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Gross, Background, and Net Anthropogenic Soil Nitrous Oxide Emissions from Soybean, Corn, and Wheat Croplands

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Abstract

Agricultural soils are the largest single source of N_2O emissions globally. However, soils left uncultivated would still release N_2O. Distinguishing anthropogenic from natural emissions (i.e., background emissions) in crops is important if we want to assess the net effect of human activity. This study aimed to characterize N_2O emissions from croplands and unmanaged grasslands to estimate the net anthropogenic emissions and to gain a better insight into their main drivers. We established a replicated manipulative field experiment in the Pampas Region of Argentina to quantify soil N_2O emissions from corn (*Zea mays* L.), wheat (*Triticum aestivum* L.), and soybean [*Glycine max* (L.) Merr.] crops, and from adjacent unmanaged grassland plots for 1 yr. We also analyzed the main controls of N_2O emissions and the correlation between the normalized difference vegetation index (NDVI) and N_2O fluxes. Background emissions represented between 21 and 32% of total emissions from croplands, depending on crop type. No differences were detected in N_2O emissions between total and background during winter and peak crop growing season. NDVI showed a significant correlation with N_2O fluxes which was positive in grasslands and negative in growing season of soybean crops. Our results showed that N_2O emissions from croplands were higher than background emissions, but also that background represented an important fraction of cropland emissions. Higher emissions in croplands occurred during pre-seeding, after harvest, and after N fertilization in fertilized crops. In addition, our study informs about N_2O emissions from crops and unmanaged systems in South America where field data are very scarce.

Core Ideas

- We measured soil N_2O emissions in South America where field data are very scarce.
- Nonanthropogenic fluxes represented 21 to 32% of crop N_2O emissions.
- NDVI, a plant productivity index, improved seasonal estimation of N_2O flux.

Human activities are changing ecosystems dramatically, with nearly 40% of the natural terrestrial surface already replaced by croplands or pastures (Tilman et al., 2001). Human activities are increasing the concentration of N_2O in the atmosphere, one of the largest stratospheric ozone-depleting substances and an important greenhouse gas (Ravishankara et al., 2009; IPCC, 2013). Most N_2O emissions come from soils, where different microorganisms are involved in their production through nitrification and denitrification processes (Firestone and Davidson, 1989). Particularly, agricultural soils are the largest single source of N_2O emissions globally (Tubiello et al., 2015). However, are all N_2O emissions from crops a consequence of human activities?

Agricultural practices stimulate soil N_2O emissions compared with unmanaged soils through N fertilization or cultivation of N-fixing species, cultivation of annual crops (with long fallow periods between growing periods), impacts in the hydrological and N cycle, and changes in microbial structure and functioning (Robertson, 1997; Robertson et al., 2000; Song et al., 2018). However, soils are a net source of N_2O even in the absence of human activities (Firestone and Davidson, 1989). A recent meta-analysis showed that soils under different natural vegetation cover emit a mean value of 1.75 kg N ha^{-1} yr^{-1} with a broad range between −0.5 and 95.2 (Kim et al., 2013). Although many studies have measured N_2O emissions in croplands, surprisingly few have considered the nonanthropogenic or background emissions. Indeed, the concept of background emissions in agriculture has been used in many ways. For example, background was defined as N_2O emissions from unmanaged natural patches (Kessavalou et al., 1998; Perdomo et al., 2008), successional systems (Robertson et al., 2000), set-aside pastures (Ruser et al., 2001; Dusenbury et al., 2008), bare soil, or unfertilized crops (Kim et al., 2013). Similarly, the emission factor methodology accounts for anthropogenic emissions as a fraction of the N added via fertilization and crop residues yearly, so the background concept is partially incorporated (Eggleston et al., 2006). With the aim of defining anthropogenic emissions from production systems, we define

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Abbreviations: GC, gas chromatograph; NDVI, normalized difference vegetation index; SEM, structural equation model; WFPS, water-filled pore space.

background emissions as those that would occur in the absence of (or with minimal) human alteration of ecosystems. As such, we consider as background emissions the emissions from an ecosystem located in the same environmental conditions as the cropland, generally covered with spontaneous vegetation (grasslands, forests, or savanna according to local situations), with no anthropic effect (i.e., unfertilized, ungrazed by domestic herbivores, etc.). In the same way, we define net anthropogenic emissions as the change in N_2O fluxes due to agriculture activity considering the background (i.e., gross emissions from crops minus background emissions).

The regulating factors of soil N_2O emissions have been classified as direct if they control the nitrification or denitrification processes and as indirect if they exert a control on the direct factors (Robertson, 1989). Soil temperature, water-filled pore space (WFPS, a measure of soil moisture and O_2 availability), labile soil C, and soil mineral N are considered the main direct factors (Mosier et al., 1998; Davidson et al., 2000). Soil mineral N requires special attention when analyzing soil N_2O emissions, since both NH_4^+ and NO_3^- represent small and transient pools in soils, with very high turnover (Robertson, 1997). Therefore the correlation between N_2O emissions and soil NH_4^+ or NO_3^- may be weak (Rochette et al., 2004; Gelfand et al., 2016), and estimates of N fluxes (i.e., N mineralization, plant N uptake) rather than N pools may represent better estimates of N_2O emissions (Davidson et al., 2000).

Apart from these direct factors, indirect or distal factors are related to soil properties, weather conditions, plant cover, and land use or crop management (Robertson, 1989; Mosier et al., 1998). Soil temperature and WFPS can exert direct and indirect effects on soil N_2O emissions, affecting NH_4^+ and NO_3^- supply via N mineralization and nitrification (Curtin et al., 2012). Similarly, plant productivity is tightly correlated with mineral N uptake (Bender et al., 2013, 2015), so a measure of plant productivity and its temporal dynamics might represent a useful variable for modeling temporal changes in N_2O emissions. In this way, the normalized difference vegetation index (NDVI; Tucker 1979), a proxy of aboveground net primary productivity, arises as an alternative to enhance N_2O emissions models.

The main objectives of this study were (i) to characterize N_2O emissions from croplands and unmanaged grasslands (considered as background emissions) in commercial (nonexperimental) field conditions to estimate the net anthropogenic emissions; (ii) to investigate the seasonal dynamics of net anthropogenic emissions; and (iii) to gain a better insight of the main drivers affecting N_2O emissions in crops and in unmanaged systems. To achieve these objectives, we established twin manipulative field experiments in two different farms in the Pampas Region of Argentina, one of world's main agricultural regions, with a humid-temperate climate and fertile soils (Hall et al., 1992).

Materials and Methods

Study Sites

The study was performed in two agricultural farms, located 370 km apart, in different subregions of the Pampas grasslands of Argentina: Estancia San Claudio in the Inland Pampas (35°56′ S, 61°10′ W), and Estancia Don David in the Mesopotamic Pampas (33°18′ S, 58°41′ W; Soriano 1992). San Claudio has loam Thapto Argic Hapludolls soils, with a greater sand fraction and higher total C and N contents than Don David, which has silt loam Aquic Argiudolls, with higher clay and P contents. Mean annual precipitation is 1070 mm in Don David and 997 mm in San Claudio. Extra climate and soil information of the study sites is available in Supplemental Table S1. Both subregions are devoted to agriculture production, mainly soybean [*Glycine max* (L.) Merr.], corn (*Zea mays* L.), and wheat (*Triticum aestivum* L.) crops.

Experimental Design

We performed a manipulative field experiment during 1 yr in both farms to estimate N_2O emissions from the main crops and compare them with background emissions from unmanaged grasslands developed under the same environmental conditions. Temperature and precipitation during the experiment were close to average values in both farms (Supplemental Table S1, Supplemental Fig. S2). At each farm, we selected four sites located between 1 and 5 km from each other, which represented statistically independents blocks. Each block contained four plots (25×8 m^2) located one next to the other corresponding to each of the four treatments (Supplemental Fig. S4). The treatments were corn, soybean, double crop wheat–soybean, and unmanaged grassland. Cultivated plots were located within a commercial production field, and the background plot was located adjacent to it, in an unmanaged grassland field (a total of 32 plots, 16 plots in each farm). The double cropping treatment involved a late soybean crop seeded after wheat harvest (early summer), which is a practice widely used in Argentina. The grasslands fields were successional plots that had not been cultivated or fertilized for at least 20 yr (some of them had never been cultivated) and were rarely grazed by cattle. These plots were covered by native and exotic C_3 and C_4 grass species [i.e., *Paspalum dilatatum* Poir., *Paspalum quadrifarium* Lam., *Cynodon dactylon* (L.) Pers., *Bromus unioloides* Vahl, and *Schedonorus arundinaceus* (Schreb.) Dumort.]. Grassland soils had higher total C and lower bulk density than crop soils in both farms (Supplemental Table S1).

All crops were established under no till. Wheat plots received 55 Kg N ha^{-1} at seeding in both farms, whereas corn plots received 60 and 69 Kg N ha^{-1} at seeding in San Claudio and Don David, respectively. Soybean crops at both farms were fertilized with triple superphosphate, without N addition. Fertilizer and herbicide applications were conservative and followed business-as-usual practices for the region. All management practices of crops are detailed in Supplemental Table S3.

The experiment started in August 2012, after wheat seeding, and spanned until August 2013. We measured N_2O emissions with a monthly time step during the whole year. We used the static chamber method (Parkin and Venterea, 2010), and on each sampling date, we established two chambers in each plot (2 farms × 4 blocks × 4 treatments × 2 chambers × 12 dates = 768 gas samples).

Gas Sampling, Collection, and Analysis

To estimate soil N_2O emissions we used plastic chambers deployed on iron bases buried into soil (Supplemental Fig. S5). Plastic (polyvinyl chloride [PVC]) chambers were 37 cm long × 25.5 cm wide × 14 cm high, covered by a light-reflecting aluminum film, and vented with a 10-cm-long stainless steel tube according to USDA protocol (Parkin and Venterea, 2010).

During deployment time, the chambers were placed on iron bases previously installed to a depth of 8 cm and sealed with water. In crop fields, the bases were located across the crop row, covering the row and inter-row area, with plants rooted inside. On each sampling date, if necessary, we cut the plants growing inside the base, leaving 5-cm height of stems.

We extracted 30-mL gas samples from the chambers at 0, 15, and 30 min after chamber placement and stored 10-mL subsamples in 10-mL vials with butyl-rubber seals. Before each extraction, we evacuated the vial and generated 85 kPa vacuum using a hand vacuum pump (Mytivac) in the vial. Within 10 d of collection, we analyzed the samples by injecting a 0.5-mL subsample with a syringe, to a gas chromatograph (GC, 6890 Agilent Technologies Network) with ^{63}Ni electron capture detector Agilent, equipped with a column HP-Plot Molesieve (30 m × 530 μm × 25 μm). The GC was calibrated with five different concentrations of N_2O reference gas, ranging from 0.05 to 1 μL L^{-1}. Furthermore, during each run we included a reference gas sample to examine the GC performance. Reference gas samples were injected to 10-mL vials, and then we extracted a 0.5-mL subsample to inject into the GC. The N_2O fluxes were calculated using linear regression model (Venterea, 2010).

Ancillary Variables

We recorded air and soil (0–10 cm) temperature adjacent to each chamber during each sampling period. We also recorded phenological stages of wheat, soybean, and corn crops using Zadoks et al., (1974), Fehr and Caviness, (1977), and Ritchie and Hanway, (1982) scales, respectively. After gas collection, we took three 10-cm-deep soil cores from inside each iron base using a 2-cm-diam. soil core and made a composite sample for analysis. We analyzed soil samples for water content and NH_4^+ and NO_3^- concentrations in the laboratory within 10 d after collection. We dried a 5-g subsample at 105°C during 48 h to estimate gravimetric soil water content (g g^{-1}), and then we calculated WFPS using the bulk density, assuming a particle density of 2.65 g cm^{-3}. We extracted soil subsamples with K_2SO_4 to estimate NH_4^+ and NO_3^- contents (Keeney and Nelson 1982). On each sampling date, we also recorded NDVI at the plot level using a manual radiation sensor (SpectroSense2, Skye Instruments) to provide a proxy for aboveground primary production. After each sampling, we removed the bases and relocated them in a different position within the same experimental plot to avoid disturbing the soil and allow stabilization of soil before the next sampling date. This relocation was also useful to avoid temporal correlation among sampling dates.

Data Analysis

We analyzed the direct regulating factors of the N_2O emissions separately for each land cover (grassland, corn, soybean, and wheat–soybean) and for each of the three crops considering only the growing season (seven subsets) through linear mixed models in R statistical language (*nlme* package; R Core Team 2013; Pinheiro et al., 2016). Each subset included the daily values of N_2O flux, soil temperature, WFPS, and soil NH_4^+ and NO_3^- content of the different farms, blocks, and sampling dates. Nitrous oxide flux data were log-transformed to achieve normal distribution. To build the models, soil temperature, WFPS, and soil NH_4^+ and NO_3^- content were set as fixed-effect factors, whereas farm and phenological stage were included as random factors. We selected the best combination of fixed factors to build the model of each subset through Akaike information criteria and then evaluated their significance. Parameters of the models were estimated by maximum likelihood. The coefficients of the models were standardized so they can be interpreted as relative effect size of the different variables to explain the changes in the N_2O emission (Pinheiro et al., 2016). Marginal and conditional coefficients of determination (R^2_m and R^2_c, respectively) were calculated for each model using the methodology proposed by Nakagawa and Schielzeth (2013). The R^2_m and R^2_c can be interpreted as the coefficients of determination of ordinary least squares models, but R^2_m represents the proportion of variability of N_2O emission explained by the fixed term of the model and R^2_c represents the proportion of variability explained by the complete model (fixed plus random factors). Nitrous oxide emissions were similar in both farms; therefore, we considered farm as a random factor to improve statistical power. Since we used commercial plots, we had differences in the seeding and harvesting dates among the different crops and farms. Therefore, instead of using fixed dates for our analyses, we established our comparison grouping by phenological stages for each crop (Rochette et al., 2004).

We evaluated the direct and indirect relationships between variables and N_2O through structural equation models (SEMs). We tested the direct relationship of soil temperature, WFPS, NH_4^+, NO_3^-, and NDVI with N_2O emissions and the indirect relationship of soil temperature, WFPS, and NDVI with N_2O emissions through their relationship on soil NH_4^+ and NO_3^- availability (see Supplemental Fig. S6 for an a priori conceptual model). We used the *piecewiseSEM* package for R statistical language (Lefcheck, 2016), which allows the use of mixed effect models to build the SEM structure.

Results

Nitrous Oxide Emissions and their Temporal Dynamics

Mean N_2O emissions from the double crop wheat–soybean, corn, and soybean crops were 34.8, 36.2 and 52.9 μg N_2O-N m^{-2} h^{-1}, respectively, whereas background emissions were 11.1 μg N_2O-N m^{-2} h^{-1} (Fig. 1). Emissions from corn and soybean plots were significantly different from grasslands plots ($p = 0.034$ for corn and $p < 0.0001$ for soybean), but differences were only marginally significant ($p = 0.088$) for wheat–soybean plots. Indeed, background emissions represented between 21 (in soybean plots) and 32% (in wheat–soybean plots) of gross emissions.

Daily emissions from crops ranged from null (even some negative fluxes were observed) to 133 ± 73 μg N_2O-N m^{-2} h^{-1}

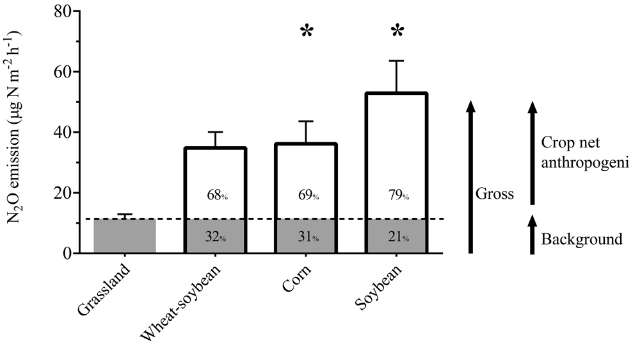

Fig. 1. Mean soil N_2O emissions from unmanaged grasslands (background) and crops. Asterisks show significant differences between each crop and grasslands ($p < 0.05$).

at the maturity stage in soybean, whereas grassland emissions rarely exceeded 25 μg N_2O-N m^{-2} h^{-1} (Fig. 2). Spatial variability of N_2O emissions in croplands was higher during emission peaks (i.e., the highest mean values showed the highest SE; Fig. 2). By contrast, unmanaged grasslands showed low variability during the whole sampling period, with highest emissions during spring and early summer (Fig. 2). As expected, corn crop showed two emission peaks: after seeding or fertilization date and after harvest (Fig. 2). High emissions were also observed at late spring during fallow period. For the double crop wheat–soybean, which did not have a fallow period prior to wheat seeding, the emission peak was observed ∼1 mo after wheat seeding and fertilization (the three-tiller stage, 77 ± 19 μg N_2O-N m^{-2} h^{-1}, Fig. 2). The soybean crop showed higher emissions before seeding (during the fallow period), and both soybean and late soybean had high emissions before harvesting too, during their maturity stages. During the moments of greater biomass productivity of all crops, N_2O emissions showed the lowest values (Fig. 2, Supplemental Fig. S7).

Direct Regulating Factors

The direct factors regulating N_2O emissions analyzed differed between cropland and grassland plots and changed when considering only the crop growing season or including the fallow periods (Table 1). Nitrous oxide emissions in croplands were controlled by soil temperature, NO_3^- content (except for corn), and WFPS when considering the complete year, whereas in unmanaged grasslands, only WFPS was the main significant regulating factor. When excluding the fallow period from the analysis, only considering the growing season, emissions were controlled by WFPS for soybean, late soybean, and corn crops, and by soil NO_3^- content in wheat crops, whereas soil temperature was not present in the models. Water-filled pore space was present in all but one (wheat growing season) model (Table 1). Soil NH_4^+ content was not present in any model as a direct factor regulating the N_2O flux.

NDVI and Nitrous Oxide Emissions

Values of NDVI were significantly correlated with N_2O emissions for soybean crops and grasslands, but in opposite directions (Fig. 3). Strong negative correlations between NDVI and N_2O emissions were evident in soybean ($R^2 = 0.74$) and late soybean ($R^2 = 0.57$) crop growing seasons (Fig. 3a), whereas a positive correlation was evident in unmanaged grasslands (Fig. 3c). In fertilized crops (wheat and corn), there were nonsignificant relationships between NDVI and N_2O emissions (Fig. 3b and 3d).

Structural Equation Model Analysis

The structural equation models supported by the data match with the a priori conceptual SEMs for soybean crops and unmanaged grasslands during the growing season (p for the χ^2 test were >0.05, Fig. 4). Because fertilized crops (wheat and corn) showed no relationship between NDVI and N_2O emissions, we did not include them in this analysis. We found a significant direct effect of WFPS, soil temperature, and NDVI on N_2O emissions from soybean crops during the growing season (considering both soybean and late soybean in the model, Fig. 4a). The WFPS and soil temperature had a positive effect on N_2O emissions (as shown in Table 1), whereas NDVI had a negative direct correlation. Mineral N pools did not significantly control N_2O emissions, so potential indirect relationships of soil temperature, WFPS, and NDVI were not observed. Furthermore, soil temperature, WFPS, and NDVI explained 39% of NH_4^+ variability, and NDVI explained 23% of NO_3^- variability (Fig. 4a).

For grasslands, NDVI was the main variable explaining N_2O emission variability with a significant direct relationship and an indirect relationship through soil NO_3^- availability (Fig. 4b, Supplemental Fig. S7). The WFPS and soil NO_3^- content had a minor direct effect. Neither soil temperature nor NH_4^+ content seem to control N_2O fluxes in unmanaged grasslands (Fig. 4b).

Discussion

Our results showed that N_2O emissions from croplands were higher than background emissions, but also that background emissions represented an important fraction of emissions measured in croplands. Higher emissions in croplands occurred during pre-seeding, after harvest and after N fertilization in fertilized crops (corn and wheat). As expected, soil temperature, WFPS, and NO_3^- contents had a positive effect on N_2O fluxes in all vegetation covers. In addition to these direct effects, our study demonstrated that NDVI, a proxy of plant productivity, was tightly correlated with N_2O fluxes in soybean crops and unmanaged grasslands, although with opposite relationships.

In this study, we reinforce the need to include background emissions to accurately estimate anthropogenic soil N_2O

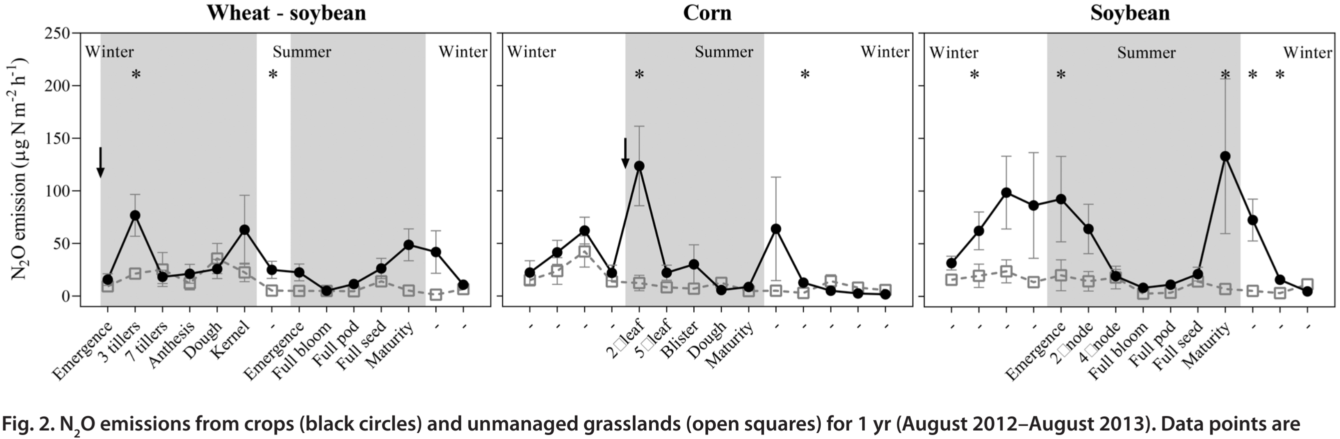

Fig. 2. N_2O emissions from crops (black circles) and unmanaged grasslands (open squares) for 1 yr (August 2012–August 2013). Data points are mean values of μg N_2O-N m^{-2} h^{-1}, ±1 SE and are deployed according to the phenological stage of each crop. Shaded areas correspond to crop growing season (from seeding to harvest), with the rest being the fallow period (pre-seeding and post-harvest). Arrows indicate nitrogen fertilization dates. Asterisks show significant differences between crop and grassland plots (p < 0.05).

Table 1. Direct regulating factors of N_2O emissions for different land covers evaluated using mixed-effect models. For each crop, we analyzed the effect of the different factors for the complete sampling period and for the growing season period (gs). Each line shows the size of the subset (*n*), the standardized coefficients of the model, and the marginal and conditional coefficients of determination (R^2_m and R^2_c, respectively).†

Land cover	*n*	Intercept	WFPS‡	Soil temperature	NO_3^-	R^2_m§	R^2_c¶
Corn	78	2.04	0.020 ± 0.005**	0.020 ± 0.009*		0.23	0.23
Wheat–soybean	56	2.03	0.014 ± 0.006*	0.027 ± 0.011*	0.086 ± 0.030**	0.32	0.49
Soybean	86	1.41	0.024 ± 0.005**	0.037 ± 0.01**	0.104 ± 0.041*	0.35	0.36
Grassland	88	2.67	0.012 ± 0.004*			0.15	0.15
Corn gs	52	2.70	0.016 ± 0.007*			0.20	0.21
Wheat gs	35	3.44			0.101 ± 0.036**	0.27	0.53
Late soybean gs	21	2.56	0.018 ± 0.008#			0.36	0.36
Soybean gs	53	2.66	0.022 ± 0.006**			0.27	0.27

*, ** Significant at the 0.05 and 0.01 probability levels, respectively.

† NH_4^+ is not included in the table because it was not significant in any model.

‡ WFPS, water-filled pore space.

§ R^2_m represents the proportion of variability explained by the fixed terms of the model.

¶ R^2_c represents the proportion of variability explained by the complete model (fixed plus random terms).

# $P < 0.1$.

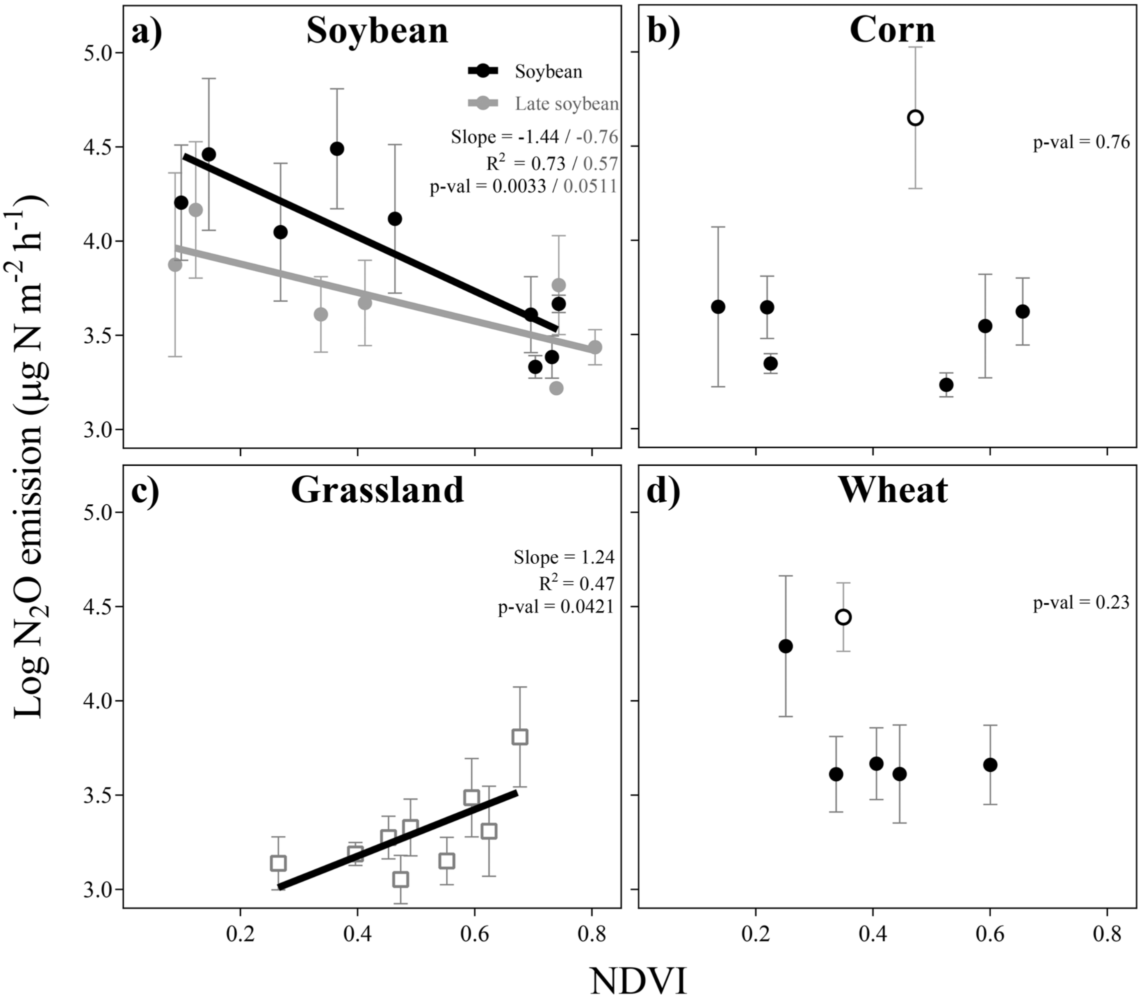

Fig. 3. Relationship between N_2O emissions (log-transformed µg N m^{-2} h^{-1}) and normalized difference vegetation index (NDVI, unit-less) for (a, b, and d) each crop's growing season (including pre-seeding and post-harvest stages), and (c) in unmanaged grasslands. Each point represents mean values ±1 SE of the phenological stages in crops and sampling dates in grasslands. In Panel a, gray points and lines correspond to late soybean plots. Open points in Panels b and d represent post-fertilization stages.

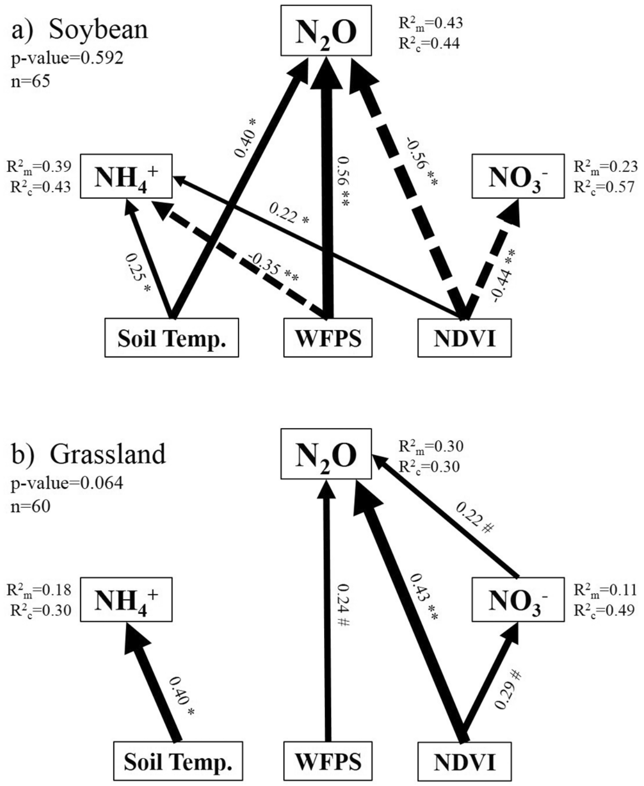

Fig. 4. Structural equation models (SEM) showing direct and indirect relationships (throughout mineral N availability) between the analyzed variables (N_2O, NH_4^+, NO_3^-, soil temperature [soil temp.], water-filled pore space [WFPS], and normalized difference vegetation index [NDVI]) and N_2O emissions for (a) soybean crops and (b) unmanaged grasslands during the growing season. Boxes represent variables and arrows represent positive (solid lines) or negative (dashed lines) relationships between variables. Arrow thickness show the relative effect of each variable on the response variable. Effect significance: * $p < 0.05$, ** $p < 0.01$, # $p < 0.1$. The proportion of the variability explained by the fixed terms (R^2_m) and fixed plus random terms of the model (R^2_c) are indicated for each response variable beside the box. The hypothesized model is consistent with data when p value for χ^2 test is greater than the threshold ($\alpha = 0.05$).

emissions. The definition of background emissions and the experimental design used in this study allow us to account not only for the effect of adding N to the soil, but also other anthropogenic effects on N_2O emissions such as changes in water and N cycles, seasonality of plant productivity, and changes in microbiological structure and functioning. Our data showed that between 21 and 32% of emissions from crops are nonanthropogenic. Similar rates were observed in the Brazilian Cerrado, where emissions of the native savanna represented 20, 28, and 40% of the emissions observed in nearby soybean, soybean–sorghum [*Sorghum bicolor* (L.) Moench], and corn–pigeonpea [*Cajanus cajan* (L.) Millsp.] croplands, respectively (dos Santos et al., 2016). Other studies showed that this percentage ranged from 4 to 100%: background emissions were almost negligible in a corn field that received 135 kg N ha^{-1} as chemical fertilizer in Indiana, USA (Hernandez-Ramirez et al., 2009), whereas background almost equaled gross emissions in a corn–soybean rotation in Argentina (Alvarez et al., 2012). Therefore, according to these studies, agriculture can represent no changes in N_2O emission compared with an unmanaged system or an increase up to 24-fold. The estimation of net anthropogenic emissions by subtracting the background emissions was applied in the US greenhouse gases inventories up to 2006, where background emissions from potential native ecosystems were estimated using a simulation model and subtracted from gross agricultural emissions (Del Grosso et al., 2006; USEPA, 2006).

Regarding temporal variability of the N_2O emissions, higher values in croplands have been generally observed and studied after tillage, fertilization, and harvest (Groffman et al., 2009). Our experiments further demonstrate that elevated emissions can occur before seeding (at late fallow period) and just before harvesting (in crop maturity stages) in annual crops. In these periods, low or null plant N uptake together with high decomposition and N mineralization rates (of previous crop biomass during pre-seeding or of the actual crop biomass in maturity stages) are expected, so mineral N would be available for microbe nitrification and denitrification (Supplemental Fig. S7; Robertson, 1997). During these periods neither mineral N nor temperature would limit N_2O production, so changes in WFPS would trigger the N_2O emissions as proposed in the "hot moment" approach by Groffman et al. (2009) and Molodovskaya et al. (2012). The mismatch in N mineralization and N uptake is intensified in crops with low C/N residues, like soybean, compared with high C/N residues (i.e., corn or wheat) as observed in our experiment. These findings highlight that considering the fallow period becomes essential when quantifying the annual crop N_2O emission.

The higher emissions observed in soybean than with double cropping (wheat–soybean) can be attributed to the shorter growing season of soybean single crops and the long fallow period that increases NO_3^- contents in the soil available for denitrification, particularly in autumn and spring when temperatures are high. Double cropping maintains active vegetation and plant uptake during 10 to 11 mo of the year, leading to short fallow periods in winter (between 30 and 50 d long) and summer (2–15 d long), reducing N availability for denitrification. In addition, corn had higher emissions than wheat because although both crop received low doses of N fertilization, wheat was fertilized in winter when temperature limits N_2O emissions, whereas corn fertilization occurs in spring-summer (Cosentino et al., 2013), favoring N_2O emissions. In contrast with what occurs in annual crops, in mixed communities of unmanaged natural ecosystems, N mineralization and plant N uptake are expected to be temporally and spatially coupled, so less mineral N is available for soil microbial transformation, as observed by Gelfand et al. (2016), Robertson, (1997), and Robertson et al. (2000). Coupling N mineralization and plant N uptake in unmanaged ecosystems can explain the low temporal variability and the absence of emission peaks observed in perennial grasslands of the Pampas Region in the present study. Apart from changes in N cycle, a recent study found that higher N_2O emissions in crops compared with unmanaged lands can be explained through changes in the microbiome functioning and composition (Song et al., 2018).

Several studies have reported WFPS as the main regulating factor of soil N_2O emissions (Dobbie and Smith, 2003; Alvarez et al., 2012; Cai et al., 2016). The observation that soil temperature was a significant factor when considering the whole year, but not when considering only the growing season, suggests that there might be a "threshold" effect of soil temperature as proposed by Cosentino et al., (2013). According to these authors, emissions are low when soil temperature is below 14°C, whereas temperatures above this value produce medium to high emissions, depending on WFPS level. The effect of mineral N content is more intriguing, as many studies have reported no relationship between these N pools and N_2O fluxes (Jarvis et al., 1996; Rochette et al., 2004; Gelfand et al., 2016). Furthermore, recent studies suggest that NO_2^- concentration would be a better estimator of N_2O emission than NH_4^+ or NO_3^- due to the role of NO_2^- as a central substrate in nitrification, denitrification, and chemodenitrification (Maharjan and Venterea, 2013; Breuillin-Sessoms et al., 2017). Furthermore, it has been shown that estimating fluxes of reactive N can give different and supplementary information regarding N_2O fluxes (Davidson et al., 2000; Gelfand et al., 2016). Therefore, high emission pulses result from the confluence of critical environmental factors (mainly temperature, WFPS, and mineral N), but predicting them at a daily timescale still entails low confidence and great error (Del Grosso et al., 2008; Groffman et al., 2009). Although N fluxes (mineralization, nitrification, or plant uptake) are more difficult to quantify than N pools, it seems to be crucial to estimate them to enhance the performance of daily N_2O emission models.

Our results suggest that plant productivity is tightly correlated to N_2O emission in crops and unmanaged systems in opposite directions, and that NDVI is a promising tool to enhance model predictability for seasonal N_2O emissions. This index has been widely used as a proxy of aboveground net primary productivity and live biomass, and it has also been used to describe N uptake in crops (Freeman et al., 2007; Yao et al., 2013). Nitrogen uptake by annual crops has a strong seasonality: uptake is null during fallow periods and is strongly correlated with aboveground dry matter production during the growing season, reaching its maximum at mid-growing season (Bender et al., 2013, 2015). In addition, a decrease in crop aboveground net primary productivity toward the end of the growing season reflects the start of root death and biomass decomposition, in which N-fixing species, such as soybean, contribute important N loadings from root nodules (Rochette et al., 2004). Normalized difference vegetation index has not been included previously in crop N_2O emission models. According to our results, its use is applicable to unfertilized crops where soil N availability is not influenced by very high external N inputs in short periods like fertilization.

The opposite pattern (a positive correlation between NDVI and N_2O emissions) was observed in unmanaged perennial grasslands. Our findings agree with two prior studies that observed a positive correlation between N_2O and proxies of biomass productivity in perennial ecosystems (Groffman and Turner, 1995; Wolf et al., 2011); Groffman and Turner (1995) even used NDVI data from satellite imagery as a plant productivity proxy. These studies observed a positive plant productivity and N_2O emission relationship at an interannual timescale for different topographic positions (slope and elevation) or management (burning and grazing). The authors interpreted their findings considering N-limited ecosystems, where plant productivity and soil N_2O flux are controlled by the same two factors, soil mineral N and water availability. Therefore, higher N availability promoted both plant productivity and N_2O emissions. Considering that soil N limits grassland productivity in the Pampas Region of Argentina (Chaneton et al., 1996), our results show that the positive correlation between N_2O emissions and primary productivity is present in the intra-annual temporal variability. These findings highlight that N_2O controls are indeed complex, and that NDVI had direct and indirect effects on N_2O emissions in soybean and grasslands, as revealed by the SEMs. The NDVI improved the models' predictability when describing seasonal variability of the N_2O emissions. Further information is required to test the control at a daily time step. The NDVI is a very promising and versatile tool to include in N_2O emission studies, since it is easily attainable and widely available at several temporal and spatial levels, from plot scale assessed with manual sensors, to regional scales, using data from satellite images.

Conclusions

Background emissions represented a significant fraction of the N_2O flux observed in crops; therefore, including background emissions in crops studies seems important to quantify anthropogenic N_2O emissions. Our study offers valuable information to discriminate natural from anthropogenic emissions because plots were located adjacently in independent blocks and, therefore, environmental conditions were the same for crops and unmanaged plots. As expected, higher emissions were observed after fertilization in corn and wheat crops. However, in soybean crops, we observed high N_2O emissions during fallow periods (before seeding) and in maturity stages (before harvesting) and very low emissions at mid-growing season stages. In addition, we tested NDVI, an easily attainable index of plant productivity related to plant N uptake, and we found that NDVI was negatively correlated with soil NO_3^- and with N_2O emissions during the soybean growing season. On the contrary, in unfertilized grasslands, the N cycle is better coupled between plants and soils, and therefore NDVI was positively related with N_2O emissions.

Supplemental Material

Detailed information on study sites (soil characteristics, climate, and crop management) and photos of the experimental plots and sampling devices are available online. Furthermore, the file contains raw N_2O, NDVI, soil temperature, WFPS, NO_3^-, and NH_4^+ data.

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References

Alvarez, C., A. Costantini, C.R. Alvarez, B.J.R. Alves, C.P. Jantalia, E.E. Martellotto, and S. Urquiaga. 2012. Soil nitrous oxide emissions under different management practices in the semiarid region of the Argentinian Pampas. Nutr. Cycl. Agroecosyst. 94:209–220. doi:10.1007/s10705-012-9534-9

Bender, R.R., J.W. Haegele, and F.E. Below. 2015. Nutrient uptake, partitioning, and remobilization in modern soybean varieties. Agron. J. 107:563–573. doi:10.2134/agronj14.0435

Bender, R.R., J.W. Haegele, M.L. Ruffo, and F.E. Below. 2013. Nutrient uptake, partitioning, and remobilization in modern, transgenic insect-protected maize hybrids. Agron. J. 105:161–170. doi:10.2134/agronj2012.0352

Breuillin-Sessoms, F., R.T. Venterea, M.J. Sadowsky, J.A. Coulter, T.J. Clough, and P. Wang. 2017. Nitrification gene ratio and free ammonia explain nitrite and nitrous oxide production in urea-amended soils. Soil Biol. Biochem. 111:143–153. doi:10.1016/j.soilbio.2017.04.007

Cai, Z., S. Gao, A. Hendratna, Y. Duan, M. Xu, and B.D. Hanson. 2016. Key factors, soil nitrogen processes, and nitrite accumulation affecting nitrous oxide emissions. Soil Sci. Soc. Am. J. 80:1560–1571. doi:10.2136/sssaj2016.03.0089

Chaneton, E.J., J.H. Lemcoff, and R.S. Lavado. 1996. Nitrogen and phosphorus cycling in grazed and ungrazed plots in a temperate subhumid grassland in Argentina. J. Appl. Ecol. 33:291–302. doi:10.2307/2404751

Cosentino, V.R.N., S.A. Figueiro Aureggui, and M.A. Taboada. 2013. Hierarchy of factors driving N_2O emissions in non-tilled soils under different crops. Eur. J. Soil Sci. 64:550–557. doi:10.1111/ejss.12080

Curtin, D., M.H. Beare, and G. Hernandez-Ramirez. 2012. Temperature and moisture effects on microbial biomass and soil organic matter mineralization. Soil Sci. Soc. Am. J. 76:2055–2067. doi:10.2136/sssaj2012.0011

Davidson, E.A., M. Keller, H.E. Erickson, L.V. Verchot, and E. Veldkamp. 2000. Testing a conceptual model of soil emissions of nitrous and nitric oxides. Bioscience 50:667–680. doi:10.1641/0006-3568(2000)050[0667:TACMOS]2.0.CO;2

Del Grosso, S.J., W.J. Parton, A.R. Mosier, M.K. Walsh, D.S. Ojima, and P.E. Thornton. 2006. DAYCENT national-scale simulations of nitrous oxide emissions from cropped soils in the United States. J. Environ. Qual. 35:1451–1460. doi:10.2134/jeq2005.0160

Del Grosso, S.J., T. Wirth, S.M. Ogle, and W.J. Parton. 2008. Estimating agricultural nitrous oxide emissions. EOS, Trans. Am. Geophys. Union 89:529–540. doi:10.1029/2008EO510001

Dobbie, K.E., and K.A. Smith. 2003. Nitrous oxide emission factors for agricultural soils in Great Britain : The impact of soil water-filled pore space and other controlling variables. Glob. Change Biol. 9:204–218. doi:10.1046/j.1365-2486.2003.00563.x

dos Santos, I.L., A.D. de Oliveira, C.C. de Figueiredo, J.V. Malaquias, J.d.D.G. dos Santos Júnior, E.A.B. Ferreira, et al. 2016. Soil N_2O emissions from long-term agroecosystems: Interactive effects of rainfall seasonality and crop rotation in the Brazilian Cerrado. Agric. Ecosyst. Environ. 233:111–120. doi:10.1016/j.agee.2016.08.027

Dusenbury, M.P., R.E. Engel, P.R. Miller, R.L. Lemke, and R. Wallander. 2008. Nitrous oxide emissions from a northern Great Plains soil as influenced by nitrogen management and cropping systems. J. Environ. Qual. 37:542. doi:10.2134/jeq2006.0395

Eggleston, S., L. Buendia, K. Miwa, T. Ngara, and K. Tanabe. 2006. 2006 IPCC guidelines for national greenhouse gas inventories, prepared by the National Greenhouse Gas Inventories Programme. Inst. Glob. Environ. Strat., Hayama, Japan.

Fehr, W.R., and C.E. Caviness. 1977. Stages of soybean development. Spec. report. Iowa State Univ. Ames, Iowa.

Firestone, M.K., and E.A. Davidson. 1989. Microbiological basis of NO and N_2O production and consumption in soil. In: M.O. Andreae and D.S. Schimel, editors, Exchange of trace gases between terrestrial ecosystems and the atmosphere. John Wiley & Sons, New York. p. 7–21.

Freeman, K.W., K. Girma, D.B. Arnall, R.W. Mullen, K.L. Martin, R.K. Teal, and W.R. Raun. 2007. By-plant prediction of corn forage biomass and nitrogen uptake at various growth stages using remote sensing and plant height. Agron. J. 99:530–536. doi:10.2134/agronj2006.0135

Gelfand, I., I. Shcherbak, N. Millar, A.N. Kravchenko, and G.P. Robertson. 2016. Long-term nitrous oxide fluxes in annual and perennial agricultural and unmanaged ecosystems in the upper Midwest USA. Glob. Chang. Biol. 22:3594–3607. doi:10.1111/gcb.13426

Groffman, P.M., K. Butterbach-Bahl, R.W. Fulweiler, A.J. Gold, J.L. Morse, E.K. Stander, et al. 2009. Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. Biogeochemistry 93:49–77. doi:10.1007/s10533-008-9277-5

Groffman, P.M., and C.L. Turner. 1995. Plant productivity and nitrogen gas fluxes in a tallgrass prairie landscape. Landsc. Ecol. 10:255–266. doi:10.1007/BF00128993

Hall, A.J., C.M. Rebella, C.M. Ghersa, and J.P. Culot. 1992. Field-Crop systems of the Pampas. In: C.J. Pearson, editor, Ecosystems of the world: Field crop ecosystems. Elsevier, Amsterdam. p. 413–450.

Hernandez-Ramirez, G., S.M. Brouder, D.R. Smith, and G.E. Van Scoyoc. 2009. Greenhouse gas fluxes in an eastern Corn Belt soil: Weather, nitrogen source, and rotation. J. Environ. Qual. 38:841–854. doi:10.2134/jeq2007.0565

IPCC. 2013. Climate change 2013: The physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Intergov. Panel Clim. Change, Cambridge, UK, and New York.

Jarvis, S.C., E.A. Stockdale, M.A. Shepherd, and D.S. Powlson. 1996. Nitrogen mineralization in temperate agricultural soils: Measurement processes and measurement. Adv. Agron. 57:187–235. doi:10.1016/S0065-2113(08)60925-6

Keeney, D.R., and D. Nelson. 1982. Nitrogen: Inorganic forms. In: A.L. Page, editor, Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. ASA and SSSA, Madison, WI. p. 643–693. doi:10.2134/agronmonogr9.2.2ed.c33

Kessavalou, A., A.R. Mosier, J.W. Doran, R.A. Drijber, D.J. Lyon, and O. Heinemeyer. 1998. Fluxes of carbon dioxide, nitrous oxide, and methane in grass sod and winter wheat-fallow tillage management. J. Environ. Qual. 27:1094–1104. doi:10.2134/jeq1998.00472425002700050015x

Kim, D., D. Giltrap, and G. Hernandez-Ramirez. 2013. Background nitrous oxide emissions in agricultural and natural lands: A meta-analysis. Plant Soil 373:17–30. doi:10.1007/s11104-013-1762-5

Lefcheck, J.S. 2016. PIECEWISESEM: Piecewise structural equation modelling in R for ecology, evolution, and systematics. Methods Ecol. Evol. 7:573–579. doi:10.1111/2041-210X.12512

Maharjan, B., and R.T. Venterea. 2013. Nitrite intensity explains N management effects on N_2O emissions in maize. Soil Biol. Biochem. 66:229–238. doi:10.1016/j.soilbio.2013.07.015

Molodovskaya, M., O. Singurindy, B.K. Richards, J. Warland, M.S. Johnson, and T.S. Steenhuis. 2012. Temporal variability of nitrous oxide from fertilized croplands: Hot moment analysis. Soil Sci. Soc. Am. J. 76:1728–1740. doi:10.2136/sssaj2012.0039

Mosier, A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger, and O. van Cleemput. 1998. Closing the global N_2O budget: Nitrous oxide emissions through the agricultural nitrogen cycle. Nutr. Cycl. Agroecosyst. 52:225–248. doi:10.1023/A:1009740530221

Nakagawa, S., and H. Schielzeth. 2013. A general and simple method for obtaining R^2 from generalized linear mixed-effects models. Methods Ecol. Evol. 4:133–142. doi:10.1111/j.2041-210x.2012.00261.x

Parkin, T.B., and R.T. Venterea. 2010. Chamber-based trace gas flux measurements. In: R.F. Follett, editor, Sampling protocols. USDA-ARS, Washington, DC. p. 3.1–3.39.

Perdomo, C., P. Irisarri, and O. Ernst. 2008. Nitrous oxide emissions from an Uruguayan Argiudoll under different tillage and rotation treatments. Nutr. Cycl. Agroecosyst. 84:119–128. doi:10.1007/s10705-008-9231-x

Pinheiro, J., D. Bates, S. DebRoy, D. Sarkar, and R Core Team. 2016. nlme: Linear and nonlinear mixed effects models. R Package version 3.1-128. R Found. Stat. Comput., Vienna.

R Core Team. 2013. R: A language and environment for statistical computing. R Found. Stat. Comput., Vienna.

Ravishankara, A.R., J.S. Daniel, and R.W. Portmann. 2009. Nitrous oxide (N_2O): The dominant ozone-depleting substance emitted in the 21st century. Science 326:123–125. doi:10.1126/science.1176985

Ritchie, S.W., and J.J. Hanway. 1982. How a corn plant develops. Spec. report. Iowa State Univ. Ames.

Robertson, G.P. 1989. Nitrification and denitrification in humid tropical ecosystems: Potential controls on nitrogen retention. In: J. Proctor, editor, Mineral nutrients in tropical forest and savanna ecosystems. British Ecol. Soc. Spec. Publ. 9. Blackwell Sci., Hoboken, NJ. p. 55–69.

Robertson, G.P. 1997. Nitrogen use efficiency in row-crop agriculture: Crop nitrogen use and soil nitrogen loss. In: L.E. Jackson, editor, Ecology in agriculture. Acad. Press, Cambridge, MA. p. 347–365.

Robertson, G.P., E.A. Paul, and R.R. Harwood. 2000. Greenhouse gases in intensive agriculture: Contributions of individual gases to the radiative forcing of the atmosphere. Science 289:1922–1925. doi:10.1126/science.289.5486.1922

Rochette, P., D.A. Angers, B. Gilles, M.H. Chantigny, D. Prévost, and G. Levésque. 2004. Emissions of N_2O from alfalfa and soybean crops in eastern Canada. Soil Sci. Soc. Am. J. 68:493–506. doi:10.2136/sssaj2004.4930

Ruser, R., H. Flessa, R. Schilling, F. Beese, and J.C. Munch. 2001. Effect of crop-specific field management and N fertilization on N_2O emissions from a fine-loamy soil. Nutr. Cycl. Agroecosyst. 59:177–191. doi:10.1023/A:1017512205888

Song, A., Y. Liang, X. Zeng, H. Yin, D. Xu, B. Wang, et al. 2018. Substrate-driven microbial response: A novel mechanism contributes significantly to temperature sensitivity of N_2O emissions in upland arable soil. Soil Biol. Biochem. 118:18–26. doi:10.1016/j.soilbio.2017.11.021

Soriano, A. 1992. Río de la Plata grasslands. Ecosyst. World 8:367–407.

Tilman, D., P.B. Reich, J. Knops, D. Wedin, T. Mielke, and C. Lehman. 2001. Diversity and productivity in a long-term grassland experiment. Science 294:843–845. doi:10.1126/science.1060391

Tubiello, F.N., M. Salvatore, A.F. Ferrara, J. House, S. Federici, S. Rossi, et al. 2015. The contribution of agriculture, forestry and other land use activities to global warming, 1990-2012. Glob. Change Biol. 21:2655–2660. doi:10.1111/gcb.12865

Tucker, C.J. 1979. Red and photographic infrared linear combinations for monitoring vegetation. Remote Sens. Environ. 8:127–150. doi:10.1016/0034-4257(79)90013-0

USEPA. 2006. Inventory of U.S. greenhouse gas emissions and sinks: 1990–2004. USEPA, Washington, DC.

Venterea, R.T. 2010. Simplified method for quantifying theoretical underestimation of chamber-based trace gas fluxes. J. Environ. Qual. 39:126–135. doi:10.2134/jeq2009.0231

Wolf, K., E. Veldkamp, J. Homeier, and G.O. Martinson. 2011. Nitrogen availability links forest productivity, soil nitrous oxide and nitric oxide fluxes of a tropical montane forest in southern Ecuador. Global Biogeochem. Cycles 25(4). doi:10.1029/2010GB003876

Yao, X., X. Yao, W. Jia, Y. Tian, J. Ni, W. Cao, and Y. Zhu. 2013. Comparison and intercalibration of vegetation indices from different sensors for monitoring aboveground plant nitrogen uptake in winter wheat. Sensors (Basel) 13:3109–3130. doi:10.3390/s130303109

Zadoks, J.C., T.T. Chang, and C.F. Konzak. 1974. A decimal code for the growth stages of cereals. Weed Res. 14:415–421. doi:10.1111/j.1365-3180.1974.tb01084.x