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METHOD FOR MEASURING OF N_2O EMISSIONS FROM FERTILIZED SOIL AFTER THE USING OF FERTILIZER SPREADER

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Abstract: The use of fertilizer spreaders is accompanied by a different quality of work these machines, which can cause local overdosing of the fertilizers. Consequently, there may occur the increased formation of nitrous oxide (N_2O) emissions from the soil to the atmosphere. The aim of the paper was to compare the field and the laboratory method, which can be used for measuring of the N_2O emissions released from the soil to the atmosphere. For the purpose of emissions measuring the INNOVA devices with measurement system based on the photo-acoustic infrared detection method was used. Experiment was conducted 10 days after the field was fertilized. During experiment were used the VICON RS-L fertilizer spreader and the Calk Ammonium Nitrate fertilizer. There were found statistically significant differences between the size of the application rate and concentration of the N_2O emissions released from soil to the atmosphere. No statistically significant differences were found in comparison of this two methods and this fact indicate the possibility to replace the field method by the laboratory method.

***Key words**: nitrogen fertilizer, soil emissions, nitrous oxide, measuring methods*

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INTRODUCTION

Nitrogen is an essential element for plant growth, which has fostered an extensive anthropogenic alternation of the natural nitrogen cycle by the application of fertilizer to optimize crop yields in agriculture and forestry [1]. Emissions of the nitrous oxide (N_2O) from agriculture are from about 60% [2] to more than 75% [3, 4] of the total global anthropogenic emissions. Lifetime of the N_2O in the atmosphere is about 150 years and it directly destruct the stratospheric ozone layer. For a better comparability emissions are commonly expressed as CO_2 equivalent using the global warming potential (GWP), which is defined as the cumulative radiative forcing between the present and selected time in the future, caused by a unit mass of gas emitted now [5]. The GWP (with a time span of 100 years) of CO_2 and N_2O is 1 and 298, respectively [2]. Nitrous oxide is produced in soils during nitrification and denitrification [6-8] and chemo-denitrification at low pH<5.5 [9]. Nitrogen fertilization strongly has influenced the releasing of the emissions. Increasing of the application rate of N fertilizer causes the increase of N_2O emissions [10-16]. There are also other factors affecting the N_2O releasing from the soil: soil texture [17-19], soil organic matter content [20], pH [21] and temperature [22]. Different types of measuring methods are used - the closed chamber technique is widely used [23-26] and there are also used both micrometeorological methods - gradient method and eddy correlation method. A comparison of these methods were done by many authors [27-30]. Cuvette surface material strongly affects the result of N2O measurement [31]. For simulating of the N_2O emissions it is possible to use a different types of models, mainly DNDC [32-36], CANDY [37], DAISY [38] and other models (DAYCENT, ExpertN). Implementation of measurement directly on the field is not always possible. From these reasons it is necessary to use the laboratory methods instead of the field methods. The laboratory method consists of collecting soil samples from the field and their subsequent analysis in laboratory. The field method measurement is placed directly on the field.

The main aim of the study was to compare these two methods for the measurement of the nitrous oxide emission released from soil to the atmosphere by using of INNOVA devices and also investigate the impact of the size of application rate of nitrogen fertilizer on amount of released N_2O emissions from soil to the atmosphere.

MATERIAL AND METHODS

During experiments we have used the INNOVA measuring devices (LumaSense Technologies, Inc., Denmark) which consist of three main parts. Photo-acoustic field gas monitor INNOVA 1412 with measurement system based on the photoacoustic infrared detection method is used for gas analysis, multipoint sampler INNOVA 1309 serves for gas sampling from 12 sampling points and transport gas samples to the INNOVA 1412 for analysis [39]. Notebook equipped with the necessary operating software is the third major component. Software is supplied by the manufacturer and it is used for setup and control of the analysis.

Sampling probes were made from seamless steel pipe with 114.3 mm outer diameter and 4 mm wall thickness.

Sampling probes were made in two variants (Figure 1):
- small sampling probes, length 170 mm (for the field method),
- big sampling probes, length 300 mm (for the laboratory method).

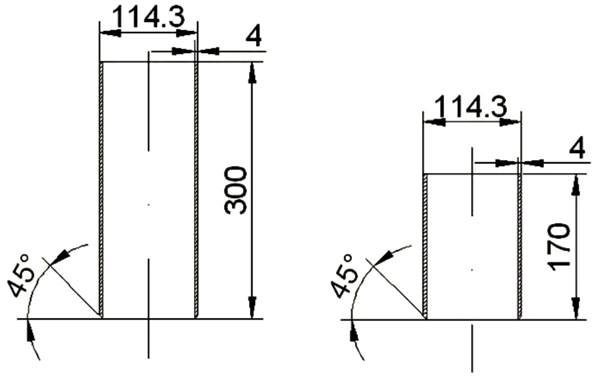

Figure 1. Big (left side) and small (right side) sampling probes

Both variants of sampling probes had on the bottom created outside bevel angle of 45° for easier penetration into the soil. As the end cap there were used „smoked cap" made of a combination of copper and steel with 118 mm diameter. Sampling probe needs one or two caps for the field and the laboratory method, respectively. Cap placed on the top of sampling probe have drilled a hole with 5 mm diameter due to the teflon suction hose introduction.

Air pipes - each of twelve air pipes consist of:
teflon suction hose EN-2007, type AFO614,
air filter EN-2026, type DS2306,
fitting for the air filter EN-2247, type UD-5041.

Table 1. Chemical composition of Calk Ammonium Nitrate [40]

Technical specification	*Content, %*
Total nitrogen content (N)	*27.0 %*
Ammonium nitrogen content	*13.5 %*
Nitrate nitrogen content	*13.5 %*
Content of total magnesium oxide (MgO)	*4.1 %*
Content of magnesium oxide (MgO) soluble in water	*1.0 %*

Table 2. Soil properties

Soil type	*Haplic luvisol*
Clay	*37.700 %*
Silt	*39.430 %*
Sand	*22.870 %*
pH H2O	*7.78*
pH KCl	*6.87*
Cox	*1.624 %*
Hm	*2.799 %*

Fertilizer CAN 27 (calk ammonium nitrate) was used in the form of a grey-white ammonium nitrate granulates with the grounded dolomite decreasing the natural acidity of the fertilizer. Fertilizer was protected by anti-caking surface treatment. Chemical composition is shown in Table 1. The official trade mark of this fertilizer produced by the manufacturer DUSLO Šala, Ltd. is LAD 27 [40].

Soil properties (Tab. 2) were analyzed on Department of Soil Science a Geology at the Slovak University of Agriculture in Nitra, Slovakia. Soil moisture content of the soil samples varied within the range 26-28 % and it was measured by gravimetric method.

Methodical procedure

Used fertilizer CAN 27 was applied on the field surface by VICON RS-L fertilizer spreader. Application of the fertilizer on the field and spread pattern measurement of distributed fertilizer were explained in our previous study [41]. In this case there was realized only one pass with no overlaps. Fertilizer applied on the field was incorporated to the soil by tillage (power harrow PÖTTINGER LION 301) during the seedbed preparation after six hours on the same day. Knowing of the real spread pattern has allowed us to determine the places with different size of the applied fertilizer. There were conducted three variants of experiment with different size of application rates. Measuring places were chosen in measuring points with equivalent application rate to 0 kg.ha^{-1}, 150 kg.ha^{-1} and 300 kg.ha^{-1}, what have corresponded to 0 kg N ha^{-1}, 40.5 kg N ha^{-1} and 81 kg N ha^{-1} of the total amount of nitrogen applied to the field. Measurement with three replications was carried out from 10 to 11 days after soil tillage during the significant N_2O emissions releasing [5, 42]. The field method measurement was placed directly on the field. Small sampling probes were incorporated to 20 mm depth into the soil (Fig. 2).

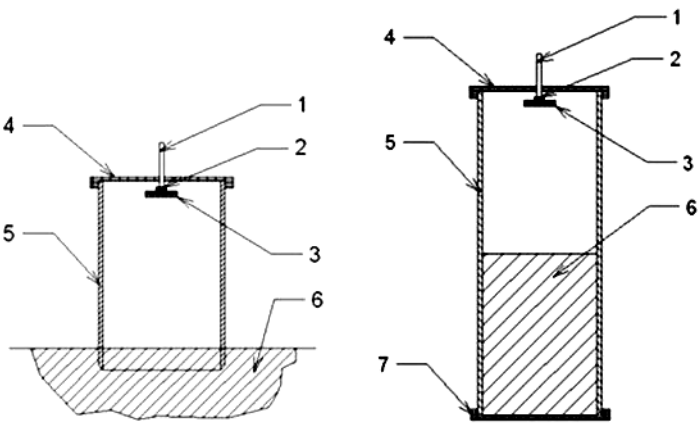

Figure 2. Sampling probes used during the measurement - small (left) and big (right), 1 - suction teflon hose, 2 - fitting for air filter, 3 - air filter, 4 - top cap, 5 - sampling probe, 6 - soil, 7 - lower cap

The laboratory method consists of collecting soil samples from field and their subsequent analysis in laboratory. Big sampling probes were incorporated to 150 mm depth into the soil, surrounding soil has been removed and the sampling probes were closed up from the bottom (Fig. 2). For this case the big sampling probes were left directly on the field with a goal to eliminate nature effects (temperature, air humidity, pressure). Air column in both methods is 150 mm [23]. Consequent close up from the top was done by top caps. Then the measuring devices INNOVA was connected. Measurement started one hour after soil sampling with the aim to eliminate the soil surface disturbance effect during incorporation of sampling probes to production nitrous oxide emissions from the soil to the atmosphere.

Statistical analysis

Data were analyzed by using of the ANOVA test after normality test provide by the Kolmogorov-Smirnov test and homogeneity of variance by using of Levene's test. With ANOVA P-Value < 0.05 we have continued post-hoc LSD Test. There was used software STATGRAPHICS Centurion XVI.I (Statpoint Technologies, Inc.; Warrenton, Virginia, USA). Graphic processing of results was performed by using of software STATISTICA 7 (Statsoft, Inc.; Tulsa, Oklahoma, USA).

RESULTS AND DISCUSSION

During the measurement we have used a design with six sets of values:

- FM-Z - Field Method - Zero application rate of fertilizer 0 $kg.ha^{-1}$ (0 kg N ha^{-1})
- FM-L - Field Method - Low application rate 150 $kg.ha^{-1}$ (40.5 kg N ha^{-1})
- FM-H - Field Method - High application rate 300 $kg.ha^{-1}$ (81 kg N ha^{-1})
- LM-Z - Laboratory Method - Zero application rate 0 $kg.ha^{-1}$ (0 kg N ha^{-1})
- LM-L - Laboratory Method - Low application rate 150 $kg.ha^{-1}$ (40.5 kg N ha^{-1})
- LM-H - Laboratory Method - High application rate 300 $kg.ha^{-1}$ (81 kg N ha^{-1})

Table 3. Analysis of variance for N2O emissions measurement

Source	*Sum of Squares*	*Df*	*Mean Square*	*F-Ratio*	*P-Value*
Between groups	*0.107258*	*5*	*0.021451600*	*26.41*	*0.0000*
Within groups	*0.116970*	*144*	*0.000812292*		
Total (Corr.)	*0.224228*	*149*			

By using of Kolmogorov-Smirnov test we have found out a normal distribution for all tested sets of values. P-Value of Kolmogorov-Smirnov test for all samples - set of values determined the normal distribution of data obtained (all P-Value > 0.5). Next, Levene's test confirmed homogeneity of variance P-Value = 0.563128 (P > 0.5). ANOVA test was used after the values verification. The P-value of the ANOVA is less than 0.05 (Table 3).

There is a statistically significant difference between the means of values of the six variables at the 95.0 % confidence level. To determine which mean values are significantly different from which others, we have selected Multiple Range Tests – LSD Test at the 99.0 % confidence level (Tab. 4). Three homogeneous groups are identified by using of different letters ($_{\mathbf{a,b,c}}$) in the column of mean. There are no statistically significant differences between the means with the same letter.

Table 4. LSD Test at 99.0% confidence level

Sample	*Count*	*Mean*
FM-Z	*25*	0.449159_a
LM-Z	*25*	0.449916_a
FM-L	*25*	0.486911_b
LM-L	*25*	0.487352_b
FM-H	*25*	0.511825_c
LM-H	*25*	0.517482_c

**Different letters ($_{a,b,c}$) in the column indicate that treatment means are significantly different at P < 0.01 according to LSD multiple-range test at the 99.0 % confidence level.*

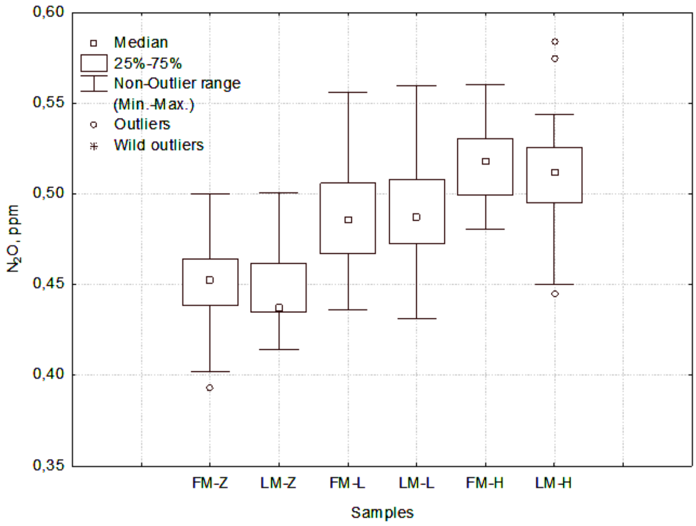

Figure 3. Box-and-Whisker diagram of concentration N_2O

Between the field and the laboratory methods are not statistically significant differences at the 99.0% confidence level at the same size of application rate N fertilizer. From this reason it is possible to replace the field method by the laboratory method. As shown in Table 4 and Figure 3, amount of nitrogen applied to the soil have an effect on the nitrous oxide emissions.

Average value of concentration of nitrous oxide emission during the field and the laboratory methods for nitrogen application rate 0, 40.5 and 81 kg N ha^{-1} were 0.4492, 0.4500, 0.4870, 0.4874, 0.5175 and 0.5118 ppm (parts per million), respectively. These results agree with previous researches [10-16, 42] where nitrogen fertilization strongly influenced releasing emissions.

Increasing application rate of N fertilizer has causes the increase of the N_2O emissions. Comparison of measuring methods and practical verification of the laboratory method allow to use this method for measuring nitrous oxide emission released from soil to the atmosphere. Used method allows measuring of nitrous oxide soil emissions from 12 points at the same time and creates the possibility for long-term complex monitoring of the fertilized soil.

CONCLUSIONS

Field experiment focused for measuring of nitrous oxid emission released from soil to the atmosphere requires specific experimental conditions. Realize a field measurement is not always possible. Traffic measurement equipment, remoteness of the field, difficulties of entry into the vegetation, the need of electric power supply and many other factors are complicating the experimental activities. From this reason it was necessary to replace the field method by the laboratory method.

Field measurement may be influenced by many factors with unwanted side effects. From this reason it is necessary to control most of these factors masking the influences of fertilization [5]. Nitrogen fertilizer application rate has affected amount of released nitrous oxide emission and increasing of the application rate of N fertilizer has caused the increas of the N_2O emissions what corresponds with the results obtained by other researchers [10-16, 42].

In this study was verified the laboratory method of measuring nitrous oxide emissions released from soil to the atmosphere. At 99.0 % confidence level there were no significant differences between methods. Used method has no statistically significant effect on the results obtained, and based on this fact, there can be replaced the field method by the laboratory method. It is possible to state that the used method allows to provide the long-term measurement of N_2O emissions released from soil to the atmosphere and for 12 points in the same time and at the same conditions what reduce the influence of a lot side effect factors.

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METOD MERENJA EMISIJA N_2O IZ ZEMLJIŠTA POSLE ĐUBRENJA RASIPAČEM MINERALNOG ĐUBRIVA

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Sažetak: Upotreba rasipača đubriva je praćena je različitim kvalitetom rada ovih mašina, što može da dovede do lokalnog predoziranja đubriva. Kao posledica toga može se javiti povećana emisija azotnog oksida (N_2O) iz zemljišta u atmosferu. Cilj ovog rada je bio poređenje poljskog i laboratorijskog metoda za merenje emisija N_2O, oslobođenih iz zemljišta u atmosferu. Za potrebe merenja emisije korišćen je uređaj INNOVA sa mernim sistemom zasnovanim na metodu foto-akustične infracrvene detekcije. Ogled je izveden 10 dana posle đubrenja parcele. Tokom eksperimenta korišćen je rasipač VICON RS-L za rasipanje azotnog đubriva. Utvrđene su statistički značajne razlike između primenjene norme đubrenja i koncentracije N_2O oslobođenog iz zemljišta u atmosferu. Poređenjem ova dva metoda nije utvrđena statistički značajna razlika, što ukazuje na mogućnost zamene poljskog laboratorijskim metodom.

Ključne reči: *azotno đubrivo, zemljišne emisije, azotni oksid, merne metode*

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