

The Effect of Nitrogenous Fertilizers on Methane Oxidation in Soil

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Abstract

One of the most prominent applications to increase agricultural yield is the application of nitrogenous fertilizers to the soil. The intermediate and final products of the mineralization/humidification that include carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) are released into the atmosphere while other final products are cycled into the soil upon completion of the related reactions that take place in soil. Released CO₂, CH₄, and N₂O are the most notable factors responsible for global warming and are claimed to be remarkably serious when one accounts for all of the agricultural lands and other similar fields all around the globe. In the present study, the impact of NH₄NO₃ with 26% N, which consisted of 19% NH₄-N (ammonium-N) and 7% NO₃-N (nitrate-N), with and without nitrification inhibitor in the soil on CH₄, CO₂ and N₂O gas emissions was monitored in a controlled laboratory environment as three parallel experiments. The amount of fertilizer applied to the soil layer was 90 kg N per hectare. The two treated soils and one control soil were incubated at 60% maximal water holding capacity at 25°C during the test period of 18 days to investigate, (a) nitrogenous fertilizer (NH₄NO₃), (b) nitrogenous fertilizer plus nitrification inhibitor (NH₄NO₃ + N.I.), and finally (c) control for CH₄, CO₂, and N₂O emissions. Gas compositions from the experimental soils were sampled at predetermined times in order to assess the CH₄ release along with N₂O and CO₂ emissions. Analyses of the headspace on the 1st, 2nd, 4th, 7th, 10th, 14th and 18th days were completed in order to evaluate gas concentrations. The overall results indicate that NH₄NO₃ fertilization and NH₄NO₃ with a nitrification inhibitor application causes a statistically significant decrease in CH₄ emissions and an increase in CO₂ emissions into the atmosphere. N₂O emissions were found to be statistically different with the NH₄NO₃ application and control treatments. Yet, no significant change was observed in, the N₂O concentrations with respect to time, based on the NH₄NO₃ with a nitrification inhibitor application compared to the control group.

Keywords: Carbon dioxide, methane oxidation, nitrogenous fertilizers, nitrous oxide, nitrification inhibitor, soil.

Toprağa Uygulanan Azotlu Gübrenin Metan Oksidasyonuna Etkisi

Özet

Azotlu gübre kullanımı, tarımsal ürün artışı sağlamak için yapılan tarımsal uygulamalardan en önemlilerinden biridir. Toprakta meydana gelen mineralizasyon ve humifikasyon olayları ile toprakta meydana gelen diğer reaksiyonların tamamlanması sonucu açığa çıkan, CH₄, CO₂ ve N₂O gibi ara ve son ürünler atmosfere verilirler. Açığa çıkan CO₂, CH₄ ve NO₂ gazları küresel ısınmaya neden olan en önemli faktörlerdendir. Dünyadaki tarım alanlarının tamamı dikkate alındığında bu durumun önemi daha çok ortaya çıkmaktadır. Bu çalışmada, toprağa uygulanan nitrifikasyon inhibitörü içeren ve nitrifikasyon inhibitörü içermeyen (%26N; %19 NH₄-N ve % 7 NO₃-N) iki azotlu gübrenin topraktan CH₄, CO₂ ve N₂O çıkışına olan etkisi kontrollü laboratuvar koşullarında araştırılmıştır. Toprağa uygulanan gübre miktarı 90kgN/ha olarak hesaplanmış olup, deneme üç yinelemeli olarak kurulmuştur. Denemede kullanılan varyantlar; a) Azotlu gübre (NH₄NO₃), b) Azotlu gübre + nitrifikasyon inhibitörü (NH₄NO₃ + N.I) ve c) Kontrol (toprak) olarak belirlenmiştir. Bu amaçla azotlu gübrelerin toprağa karıştırılmasından sonra, tarla kapasitesinin %60'ına kadar saf su ilave edilen topraklar 25°C'de 18 gün süre ile inkübasyona bırakılmıştır. Inkübasyonun 1., 2., 4., 7., 10., 14. ve 18. gününde topraklardan özel şırıngalar ile alınan gaz örneklerinde bulunan CH₄, CO₂ ve N₂O miktarları gaz kromatografisinde yapılan ölçümler ile belirlenmiştir.

Araştırma sonucunda; azotlu gübre uygulamasının topraktan çıkan CH₄ miktarını azalttığı, CO₂ çıkışını artırdığı ve N₂O çıkışında ise önemli bir farklılığa neden olmadığı belirlenirken, inkübasyon süresine bağlı

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olarak CH₄ çıkışında azalma, CO₂ çıkışında artış, N₂O çıkışında ise azalma belirlenmiştir.

Sonuç olarak; çalışmanın yapıldığı özellikteki topraklarda uygulanan azotlu gübrelerin ikisinin de metan oksidasyonunu artırarak atmosfere verilen CO₂ çıkışının artmasına neden olduğu, N₂O çıkışında etkinin önemli olmadığı, nitrifikasyon inhibitörü içermeyen gübrede etkinin daha fazla olduğu söylenebilir.

Anahtar Kelimeler: Azotlu gübre, karbon dioksit, metan oksidasyonu, nitroz oksit, nitrifikasyon inhibitörü, toprak

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INTRODUCTION

Methane (CH₄) and nitrous oxide (N₂O) are two of the most prominent greenhouse gases. Methane is 15 to 20 times stronger and nitrous oxide is 310 times stronger than carbon dioxide (CO₂) in terms of absorbance capacity of infrared radiation (Wuebbles and Hayhoe 2002, Peigné and Girardin 2004). Since the atmospheric quality of the earth has long been subjected to threats by various, specifically anthropogenic sources, CH₄ and N₂O were classified as being two major factors for both tropospheric and stratospheric air quality, because of their impacts on the ozone, water vapor, the hydroxyl radical, and numerous other atmospheric compounds, along with other gases that play important roles in global climatic change (Fuhrer 2003). Recent studies have shown that CH₄ concentration in the atmosphere is increasing at a rate of 1% each year due to increasing amount of landfill exhaustion gases, cattle grazing, biomass burning, and the inclination of rice paddies (Krupa 2003, Streese and Stegmann 2003, Chang and Yang 2003). Consumption of atmospheric CH₄ in soil should also be pointed out as one of the most notable sinks in the global cycle of CH₄ (Prinn 1994).

In many types of soil use, Maljanen et al. (2003) postulated that both uptake and formation rates of CH₄ in the forests is nearly three times larger than the rates from the agricultural areas. On the other hand, mineral N fertilization and pesticide application cause reductions in CH₄ oxidation rates in the forests (Priemé and Ekelund 2001). In rice fields, the emissions are dependent on the conditions and agricultural practices employed during cultivation, such as climate, soil characteristics, cultivation practices including water management, fertilizers and other additives used, and the different varieties of rice plants (Neue et al. 1997, Khalil et al. 1998, Sass et al. 1999, Cai and Mosier 2000). Alternatively, the addition of organic fertilizers possesses the potential to increase

emissions by over 50% relative to non-organic fertilizers (Denier van der Gon and Neue 1995, Buendia et al. 1997). Laboratory studies performed by Hütsch et al. (1993) and Willison et al. (1995) revealed that reduction of CH₄ uptake rates was caused by the application of ammonium nitrate on the agricultural fields compared to the CH₄ uptake rates from unfertilized soils. This could be explained by the competitive inhibition of CH₄ mono-oxygenase by ammonium (Bedard and Knowles 1989). Hütsch et al. (1993) suggested that the inhibition of CH₄ oxidation in soils that include inorganic N is the result of a long-term effect.

CH₄ oxidation in soil requires the availability of oxygen, the presence of the methanotrophic bacteria and suitable environmental conditions, such as temperature and soil humidity, that allow such bacteria to effectively perform their activities (Jäckel et al. 2001, Steinkamp et al. 2001). CH₄ is oxidized to CO₂ in soils as a result of the activities of a diverse group of methanotrophic bacteria.

Inhibitors that play prominent roles in the microbial processes, e.g. nitrification inhibitors, can serve as distinguishing relative contributions of chemo-autotrophic nitrifying and methanotrophic bacteria to CH₄ oxidation in the soil environment. The ideal differential inhibitor should have appreciable inhibitory effects on CH₄ oxidation and minimal effects on the other processes that take place in the soil environment. The nitrification inhibitors, such as nitrapyrin (2-chloro-6-trichloromethylpyridine (C₆H₃Cl₄N)) and acetylene (C₂H₂), have been reported as strong inhibitory agents in CH₄ oxidation (Bronson and Mosier 1994). Nitrogen is mainly applied to the soil in order to prevent losses of nitrogen through nitrification and denitrification and the product inhibits ammonia (Dan et al. 2001). Few researchers have examined the effects of nitrification inhibitors and the roles of different forms of N on CH₄ oxidation (e.g. Hellebrand et al. 2003, Liou et al. 2003). The use of fertilizers and consequently

agricultural runoff undoubtedly restricts CH₄ oxidation in the soil (King 1992, Bedard and Knowles 1989). It has been suggested that NH₃, rather than NH₄⁺, is the primary inhibitor of CH₄ oxidation despite the fact that NH₃ inhibition in soils occur in a more complex pathway (Peigné and Girardin 2004). Moreover, nitrite (NO₂⁻), produced by the completion of oxidation of NH₃ performed by methanophoric bacteria, results in a more permanent inhibition of CH₄ oxidation when compared to that by NH₃ with an unknown reaction mechanism (Schnell and King 1994). Besides, if the inhibition of methane oxidation persists for long time periods and due to the involvement of large fields, runoff is significantly prominent for CH₄ oxidation in wetlands, rice paddies, and such lands, which receive high precipitation where reduction of CH₄ potentially occurs (Le Mer and Roger 2001).

On the contrary, Willison et al. (1995) have noted that the long-term (138 years) application of NH₃ fertilizers to the experimental grassland field within the Rothamsted Facilities (UK) has caused a significant drop in methane emitted into the atmosphere, whereas the application of NO₃⁻ for the same duration at the same location has not caused any changes.

Consequently, NH₃, NO₃⁻, and NO₂⁻ on the inhibition of methane oxidation is significantly different than the ecological implications (Adams 2003). One of the most notable sinks of CH₄ in the soil oxidation of CH₄ by methanotrophic bacteria, has not yet received adequate attention. Recent work has proven that addition of N fertilizer to the soil is responsible for the decrease in CH₄ consumption rates, possibly due to competitive inhibition of CH₄ oxidation in pure cultures of methanotrophic bacteria by NH₄⁺ (and/or NH₃).

The objective of this paper is to investigate the effects of NH₄NO₃, when present on its own and when present with a nitrification inhibitor, and its role in CH₄ oxidation in sandy loam soils under stagnant ambient air temperature settings. Emissions of CH₄ and CO₂ under; (a) NH₄NO₃, (b) NH₄NO₃ + N.I., and (c) control (no extra addition) treatments are discussed and their respective ratios were tabulated. N₂O, which is 15.5 times stronger in terms of greenhouse effect than that of CH₄ (Peigné and Girardin 2004), emissions was investigated. The experimental period was

chosen as 18 days. Not only were the overall emissions of CH₄, CO₂ and N₂O under, (a) NH₄NO₃ (nitrogenous fertilizer), (b) NH₄NO₃ + N.I. (nitrogenous fertilizer and nitrification inhibitor), and (c) control treatments determined but the pair-wise relationship between them was also investigated.

MATERIALS AND METHODS

Randomly taken upper (0-20 cm) soil samples from a non-fertilizer applied field in Giessen, Germany, were examined in terms of selected physical and chemical parameters. Table 1 exhibits the results of the physical and chemical soil properties of the study site. The determinations of these parameters were completed at the Microbiologia Institute at Justus Liebig University in Giessen, Germany. Fresh soil samples were stored in polyethylene bottles at 4°C in the dark. The CH₄ oxidation activity was kept constant during the first 18 days of storage.

The percent inhibition of CH₄ oxidation posterior to the application of NH₄NO₃ that consists of 26% N, which consists of 19% NH₄-N and 7% NO₃-N by weight, and both NH₄NO₃ + N.I. were calculated after *c* days by using the modified Bundy and Bremner (1973) equation;

$$\frac{(I-C)-(I-T)}{(I-C)} \times 100 \quad (1)$$

where,

I is the initial concentration of CH₄ in the laboratory air (2.00 μmol mol⁻¹),

C is the CH₄ concentration in the headspace of the control bottle (untreated) and

T is the CH₄ concentration in the headspace over the treated soils.

Analyses of the headspace on the 1st, 2nd, 4th, 7th, 10th, 14th and 18th days were completed in order to evaluate the gas concentrations. A gas chromatograph (Perkin-Elmer® Autosystem XL Arnel peak simple chromatography data system SRI model 202 four channel serial port) fitted with an ultrasonic O₂ detector that is able to detect oxygen concentrations of between 21% and 24% was used for this analysis.

In order to assess the influence of the CH₄ mixing ratio on the induction of CH₄ oxidation in soils, the soil samples (200.0 g as raw or 145.3 g as dry weight) have been placed in sterile serum bottles then incubated using a mixing ratio of 5 μg CH₄ and

Table 1. Selected physical and chemical characteristics of the soil used in the experimentes.

Specification	Value
Soil texture	Sandy loam
pH (1:2.5 suspension with distilled water)	7.7 (slightly alkaline)
Maximum water holding capacity (WHC _{max}), per cent dry weight	60
NH ₄ -N (µg - N g ⁻¹ dry weight)	2.03
NO ₃ -N (µg - N g ⁻¹ dry weight)	92.26

25% O₂. The O₂ mixing ratio during the experiment was controlled periodically and, if there was a change, it was readjusted to a value of 25-30% O₂ in the gas phase by adding the necessary amounts of oxygen into the incubation bottles with a syringe.

At the conclusion of the incubation period, the experimental vessels were flushed with synthetic air and the CH₄ oxidation rate was measured at the initial CH₄ concentration of the soils. The soils were also used to evaluate the short term response of the CH₄ oxidation to water content, pH value, and NH₄, NO₂, and NO₃ concentrations.

The CH₄ oxidation rates were measured by transferring soil samples into 2200 mL serum bottles and 1-1 flasks, which were flushed with synthetic air beforehand and equipped with rubber stoppers. The desired CH₄ (5 µg CH₄ and 25% O₂) mixing ratio in the gas phase was adjusted by injecting computed amounts of pure CH₄ and O₂ with gassing syringes (Glenco® made, Houston, Texas, USA). Internal serum bottle pressures were set to 120 kPa and the 1-1 flasks pressures set to 105 kPa at the initiation of the experiment. All CH₄ oxidation experiments were performed at 25°C under dark conditions and analyses were conducted with three replicates in order to assure quality during the experiment. Statistical analyses and accompanying graphics were generated using SPSS (Statistical Package for Social Sciences) 10.0 and Microsoft Excel® 6.0 spreadsheet program.

RESULTS

Soil used in the experiment is sandy-loam and has a slightly basic characteristic as tabulated in Table 1. NH₄-N and NO₃-N concentrations of the soil are also noted in Table 1 along with the maximum water holding capacity.

Concentrations of CH₄, CO₂, and N₂O during the course of the experiment were also evaluated. To start with, CH₄ emission have been submitted in addition to the CO₂ emission during the experimental procedure. Finally, N₂O change during the course of the experiments has been illustrated and discussed. The CH₄ change in all treatments was detected to be slightly decreasing as

a function of time whereas, CO₂ was found to be increasing and N₂O was realized to be almost stagnant in all treatments.

Prior to completion of the adopted statistical analyses, homogeneity of the data set was tested. According to Levene statistics for CH₄ emissions, the data set was found to be homogeneous (Levene statistics = 0.599 and significant at 0.560). The one way ANOVA yielded a significant difference between treatments (F = 15.901 and significant at 0.000 level). Based on statistical computations, there are significant drops in CH₄ emissions under both the NH₄NO₃ (mean difference = 10.05 significant at 0.000) treatment and the NH₄NO₃ + N.I. (mean difference = 10.31 significant at 0.000) application when compared to the control group. However, no significant difference was computed between CH₄ emissions under NH₄NO₃ + N.I. and only NH₄NO₃ application since mean difference was computed to be 0.2629 and has a significance at 0.991.

For CO₂ emissions, no significant differences were found (F = 0.049 and significance = 0.952) between all the treatments. All applications yielded similar CO₂ emissions as illustrated in Fig.2. Levene statistics showed that the data set is homogeneous (Levene statistic = 0.219 and significant at 0.805). Since the one way ANOVA yielded insignificant difference between the treatments, mean differences were not computed.

Lastly, Levene statistics for N₂O showed that the data set is homogeneous (Levene statistic = 3.005 and significant at 0.075). N₂O emissions were found statistically different using only the NH₄NO₃ application and control treatment (mean difference = 14.407 and significant at 0.040). However, no differences were computed for N₂O between the NH₄NO₃ and NH₄NO₃ + N.I. and between NH₄NO₃+N.I. the control treatments.

DISCUSSION

CH₄ Emissions

The nitrification inhibitor with NH₄NO₃ has yielded the highest CH₄ (55.1 ng CH₄-C g⁻¹) concentration among all treatments while the fertilizer application yielded the lowest CH₄ (49.6 ng CH₄-C g⁻¹) emission on the first day of the experiment. Between the 2nd and 14th day of the experiment, the NH₄NO₃ + N.I. treatment maintained the lowest CH₄ concentration whereas, the control group yielded the highest CH₄

emissions. The significant increase of CH₄ in NH₄NO₃ and NH₄NO₃ + N.I. treatments at day 14 could be attributed to the time between the phase I -that type I methanotrophic bacteria actively takes role and phase II when nitrogenous methanotrophics are more dominant as discussed in detail by De Visscher and Van Cleemput (2003).

The significant decrease in CH₄ emission under NH₄NO₃ and NH₄NO₃ + N.I. detected was in agreement with the results reported by Kravchenko et al. (2002). Their research revealed that there is a significant change in terms of the increase in CH₄ concentration during the first five days and a sudden drop in CH₄ concentration inhibited by NH₄⁺ after the fifth day through the end of the experimental period (30 day) despite the fact that in the control group the CH₄ concentration has been found to decline after the 12th day in their medium-term experiment (Kravchenko et al. 2002). They also noted that CH₄ decreased by almost 25% in the first ten hours during their short-term experiment (Kravchenko et al. 2002) performed in similar soil type as used in the present work. However, as they also noted, microbiological communities and environmental factors might play more important roles in such mechanisms.

Fertilizer application sustained slightly, yet statistically significant, decreasing levels of CH₄ concentrations in the treatments during the course of the short-term experiment as shown in Fig. 1. This result could be interpreted that a collective use of mineral NH₄NO₃ fertilizers and an N.I. may successfully reduce CH₄ elusion thus resulting in CO₂ concentration into the atmosphere. The first day of the experiment is the period when there was the highest drop in CH₄ concentration in the NH₄NO₃ + N.I. treatment. The maximum CH₄ concentration observed in the control group at day 14 has shown results parallel to those obtained by Lopez-Real and Baptista (1996) since they noted that the maximum emission of CH₄ occurs between the 5th and 15th days when cattle manure was used.

The arithmetic averages of the CH₄ emissions with NH₄NO₃, NH₄NO₃ + N.I. and control treatments were 45.46 (± 3.33) ng CH₄-C g⁻¹, 45.20 (± 5.16) ng CH₄-C g⁻¹, and 55.51 (± 2.82) ng CH₄-C g⁻¹, respectively.

Based on the results, with the NH₄NO₃ treatment, the CH₄ emissions decreased linearly with respect to time according to the linear relation

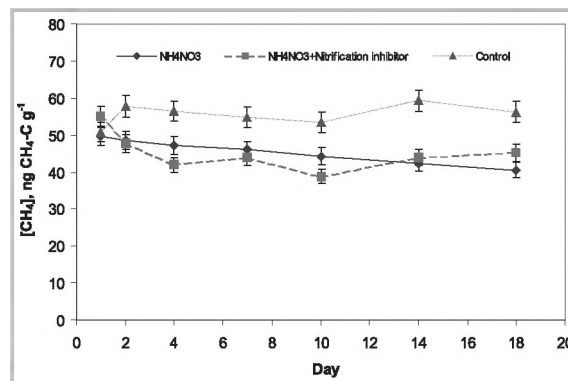


Fig 1. The change in methane concentration in all treatments.

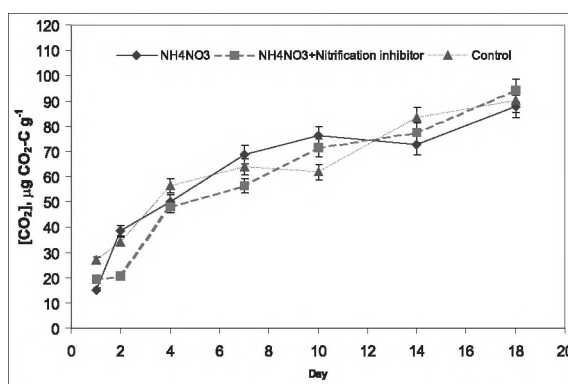


Fig 2. The change in carbon dioxide concentration in all treatments.

that can be given as

$$CH_4 \text{ concentration as ng } CH_4\text{-C g}^{-1} (NH_4NO_3) = 49.645 - (0.5321 \times t) \quad (2)$$

where,

t is the time after application of the treatment as a day, with the regression coefficient of 98.88%. The change between final and initial CH₄ emissions in the case of NH₄NO₃, NH₄NO₃ + N.I., and the control treatments have been computed to be approximately -9%, -22% and +9%, respectively. This means the increasing CH₄ detected with the control treatment, was inspite of the fact that CH₄ emission were found to have a declining order under both the NH₄NO₃ and NH₄NO₃ + N.I. treatments during the experiment. The overall decrease in CH₄ emission with NH₄NO₃ + N.I. was found to be more than twice as longer as that in only the NH₄NO₃ applied treatment.

CO₂ Emissions

High CO₂ concentration, specifically within first two days, was measured in the NH₄NO₃ applied samples. It was seen that both the nitrification

inhibited and control sample CO₂ concentrations inclined with respect to time passed as shown in Fig. 2. The general tendency of all treatments has been fitted to a continuous increase in CO₂ concentration that started approximately at 20 µg CO₂-C g⁻¹ and finally reached 90 µg CO₂-C g⁻¹ at day 18. These results could be attributed to soil microorganisms that breakdown soil organic matter in spite of the fact that the soil biological activity during the experiments is not in the scope of this work. During microbial activity, CO₂ is released into the atmosphere and due to the decreasing available food, soil microbial activity decreases and this results in decreasing CO₂ emission into the atmosphere. Therefore, it must be underlined that CO₂ formation via CH₄ oxidation could be classified as a logarithmically driven progress with respect to time. Based on Fig. 2, approximately a 475% increase in CO₂ concentration under NH₄NO₃ treatment, a 380% increase in CO₂ concentration under NH₄NO₃ + N.I. treatment and a 235% increase the CO₂ concentration in the control group between final and initial conditions were computed. These results indicate that the CO₂ concentrations are twice as much with NH₄NO₃ and approximately 1.6 times greater with NH₄NO₃ + N.I. than the CO₂ concentration increase computed for the control treatment.

The arithmetic averages of the CO₂ emission with NH₄NO₃, NH₄NO₃ + N.I., and control treatments are 58.44 (± 25.20) µg CO₂-C g⁻¹, 55.38 (± 28.22) µg CO₂-C g⁻¹, and 59.54 (± 23.23) µg CO₂-C g⁻¹, respectively.

Based on the change of CO₂ in all treatments, three logarithmic relationships for prediction of CO₂ formation during the course of the experiment from NH₄NO₃, NH₄NO₃ + N.I. and the control treatments were developed. The relationships are

$$\text{CO}_2 \text{ concentration as } \mu\text{g CO}_2\text{-C g}^{-1} \text{ (NH}_4\text{NO}_3\text{)} \\ = (23.417 \times \text{Ln } t) + 18.773 \quad (3)$$

$$\text{CO}_2 \text{ concentration as } \mu\text{g CO}_2\text{-C g}^{-1} \\ \text{(NH}_4\text{NO}_3\text{+N.I.)} = (24.498 \times \text{Ln } t) + 15.319 \quad (4)$$

$$\text{CO}_2 \text{ concentration as } \mu\text{g CO}_2\text{-C g}^{-1} \text{ (control} \\ \text{treatment)} = (21.278 \times \text{Ln } t) + 23.497 \quad (5)$$

with regression coefficients of 93.62%, 90.31%, and 88.38%, respectively.

Based on the equations given above, the CO₂ concentration with NH₄NO₃ and nitrification treatments were computed to be approximately 86 µg CO₂-C g⁻¹ and 85 µg CO₂-C g⁻¹ with the control

treatment at day 18.

N₂O Emissions

The N₂O changes during the course of the experiment have shown that mineral NH₄NO₃ applied to the soil has yielded more N₂O than in the other treatments in the first seven days of the experimental procedure. Posterior to this point of time, there is a slightly decreasing trend in N₂O from the soil with NH₄NO₃ applied. The N₂O levels evolved from the soil were found to be in the order of a fertilizer inhibitor, that were used in the control treatments during the experiment.

Fig.3 illustrates the N₂O formation from the treatments during the experiment. The results have shown that mineral nitrogen fertilization without any nitrification inhibitor, yields large mineral or organic nitrogen losses in N₂O and other nitrous oxide forms from the agrarian fields.

With the NH₄NO₃ treatment, the change in N₂O concentration has been observed as high as 40% between the 1st and 2nd day of the experiment. However, the increase in both nitrification inhibited and control treatments are notably low. The decline of N₂O with all treatments after day 14 is very similar being about 5%. After the 18th day, the change in N₂O concentration could be expected to incline steadily since as Kravchenko et al. (2002) reported, after a logarithmic increase in N₂O concentration during the first 25-30 days of long-term methanogenesis, a steady linear increase occurs in N₂O concentration following the first period (25-30) days.

The arithmetic averages of the N₂O emission with NH₄NO₃, NH₄NO₃ + N.I. and the control treatments are 135.53 (± 16.81) ng N₂O g⁻¹, 124.44 (± 2.93) ng N₂O g⁻¹, and 121.13 (± 3.98) ng N₂O g⁻¹, respectively.

A logarithmic increase in N₂O concentration with NH₄NO₃ treatment and a linear decrease in N₂O concentrations with NH₄NO₃ + N.I. and the control treatments have been shown to exist, despite some of the relationships which are weakly explainable. These relationships can be defined as;

$$\text{N}_2\text{O concentration as ng N}_2\text{O-N g}^{-1} \\ \text{(NH}_4\text{NO}_3\text{)} = (10.683 \times \text{Ln } t) + 117.44 \quad (6)$$

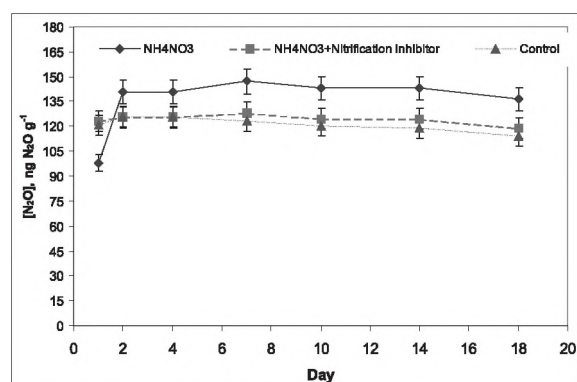
$$\text{N}_2\text{O concentration as ng N}_2\text{O-N g}^{-1} \\ \text{(NH}_4\text{NO}_3\text{+N.I.)} = (-0.2663 \times t) + 126.57 \quad (7)$$

$$\text{N}_2\text{O concentration as ng N}_2\text{O-N g}^{-1} \text{ (Control} \\ \text{treatment)} = (-0.5303 \times t) + 125.37 \quad (8)$$

with regression coefficients of 20.47%, 11.13%,

Table 2. The respective gas emission ratios with the treatments used.

Time, day	NH ₄ NO ₃			NH ₄ NO ₃ + N.I.			Control		
	CH ₄ : CO ₂	CH ₄ : N ₂ O	CO ₂ : N ₂ O	CH ₄ : CO ₂	CH ₄ : N ₂ O	CO ₂ : N ₂ O	CH ₄ : CO ₂	CH ₄ : N ₂ O	CO ₂ : N ₂ O
1	0.0032	0.5050	155.71	0.0028	0.4471	158.52	0.0019	0.4200	222.57
2	0.0013	0.3448	273.28	0.0023	0.3793	164.80	0.0017	0.4607	273.17
4	0.0009	0.3355	356.43	0.0009	0.3333	383.15	0.0010	0.4497	450.39
7	0.0007	0.3124	467.18	0.0008	0.3418	438.81	0.0009	0.4447	518.81
10	0.0006	0.3101	532.93	0.0005	0.3113	573.49	0.0009	0.4450	515.38
14	0.0006	0.2956	507.59	0.0006	0.3521	622.14	0.0007	0.4981	700.42
18	0.0005	0.2966	644.14	0.0005	0.3801	791.43	0.0006	0.4927	789.61
Mean	0.0011	0.3428	419.61	0.0012	0.3636	447.48	0.0011	0.4587	495.76
S.D.	0.0010	0.0739	167.48	0.0009	0.0443	235.34	0.0005	0.0279	206.31

**Fig 3.** The change in N₂O concentration in all treatments.

and 51.44%, respectively.

The total increase of N₂O concentration between the initiation and 18th days of the experiment with the NH₄NO₃ treatment has been computed to be approximately 40%; whereas, the total decreases of N₂O with the NH₄NO₃ + N.I. and control treatments have been, calculated as 4% and 6% respectively. Indeed, N₂O concentration with NH₄NO₃ + N.I. could be evaluated as stable, especially in the first 14 days of the experiment. To be more precise, N₂O concentration with NH₄NO₃ + N.I. increased up to the 7th day of the experiment then dropped and the N₂O concentration with the control treatment increased in the first 4 days then dropped notably. In Table 2, CH₄ to CO₂, CH₄ to N₂O and CO₂ to N₂O, ratios their mean values, and standard deviations with (a) NH₄NO₃, (b) NH₄NO₃ + N.I., and (c) control treatments are summarized. Based on these results, despite the fact that there are notable decreases in both the CH₄ to N₂O ratio with both the NH₄NO₃ and NH₄NO₃ + N.I. treatments with respect to time, there is a slight increase in the CH₄ to N₂O emission ratio with the control treatment.

According to the completed statistical calculations, no statistical differences were found between N₂O concentrations with the NH₄NO₃ application and the NH₄NO₃ + N.I. applications. On the other hand, a significant statistical difference

was obtained in N₂O with the NH₄NO₃ and the control applications.

Total Gas Emissions

As a result of the computations that were made by converting the CH₄ and N₂O gas concentrations into their equivalent CO₂ values, the best option to reduce greenhouse gas emission is NH₄NO₃ + N.I. Because of the fact that the conversion showed a decrease of 3.33 μg CO₂ g⁻¹ gas emission per day. On the other hand, only the NH₄NO₃ application caused a 3.16 μg CO₂ g⁻¹ gas increase per day compared to the control. If one considers total agricultural field and duration of agricultural aid, the total CO₂ emitted into the atmosphere would be enormous. For this computation, it is assumed that CH₄ and N₂O have a 20 and 310 times larger greenhouse impact respectively, than that of CO₂ as postulated by Peigné and Girardin (2004). The total daily CO₂-equivalent gas emitted into the atmosphere per day for NH₄NO₃, NH₄NO₃ plus N.I., and the control was computed to be 101.36 μg g⁻¹, 94.87 μg g⁻¹, and 98.20 μg g⁻¹, respectively. Therefore, the highest CO₂-equivalent gas reduction (3.39% per day compared to the control and 6.61% per day compared to the NH₄NO₃ application) is achievable using NH₄NO₃ plus a nitrification inhibitor.

CONCLUSIONS

Based on the results obtained, the CO₂ change during the experiment was found to be in substantially increasing order as a function of time. This was approximately a 380% increase in CO₂ concentration with NH₄NO₃ + N.I., a 475% increase in CO₂ emission with the NH₄NO₃ application and, a 235% increasing with the control treatments when observe whereas, the CH₄ concentrations measured during the experiment were computed to have a steadily decreasing (9 and 22%) order for NH₄NO₃ and NH₄NO₃ + N.I. treatments despite the fact that with the control treatment the CH₄ emission showed a steadily rising trend of 9% during the course of the experiment. As for the N₂O change, a slightly increasing (40%) then steadily progressing N₂O for the NH₄NO₃ applied experimental treatment and almost, a stagnant NH₄NO₃ + N.I. and control treatments were observed. Therefore, it can be concluded that the overall NH₄NO₃ + N.I. treatment offers the best option when one needs to minimize both methane and nitrous oxide, along with predominant

CO₂ emissions from agricultural fields composed of sandy loam soils.

Differences of CH₄ to CO₂ ratios during the experiment with NH₄NO₃ and NH₄NO₃ + N.I. applications have been computed to be almost three times and slightly over 2.4 times larger in comparison with those of the control treatment. On the other hand, both the NH₄NO₃ and NH₄NO₃ + N.I. applied treatments have been computed to have decreasing CH₄ to N₂O ratios (70% and 18% respectively); whereas, in the control treatment, this ratio was found to have a slightly (approximately 15%) increasing pattern. The CO₂ to N₂O ratios during the experiment in all treatments was found to be close. As many researchers underlined, along with the soils physical characteristics, soil biotic and

chemical characteristic and climatic factors are all important for the methanogenesis. It is clear that the first stages (especially the first 3 days) are critically important in CH₄ oxidation and related kinetics. In order to minimize CO₂ emission from such fields where methane oxidation takes place, a nitrification inhibitor along with NH₄NO₃ should be applied in to the soil. As one assesses importance of the global scale, careful application of NH₄NO₃ plus a nitrification inhibitor and use of the best soil management practices (effective irrigation, agricultural plant variety, etc.) could notably reduce the amount of greenhouse gases caused by agricultural activities and have an impact on the atmospheric wellbeing.

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