

Strategies to Reduce the Emission of greenhouse-gases

ABDOUSALAM A. A. ALGAIDI¹ and Hosam Bayoumi Hamuda²

¹Faculty of Agriculture, Sebha University, Libya

²Óbuda University, Rejtő Sándor Faculty of Light Industry and Environmental Protection Engineering, Hungary

Abstract

The N₂O and CO₂ concentration of gas samples was analysed by gas chromatographic methods by means of chemiluminescent detection. Concerning the results it can be stated that the temporal changes of N₂O and CO₂ concentration demonstrated the impact of the coupled microbial processes resulting in these greenhouse gases. The gas production depended on the soil moisture level, temperature and C:N ratio significantly. The inhibitory effect of toxic heavy metals (e.g. Cd) could also be affected by the C:N ratio. The appearance of Nitric Oxide as an intermediate of microbial processes was observed as well.

Introduction

Although many of these sources have been identified, researchers usually agree that agriculture is a significant contributor to the increasing CO₂ and N₂O concentration of air Hellebrand et al (2008), Akimoto et al (2005). Dissimilatory reduction of NO₂⁻ to NH₄⁺, denitrification Firestone et al (1979), other reducing biological processes by common bacteria not typically defined as denitrifiers and non-biological reactions van Hecke et al (1990). These processes cover a wide range of metabolisms, from autotrophic to heterotrophic, from oxidative to reductive. Consequently different nitrogen forms can have different effects on soil N transformations and N₂O emissions, as they kinds of soil microorganisms. Also, soil physico-chemical properties will influence the contribution of different biological processes to the overall N₂O flux from soil. Denitrification of nitrate and nitrite is generally considered as the dominant source of N₂O in heavy textured soils. The microbial reduction of NO₃⁻ to NO₂⁻ and then to gaseous N₂O and N₂ called enzymatic denitrification because each step of the process is governed by specific reductase enzymes. Most denitrification is accomplished by heterotrophic bacteria which require complex organic compounds of nitrogen and carbon for metabolic synthesis. Besides carbon availability, pH, temperature, soil water content, characteristics, fertilisation, crop species etc. influence denitrification. Most denitrifying bacteria grow best near neutral pH values. Decreasing pH decreases CO₂ and N₂O production Ellis et al (1998). Soil temperature affects denitrification directly by influencing microbial activity and indirectly for both O₂ solubility and diffusion in water depend on temperature. Although the minimum temperature for denitrification is about 5°C according to Paul and Clark (1989), there are studies (e.g. Koponen et al (2004)) which analyse the possible effect of freezing and thawing on N₂O emission. Soil moisture controls O₂ diffusion to sites of microbial activity i.e. if increased water content interferes with air diffusion, denitrification increases as well. Generally in field, denitrification is lacking or insignificant at moisture levels less than 60 % of water-holding capacity Paul and Clark (1989). Zheng et al.(2000) experienced „explosive emission of N₂O from rice-based agro-ecosystem” within 110±5% soil water holding capacity Zheng et al.(2000). Usually it is higher in case of heavy clay soils than in case of loose soils Füleky Gy. (1999). Huang et al (2004). Experienced a correlation between the N₂O and CO₂ emissions and the dissolved organic C concentration of soil, and C:N ratio of different plant residues Huang et al (2004). The residue type is

thought to be an important factor affecting N₂O emissions as well Shelp et al (2000). Collective effect of some factors was also studied and e.g. Kiese and Butterbach. (2002) found that soil moisture had a stronger effect on N₂O emissions than on CO₂ emission. They also observed that changes in soil moisture influenced more significantly the N₂O and CO₂ emission than changes in soil temperature Kiese and Butterbach. (2002). Different experimental methods have been developed for years to measure the direct agricultural effect on greenhouse gas emission e.g. various isotope methods, chamber methods, measurement of N₂O concentration in soil and micrometeorological methods. Besides field measurements, mesocosm greenhouse experiments are also conducted. Both of them are quite time-consuming and expensive, so the development of suitable microcosm experimental methods is essential. Considering the analytical techniques, gas chromatographic measurement of greenhouse gases is the most used means in the analysis of gas samples. Traditionally Electron Capture Detector (ECD) and Thermal Conductivity Detector (TCD) are used to measure the N₂O and CO₂ concentration of samples (Christensen et al. 1996, Granli and Bøckman 1994, Clayton et al. 1994, Smith and Arah 1992). The objectives of present study are development a microcosm method for estimating the rate of environmental polluting gas production of denitrification origin mostly and the effect of different factors affecting the gas emission. This experiment was a part of a two level agricultural experiment in which field, mesocosm and microcosm experiment were performed with the same cultivated soil. For this reason in present microcosm experiment sets different typed and sized vessels, amount of soil, N-fertiliser and water were applied. The length of the preliminary incubation period, the type of the additives and the incubation temperature were also changed in order that different and more detectable effects could be observed. O₂, N₂, N₂O, and CO₂ emissions were measured from the headspace gas by the use of a gas chromatograph (GC).

Materials and methods

The microcosm experiment: The microcosm experiments were conducted in glass vessels of 800-1200 cm³ covered by septa. 100-200 g homogenised (<2 mm) soil was placed into the vessels and then it was treated by the addition of plant residue and inorganic N-source singly or in combination form as well as different doses in the presence or absence of Collembola (Springtails) (*Folsomia Candida*) and cadmium ion and various moisture degrees. The vessels were incubated in a laboratory thermostat at two different constant temperatures during 30-100 days. On the basis of its physical properties it is adobe. The chemical properties of the used soil in details are: pH_(KCl) 7.55, Density 2.41 g/cm³, total salt content 0.08%, CaCO₃ 1.91%, Humus 1.06%, total organic C 1.08%, total N 0.08%, NH₄⁺-N 0.99 mg/100g, NO₃⁻-N 7.16 mg/100g, C/N ratio 13.15, K₂O (AL*) 13.97 mg/100g, P₂O₅ (AL*) 84.68 mg/100g, (*measured by the ammonium-lactate extraction method).

Analysis of headspace gases

During the experiments, N₂O and CO₂ concentrations of gas samples taken from the headspace of each vessel were measured regularly. Packed columns were used to separate the different constituents of gas samples. ECD and TCD detected N₂O and CO₂ concentrations, respectively in a gas chromatograph. (In Experiment I. the N₂ and O₂ content of gas samples was also measured by TCD.) The CO₂ measurements were carried out according to the usual technique but a baseline correction and a CO₂ adsorbing pre-column had to be applied in the case of the N₂O measurements in Experiment I.-II. Respectively due to the high concentration of CO₂ which resulted in CO₂ blank values detected together with N₂O peaks by the ECD.

Results and discussion

The changes of the concentrations of the different measured gases plotted against time can be seen in summarising the results, it can be stated that even the first experiment proved that the applied microcosm experimental method can be used successfully to study the N₂O and CO₂ productions of denitrification origin mostly from soil. The effect of different factors and temporal changes could also be observed. In the second experiment the amount of the applied N-fertiliser and soil moisture were increased to make the concentration changes of the released gases more significant and an increased CO₂ production was detected.

Table1 The most important characteristics of GC

GC analysis of gas samples	HP 5980 Series II type gas chromatograph	
Analysed gases	N ₂ O	CO ₂
Carrier gases and flow rates	N ₂ : 23ml/min	He: 27ml/min
Temperature of Injector	70°C	70°C
Columns (temperature of oven is 50°C in Exp. I-II.)	Porapak Q (80/100 mesh, 6ft)	Porapak Q (80/100 mesh, 6 ft)
Detectors (temperature)	ECD (250°C)	TCD (150°C)
Calibration	external standard	
Calibration gas mixture contains	7.9 vpm N ₂ O (in Exp. I-II.)	9.7 v/v% CO ₂ (in Exp. I-II.)
Evaluation of chromatograms	HP 3390 Ser. II integrator, HP CHEM	

However the N₂O concentration decreased slightly on average. Similarly to the second experiment, an increased amount of N₂O emitted was detected to the effect of N fertilisation and added organic matter. The changes of the gas concentrations in time showed similar tendencies compared with the results of the first experiment. The presence of the organic matter buffered the effect of the cadmium contamination i.e., the addition of heavy metal did not restrict the microbial activity so much in the presence of maize plant residue than it did without organic matter. The presence of NO as an intermediate during N₂O production was also detected. The maximal values occurred at about half time of the appearance of the N₂O maximums.

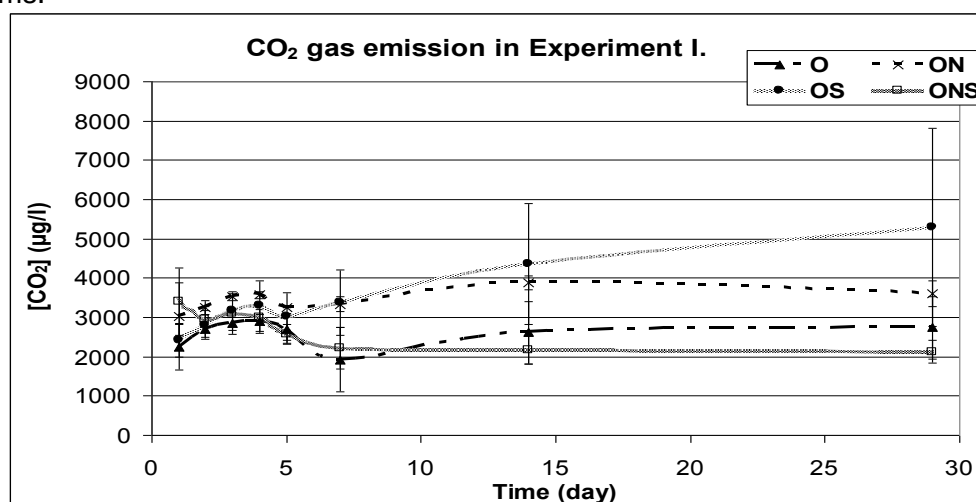


Fig. 1.A. CO₂ gas emission vs. time in Experiment I. Treatments are O, ON, OS and ONS.

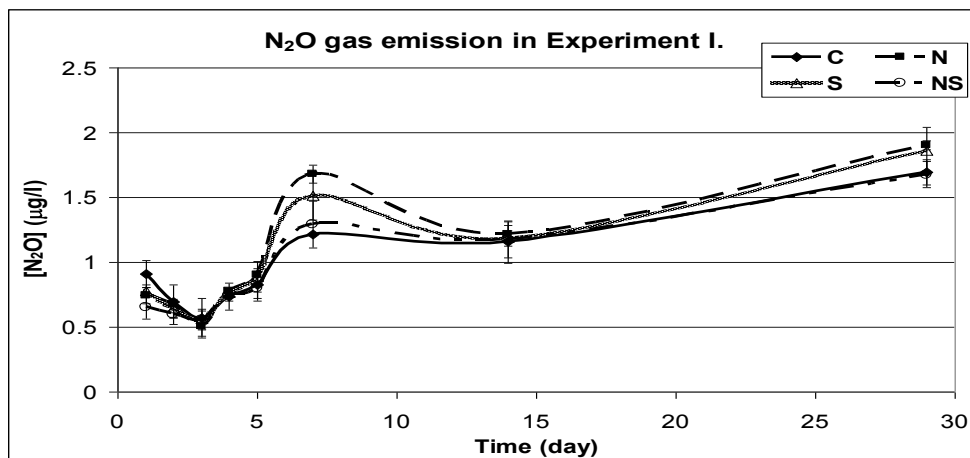


Fig. 1.B. N₂O gas emission vs. time in Experiment I. Treatments are C, N, S and NS.

The results of the first experiment indicate that after one week preconditioning period, although the change of N₂ and O₂ concentration could not be detected reliably by the applied GC method in agreement with Paul and Clark (1989), changes in N₂O and CO₂ productions could be measured. At normal atmospheric N₂ and O₂ concentrations, this technique (mole sieve column and TCD in a gas chromatograph) cannot detect such small changes in N₂ and O₂ concentrations. (Hence these diagrams are not included in present study.) Considering the temporal changes in N₂O and CO₂ concentrations, it can be observed that after a constant period of some days, there are increasing concentrations both in the cases of N₂O and CO₂. The local maximums occurred earlier in the case of CO₂ (on the 4th day approximately) than it happened in the case of N₂O (7th day). This phase delay might be explained by the fact that there is a more direct correlation between the increasing microbial activity and CO₂ concentration, than between the enhanced microbial life and the N₂O production. Another reason for this phenomenon might be that the micro-organisms consumed the soil O₂ content for oxidising organic compounds at first and only later, in the absence of O₂ the NO₃⁻ content of soil was used for accepting electrons resulting in N₂O. The long term effect of the different treatments could be detected more unambiguously in the case of N₂O whose concentration shows a definite increase again after the first maximums. Although the evaluation of the influence of spring tails is quite difficult, the improving effect of the organic additive on microbial activity can be seen clearly. Therefore, in Experiment II., the impact of N-fertilisation and organic additives were investigated setting higher soil moisture as well. As far as the results of Experiment I. are concerned, it can be stated that the applied microcosm experimental method proved to be an appropriate tool to investigate the soil greenhouse gas emission of denitrification origin mostly. To obtain more definite results and temporal changes in gas concentrations, Experiment II., was performed.

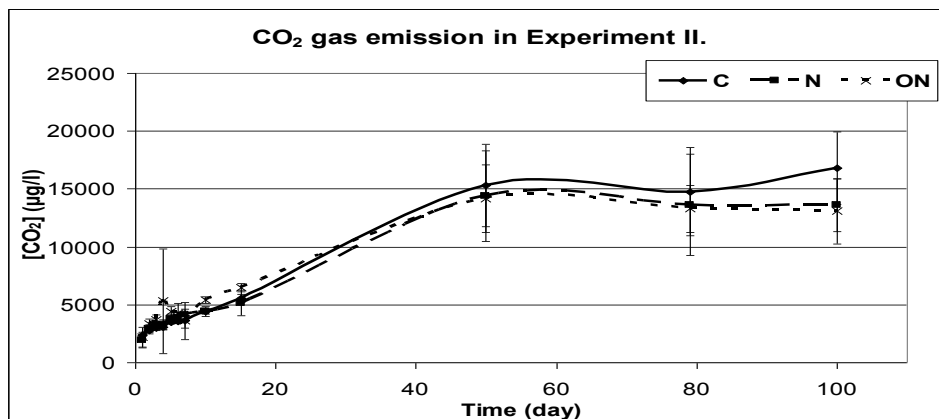


Fig. 2.A. CO₂ gas emission vs. time in Experiment II. Treatments are C, N and ON.

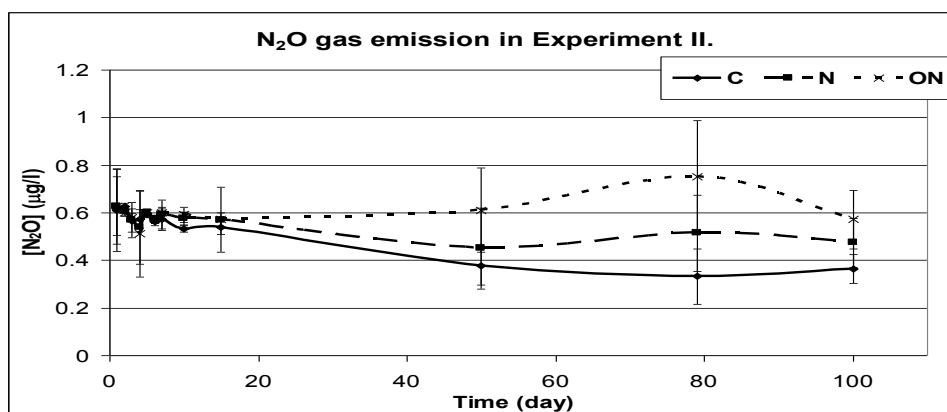


Fig. 2.B. N₂O gas emission vs. time in Experiment II. Treatments are C, N and ON.

In the second experiment the amount of the applied N-fertiliser and soil moisture were increased to make the concentration changes of the released gases more significant. The N-fertiliser was applied in dissolved form also to make the N-uptake of soil microorganisms easier. The CO₂ production increased in a well detectable way due to the different treatments. (By the end of the experiment it reached about the 3-5 times level of its concentration measured in Experiment I.) However the N₂O concentration decreased slightly on average in spite of the increased amount of the applied N-fertiliser. The fluctuation of the concentrations observed in the beginning of Experiment I., could hardly be detected in either cases. The presence of the dissolved form of the applied fertiliser might have made the microbiological processes more balanced. The increased moisture level might have created more anaerobic circumstances for the denitrifiers, ensuring a more complete denitrification and reduced N₂O/N₂ Granli and Bøckman. (1994). To eliminate the disturbing impact of the quite high standard deviations, to confirm and explain the phenomena experienced in Experiment I and II.

Similarly to the results of the second experiment, an increased amount of N₂O and CO₂ emitted was detected to the effect of N fertilisation and added organic matter, which is in accordance with the results of Huang et al (2004). Flessa et al (2010). The changes of gas concentrations in time showed similar tendencies compared with the results of the first experiment. The phase delay of the N₂O production maximum was detected again. Compared with Experiment II., the appearance of two local maximums could be observed in the case of N-fertilisation and cadmium contamination. Cadmium reduced microbial life significantly as Bleuel et al. (2009) also considered cadmium used in their experiment an

extremely toxic heavy metal. Considering the results of the CO₂ concentration measurements, which might be more characteristic to microbial life than N₂O production it can be concluded that the presence of organic matter buffered the effect of the cadmium contamination so the addition of heavy metal did not restrict the microbial activity so much in the presence of maize plant residue than it did without organic matter, although this dose (340 mg Cd²⁺/ kg) exceeded the maximal amount of Cd²⁺ of sewage sludge i.e. 10 mg/kg which is permitted to be placed to fields MI-08-1735-(1990).

The phenomenon might be explained by the occurrence of completed denitrification and the N₂O transformation to N₂. The explanation of the observations are not quite clear, although e.g. Ellis et al.(1998), raised the question of NO₃⁻ storage or assimilation within the microbial biomass and thus the possibility of mismatch between NO₃⁻ content and N₂O production of soil Ellis et al (1996). Linzmeier et al (2001) found that at the beginning of their experiment the proportion of the fertiliser-N-derived N₂O to the total N₂O emission reached 30-40% and later it decreased to 10-20%. The remaining part was assigned to soil-N. They also found a direct connection between high N₂O production and intensive rainfall events, rather than the timing of fertilisation.

Conclusion

In conclusion it can be stated that the developed microcosm experimental method proved to be suitable for estimating the potential of N₂O and CO₂ emission from cultivated soil. The response of the applied experimental system can be observed and explained considering the coupled microbial processes resulting in the detected gases.

References

- Akimoto F.; Matsunami A.; Kamata Y.; Kodama I.; Kitagawa K.; Arai N.; Higuchi T.; Itoh A.; Haraguchi H. (2005): Cross-correlation analysis of atmospheric trace concentrations of N₂O, CH₄ and CO₂ determined by continuous gas-chromatographic monitoring. *Energy*, **30**: 299-311.
- Bleuel C.; Wesenberg D.; Sutter K.; Miersch J.; Braha B.; Bärlocher F.; Krauss G.-J. (2009): The use of the aquatic moss *Fontinalis antipyretica* L. Ex Hedw. as a bioindicator for heavy metals: 3. Cd²⁺ accumulation capacities and biochemical stress response of two *Fontinalis* species. *Sci. Tot. Environ.*, **345**: 13-21.
- Christensen S.; Ambus P.; Arah J.R.M.; Clayton H.; Galle B.; Griffith D.W.T.; Hargreaves K.J.; Klemetsson L.; Lind A.M.; Maag M.; Scott A.; Skiba U.; Smith K.M.; Welling M.; Wienhold F.G. (1996): Nitrous oxide emission from agricultural field: comparison between measurements by flux chamber and micrometeorological techniques. *Atmospheric Environ.*, **30**: 4183-4190.
- Clayton, H.; Arah, J.R.M.; Smith K.A. (1994): Measurement of nitrous oxide emissions from fertilized grassland using closed chambers. *J. Geophys. Res.*, **99**: 599-607.
- Ellis S.; Howe M.T.; Goulding K.W.T.; Mugglestone M.A.; Dendooven L. (1998): Carbon and nitrogen dynamics in a grassland soil with varying pH: effect of pH on the denitrification potential and dynamics of the reduction enzymes. *Soil Biol. Biochem.*, **30**: 359-367.
- Ellis S.; Dendooven L.; Goulding K.W.T. (1996): Quantitative assessment of soil nitrate disappearance and N₂O evolution during denitrification. Nitrate disappearance during denitrification. *Soil Biol. Biochem.*, **28**: 589-595.
- Füleky Gy. (1999): Nutritive management (In Hungarian). *Mezőgazda Kiadó, Budapest*. pp. 119, 238.
- Granli T.; Bøckman O.C. (1994): Nitrous Oxide from Agriculture. *Norweg. J. Agric. Sci.*, **12**: 7-128.

- Hellebrand H.J.; Kern J.; Scholz V. (2008): Long-term studies on greenhouse gas fluxes during cultivation of energy crops on sandy soils. *Atmospheric Environment*, **37**: 1635-1644.
- Huang Y.; Zou J.; Zheng X.; Wang Y.; Xu X. (2004): Nitrous oxide emissions as influenced by amendment of plant residues with different C:N ratios. *Soil Biol. Biochem.*, **36**: 973-981.
- Firestone M.K.; Firestone R.B.; Tiedje J.M. (1979): Nitrous oxide as an intermediate in denitrification: Evidence from nitrogen-13 isotope exchange. *Biochem. Biophys. Res. Commun.*, **91**: 10-16.
- Flessa H.; Ruser R.; Dörsch P.; Kamp T.; Jimenez M.A.; Munch J.C.; Beese F. (2010): Integrated evaluation of greenhouse gas emissions (CO₂, CH₄, N₂O) from two farming systems in southern Germany. *Agriculture, Ecosys. Environ.*, **91**: 175-189.
- Kiese R.; Butterbach-Bahl, K. (2002): N₂O and CO₂ emissions from three different tropical forest sites in the wet tropics of Queensland, Australia. *Soil Biology & Biochemistry*, **34**: 975-987.
- Koponen H.T.; Flöjt L.; Martikainen P.J. (2004): Nitrous oxide emission from agricultural soils at low temperatures: a laboratory micocosm study. *Soil Biol. Biochem.*, **36**: 757-766.
- Linzmeier W.; Gutser R.; Schmidhalter U. (2001): Nitrous oxide emission from soil and from a nitrogen-15-labelled fertilizer with new nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP). *Biol. Fertil. Soils*, **34**: 103-108.
- MI-08-1735-1990 [Hungarian Technical Directive] (1990): Allowable amount of toxic and undesirable components for using sludges in landscape (In Hungarian).
- Paul E.A.; Clark F.E. (1989): *Soil Microbiology and Biochemistry*. Academic Press, Inc. San Diego. pp. 133-164.
- Shelp M.L.; Beauchamp E.G.; Thurell G.W. (2000): Nitrous oxide emissions from soil amended with glucose, alfalfa, or corn residues. *Communication Soil Science Plant Annals*, **31**: 877-892.
- Smith K.A.; Arah J.R.M. (1992): Measurement and modelling of nitrous oxide emissions from soils. *Ecol. Bull.* **42**: 116-123.
- van Hecke K.; van Cleemput O.; Baert L. (1990): Chemodenitrification of nitrate-polluted waters. *Environ. Poll.*, **63**: 261-274.
- Zheng X.; Wang M.; Wang Y.; Shen R.; Gou J.; Li J.; Jin J.; Li L. (2000): Impacts of soil moisture on nitrous oxide emission from croplands: a case study on the rice-based agro-ecosystem in Southeast China. *Chemosphere-Global Change Science*, **2**: 207-224.