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The effect of nitrification inhibitors on nitrous oxide flux from haplic luvisol soil of DASA® 26/13 and ENSIN® fertilisers in a laboratory experiment

T. Šima[1,]*, L. Nozdrovický[1], K. Krištof[1], M. Dubeňová[2] and J. Krupička[3]

[1]Slovak University of Agriculture in Nitra, Faculty of Engineering, Department of Machines and Production Systems, Tr. A. Hlinku 2, 94976 Nitra, Slovak Republic;
*Correspondence: tomasko.sima@gmail.com
[2]Slovak University of Agriculture in Nitra, Faculty of Engineering, Department of Production Engineering, Tr. A. Hlinku 2, 94976 Nitra, Slovak Republic
[3]Czech University of Life Sciences Prague, Faculty of Engineering, Department of Agricultural Machines, Kamýcká 129, 16521 Prague, Czech Republic

Abstract. The aim of the paper was to compare the effects of two very similar fertilisers on nitrous oxide (N_2O) flux from soil to the atmosphere in laboratory conditions. The following fertilisers were used: granulated nitrogenous fertiliser DASA® 26/13 with the nitrogen content of 26%, sulphur content of 13%, and nitrogen fertiliser ENSIN® with the nitrogen content of 26%, sulphur content of 13% and nitrification inhibitors dicyandiamide DCD and 1, 2, 4-triazole (TZ). Both fertilisers are produced by the same manufacturer, DUSLO, Inc., Šala, Slovakia. For both fertilisers, there variants of experiments were carried out for application rates equivalent to 0, 250 and 500 kg ha^{-1}. The amount of the N_2O emissions released from soil to the atmosphere was measured by a photo-acoustic field gas monitor INNOVA 1412 connected to a multipoint sampler INNOVA 1309. The experiments were conducted for 30 days in laboratory conditions. The fertiliser was incorporated into the soil in sampling tubes to a depth of 80 mm after 24 hours of measurement. Subsequently, after every 24 hours of measurement, another 48 hours was carried out, and this measuring cycle was repeated 10 times. The results of our experiment have confirmed that the fertiliser application rate and type of the fertiliser used have a significant effect on N_2O flux and have confirmed the importance of accurate and uniform application of fertilisers in field conditions in order to eliminate the negative environmental effects.

Key words: nitrification inhibitors, nitrous oxide, soil emissions, fertilising, application rate

INTRODUCTION

One of the most important factors affecting crop yields is nitrogen fertilisation (Ložek et al., 1997; Ambus et al., 2011; Kajanovičová et al., 2011). The use of fertilisers has significant effects on intensification of crop production (Šima et al., 2011). Nitrous oxide emissions produced by agriculture in the world range from 60% (IPCC, 2007) to 75% (Jackson et al., 2009). Stratospheric O_3 (ozone) depletion is generally caused by nitrous oxide (Skiba et al., 2001) which is mostly produced by agricultural soils (Ruser et al., 2001). The use of fertilisers is currently connected with the increased flux of N_2O emissions from the soil into the atmosphere (Jones et al., 2007; He et al., 2009; Pang et al., 2009; Lin et al., 2010; Šima et al., 2014 in press). Nitrous oxide is produced in the soil mainly by two biological processes: nitrification and denitrification (Davidson, 1991; Williams et al., 1992; Ložek et al., 1997; Ambus et al., 2006). Inaccurate application of fertiliser causes the local overdosing of fertiliser on the field surface resulting in an increased release of CO_2 and N_2O from the soil into the atmosphere (Šima et al., 2012b; Šima et al., 2012d; Šima et al., 2013d; Šima et al., 2013g). It is apparent than an improved operating quality of a fertiliser spreader has a positive environmental effect. For effective application, it is necessary to know the transversal uniformity of the fertiliser distribution on the field surface, since local overdosing of fertiliser caused by incorrect setup of the fertiliser spreader has negative economical and environmental effects (Šima et al., 2011; 2012b; 2012d; 2013d). The need for using fewer amounts of fertilizers means that it must be applied in a right way, and fertiliser losses are reduced to an absolute minimum. An optimal application of fertilizers, minimisation of spoilage of fertilizers, improvement of existing and development of possible new application techniques - all this requires detailed knowledge of the processes and factors that affect the spreading of fertilisers (Hofstee, 1993). Many factors such as weather conditions, soil properties and mostly nitrogen application rate affect the amount of nitrous oxide emissions flux. Based on this fact, is very important to pay attention to the quality of the work of the fertiliser spreader (Šima et al., 2013a). And, at the same time, an increased amount of nitrogen fertiliser is unusable for plants and in many cases is harmful to the environment. The next factor is the content of nitrification inhibitors in the fertilisers, which may also be considered very important. These inhibit the biological oxidation of ammonium nitrogen into the nitrate nitrogen in the soil. Nitrification inhibitors affect on the granulometric composition (Šima et al., 2013b) of fertilisers and the electrical conductivity (Šima et al., 2013c) of the fertiliser.

The aim of the paper is the study the effects of nitrification inhibitors of two very similar nitrate fertilizers from the same manufacturer on the production of N_2O emissions released from soil to the atmosphere under laboratory conditions – in a laboratory experiment. The fertilizers used were the granulated nitrogen fertilizer with sulphur content, DASA® 26/13, and nitrogen fertilizer ENSIN® containing sulphur and nitrification inhibitors dicyandiamide DCD and 1, 2, 4 triazole – TZ.

MATERIAL AND METHODS

During the experiments, soil samples were collected by five sampling probes from one specific soil location. For collecting the soil samples, sampling probes of own design were used (Šima et al., 2012a; 2012c; Šima & Dubeňová, 2013; Šima et al., 2013e; 2013f). The aim was to obtain soil samples with uniform soil properties and therefore avoid the effect of the natural heterogeneity of soil properties across the arable fields (Šima et al., 2013a). The nitrous oxide released from the soil into the atmosphere was measured in collected non-fertilising sampling probes for 24 hours. Subsequently, equivalent amount of application rates of the fertiliser were incorporated into the soil in the sampling probes under laboratory conditions. Three variants of fertiliser application rate were used: 0 kg ha^{-1}, 250 kg ha^{-1}, 500 kg ha^{-1} and with two repetitions for each variant of non-zero application rate. Measurements were started

48 hours after fertiliser incorporation and were carried out for 24 hours with 48 hours of rest between the measurements, and this measuring cycle was repeated 10 times.

The soil properties (Table 1) were analysed at the Department of Soil Science and Geology at the Slovak University of Agriculture in Nitra, Slovak Republic. The soil moisture content of the soil samples was measured by the gravimetric method. The soil type was identified as haplic luvisol with a slightly alkaline pH reaction and medium humus content.

Table 1. Soil properties

Soil type	Haplic luvisol
Soil moisture content	32–34%
Clay content	37.7%
Silt content	39.43%
Sand content	22.87%
pH H_2O	7.78
pH KCl	6.87
CO_X	1.624%
Hm	2.799%
Bulk density	1.41 g cm^{-3}

During the experiments, we used two very similar fertilizers from the same manufacturer DUSLO, Inc. The granulated nitrogen fertilizer with sulphur content, DASA® 26/13, was used. Nitrogen is in ammonium and nitrate form and sulphur is in water-soluble sulphate form. The granulate has pink to brown colour and the surface is treated with a coating agent. As the second fertilizer, we used the granular nitrogen fertilizer ENSIN® containing sulphur and nitrification inhibitors dicyandiamide DCD and 1, 2, 4 triazole – TZ. The granulate is treated with a coating agent and has green colour. The nitrification inhibitors ensure transformation of ammonium nitrate to nitrogen nitrate in the soil. The advantages of ENSIN® usage compared to DASA® 26/13 are that the fertilizer is applied in 1 dosage and re-application of the fertilizer is not necessary. It allows farmers to save the time and money to increase the crop yields and allows better quality of crops.

The chemical compositions of the DASA® 26/13 and ENSIN® fertilizers are presented in Tables 2 and 3, respectively. The grain-size distribution of the DASA® 26/13 and ENSIN® fertilizers are shown in Table 4.

Table 2. Chemical composition of the DASA® 26/13 fertilizer

Technical specification	Content, %
total nitrogen content (N)	26
ammonium nitrogen content	18.5
nitrate nitrogen content	7.5
sulphur (S) soluble in water	13

Equivalent amounts of application rate of the fertiliser were calculated depending on the diameter of the sampling probes. In our case, the inlet diameter was 106.4 mm and the equivalents of the application rates 250 and 500 kg ha^{-1} were 0.2219 and 0.4437 g of fertiliser, respectively.

Table 3. Chemical composition of the ENSIN® fertilizer

Technical specification	Content, %
total nitrogen content (N)	26
ammonium nitrogen content	18.5
nitrate nitrogen content	7.5
sulphur (S) soluble in water	13
dicyandiamide DCD and 1,2,4 triazole content	0.37–0.74
DCD:TZ ratio	10:1

Table 4. Grain-size distribution of the DASA® 26/13 and ENSIN® fertilizers

	Content of particles, %	
Dimension, mm	DASA® 26/13	ENSIN®
< 1	max. 1	max. 1
2–5	min. 90	min. 90
> 10	0	0

The amount of the N_2O emissions emitting from the soil was measured by INNOVA devices (Lumasense Technologies, Inc.) with the measurement system based on the photo-acoustic infrared detection method. A photo-acoustic field gas monitor INNOVA 1412 and a multipoint sampler INNOVA 1309 were used due to the possibility to analyse a number of samples simultaneously (Dubeňová et al., 2013).

The data obtained were analysed by using the ANOVA test, after a normality test by using the *Kolmogorov-Smirnov* test and a homogeneity of variance by using the *Levene's* test. With ANOVA $P < 0.05$, we continued with the post-hoc LSD multiple range test. We used the software STATGRAPHICs Centurion XVI.I (Statpoint Technologies, Inc.; Warrenton, Virginia, USA). The graphic processing of the results was performed by using the software STATISTICA 7 (Statsoft, Inc.; Tulsa, Oklahoma, USA).

RESULTS AND DISCUSSION

The concentration of N_2O emissions in the sampling probes considerably fluctuated in comparison with the emission concentration before fertilising due to the time period (Fig. 1 and Table 5).

Based on the obtained results, we found the effect of nitrification inhibitors to the intensity and time interval of nitrous oxide emissions released from the soil to the atmosphere in laboratory conditions. The content of nitrification inhibitors in fertilisers slows down the intensity of nitrous oxide emissions releasing. The maximum values, the peak of nitrous oxide flux, after using the 'non inhibitors fertiliser' DASA® 26/13 were measured for 18 and 21 days after application of the fertiliser to the soil for the application rates of 250 and 500 kg ha^{-1}, respectively. The peak of nitrous oxide flux after using the ENSIN® fertiliser was measured 27 days after application of the fertiliser for both application rates. These results correspond with the results obtained by other researchers (e.g., Eichner, 1990; Bouwman, 1996; Verma et al., 2006; Jones et al., 2007; He et al., 2009; Pang et al., 2009; Lin et al., 2010; Mapanda et al., 2011) and also extend the evidence into more detail in this study area concerning the nitrification inhibitors effects on releasing of soil emissions and the properties of fertilisers.

Table 5. The average values of nitrous oxide concentration, ppm

Time,	Application rate of fertiliser, kg ha^{-1}				
days	NF	Dasa250	Dasa500	Ensin250	Ensin500
0	0.5502_{a}^{s}	0.5594_{a}^{s}	0.5656_{a}^{s}	0.5587_{a}^{st}	0.5613_{a}^{s}
3	0.5620_{ab}^{st}	0.5714_{bc}^{s}	0.5776_{c}^{s}	0.5552_{a}^{st}	0.5649_{abc}^{s}
6	0.5651_{a}^{t}	0.6095_{b}^{t}	0.6178_{b}^{s}	0.5509_{a}^{s}	0.5540_{a}^{s}
9	0.5641_{a}^{t}	0.6149_{c}^{tu}	0.6997_{d}^{t}	0.5830_{ab}^{tu}	0.6124_{bc}^{t}
12	0.5601_{a}^{st}	0.6433_{c}^{uv}	0.8192_{e}^{u}	0.6014_{b}^{uv}	0.6818_{d}^{u}
15	0.5616_{a}^{st}	0.6892_{c}^{xy}	0.9104_{d}^{v}	0.6216_{b}^{v}	0.7140_{c}^{u}
18	0.5579_{a}^{st}	0.7102_{c}^{y}	1.0019_{e}^{x}	0.6548_{b}^{x}	0.7720_{d}^{v}
21	0.5553_{a}^{st}	0.7109_{b}^{y}	1.0726_{d}^{y}	0.6794_{b}^{xy}	0.8331_{c}^{x}
24	0.5581_{a}^{st}	0.6993_{b}^{y}	0.9983_{d}^{x}	0.6931_{b}^{yz}	0.8657_{c}^{xy}
27	0.5595_{a}^{st}	0.6571_{b}^{vx}	0.8451_{d}^{u}	0.7099_{c}^{yz}	0.8778_{d}^{y}
30	0.5650_{a}^{t}	0.6459_{b}^{uv}	0.8055_{c}^{u}	0.6905_{b}^{z}	0.8571_{d}^{xy}

Different letters in the rows ($_{a,b,c,d,e}$) mean the effect of the application rate and in the columns (^{s,t,u,v,x,y,z}) mean the effect of the time. It indicates that the means are significantly different at $P < 0.05$ according to the LSD multiple-range test at the 95.0 % confidence level.

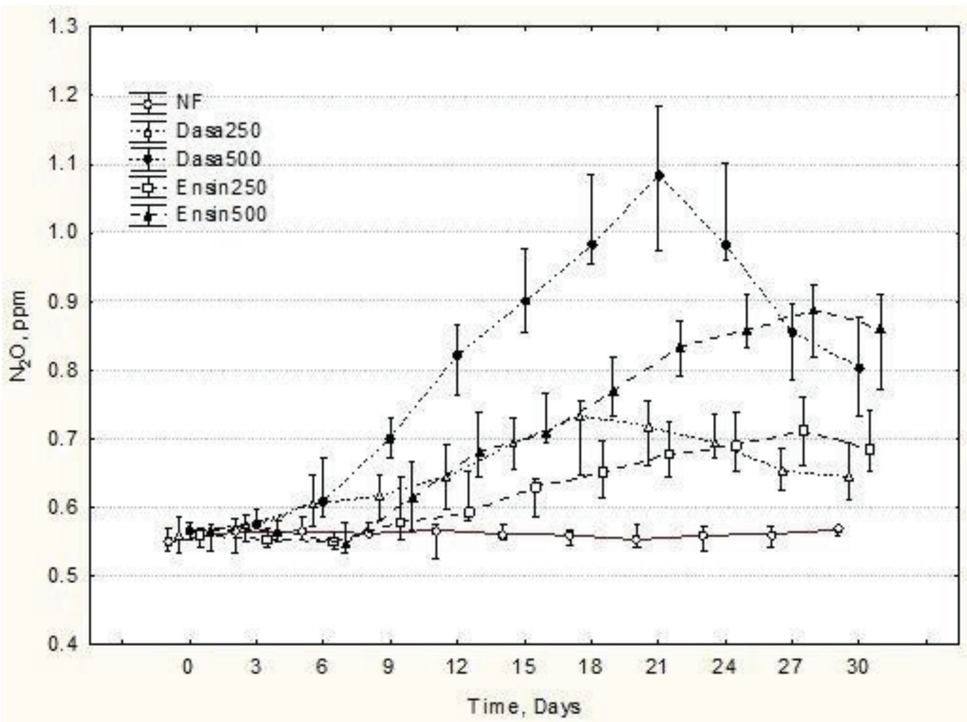

Figure 1. Nitrous oxide concentration in ppm (parts per million), NF – non-fertilizing, point – median, whisker – min.-max. values.

The effect of the size of the application rate to the nitrous oxide emissions released from soil to the atmosphere was also found, and was in agreement with our previous studies (e.g.: Šima et al., 2012c; 2013a; Šima et al., 2014 in press). Nitrification inhibitors slowed the disintegration of fertiliser in the soil and sequentially caused slower nitrogen releasing. It is necessary to include this particular effect in complex research from the perspective of plants and all environmental aspects such as groundwater and leaching of nutrients.

CONCLUSIONS

The aim of the study was to analyse the effects of nitrification inhibitors of two very similar nitrate fertilizers (with and without inhibitors) on the production of N_2O emissions released from the soil to the atmosphere under laboratory conditions – in a laboratory experiment. Increasing the amount of fertiliser results in increasing the amount of nitrous oxide emissions released from soil to the atmosphere. An effect of nitrification inhibitors to nitrous oxide flux was also found. Nitrification inhibitors caused slower disintegration of the fertiliser in the soil and sequentially caused slower nitrogen releasing which allows nutrients to be used by plants rather than to be released as nitrous oxide emissions.

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