Adding Nitrogen Fertilizers to the Soil Affects the Production of Carbon Dioxide(CO_2), Nitrous Oxide(N_2O), and Nitrogen Oxide (NO)

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الخلاصة:

في هذا البحث تم العمل على مجموعة تجارب بسيطة حيث تم حساب انبعاث ثاني أكسيد الكربون (CO_2) وأكاسيد النيتروجين وبعض العوامل مثل درجة الحرارة والنيتروجين المعدني المختلف (N) والنيتروجين العضوي ومصادر الكربون (C) التي تؤثر على إنتاج الغاز. حيث. تم تحليل تركيبة الغاز في مساحة الجهاز الزجاجي المغلق التي يحتوي على عينة التربة بواسطة طريقة كروماتوجرافيا الغاز والتألق الكيميائي. أثبت النموذج التجريبي المصغر المطبق أنه أداة مناسبة لتقدير تأثير العوامل المؤثرة على إطلاق ثاني أكسيد الكربون وأكسيد النيتروجين وأكسيد النيتروز. أدى ارتفاع درجة الحرارة ونسبة C / Nللإمدادات العضوية C إلى زيادة انبعاثات الغازات الدفينة.حيث يسبب إضافة سماد الأمونيوم أيضًا في انبعاث غازات أكثر من سماد النترات. ولوحظ أيضًا ظهور NO كوسيط في التحولات الميكروبية.

الكلمات الافتتاحية: الغازات الدفينة، النترتة، نزع النتروجين ، CO_2 ، N_2O، NO

ABSTRACT:

In the present paper a simple microcosm experiment set is reported in which the carbon dioxide (CO_2) and nitrogen oxides emission and some factors as temperature, different mineral nitrogen (N) and organic N, and carbon (C) sources influencing the gas production were investigated. The headspace gas composition of closed glass vessels containing soil sample was analysed by gas chromatographic and chemiluminescent methods. The applied microcosm experimental model proved to be a suitable tool for estimating the effect of factors affecting the CO_2, NO and N_2O release. The rising temperature and C/N ratio of the organic C supply increased the greenhouse gas emission. The applied ammonium fertiliser also induced more gas emission than nitrate fertiliser. The appearance of NO as an intermediate in microbial transformations was observed as well.

Keywords: Denitrification, Greenhouse gases, Nitrification, CO_2, N_2O, NO.

الملخص:

في هذا البحث تم العمل على مجموعة تجارب بسيطة حيث تم حساب انبعاث ثاني أكسيد الكربون (CO_2) وأكاسيد النيتروجين وبعض العوامل مثل درجة الحرارة والنيتروجين المعدني المختلف (N) والنيتروجين العضوي ومصادر الكربون (C) التي تؤثر على إنتاج الغاز. حيث. تم تحليل تركيبة الغاز في مساحة الجهاز الزجاجي المغلق التي يحتوي على عينة التربة بواسطة طريقة كروماتوجرافيا الغاز والتألق الكيميائي. أثبت النموذج التجريبي المصغر المطبق أنه أداة مناسبة لتقدير تأثير العوامل المؤثرة على إطلاق ثاني أكسيد الكربون وأكسيد النيتروجين وأكسيد النيتروز. أدى ارتفاع درجة الحرارة ونسبة C / N للإمدادات العضوية C إلى زيادة انبعاثات الغازات الدفينة.حيث يسبب إضافة سماد الأمونيوم أيضًا في انبعاث غازات أكثر من سماد النترات. ولوحظ أيضًا ظهور NO كوسيط في التحولات الميكروبية.

الكلمات الافتتاحية: الغازات الدفينة، النترتة، نزع النتروجين ، CO_2 ، N_2O، NO

INTRODUCTION:

The extended application of manure, plant residues and fertilisers causes agricultural and environmental problems. To a certain extent nutrients might be utilised by soil microorganisms instead of plants resulting in greenhouse gases which contribute to global climate change. Although there are several anthropogenic greenhouse gas sources and it is important to study the possibilities of reducing the emission originating from e.g. nitrogen fertiliser industry (Cao, R., L et al.,.. 2021; A. Langarica-Fuentes et al. 2018) and wastewater treatment plants (Préndez and Lara-González, 2007), researchers usually agree that besides fuel burning technologies, the main anthropogenic source is agriculture (Mørkved et al., 2006; Ruser et al., 2006). CO_2 is the most important greenhouse gas considering its amount in air but the global warming potential of nitrous oxide (N_2O) is about 300 times that of CO_2 (Koponen et al., 2004; Khalil et al., 2002; IPCC, 2001). The atmospheric concentration of N_2O has been increasing continuously at the rate of 0.2 %

annually (Khalil et al., 2002) and the globally experienced climate change induces more and more new surveys and simulation models (Calanca et al., 2007; Levy et al., 2007) in which the greenhouse gas emitting processes, the factors influencing them, the resulted global warming potential and the possible mitigation strategies (Guo and Zhou, 2007; Liu, Y., et al., 2019) are investigated. Soil microbial processes are presumed to contribute significantly to the agricultural CO_2 emission. In the case of NO and N_2O emission, generally also microbial activities, namely nitrification and denitrification, are considered to be the processes of primary importance. Although the basic factors determining the rate of these microbial events are soil moisture, temperature and C and N availability (Ma et al., 2007; Guo and Zhou, 2007; Chu et al., 2017; Ruser et al., 2006), the effects of a lot of other factors are studied comprehensively. Thus, besides basic climatic conditions, soil properties (texture, organic matter content, bulk density, porosity, infiltration rate, pH, etc.), microbial population density (Kravchenko and Yu, 2006; Leiber-Sauheitl et al. 2015), the way of tillage (Liu et al., 2020; Oorts et al., 2007) and fertilisation (Chu et al., 2017; Guo and Zhou, 2007; Huang et al.; 2004), crop management (Guo and Zhou, 2007; Cheng et al., 2017; Chen et al., 2016) and even the presence or absence of earthworms (Congreves, K. A. et al., 2019) and their selecting and amplifying influences to microbial processes are investigated in field, meso- and microcosm experiments. Though the effect of some determining factors e.g. tillage cannot be studied in microcosm experiments, their relatively low financial needs compared to field studies favour their application in research projects (e.g. Mørkved et al., 2006; Ludwig et al., 2006). Laboratory experiments make also possible the analysis of the influence of different factors separately from each other, their investigation in certain combinations and the repetition of the experiments under the same conditions used earlier.

The microcosm experiment reported by the present paper was a part of a three level agricultural experiment set in which field, mesocosm and microcosm experiments were performed with the same cultivated soil. (Debreczeni et al.,1997; Notas et al., 2002) to study the different transformation processes of soil C-N cycles. Though the applied microcosm system was quite simple, by its means it was possible to investigate the CO_2, NO and N_2O emission of nitrification and denitrification origin mostly and some factors such as temperature, different mineral N and organic N, and C sources influencing the gas production of agricultural soil.

During the experiments the headspace gas composition of closed glass vessels containing soil sample was analysed. The CO_2 and N_2O concentrations of gas samples were analysed by gas chromatographic methods and NO-content by means of chemiluminescent detection.

MATERIALS AND METHODS:

The microcosm experiment was conducted in glass vessels covered gas tightly by silicone septa. A 200 g homogenised (<2 mm) slightly alkaline solonchak arable land soil sample of low humus content were placed into the vessels of 1200 cm^3. The most important physical and chemical properties of the soil are the next: pH (KCl): 7.55, total salt content: 0.08 %, $CaCO_3$: 1.91 %, humus: 1.06 %, total organic C: 1.08 %, total N: 0.08 %, NH_4^+-N: 0.99 mg $(100g)^{-1}$, NO_3^-–N: 7.16 mg $(100g)^{-1}$, K_2O (AL*): 13.97 mg $(100g)^{-1}$, P_2O_5 (AL*): 84.68 mg $(100g)^{-1}$, density: 2.41 g cm^{-3} and C/N ratio: 13.15. The soil samples were treated by the addition of plant residue, manure and inorganic N-sources singly or in combination form, as well at a moisture level of 60 % water holding capacity. The treatments were applied in three replications. The vessels were incubated in a laboratory thermostat in two experiment sets at 28 °C and 37 °C temperature, respectively during 35 days. The most important features of the treatments applied in the experiment performed in 2005 and 2006 are summarised in *Table 1*.

Label of treatments	Meaning of treatments	Treatments / Additives (doses)
C	Control soil	
C+N1	Control soil amended with KNO_3	• KNO_3: 500 kg N ha^{-1}
C+N2	Control soil amended with NH_4NO_3	• NH_4NO_3: 500 kg N ha^{-1}
R	Control soil amended with plant residue	• Maize straw: 0.5 t ha^{-1}
R+N1	Control soil, plant residue and KNO_3	• KNO_3: 500 kg N ha^{-1} • Maize straw: 0.5 t ha^{-1}
M	Control soil amended with manure	• Manure: 52 t ha^{-1}

Table 1. The most important features of the treatments applied in the different xperiments.

During the experiments, N_2O and CO_2 concentrations of gas samples taken from the headspace of each vessel were determined regularly by gas chromatographic method. A 250 – 250 μl gas sample was taken manually by

* measured by the **A**mmonium-**L**actate extraction method.

gas tight Hamilton® syringes (See *Figure 1.*) and was injected from each vessel to the HP 5890 Series II® gas chromatograph.

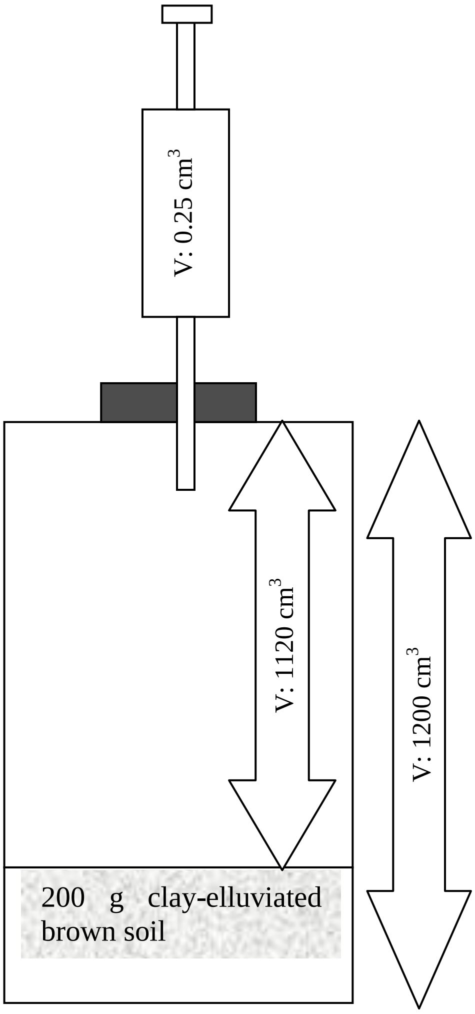

Figure 1. The microcosm experimental system

Packed columns (Porapak Q) were used to separate the different constituents of gas samples. Electron Capture Detector (ECD) and Thermal Conductivity Detector (TCD) detected N_2O and CO_2 concentrations, respectively. The NO-content of the gas samples was analysed by the chemiluminescent detector of Antek 7050 NO-analyser®. Each gas content was measured three times per day whenever measurements were carried out using external standard and one point linear calibration.

RESULTS AND DISCUSSIONS:

The changes of the concentrations of the different measured gases plotted against time can be seen in *Figures 2.* and *3.* The horizontal axes represent the time of incubation (Time) and the vertical axes denote gas concentration (c). Vertical bars symbolise standard deviations.

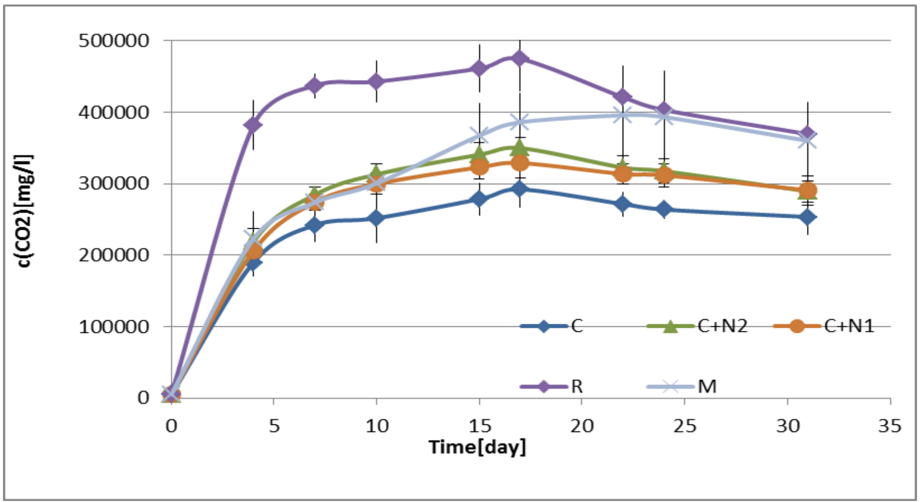

Figure 2.a. CO_2 gas concentration at 37 °C vs. time. Treatments are **C, R, M, C+N1** and **C+N2**. The meanings of the symbols are listed in Table 1.

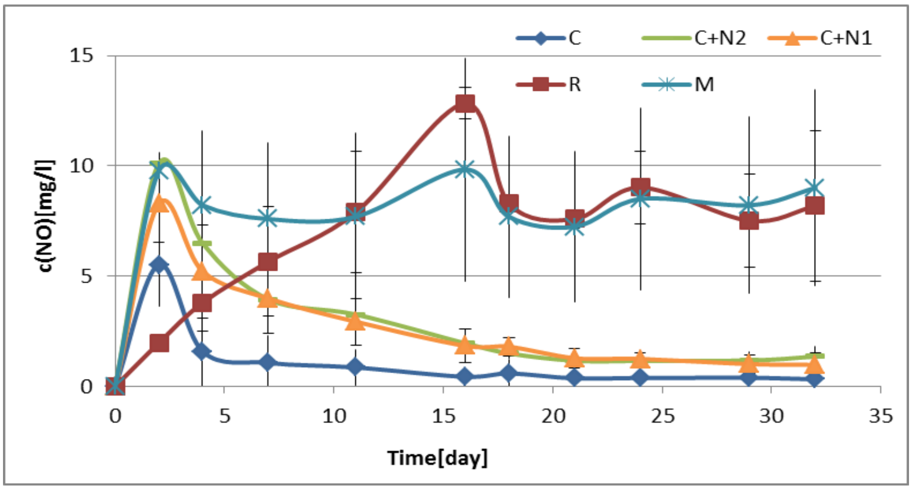

Figure 2.b. NO gas concentration at 37 °C vs. time. Treatments are **C, R, M, C+N1** and **C+N2**. The meanings of the symbols are listed in Table 1.

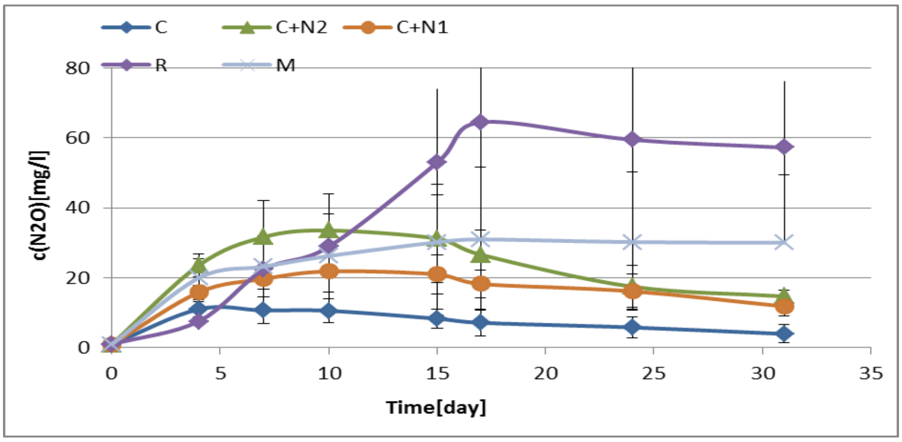

Figure 2.c. N_2O gas concentration at 37 °C vs. time. Treatments are C, R, M, C+N1 and C+N_2. The meanings of the symbols are listed in Table 1

In *Figures 2.* the temporal changes of greenhouse gas emission affected by the application of different organic (R and M) and inorganic fertilisers (N1 and N2) are represented. Considering the shapes of the curves, it can be stated that maximums can be observed approximately on the 15th day of the experiments. In the case of the NO and N_2O production these maximums occur earlier i.e. on the 10th day during N_2O emission and even earlier for NO productions from inorganic fertiliser amended soil. In the latter cases the microorganisms utilised the great amount of available mineral N faster than in the soil samples containing organic additives, where the mineralisation of the organic N-content needed some time, as well.

The higher available C amount (R and M) resulted in significantly higher microbial activity and increased gas production of denitrification and heterotrophic nitrification origin (Guo and Zhou, 2007). Although the amount of the applied plant residue was smaller than the quantity of manure, the higher C/N ratio of the plant remnants caused higher gas emission in treatment (R) than in (M).

Analysing the effect of the different types of inorganic N fertilisers, it can be seen, that although the differences were not always significant, usually increased gas emission from treatments containing NH_4^+ (N2), as well was observed compared to the gas production of soil samples of equivalent N content of NO_3^- (N1) fertiliser origin. This phenomenon might be explained by the occurrence of nitrification at the given moisture level and the priming effect of ammonium fertilisers (Stout, 1995).

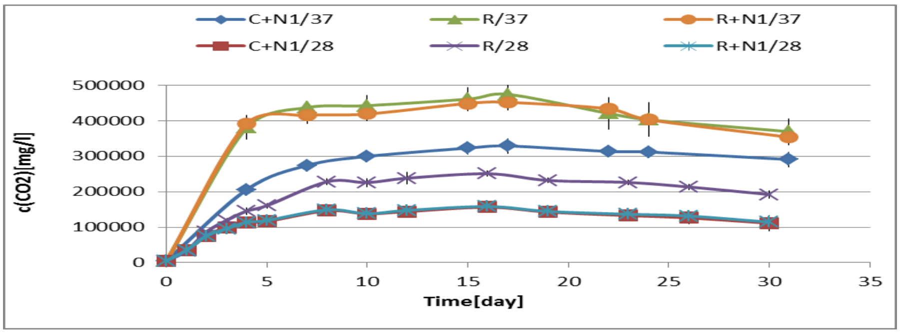

Figure 3.a. CO_2 gas concentration at 37 °C and 28 °C vs. time. Treatments are **R, C+N1** and **R+N1**. The meanings of the symbols are listed in Table 1.

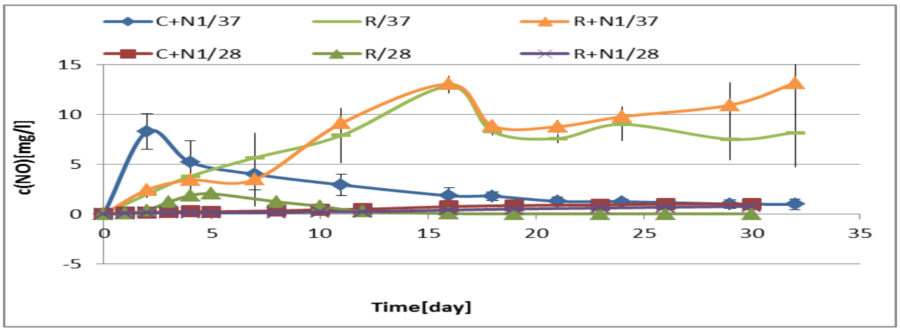

Figure 3.b. NO gas concentration at 37 °C and 28 °C vs. time. Treatments are **R, C+N1** and **R+N1**. The meanings of the symbols are listed in Table 1.

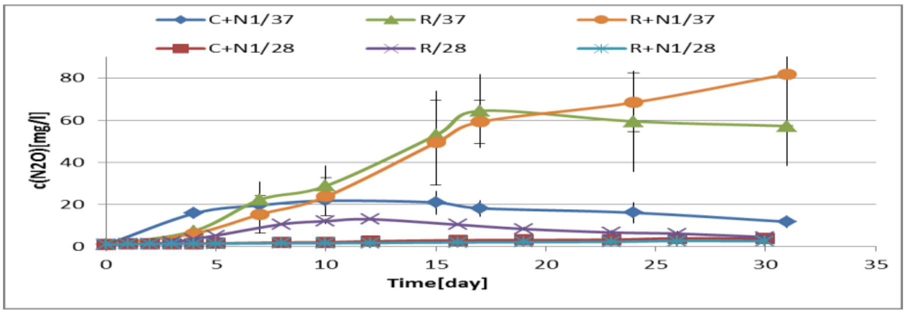

Figure 3.c. N_2O gas concentration at 37 °C and 28 °C vs. time. Treatments are **R, C+N1** and **R+N1**. The meanings of the symbols are listed in Table 1.

In *Figures 3.* the temporal changes of greenhouse gas emission affected by the application of organic (R) and inorganic (N1) fertilisers at different incubation temperatures are represented. The shapes of the curves correspond to those represented by *Figures 2.* The microbial activity enhancing effect of temperature can be observed in all figures, i.e. the increased microbial processes resulted in higher gas productions. A temperature increase of approximately 10 °C caused 2-6 times higher gas concentrations. The order of the maximal gas production originating from the different treatments is approximately the same at both applied temperature namely (R/37, R+N1/37), C+N1/37, R/28, (R+N1/28 and C+N1/28). The gas emissions from the treatments whose symbols are in parentheses do not differ from each other significantly. The above order can be attributed to the increased available C content and higher C/N ratio which improve the microbial activity compared to the cases of lower C/N ratio in only N amended treatments. The detected gas concentrations from the different treatments indicate the determining role of C supply for microbial processes which was more apparent in the reported experiments than the effect of N supply. This experience is in agreement with the results of other studies which also report the microbial activity raising effect of decomposable organic C e.g. after drying and rewetting of soil (Ruser et al., 2006) and freeze-thaw cycles (Mørkved et al., 2006; Ludwig et al., 2006), although Kravchenko et al. (2006) found that microbial life is stimulated by C/N ratios below (<10) and above (>14) certain C/N ratio limits. (Considering the standard deviations, it seems to be reasonable to presume that in soils treated with organic C supply and at higher temperature, the faster microbial processes caused faster changes in the gas productions resulting in bigger standard deviations during the measurements. This phenomenon could be observed mainly in the case of the production of the more transient NO and N_2O than it happened during the CO_2 emission.)

In conclusion, it can be stated that the applied simple microcosm experimental model proved to be a suitable tool for estimating the effect of factors influencing the CO_2, NO and N_2O release from agricultural soil. The temporal changes of the gas production depended on the soil temperature, the type of the applied mineral N and organic N, and C sources significantly. From 28 °C to 37 °C, the rising temperature increased the microbial activity of soil resulting in higher greenhouse gas emission. The appearance of NO as an intermediate of microbial processes was observed as well. Comparing the gas productions due to the effect of equivalent N-amount of KNO_3 and of NH_4NO_3, higher gas concentrations were observed in the case of NH_4NO_3 than that of KNO_3. Smaller doses of plant residue caused higher gas emission as a consequence of its higher C/N ratio than it was experienced in the case of manure utilisation. Based on the result of the reported experiment it can be stated that to reduce the greenhouse gas production of agricultural origin and to ensure optimal C and N content and supply of cultivated soil, organic fertilisers with lower C/N ratio and the co-application of organic matter and N supplies are necessary mainly at warm regions to avoid high gas loss of microbial origin.

In the case of future experiments, the development of the applied microcosm model might be necessary for the measurement of short term changes by this static approach or for the investigation of long term tendencies by a dynamic system. This would also result in a better correlation with the results of field experiments and by means of an improved experiment system, the effect of other factors such as water supply, soil physical properties etc. might be studied as well.

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