical studies (Passianoto et al. 2004; Baggs et al. 2006; Bauer et al. 2006; Álvaro-Fuentes et al. 2007; Carmo et al. 2007; Chatskikh and Olesen 2007; Bono et al. 2008; Jabro et al. 2008; Akbolat et al. 2009; Almaraz et al. 2009). Thus, the large $CO_2$ emissions from the Guárico T-06 site could be attributable to an increase of (1) soil total porosity enhancing gas diffusion, (2) root respiration (by a larger soil-atmosphere exchange) and (3) perturbation of soil aggregates and the previously protected organic matter becoming available for decomposition (Paul 2007;

**Table 4** Significant Pearson coefficients for variables measured

| | log(NO) | $log(NO_2)$ | $log(CO_2)$ | $NO_3^-$ | $NH_4^+$ | TIN | *g* | WFPS | pH | Precipitation | Clay | Sand | Silt |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| log(NO) | 1 | | | | | | | | | | | | |
| $log(NO_2)$ | 0.420** | 1 | | | | | | | | | | | |
| $log(CO_2)$ | 0.282** | 0.442** | 1 | | | | | | | | | | |
| $NO_3^-$ | 0.222* | 0.278** | | 1 | | | | | | | | | |
| $NH_4^+$ | 0.218* | 0.260** | | 0.541** | 1 | | | | | | | | |
| DIN | 0.250** | 0.297** | | 0.842** | 0.909** | 1 | | | | | | | |
| *g* | 0.172** | 0.297** | 0.279** | 0.431** | 0.295** | 0.380** | 1 | | | | | | |
| WFPS | | 0.357** | | 0.377** | 0.287** | 0.355** | 0.903** | 1 | | | | | |
| pH | −0.438** | −0.303** | −0.228** | −0.297** | | −0.263* | −0.577** | | 1 | | | | |
| Precipitation | | | | | | | 0.261** | 0.298** | | 1 | | | |
| Clay | 0.445** | 0.457** | 0.278** | 0.278** | 0.264** | 0.304** | 0.546** | 0.280** | −0.930** | | 1 | | |
| Sand | −0.264** | −0.242** | −0.243** | −0.219* | −0.301** | −0.288** | −0.723** | −0.640** | 0.459** | | −0.582** | 1 | |
| Silt | −0.428** | −0.411** | −0.242** | −0.249** | −0.203* | −0.255** | −0.390** | | 0.926** | | −0.961** | 0.335** | 1 |

*DIN* = $NO_3^-$ + $NH_4^+$ soil concentrations

* Significance at the 0.05 probability level; ** significance at the 0.01 probability level

La Scala et al. 2008). On the other hand, $CO_2$ fluxes from T and NT corn fields from the Portuguesa sites did not show significant differences (T-07 and NT-07; Table 3) because of their higher land management intensity (up to 4 crop rotations per year for 40 years). Higher $CO_2$ emissions from one rotation per year soils than those from more than one crop rotation per year (for example, maize-soybean (*Glycine max* L.), Amos et al. 2007) are associated with larger soil C and N losses (Stevenson and Cole 1999a). The larger dehydrogenase enzyme activity in the Guárico soils compared to that found in the Portuguesa crop soils is consistent with greater land management intensity in the latter, given that this enzymatic activity is an indicator of soil microbial organic matter decomposition activity and soil biomass availability (Stevenson and Cole 1999b). For this, Guárico State crop soils (one crop rotation per year) have larger microbial activity related to soil decomposition than those from Portuguesa State (3–4 crop rotations per year), in turn affecting the magnitude of the trace gas emissions evaluated here (Table 3). The combination of microbial activity (influenced by land management intensity), fertilization regimes and N application rates within each region (e.g., application of ammonium nitrate in Guárico State) induced larger N losses from Guárico soils (3.4–6.1 % as $N_2O$ and 0.6–2.1 % as NO) than those from Portuguesa soils (0.8–6.1 % as $N_2O$ and 0.26–0.34 % as NO) (Marquina et al. 2013).

Our results support the view that the N content is also an important soil variable controlling $N_2O$ and NO production and emissions (Firestone and Davidson 1989; Davidson et al. 2000), as evident from the positive correlation of $N_2O$ and NO emissions with $NH_4^+$ and $NO_3^-$ (Table 4). The N-fertilizer application method (superficial or buried in soil furrows), fertilizer chemical formulation and also N-fertilizer rate influenced the magnitude of trace gas emissions from our crop soils (Marquina et al. 2013) mainly because of enhancement in soil microbial activity (nitrification and denitrification). Park et al. (2011), by means of a $^{15}N$ natural abundance stable isotope study evaluated in the NT-05 site (same sampling of this study), found that nitrifying denitrification might be the most important process related to $N_2O$ production from this Guárico State soil. In order to find general trends, we compared variables of all the data of this current study and found a positive correlation between the log(NO + $N_2O$) and soil $NO_3^-$ concentrations

(Fig. 4), and also $N_2O/NO$ ratios >1 (Table 3), suggesting that denitrification could be the main microbial reaction responsible for producing NO and $N_2O$ in our corn fields. Similar correlations were found in the forests of Brazil, Costa Rica and Puerto Rico, where variations in NO and $N_2O$ emissions with the indexes of N availability can be used as proxies in the hole-in-the-pipe model (Davidson et al. 2000). Similarly to the Davidson et al. (2000) and Davidson and Verchot (2000) studies, we found a positive correlation between $\log(NO + N_2O)$ and soil nitrate ($p < 0.01$) (Fig. 4), although our slope was smaller. This smaller effect in our study is probably derived from the influence of intensive agriculture on the size and distribution of production sites (Ball 2013) and N being an infinite pool in fertilized crop soils. Our larger fluxes of NO and $N_2O$ from Guárico soils related to larger soil $NO_3^-$ concentrations imply that when nitrate is the dominant form of inorganic N, there is an excess of N relative to the ability of plants and microorganism to assimilate $NO_3^-$; therefore, an open and leaky N cycle that promotes $NO_3^-$ leaching and generally enhances N gas emissions is found (Davidson et al. 2000).

## Influence of soil moisture and texture on trace gas soil emissions

All trace gas emissions evaluated in this study were positively correlated with soil water and clay contents but negatively correlated with sand and silt contents (Table 4). Clay soils promote optimal conditions for production and emission of these trace gases, which is consistent with findings in other studies (Weier et al. 1996; Silver et al. 2000; Skiba and Ball 2002; Ball 2013). Clay soils also exhibit higher initial concentrations of $NO_3^-$, greater rates of potential net $NO_3^-$ production (Silver et al. 2000), and also a larger WFPS and total denitrification than other soil textures (Weier et al. 1993). The positive correlation found between gas fluxes and clay content could be related to the positive correlation between inorganic N concentrations and clay contents (Table 4), which provides larger nutrient availability for microbial activity (denitrification) in clay soils. Also, NO, $N_2O$ and $CO_2$ soil emissions from Portuguesa State corn fields were lower than those from Guárico State (Table 3), probably because of the lower clay content and derived lower nutrient concentrations of Portuguesa crop soils (Table 2).

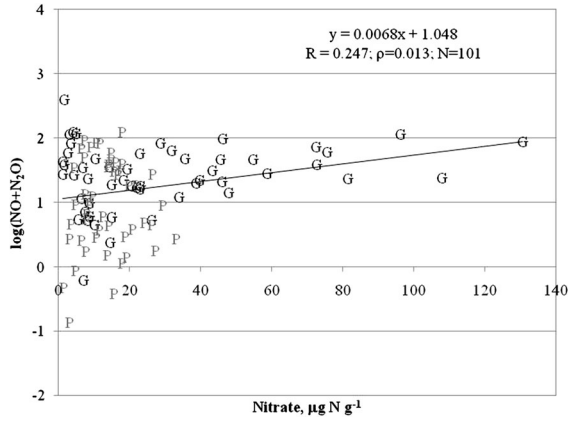


**Fig. 4** Logarithm of NO plus $N_2O$ emissions ($\log(NO + N_2O)$) versus soil nitrate concentrations. *G* Guárico soils and *P* Portuguesa soils

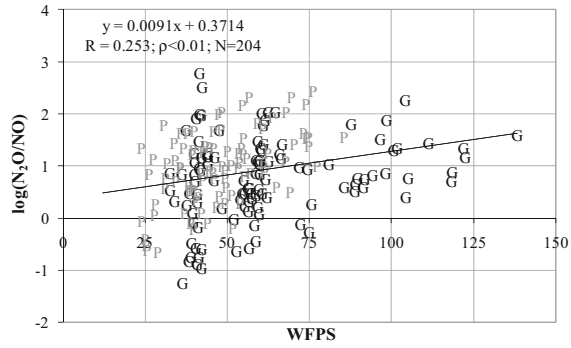


**Fig. 5** Logarithm of the ratio of $N_2O$ and NO emissions ($\log(N_2O/NO)$) as a function of the percentage of WFPS. *G* Guárico soils and *P* Portuguesa soils

Soil moisture was affected by land management. In general, WFPS values were twice higher in NT than in T soils, confirming that NT management enhanced soil water retention (Chapius-Lardy et al. 2009). However, during the crop-growing season, in all evaluated soils, WFPS values were optimal for both nitrification and denitrification reactions to occur (Davidson et al. 2000). We found a positive correlation between $\log(N_2O/NO)$ and WFPS (Fig. 5) supporting the idea that soil moisture is an important factor controlling NO and $N_2O$ emissions as found elsewhere (Davidson et al. 2000; Davidson and Verchot 2000). For our crop soils, the ratio of $N_2O/NO$ was 1 when WFPS equaled 69 % (Fig. 5), which contrasts with the results of Davidson et al. (2000) ($N_2O/NO = 1$ when WFPS = 63 % for tropical forest soils). Again, we

proposed that intensive agriculture is changing the variables that govern soil emissions of these trace gases compared to those found for natural ecosystems. Then, considering (1) $N_2O/NO$ ratios >1, (2) the positive correlations between $\log(NO + N_2O)$ and $NO_3^-$, and (3) the positive correlation between $\log(N_2O/NO)$ and WFPS, we reiterate that denitrification is the largest contributing microbial reaction to the trace gas production in these soils.

The largest $CO_2$ emissions from the T-06 site (Guárico State) (Table 3) could be attributable to shrinking and cracking of clayed soils when dry (Sabburg et al. 1997), and also to soil T, as mentioned in the previous section. Both situations promote high gas diffusion and high oxygen availability, which in turn enhance organic matter decomposition and produce $CO_2$. Also, the T-06 site had the largest clay content, which allows water retention and promotes soil respiration.

## Conclusions

Trace gas emissions from Venezuelan corn fields are affected largely by N application, as found in most studies. However, trace gas magnitude differences are also influenced by land management, soil moisture and clay content. In general, T sites had the highest values of NO and $CO_2$ fluxes, implying that this agricultural practice, besides contributing to soil erosion, also increases the emission of trace gases of atmospheric importance, as has been suggested previously. Additionally, NT agricultural practice could be adopted as a better option for soil fertility, but its effect on $N_2O$ emissions, which are larger, needs to be addressed for mitigation strategies, such as reduction of the applied N fertilizer. For this, it is necessary to examine not only the effect of soil T, but also all variables related to intensive agriculture, such as the N-fertilization rate, chemical composition, placement and timing, crop varieties and rotation, and previous soil treatment, among others. The results from this study can be applied to estimate the national GHG inventory based on the N fertilization application rate, soil texture and water content from Venezuelan agricultural crops.

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