AUTOMATED CAVITY RING DOWN SPECTROSCOPY USAGE FOR NITROUS OXIDE EMISSION MEASUREMENTS FROM SOIL USING RECIRCULATION SYSTEM

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Abstract. The nitrous oxide accounted for the year 2015 gives 60 % of Latvia`s greenhouse gas emissions from the agricultural sector. Majority of nitrous oxide comes from mineral fertiliser application and manure management. Nitrous oxide emission from soils is strongly correlated with the soil moisture and temperature. Since nitrous oxide has very low concentrations in natural environment, there is a risk to overestimate or underestimate nitrous oxide emission. Automated cavity ring down spectroscopy for nitrous oxide emission measurements is a relatively new technology and there is a need for development of proper methodology. The aim of this study is to identify proper measurement time for nitrous oxide emission from soil by using automated cavity ring down spectroscopy with recirculation system. The automated cavity ring down spectroscopy, namely Picarro G2508, was connected in a closed recirculation system with the chamber of total volume 2 litres. Dray soil samples were weighted in containers and different amounts of water and ammonium nitrate were added. Totally 36 samples were used in the experiment. Each sample was measured 10 minutes and the nitrous oxide concentration was recorded for each second. For each sample measurements were repeated three times. The linear regression method was used to calculate the emission amount for different time periods from 30 seconds till 600 seconds. The results of the research show quite high variation of nitrous oxide emission from the soil samples. Data analysis showed that the minimal measurement time has to be at least 250 seconds.

Keywords: CRDS, Picarro G2508, chamber enclosure time.

Introduction

The measurements of nitrous oxide (N_2O) emissions have become an actual topic during the last 20 years[1]. N_2O emissions from soil are measured by using closed static chembers [2]. The cavity ring down spectroscopy (CRDS) has pre-eminent detection limit and high precision [3; 4]. However, the CRDS device Picarro G2508 is limited by one outlet [5]. The chamber enclosure time is limitation for the experiment design. The N_2O concentration in atmosphere is 0.325 ppm [6] and during the measurement N_2O fluctuated. The measurement error of N_2O is 0.005 ppm [5]. The fluctuaction of N_2O is related with concentrations of other gases as well as climatic factors. The previous research shows that appropriate chamber closure time for measurements with CRDS is from 200 till 400 seconds [3].

The aim of this study is to identify the GHG measurement time for cavity ring down spectroscopy Picarro G2508 by using the recyrculation system for soil flux experiments in laboratory conditions.

Materials and methods

The experiment was conducted in laboratry conditions with fixed air temperature, air presure and humidity. 36 soil samples with weight of 100g and moisture of 20 % were colected in plastic containers. The amonia nitrate dosings were 0 g, 1 g, 2 g, 3 g, 4 g and 5 g. The water dosings were 0 ml, 10 ml, 20 ml, 30 ml, 40 ml and 50 ml. Water and amonia nitrate in each sample were added before the measurement. The CRDS device Picarro G2508 was connected with the chamber by using zero leaching conectors and the zero leaching external vacuum pump Picarro [5]. Each soil sample with the container were inserted into the chamber. After closure of the chamber, the gas concentrations of N_2O were measured for 600 seconds. The gas concentration data of the 600 seconds period for each sample of each gas were used for further data analysis. The slope of concentration change is the main parameter for further calculations of GHG emmisions from soil. The linear regression (1) was used to calculate the slope of concentration fluctuactions for each data set.

$$C = S \cdot T + c ,\qquad(1)$$

where C – concentrations, ppm;
S – slope, ppm·s^{-1};
T – time, s;
c – intercept, ppm.

The slope (2) of linear regression and the coefficient of determination (3) were calculated for 1 minute ($n = 60$) time period by using a step of 1 second. 286 slopes and coefficients of determination were calculated for each sample. The same procedure were repeated for 4 minutes ($n = 240$) time period by using slope calculation for each sample. 160 slopes and coefficients of determination were calculated for 4 minutes time period.

$$S = \frac{n\sum(TC) - \sum T \sum C}{n\sum(T^2) - (\sum T)^2},$$ (2)

where n – count of measurements;

Coefficient of determination (R^2) was calculated as follows:

$$R^2 = \left(\frac{n\sum(TC) - \sum T \sum C}{\sqrt{[n\sum(T^2) - (\sum T)^2][n\sum(C^2) - (\sum C)^2]}}\right)^2$$ (3)

The slope (2) and coefficient of determination (3) values were used to calculate the slope (5) and relative changes of the determination coefficient per time unit (4):

$$\Delta R^2 = \frac{R_{i-1}^2 - R_i^2}{R_i^2} \cdot 100,$$ (4)

where ΔR^2 – relative change of determination coefficient, %;
   i – current observation

$$\Delta S = \frac{S_{i-1} - S_i}{S_i} \cdot 100,$$ (5)

where ΔS – relative change of slope, %.

The calculated relative changes of slope and coefficient of determination in time unit were used for further analysis by using XLSTAT program package.

Results and discussion

The measurement session was done at 25 ºC soil and air temperature and the air pressure 1032 bar. The N_2O concentrations of 36 soil samples were verifyed for slope and R^2 calculations.The descriptive statistics of the N_2O concentration data is presented in Table 1. The total number of the analysed N_2O concentration data is 14,405. There are no missing values. The mean concentrattion of N_2O is 0.348 ppm, the standart deviation is 0.014 ppm.

Table 1

Descriptive statistics of N_2O concentration data

Nr.	Statistic	N_2O, ppm
1.	Number of observations	14,405
2.	Number of missing values	0
3.	Minimum	0.215
4.	Maximum	0.407
5.	Range	0.192
6.	1st Quartile	0.339
7.	Median	0.347
8.	3rd Quartile	0.356
9.	Mean	0.348
10.	Variance (*n*-1)	0.000
11.	Standard deviation (*n*-1)	0.014

The relative change of slope was analysed on one second step base. The 36 relative slope change data points were analysed for each second. The mean of the relative change of slope is not stable and it is fluctuating between 20 % and -20 % (see Figure 1).
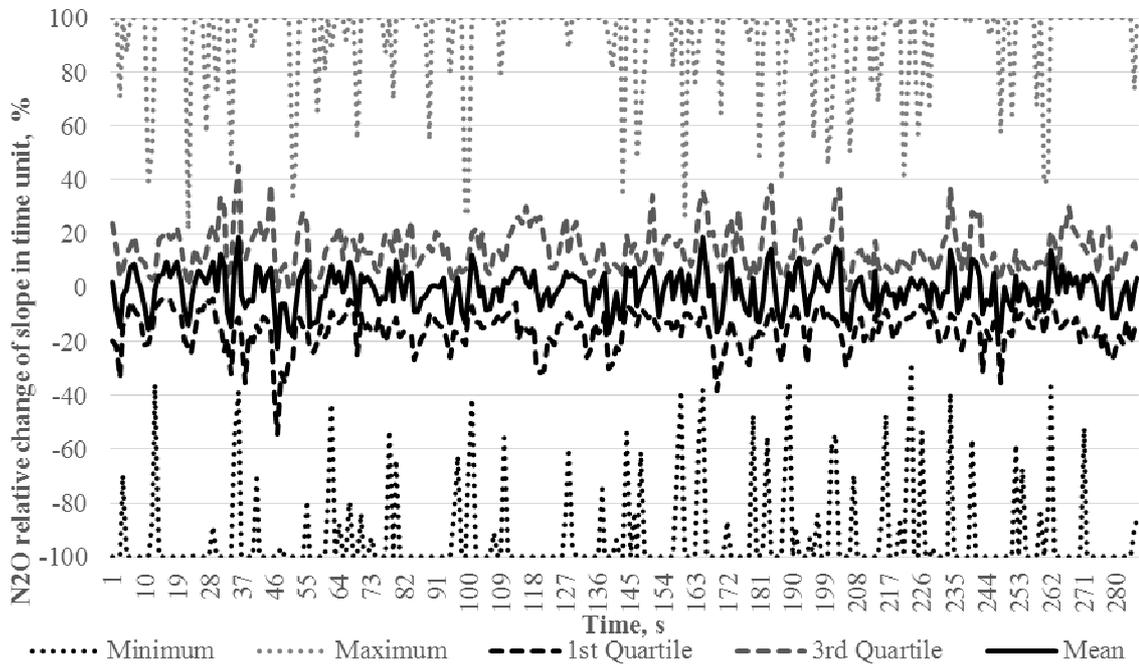

Fig. 1. **Relative change of slope for 1 minute slope calculation period**

The 1st quartile and 3rd quartile are close to mean, but the fluctuaction amplitude is between 40 % and -40 %. The minimal and maximal values are close to 100 % and -100 %. The relative change of slope was analysed for 4 minutes time period and it showed acceptable satbilistation of the slope change. The amplitude is between 20 % and -20 % (see Figure 2).
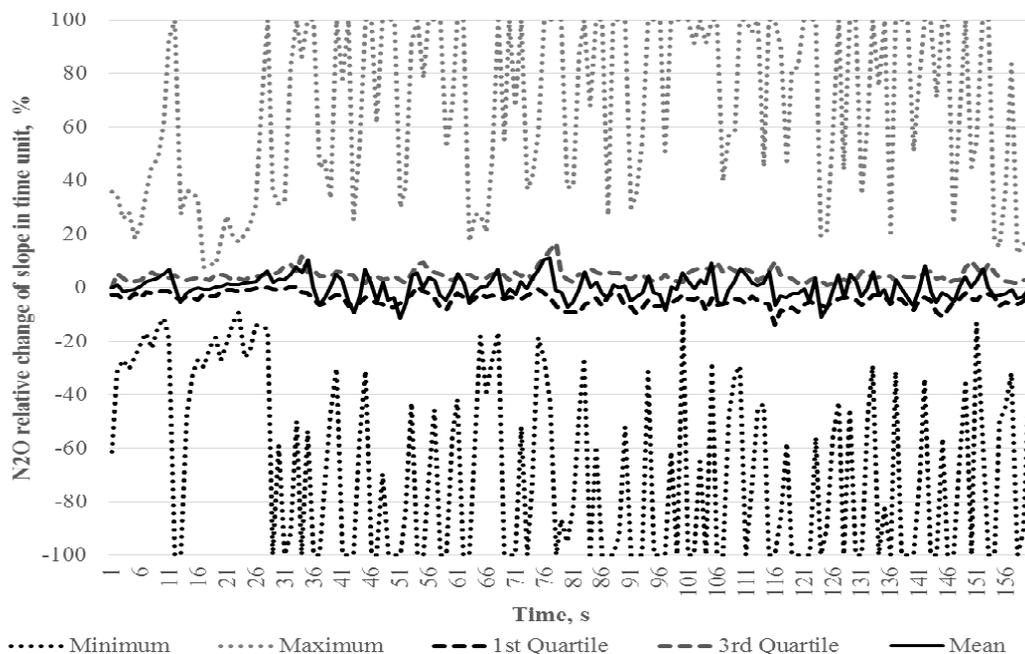

Fig. 2. **Relative change of slope for 4 minutes slope calculation period**

However, there are still high maximal and minimal values of the relative slope change. The relative change of the determination coefficient is analysed on one second step base. 36 relative changes of data point of the coefficient of determination were analysed for each second. The mean of

the relative change of the coefficient of determination is not stable and it is fluctuating between 30 % and -20 % (see Figure 3).
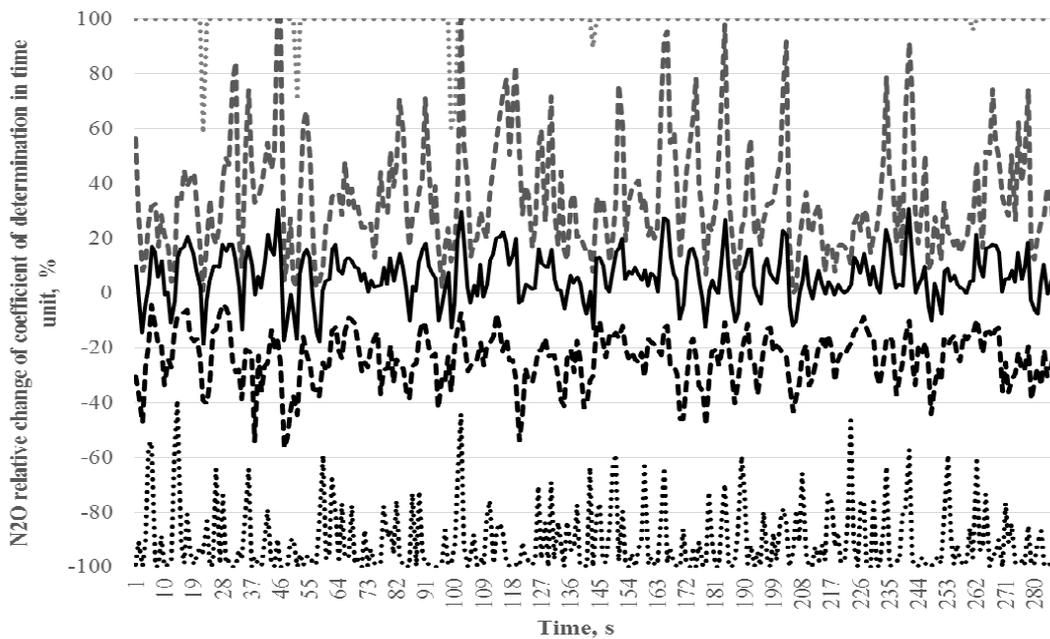

Fig. 3. **Relative change of coefficient of determination for 1 min slope calculation period**

The 1st quartile and 3rd quartile are close to mean, but the fluctuaction amplitude is between 100 % and -60 %. The minimal and maximal values are close to 100 % and -100 %. The relative change of the coefficient of determination was analysed for 4 minutes time period. It shows acceptable satbilistation of the change of the determination coefficient and it is in the amplitude from 5 % till -1 % (see Figure 4). However, there are still high maximal values of the relative slope change.
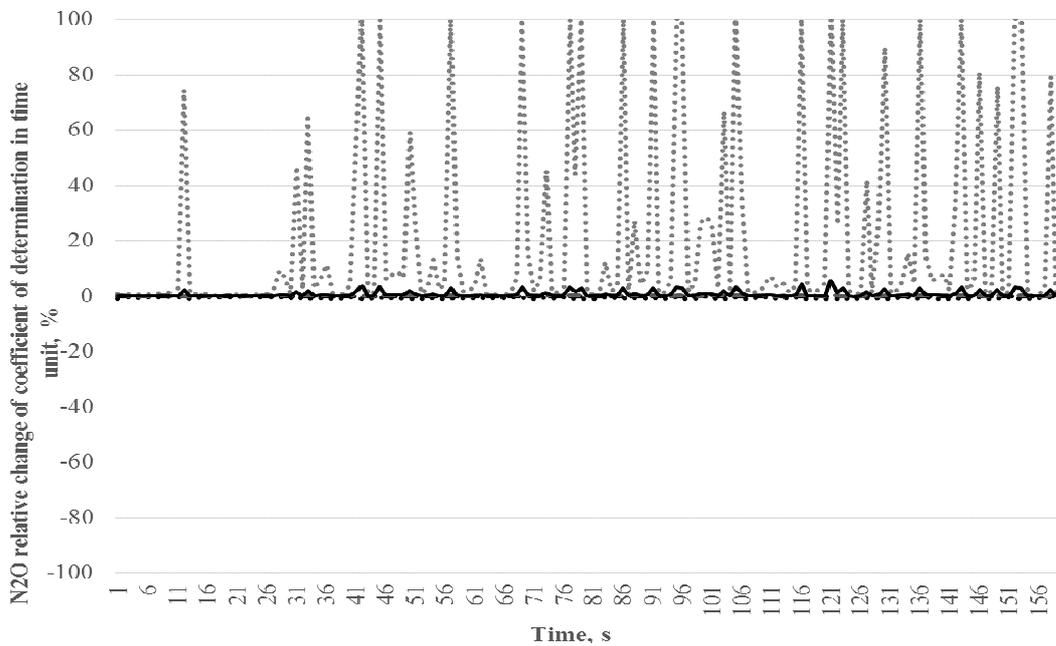

Fig. 4. **Relative change of coefficient of determination for 4 min slope calculation period**

The 1st quartile and 3rd quartile are close to mean, but the fluctuaction amplitude is between 100 % and -60 %. The minimal and maximal values are close to 100 % and -100 %. The relative change of the coefficient of determination was analysed for 4 minutes time period. It shows acceptable stabilistation of the change of the coefficient of determination and it is in the amplitude from 5 % till -1 % (see Figure 4). However, there are still high maximal values of the relative slope change. The

acceptable slope calculation start is from 10 till 20 seconds from the measurement start. The first 10 seconds of the measurement are optional to exclude for further calculations.

The acceptable measurement data are presented in Figure 5, where the graph on the left shows the measured concentration with minimal positive slope. However, the trend of concentrations is clearly positive. The graph in the middle presents the slope and R^2 relation with the slope calculation period 1 min. The graph on the right side presents the slope and R^2 relation with the slope calculation period 4 min. There is clear correlation between the slope and R^2. The highest slope values are with higher R^2.
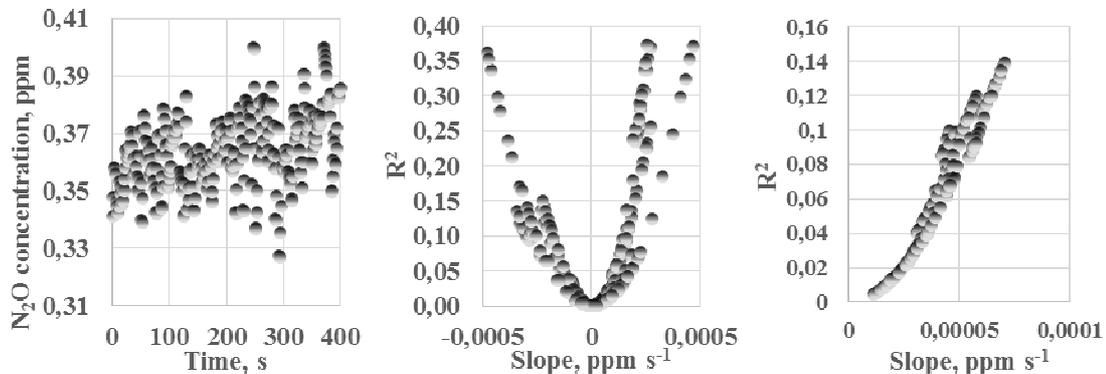

Fig. 5. **Acceptable example of measurement (left-measured concentartions; middle – R^2 and slope relation at 1minute calculation period; right – R^2 and slope correlation at 4 minute calculation period)**

The unacceptable measurement data are presented in Figure 6, where the graph on the left shows the measured concentration with unclear slope. The concentrations fluctuacte, but there is too wide fluctuaction amplitude. The graph in the middle presents the slope and R^2 relation with the slope calculation period 1 min. The relation is not symmetrical and it shows 3 outliers. The graph on the right side presents the slope and R^2 relation with the slope calculation period 4 min. There is clear correlation between the slope and R^2. However, the N_2O slope is negative or close to 0.
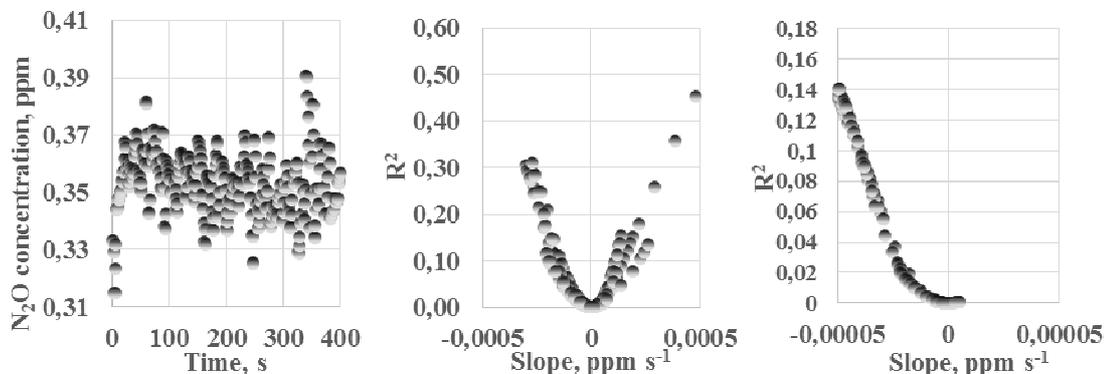

Fig. 6. **Unacceptable example of measurement (left-measured concentartions; middle – R^2 and slope correlation at 1minute calculation period; right – R^2 and slope correlation at 4 minutes calculation period)**

Conclusions

1. The CRDS device Picarro G2508 can be used for N_2O emission measurements at laboratory and field conditions. The recirculation system is sensitive to fluctuaction of N_2O concentrations as well as the concentration of other gases is an important factor.
2. The minimal measurement time is 4 minutes and 10 seconds for N_2O emissions. The previous timescale can be used for laboratory experiments with the air temperature and soil temperature range from 20 ℃ till 30 ℃.
3. Each measurement data set has to be veifyed and evaluated before calculation and repeated measurements have to be optional.
4. The multiple slope calculation aproach can be used for slope calculations, where the slope of samples is calculated as average from several slopes.

References

1. Hutchinson G.L., Mosier A.R. Improved soil cover method for field measurement of nitrous oxide fluxes. Soil Sci. Soc. Am. J. vol. 45, 1981, pp. 311-315.
2. Pihlatie M.K., Christiansen J.R., Aaltonen H., Korhonen J.F.J., Nordbo A., Rasilo T., Benant, G., Giebels M., Helmy M., Sheehy J., Jones S., Juszczak R., Klefoth R., Lobo-do-Vale R., Rosa A.P., Schreiber P., Serc D., Vicca S., Wolf B., Pumpanen J. Comparison of static chambers to measure CH4 emissions from soils. Agric. For. Meteorol. vol. 171-172, 2013, pp. 124-136.
3. Christiansen J. R., Outhwaite J., Smukler S. M. Comparison of CO2, CH4 and N2O soil-atmosphere exchange measured in static chambers with cavity ring-down spectroscopy and gas chromatography. *Agricultural and Forest Meteorology*, vol. 211, 2015, pp. 48-57.
4. Hensen A., Skiba U., Famulari D. Low cost and state of the art methods to measure nitrous oxide emissions. Environ. Res. Lett. Vol. 8, 2013, pp. 1-10
5. Fleck D., He Y., Alexander C., Jacobson G., Cunningham K.L. Simultaneous soil flux measurements of five gases – N2O, CH4, CO2, NH3, and H2O – with the Picarro G2508 1-11. Picarro Inc., Santa Clara, CA, USA. 2013. 11 p.[online] [21.03.2017]. Available at: https://picarro.app.box.com/s/z2gpj3hpl11xye9csz6mdpixltc1i5hl.
6. IPCC. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T. F., D. Qin, G.-K. Plattner, M. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P. M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA. 2013. 87 p.[online] [21.03.2017] Available at: http://www.climatechange2013.org/images/report/WG1AR5_TS_FINAL.pdf