

Nitrogen Oxide Soil Emission Measurements Using Passive Samplers and Static Chamber Method

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Abstract

Nitrogen oxides play a major role in atmospheric chemistry, like primary pollutants, in the formation of secondary air pollutants or greenhouse gases (GHGs). This research study was conducted in the Western Pannonian sub-region of Croatia with the aim to determine the suitability of our internally developed passive sampler and static chamber method for N-NO₂ concentration measurement. The aim was also to determine the impact of mineral soil fertilization on the N-NO₂ flux during triticale vegetation. The research showed that the method used was suitable. Average daily N-NO₂ flux ranged from 2.78 to 5.09 mg ha⁻¹ day⁻¹ depending on phenophase and treatment. Statistically significant differences in N-NO₂ flux between two monitored treatments (300 kg N ha⁻¹ and 0 kg N ha⁻¹) were not observed, nor between two investigated phenophases.

Keywords

Croatia, N-NO₂ flux, fertilization, triticale vegetation, agroecosystem

1 Introduction

Greenhouse gas emissions represent a global environmental concern.¹ After the energy sector, the agricultural sector represents the world's second-largest emitter of greenhouse gases. Carbon dioxide (CO₂), methane (CH₄), and nitrogen oxide (N₂O) directly influence the greenhouse effect, whereas ammonia (NH₃) and nitrogen oxides (NO and NO₂, known together as NO_x) represent primary pollutants. According to *Duxbury*² and *Isermann*³, agriculture contributes between 55 % and > 95 % of the anthropogenic NH₃ released annually into the atmosphere, where NH₃ in the presence of oxygen very rapidly turns into some type of oxide. Furthermore, some primary pollutants (NO_x) have an effect on the formation of ozone (O₃),⁴ which is a common greenhouse gas responsible for a non-negligible part of radiative forcing⁵, and have a crucial role in the oxidizing capacity of the atmosphere. Nitrogen oxides are released into the atmosphere from biomass burning and fossil fuel combustion.⁶ However, soil microbial emissions are also of high interest, especially since microorganisms as diffusive sources affect the atmospheric chemistry over large areas.⁷ Soil NO emissions from agricultural soils are estimated to represent 40 % of the total NO emission from all sectors.^{8,9} According to *Hall and Matson*¹⁰, biological production and consumption processes of microorganisms represent a combination by which nitric oxide emissions from the soil are controlled. Soil nitric oxide emissions occur mainly through the nitrification and denitrification processes, and depend on several factors, such as the amount of nitrogen, soil temperature, and soil moisture.¹¹ Accordingly, in the research of *Troy and Tang*,¹² increased

production of nitrous oxide was found in response to treatments with higher temperature and moisture levels. Also, numerous studies have shown that factors such as fertilization or tillage practice, vegetation presence, and vegetation type influence soil NO emissions in agricultural production. Many studies of NO_x in agricultural systems indicate that the application of nitrogen fertilizers results in elevated NO_x emissions as compared with background levels, regardless of the type of fertilizer used.^{13,14,15} A few studies have observed increased fluxes of NO_x from soil with clipped vegetation, as well as from cleared or plantless soil, compared to undisturbed, vegetated sites.^{16,17}

With the population increase and rapid industrialization and urbanization growth in recent decades, air pollution has been recognized as a global problem.¹⁸ Thus, together with air quality guidelines¹⁹, air quality standards have been established in many countries around the world.²⁰ Accordingly, WHO¹⁹ announced methods for testing air quality and nitrogen oxide measurements divided into: measurement using passive collectors, active measurement, measurement with automatic devices and remote sensing. All of these methods have advantages and disadvantages. Over the past two decades, the use of passive samplers has received increased attention for determining temporal and spatial distributions of key air pollutants.^{18,21}

In this research, the main goal was to determine the suitability of the passive sampler method for N-NO₂ concentration measurement. It was presumed that the method will be detectable and quantifiable enough for the determination of the potential impact of mineral soil fertilization on the N-NO₂ emission (two treatments with 0 and 300 kg N ha⁻¹). Also, the intention was to compare N-NO₂ emission between two sets of measurements in phenophases (tillering and jointing) of triticale.

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2 Experimental

2.1 Study area and cover crop

The field experiment with two different fertilization treatments was conducted in the Western Pannonian sub-region of Croatia, in Popovača (N 45° 33' 21.42", E 16° 31' 44.62") (Fig. 1). In 1996, a study was initiated to establish optimal fertilization with a positive effect on yield and without adverse effect on the environment, and in 2011, it was expanded to the research on soil C-CO₂ flux measurements due to the climate change issues (carbon balance). The total area of the experiment was 39 000 m². The soil type was classified according to *Husnjak*²² as deep distric pseudogley (Stagnosol). The soil reaction was strongly to weakly acidic, and ranged from 3.93 to 5.06 depending on the treatment. The content of organic matter varied from 1.33 wt% to 2.48 wt%. The plant available phosphorus was moderate to rich (10.1–22.4 mg/100 g of soil), and available potassium moderate to very rich (14.3–31.4 mg/100 g of soil). The soil was moderately to well supplied with total nitrogen content, and the value ranged 0.080–0.158 %, while the CN ratio ranged from 10–11.²³

For the NO₂ measurements in this research, applied were treatment without mineral nitrogen fertilization (N₀ + P + K), and treatment with a high dose of nitrogen fertilization (N₃₀₀ + P + K). The fertilization with phosphorus (P) and potassium (K) was uniform for both investigated treatments (120 kg P ha⁻¹ and 180 kg K ha⁻¹). The dimension of each trial treatment was 30 × 130 m² including blank space.

The cover crop at the experimental field was triticale (*x. Triticosecale* – Goran BC). Triticale was sown in the amount of 250 grains/m² on October 24, 2013 following agrotechnical measures of ploughing at a depth of 25–30 cm, fertilizing with UREA-N 30 %, 100 % K, 100 % P, and soil preparation for sowing. Nitrogen addition was carried out on March 13, 2014 with KAN (70 % N).²⁴ The triticale was harvested on July 18, 2014.

2.2 Meteorological conditions

The meteorological conditions for the reference period (1961–1990) and the studied period (2014) were presented according to the official meteorological data from the main meteorological station of the Meteorological and Hydrological Service of Croatia located in Sisak.²⁵ The meteorological conditions are described by Lang's rain factor and Walter climate diagram. Interpretation of Lang's rain factor was conducted according to Gračanin's climate classification.²⁶

2.3 Measurements of NO₂ concentration and agro-ecological factors

During the vegetation period, soil-emitted NO₂ concentrations and agro-ecological factors were measured twice (in the tillering phase – March 2014, and in the jointing phase – April 2014) in three repetitions on each treatment. For the measurements of NO₂ concentration, a combination of two methods including passive samplers and static chambers were used (Fig. 2). The chambers were made of lightproof metal to avoid the sunlight effect on the measurements. The chambers consisted frames and caps. The circular frames were inserted around 10 cm into the soil. If necessary, the vegetation was removed from the frames before the beginning of measurement. The tube-type passive samplers were made of hard plastic 4.7 cm long and 7.07 cm³ absorption area, and were positioned inside the chamber on the soil. The mesh at the opened end of the sampler was installed as protection against foreign bodies (e.g., insects), while an impregnated filter for NO₂ collection was positioned at the other end of the sampler. The passive samplers remained in the chambers for 24 h, after which they were hermetically closed and removed for further analysis in the laboratory.

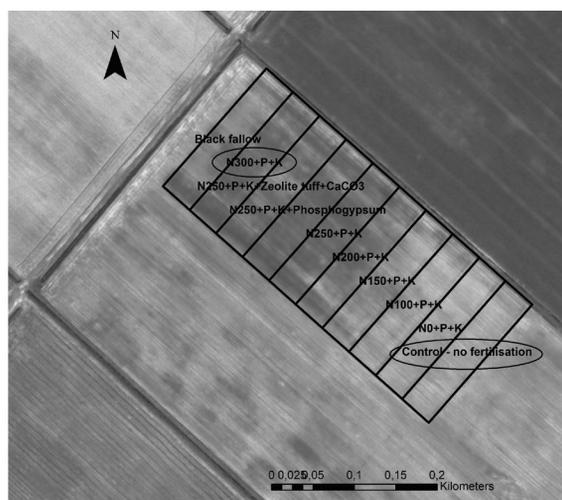
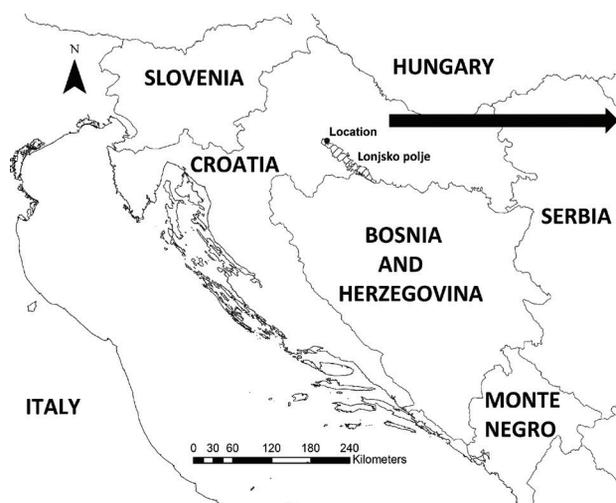


Fig. 1 – Study location
Slika 1 – Pokusno polje



Fig. 2 – Passive samplers and static chambers method
Slika 2 – Metoda pasivnih sakupljača i statičkih komora

At the beginning and end of each measurement, air temperature and relative air humidity were measured with a Testo 610 (2011) humidity and temperature meter, air pressure was measured with a Testo 511 (2011) absolute pressure meter. CO₂ concentrations in air were measured with a GasAlertMicro5 IR, BW Honeywill, 2011. Soil temperature and soil moisture were measured three times with an IMKO HD2 – probe Trime, Pico64 (2011) at 10 cm depth in the vicinity of the chambers.

2.4 Laboratory methods for passive sampler preparation and sample analysis

2.4.1 Passive sampler preparation

The impregnated Whatman 1 (W1) filter paper inside the sampler was soaked in a mixture of acetone and triethanolamine (1 : 1). After a few minutes, impregnated filter paper was removed from the solution and placed on paper to eliminate excess solution.^{27,4}

2.4.2 Sample analysis

Sample analysis was performed according to *Paukovic*²⁷ and UNEP/WHO¹⁹ protocol. The exposed filter papers were immersed in the absorption solution of triethanolamine. Thereupon, 10 ml of the colour solution (*N*-(1-naphthyl)ethylenediamine dihydrochloride/sulphonamide) was added to the 10 ml of sample solution, and left for 20 min to develop colour. The NO₂ concentration was determined on a CECIL 9200 UV/VIS (2009) spectrophotometer. The colour intensity of the prepared solution was determined by measuring absorbance at 540 nm. Blanks (unexposed filters) were prepared and analysed for each set of measurements, and blank value was subtracted from each sample.

The calibration was prepared at six levels using sodium nitrite standard solution. The middle standard (2 μg ml⁻¹ NO₂⁻) was used as a check standard at the beginning and end of each set of measurements.

2.4.3 Calculation of N-NO₂ flux

After the laboratory analysis, the average ambient NO₂ concentration (μg m⁻³) for 24-h sampling period was calculated. The mass concentration of NO₂ in the sample was calculated according to the following equation:

$$\gamma(\text{NO}_2) = m \cdot k / t \quad (1)$$

where: $\gamma(\text{NO}_2)$ – mass concentration of NO₂ in air (in μg m⁻³), m – mass of NO₂ (in μg) collected on filter during sampling, k – 628.07 constant (calculated considering the diffusion surface, length of diffusion column, and diffusion coefficient D_{12} for NO₂), and t – time of sampling in hours (24 h).

The emission (flux) of NO₂ (F) was calculated according to the equation based on Fick's first law of diffusion and the equation of state of an ideal gas:

$$F = \left(\frac{V}{A} \right) \cdot \left(\frac{pM}{RT} \cdot \frac{c_2 - c_1}{t_2 - t_1} \right) \quad (2)$$

where: F – NO₂ flux or NO₂ emission [gm⁻² s⁻¹] kg ha⁻¹ × day (10 000 m² = 1 ha), M – NO₂ molar mass [g mol⁻¹] (46 g mol⁻¹), V – chamber volume [m³] ($V = 0.002955$ m³), A – chamber surface [m²] ($A = 0.0314$ m²), c_1 – NO_x concentration at the beginning of measurement [10⁻³ mol m⁻³], c_2 – NO_x concentration at the end of measurement [10⁻³ mol m⁻³], T – air temperature 273 + $T/^\circ\text{C}$, p – air pressure [Nm⁻²], R – gas constant (8,314 J mol⁻¹ K⁻¹) J = Nm, $t_2 - t_1$ – time of measurement [s]: 1 day = 24 h = 1440 min = 86400 s

In this research, the results are presented as the N-NO₂ flux in mg ha⁻¹ per day.

2.6 Data analysis

All measured data were analysed using statistical Software SAS (SAS Institute Inc., USA). Variability between investigated treatments for all investigated parameters was evaluated with analysis of variance (ANOVA) and tested with Fisher's least significant difference procedure. In all statistical tests the significance level was 5 %.

3 Results and discussion

3.1 Meteorological conditions of study area

Mean annual amount of precipitation in Sisak during the 30-year reference period was 865 mm. Mean annual temperature was 10.6 °C indicating a temperate continental climate. According to Lang's rain factor (L_r), the reference period was characterised as a semi-humid climate ($L_r = 82$).²⁶ The year of investigation (2014) was more humid (+585 mm) and warmer (+2.3 °C) compared to the reference period, with mean annual precipitation amount of 1451 mm and mean annual temperature of 12.9 °C. According to Lang's rain factor, the year 2014 was character-

used as a humid climate ($L_f = 112$). According to Walter's climate diagram, the average climatic conditions show no record of dry periods during the reference period (Fig. 3a) and the studied year (2014) (Fig. 3b).

The real evapotranspiration in 2014 was higher by 80 mm than in the reference period. In the reference period, water deficit was recorded in August and September. The water surplus occurred mostly during the winter months until April. In 2014, water surplus occurred during all months except June and July, while no water deficit had occurred in any month (Figs. 4a and 4b).

3.2 Agro-ecological factors and N-NO₂ flux

According to Schindlbacher and Zechmeister-Boltenstern²⁸, soil temperature and soil moisture represent key variables influencing emission rates. In this research, soil temperature in March 2014 (22.3 °C) was significantly higher than in April 2014 (10.9 °C) (SAS 9.1, $P < 0.05$) (Fig. 5). While most studies have detected a positive relationship between soil temperature and NO_x emissions^{29,30,28}, there are also contrasting results concerning high-temperature responses of soil NO_x emission.^{31,32} In this research, average daily N-NO₂ flux increased with temperature (Fig. 5), showing linear dependence. However, temperature was considered as one of the reasons why a statistical difference be-

tween N-NO₂ flux was not recorded because of unusual weather, where April was colder by 9.1 °C than March. It is considered that soil moisture is a major driver of nitrogen oxide emissions as it regulates the oxygen availability to soil microbes.³³ According to Schindlbacher and Zechmeister-Boltenstern²⁸, each soil has specific soil moisture which optimises soil NO emissions. In Troy and Tang¹² research, in the soils that were subjected to 30 % soil moisture, the values of nitrous oxide production were relatively higher than the samples subjected to lower soil moisture levels. In this research, soil moisture showed no significant difference between the tillering and jointing phases (SAS 9.1, $P < 0.05$) (Fig. 6). Average daily N-NO₂ flux was inversely proportional to soil moisture (Fig. 6). In Medinets et al.³⁴, no correlations between soil NO emissions and soil moisture content at both organic and mineral soil layers for the entire cold season observation period were recorded. Many investigations have identified moisture and temperature as the key controls in nitrous oxide trace gas production.³⁵ Several authors revealed strong temporal patterns in nitrous oxide fluxes corresponding closely with seasonal changes in moisture and temperature.^{36,37,38} In agro-ecological factors, the plant cover and plant root influence should not be disregarded. The strong impact of plant cover on NO emission rates may partially be due to the reduced soil temperature and higher soil moisture content, causing a higher uptake of NO₂ on the moist soil surfaces.³⁹

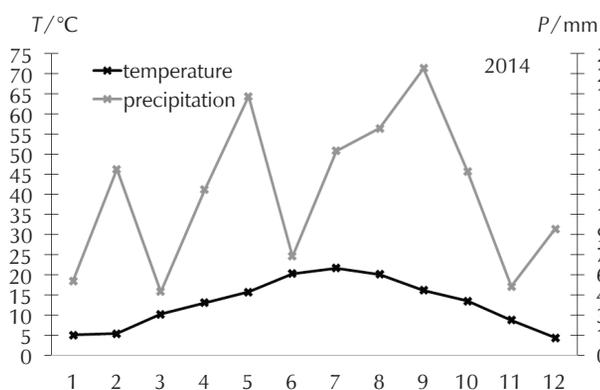
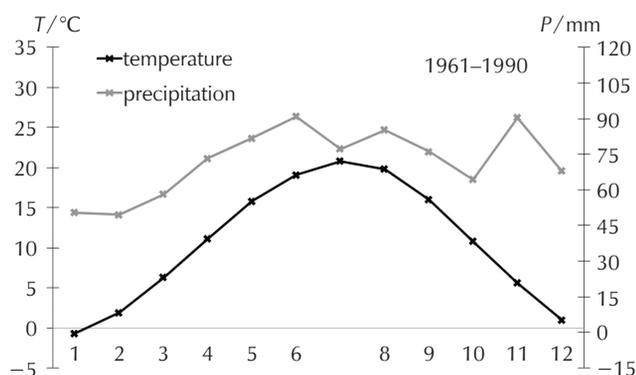


Fig. 3 – Weather conditions according to Walter climate diagram for the reference period and investigated year of 2014

Slika 3 – Vremenski uvjeti prema Walterovom klimatskom dijagramu za referentno razdoblje i istraživanu 2014.

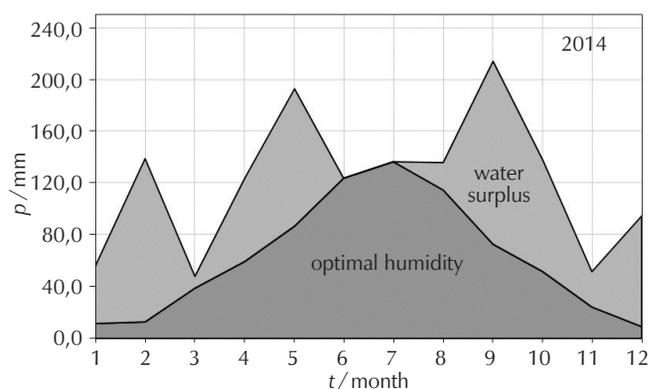
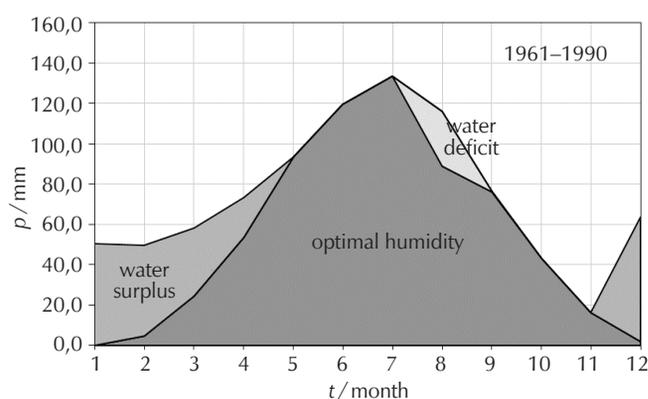


Fig. 4 – Water balance in the soil according to Thornthwaite method for the reference period and investigated year of 2014

Slika 4 – Bilanca vode u tlu prema metodi Thornthwaite za referentno razdoblje i istraživanu 2014.

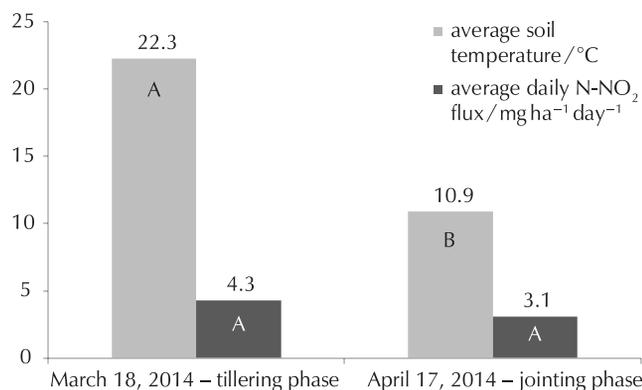


Fig. 5 – Difference in mean values marked with the same letter between soil temperature (°C) are not statistically significant; Difference in mean values marked with the same letter between average daily N-NO₂ flux are not statistically significant (SAS 9.1 p < 0.05)

Slika 5 – Srednje vrijednosti označene istim slovom između temperatura tla (°C) međusobno se statistički ne razlikuju; srednje vrijednosti označene istim slovom između prosječnih dnevnih protoka N-NO₂ međusobno se statistički ne razlikuju (SAS 9,1 p < 0,05)

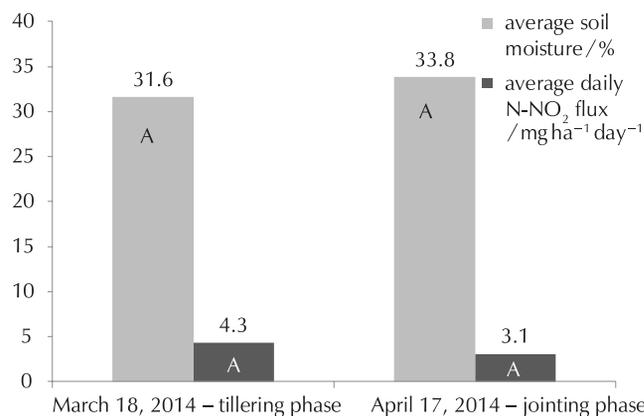


Fig. 6 – Difference in mean values marked with the same letter between soil moisture (%) are not statistically significant; Differences in mean values marked with the same letter between average daily N-NO₂ flux are not statistically significant (SAS 9.1 p < 0.05)

Slika 6 – Srednje vrijednosti označene istim slovom između vlage tla (%) međusobno se statistički ne razlikuju; srednje vrijednosti označene istim slovom između prosječnih dnevnih protoka N-NO₂ međusobno se statistički ne razlikuju (SAS 9,1 p < 0,05)

3.3 Variability of nitrogen oxide flux considering nitrogen fertilization

Agricultural management practices of fertilization and irrigation affect environmental variables such as inorganic nitrogen availability, water-filled pore space, soil temperature and moisture, and thus have the potential to dramatically alter soil NO_x emissions.¹⁰ Around a quarter of global NO_x production derives from soils, mainly from fertilized agriculture.⁴⁰ However, estimates of global soil NO_x emissions vary widely from 9 to 27 Tg per year.^{41,42,43} The first data on field measurements of NO_x emissions were published by Makarov.⁴⁴ His experiments with mineral fertilizers showed that 0.2 % of the applied nitrogen was lost as NO₂ to the atmosphere, demonstrating that the increased

application of mineral fertilizer may have an effect on the atmospheric NO_x budget. In this research, there was no significant difference in N-NO₂ flux between treatments with mineral nitrogen fertilizer (300 kg N ha⁻¹) and treatment without nitrogen fertilizer (0 kg N ha⁻¹) in the tillering and jointing phases (Figs. 7a and 7b). Although there was no significant difference between investigated treatments, in both phenophases, N-NO₂ flux was higher in treatment where 300 kg N ha⁻¹ was applied. Depending on treatment and phenophase, daily values in this research ranged from 1.66 mg ha⁻¹ day⁻¹ to 7.18 mg ha⁻¹ day⁻¹. The insignificant difference between the studied treatments can be explained by several reasons: (i) the sample was too small (only two measurements), (ii) very low measured concen-

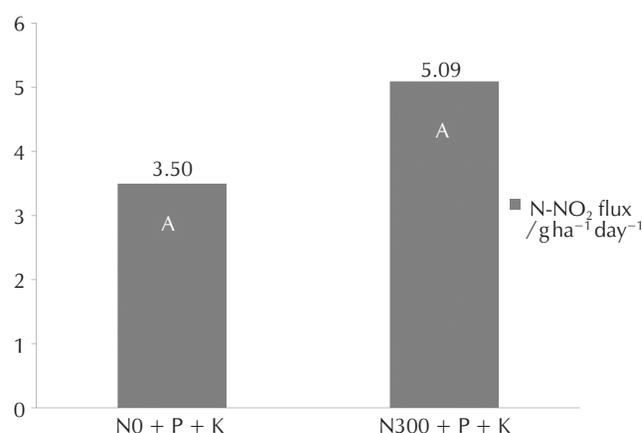
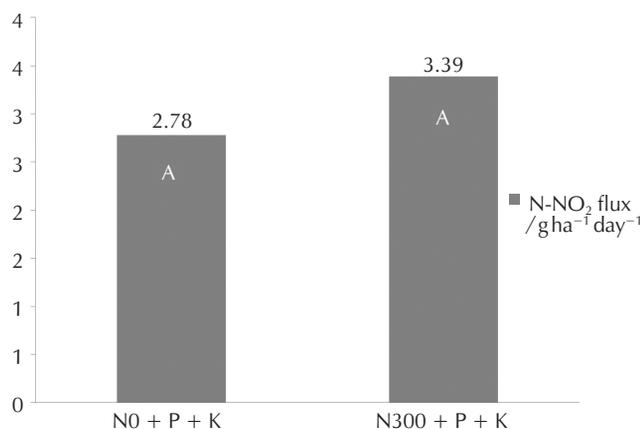


Fig. 7 – a) Mean values of N-NO₂ flux per treatment in the tillering phase – 18.03.2014; b) and in the jointing phase – 17.04.2014 (Differences in mean values marked with the same letter are not statistically significant (SAS 9.1 P < 0.05))

Slika 7 – a) Srednje vrijednosti fluksa N-NO₂ po tretmanima u fazi busanja – 18. 3. 2014.; b) i u fazi vlatanja – 17. 4. 2014. (desno) (srednje vrijednosti označene istim slovom međusobno se statistički ne razlikuju (SAS 9.1 P < 0,05))

tration, (iii) high data variability – high RSD in the range 3–55 %, (iv) soil temperature inversion. In a research conducted in California, soil NO_x emissions varied nonlinearly with environmental and land management factors, including temperature, soil moisture, and different levels of fertilization (20, 50, and 100 kg N ha^{-1}).⁴⁰ Conversely, in the research of *Shepherd et al.*⁴⁵, the fluxes increased linearly with fertilizer application, where 11 % of the nitrogen in the fertilizer converted to NO_x and 5 % to N_2O . In *Almaraz et al.*⁴⁶ study, NO_x emissions were greatest from agricultural soils where N fertilizer applications can reach $> 600 \text{ kg N ha}^{-1} \text{ year}^{-1}$. The importance of N inputs through fertilizer in accelerating NO_x emissions from soil microbial communities is presented by *Firestone*⁴⁷ through the comparison of high mean efflux from agricultural soils (average of 19.8 $\text{kg N ha}^{-1} \text{ year}^{-1}$) compared to much lower NO_x emissions from natural ecosystems (average of 1.0 $\text{kg N ha}^{-1} \text{ year}^{-1}$). In this research, average annual cumulative N- NO_2 flux was 1.15 $\text{g ha}^{-1} \text{ year}^{-1}$ on treatment without nitrogen fertilizer (0 kg N ha^{-1}) and 1.55 $\text{g ha}^{-1} \text{ year}^{-1}$ on treatment with mineral nitrogen fertilizer (300 kg N ha^{-1}).

3.4 Soil nitrogen oxide flux measurement technique

Many techniques have been developed to measure nitrogen dioxide, but few can measure soil NO emissions at concentrations below parts per billion⁴⁸. Accordingly, there is a growing demand and interest among air pollution \pm vegetation effects scientists for the use of passive sampling systems for quantifying pollutant concentrations.²¹ According to *Cruz et al.*⁴⁹, passive samplers represent simple devices capable of capturing gas pollutants from the atmosphere without an air pump or a flow meter. They require no power source or calibration, and can be placed on almost any surface. Moreover, they are inexpensive, easy to use and require no highly qualified persons.^{50,4} Therefore, they are very attractive and actual for air quality assessments on the regional-scale. Passive samplers allow quantification of cumulative air pollutant exposures, as total or average pollutant concentrations over a sampling period.²¹ On the negative side, they are characterized by high detection limits for short-term (e.g., 1 or 2 h) sampling periods, regulatory noncompliance, and provide only the average value for prolonged exposure, low relevance to vegetation effects relationships, and meteorological interference can be high. For low time resolution, they are not as accurate as automatic devices.^{51,52} A few studies have been carried out to evaluate the effect of temperature on the performance of passive samplers. The effect of extremely low temperature on passive sampler performance has been studied by several authors.^{53,54} According to the method used in this research, *Moschandreas et al.*⁵³ also used Whatman glass filter paper impregnated with triethanolamine as an absorbing material, and noticed that the passive sampler underestimates NO_2 at extremely low temperatures (-23 to 10 °C). The effect of humidity on passive sampler performance has not been extensively studied, but some earlier studies have reported that humidity affects its performance.^{55,56} *He et al.*¹⁸ used four different types of passive samplers in a tropical urban environment to measure soil NO emissions, including: (i) ogawa sam-

plers, (ii) NUS samplers, (iii) CSIR samplers, and (iv) capillary samplers. In his research, statistical analysis showed no significant difference between the measurement data obtained by different types of passive samplers, but all four types of passive samplers can be used for monitoring soil NO emissions. Furthermore, *Mulik et al.*⁵⁷ compared the results from passive (triethanolamine, TEA absorbent) and continuous (tunable diode laser) measurement methods for soil NO emissions. The overall mean values between the two methods were very close but the individual daily means were highly variable. *Stevenson et al.*⁵⁸ presented a summary of the results collected during five years, where the primary aim was to assess the spatial and temporal distribution of soil NO emissions throughout the UK, using diffusion tube samplers. The results showed that the highest concentrations occur in urban areas of the UK, and average soil NO concentrations were remarkably similar for most of the five years throughout the UK. In addition to the mentioned field measurement, passive samplers were also used for measuring indoor soil NO emissions.^{59,60} In his research, *Campos et al.*⁵⁰ concluded that passive samplers are an excellent tool for low cost atmospheric monitoring considering the growing demands for environmental monitoring.

As it stated in *Rolston*,⁶¹ the closed-chamber method is the most common method used for measuring gas exchange between the soil and the atmosphere. Closed static chamber methods allow the users to obtain instantaneous flux estimates over a short period (15 to 30 min), and measurements can be taken multiple times during the year for estimating seasonal or annual flux.^{62,63} In general, chamber methods are relatively low-cost and simple to operate, so they are used extensively in various ecosystems. Thus, chamber methods can be used for field and laboratory measurements. Incubation of soil samples in the laboratory under controlled temperatures and soil water content, allows the study of the dynamics of the emission process in a wide range of environmental variables.⁶⁴ However, like all methods, the chamber method also has certain disadvantages. Because of the very complex process of GHG exchange between soil and atmosphere, measurements by chamber systems are subject to many potential sources of disturbance and errors.⁶⁵ Therefore, chambers must not be used during precipitation because of condensed water in the chamber which can affect photosynthesis. Also, when the chambers are placed on a moist soil surface, gas concentration can be diluted and consequently less than it really is.⁶⁴ According to *Rochette and Hutchinson*⁶⁶, placing the chamber on the soil surface disrupts natural conditions and can change emissions no matter what type of chamber is used. As it is stated in *Powers and Capelari*⁶², a suitable number of chambers must be placed to represent the surface area of emission, thus it is necessary to own at least several chambers, which represents a certain investment. Considering the possibility of users to investigate the interannual variations of soil GHGs efflux, because of manual chamber measurements, they may not be consistent throughout the year.⁶⁵

In this research, the passive sampler and static chamber method has proven to be a suitable method for measuring NO_2 concentrations. Because of its mentioned benefits, this method is suitable for application on agricultural land.

4 Conclusion

A study of the NO₂ emissions from a field with controlled fertilizer applications has been performed. In March and April 2014, nitrogen oxide flux from soil into the atmosphere was measured in the Western Pannonian sub-region of Croatia using an internally developed method, i.e., a combination of passive collectors and static chambers. In this research, average daily N-NO₂ flux ranged from 2.78 on treatment without nitrogen fertilizer up to 5.09 mg ha⁻¹ day⁻¹ on treatment with mineral nitrogen fertilizer (300 kg N ha⁻¹), depending on the treatment and phenophases, and was not significantly different. During the tillering phase, average soil temperature at 10 cm depth was 22.3 °C, and 10.9 °C during the jointing phase, and the difference was significant (SAS 9.1, P < 0.05). Average daily N-NO₂ flux increased with temperature showing their positive relationship but was inversely proportional to soil moisture. Considering the benefits of the passive sampler and static chamber method, in this research, the method has proven to be suitable for measurements of NO₂ concentrations at observed N-NO₂ fluxes.

List of abbreviations

Popis kratica

GHG	– greenhouse gas – staklenički plinovi
NO	– nitrogen(II) oxide – dušikov(II) oksid
O ₃	– ozone – ozon
NO _x	– nitrogen oxide – dušikov oksid
NO ₂	– nitrogen(IV) oxide – dušikov(IV) oksid
N ₂ O	– nitrogen(I) oxide – dušikov(I) oksid
CH ₄	– methane – metan
CO ₂	– carbon dioxide – ugljikov dioksid
NH ₃	– ammonia – amonijak
WHO	– World Health Organization – Svjetska zdravstvena organizacija
P	– phosphorus – fosfor
K	– potassium – kalij
KAN	– nitrogen fertilizer – dušično gnojivo
N	– nitrogen – dušik
W1	– Whatman 1 – Whatman 1

L _f	– Lang's rain factor – Langov kišni faktor
RSD	– relative standard deviation – relativna standardna devijacija

References

Literatura

1. K. Nishitani, S. Kaneko, S. Komatsu, H. Fujii, How does a firm's management of greenhouse gas emissions influence its economic performance? Analyzing effects through demand and productivity in Japanese manufacturing firms, *J. Prod. Anal.* **42** (2014) 355–366, <https://doi.org/10.1007/s11123-015-0432-4>.
2. J. M. Duxbury, The significance of agricultural sources of greenhouse gases, *Fert. Res.* **38** (1994) 151–163, <https://doi.org/10.1007/BF00748775>.
3. K. Isermann, Agriculture's share in the emission of trace gases affecting the climate and some cause-oriented proposals for sufficiently reducing this share, *Environ. Pollut.* **83** (1994) 95–111, [https://doi.org/10.1016/0269-7491\(94\)90027-2](https://doi.org/10.1016/0269-7491(94)90027-2).
4. M. Kolman, Metode mjerenja dušikovih oksida iz tla, Diplomski rad, Zagreb, 2019.
5. IPCC, Summary for Policymakers, in S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt (ed.), *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, 2007, URL: <https://www.ipcc.ch/report/ar4/wg1/>.
6. P. Stella, B. Loubet, P. Laville, E. Lamaud, M. Cazaunau, S. Laufs, F. Bernard, B. Grosselin, N. Mascher, R. Kurtenbach, A. Mellouki, J. Kleffmann, P. Cellier, Comparison of methods for the determination of NO-O₃-NO₂ fluxes and chemical interactions over a bare soil, *Atmos. Meas. Tech.* **5** (2012) 1241–1257, doi: <https://doi.org/10.5194/amt-5-1241-2012>.
7. R. Delmas, D. Serca, C. Jambert, Global inventory of NO_x sources, *Nutr. Cycl. Agroecosys.* **48** (1997) 51–60, doi: <https://doi.org/10.1023/A:1009793806086>.
8. J. J. Yienger, H. Levy, Empirical model of global soil-biogenic NO_x emissions, *J. Geophys. Res. Atmos.* **200** (1995) 11447–11464, doi: <https://doi.org/10.1029/95JD00370>.
9. V. P. Aneja, W. P. Robarge, Soil-biogenic NO_x emissions and air quality, in Y. Steinberger (ed.), *Preservation of Our World in the Wake of Change. Vol. 6A*, Israel Society for Ecology, Israel, 1996, p. 50–52.
10. S. J. Hall, P. A. Matson, NO_x emissions from soil: Implications for Air Quality Modeling in Agricultural Regions, *Annu. Rev. Energy Environ.* **21** (1996) 311–346, doi: <https://doi.org/10.1146/annurev.energy.21.1.311>.
11. P. Laville, D. Flura, B. Gabrielle, B. Loubet, O. Fanucci, M. N. Rolland, P. Cellier, Characterisation of soil emissions of nitric oxide at field and laboratory scale using high resolution method, *Atmos. Environ.* **43** (2009) 2648–2658, doi: <https://doi.org/10.1016/j.atmosenv.2009.01.043>.
12. C. Troy, J. Tang, Effects of Temperature and Moisture Stress on Nitrous Oxide Production in Agricultural Soil. Semester in environmental science, PROJECT 2011 (2011).
13. P. A. Matson, C. Billow, S. Hall, J. Zachariassen, Fertilization practices and soil variations control nitrogen oxide emissions from tropical sugar cane, *Atmos. Chem. Phys.* **101** (1996) 18533–18545, doi: <https://doi.org/10.1029/96JD01536>.

14. F. C. Thornton, R. J. Valente, Soil emissions of nitrous oxide from no-till corn, *Sci. Soc. Am. J.* **60** (1996) 1127–1133, doi: <https://doi.org/10.2136/sssaj1996.03615995006000040024x>.
15. S. Fang, Y. Mu, NO_x fluxes from several typical agricultural fields during summer-autumn in the Yangtze Delta, China, *Atmosph. Environ.* **43** (2009) 2665–2671, doi: <https://doi.org/10.1016/j.atmosenv.2009.02.027>.
16. F. Slemr, W. Seiler W, Field study of environmental variables controlling NO emissions from soil and the NO compensation point, *J. Geophys. Res.* **961** (1991) 13017–13031, doi: <https://doi.org/10.1029/91JD01028>.
17. S. Fang, Y. Mu, NO_x fluxes from three kinds of agricultural lands in the Yangtze Delta, China, *Atmosph. Environ.* **41** (2007) 4766–4772, doi: <https://doi.org/10.1016/j.atmosenv.2007.02.015>.
18. J. He, H. Xu, R. Balasubramanian, C. Y. Chan, C. Wang, Comparison of NO₂ and SO₂ Measurements Using Different Passive Samplers in Tropical Environment, *Aerosol Air Qual. J.* **14** (2014) 355–363, doi: <https://doi.org/10.4209/aaqr.2013.02.0055>.
19. UNEP/WHO, GEMS/AIR Methodology Reviews: Passive and Active Sampling Methodologies for Measurement of Air Quality. WHO/EOS/94.4, UNEP/GEMS/94.A.5, UNEP Nairobi, Vol. 4, 1994.
20. L. L. Lim, S. J. Hughes, E. E. Hellawell, Integrated decision support system for urban air quality assessment, *Environ. Model. Soft.* **20** (2005) 947–954, doi: <https://doi.org/10.1016/j.envsoft.2004.04.01>.
21. S. V. Krupa, A. H. Legge, Passive sampling of ambient, gaseous air pollutants: an assessment from an ecological perspective, *Environ. Poll.* **107** (2000) 31–45, doi: [https://doi.org/10.1016/S0269-7491\(99\)00154-2](https://doi.org/10.1016/S0269-7491(99)00154-2).
22. S. Husnjak, *Sistematika tala Hrvatske*, Hrvatska sveucilisna naklada, Zagreb, 2014.
23. Ž. Zgorelec, M. Mesić, I. Kisić, D. Bilandžija, A. Jurišić, F. Bašić, I. Šestak, I. Bogunović, Utjecaj različitih načina korištenja tla na klimatske promjene, *Izvešće*, 2015.
24. T. Hodalić, Mjerenje emisije ugljikovog dioksida iz tla u vegetaciji ozime pšenoraži, *Diplomski rad*, 2015.
25. URL: <http://meteo.hr/index.php> (28. 3. 2020).
26. A. Butorac, Department of General Agronomy-practicum, Faculty of Agriculture, University of Zagreb, Zagreb, Croatia, 1988.
27. R. Pauković, Određivanje dušik-dioksida u zraku primjenom pasivnih sakupljača, *Arh. Hig. Rada Toksikol.* **38** (1987) 17–23.
28. A. Schindlbacher, S. Zechmeister-Boltenstern, Effects of soil moisture and temperature on NO, NO₂, and N₂O emissions from European forest soils, *J. Geophys. Res.* **109** (2004) 1–12, doi: <https://doi.org/10.1029/2004JD004590>.
29. D. W. Stocker, D. H. Stedman, K. F. Zeller, W. J. Massman, D. G. Fox, Fluxes of nitrogen oxides and ozone measured by eddy correlation over a short grass prairie, *J. Geophys. Res.* **98** (1993) 619–630, doi: <https://doi.org/10.1029/93JD00871>.
30. X. Pang, Y. Mu, X. Lee, S. Fang, J. Yuan, D. Huang D, Nitric oxides and nitrous oxide fluxes from typical vegetables cropland in China: Effects of canopy, soil properties and field management, *Atmosph. Environ.* **43** (2009) 2571–2578, doi: <https://doi.org/10.1016/j.atmosenv.2009.02.016>.
31. A. L. O. Saad, R. Conrad, Temperature dependence of nitrification, denitrification, and turnover of nitric oxide in different soils, *Biol. Fertil. Soil.* **15** (1993) 21–27, doi: <https://doi.org/10.1007/BF00336283>.
32. M. Gödde, R. Conrad, Immediate and adaptational temperature effects on nitric oxide production and nitrous oxide release from nitrification and denitrification in two soils, *Biol. Fertil. Soil.* **30** (1999) 33–40, doi: <https://doi.org/10.1007/s003740050584>.
33. K. Butterbach-Bahl, E. M. Baggs, M. Dannenmann, R. Kiese, S. Zechmeister-Boltenstern, Nitrous oxide emissions from soils: how well do we understand the processes and their controls?, *Philos. Trans. R. Soc. Lond. B. Biol. Sci.* **368** (2013) 1–13, doi: <https://doi.org/10.1098/rstb.2013.0122>.
34. S. Medinets, R. Gasche, U. Skiba, A. Schindlbacher, R. Kiese, K. Butterbach-Bahl, Cold season soil NO fluxes from a temperate forest: drivers and contribution to annual budgets, *Environ. Res. Lett.* **11** (2016) 1–11, doi: <https://doi.org/10.1088/1748-9326/11/11/114012>.
35. G. J. Luo, R. Kiese, B. Wolf, K. Butterbach-Bahl, Effects of soil temperature and moisture on methane uptake and nitrous oxide emissions across three different ecosystem types, *Biogeosci.* **10** (2013) 3205–3219, doi: <https://doi.org/10.5194/bg-10-3205-2013>.
36. W. T. Peterjohn, J. M. Melillo, P. A. Steudler, K. M. Newkirk, F. B. Bowles, J. D. Aber, Responses of Trace Gas Fluxes and N Availability to Experimentally Elevated Soil Temperatures, *Ecol. Appl.* **4** (1994) 617–625, doi: <https://doi.org/10.2307/1941962>.
37. X. Wu, N. Brüggemann, R. Gasche, Z. Y. Shen, B. Wolf, K. Butterbach-Bahl, Environmental controls over soil atmosphere exchange of N₂O, NO, and CO₂ in a temperate Norway spruce forest, *Global Biogeochem. Cy.* **24** (2010a) 1–16, <https://doi.org/10.1029/2009GB003616>.
38. X. Wu, Z. Yao, N. Brüggemann, Z. Y. Shen, B. Wolf, M. Dannenmann, X. Zheng, K. Butterbach-Bahl, Effects of soil moisture and temperature on CO₂ and CH₄ soil atmosphere exchange of various land use/cover types in a semi-arid grassland in Inner Mongolia, China, *Soil Biol. Biochem.* **42** (2010b) 773–787, doi: <https://doi.org/10.1016/j.soilbio.2010.01.013>.
39. F. Slemr, W. Seller, Field Measurements of NO and NO₂ Emissions from Fertilized and Unfertilized Soils, *J. Atmosph. Chem.* **2** (1984) 124, doi: <https://doi.org/10.1007/BF00127260>.
40. P. Y. Oikawa, C. Ge, J. Wang, J. R. Eberwein, L. L. Liang, L. A. Allsman, D. A. Grantz, G. D. Jenerette, Unusually high soil nitrogen oxide emissions influence air quality in a high-temperature agricultural region, *Nat. Commun.* **6** (2015) 8753, doi: <https://doi.org/10.1038/ncomms9753>.
41. J. Steinkamp, M. G. Lawrence, Improvement and evaluation of simulated global biogenic soil NO emissions in an AC-GCM, *Atmos. Chem. Phys.* **11** (2011) 6063–6082, doi: <https://doi.org/10.5194/acp-11-6063-2011>.
42. R. C. Hudman, N. E. Moore, A. K. Mebust, R. V. Martin, A. R. Russell, L. C. Valin, R. C. Cohen, Steps towards a mechanistic model of global soil nitric oxide emissions: implementation and space based-constraints, *Atmos. Chem. Phys.* **12** (2012) 7779–7795, doi: <https://doi.org/10.5194/acp-12-7779-2012>.
43. G. Vinken, K. Boersma, J. Maasackers, M. Adon, R. Martin, Worldwide biogenic soil NO_x emissions inferred from OMI NO₂ observations, *Atmos. Chem. Phys.* **14** (2014) 10363–10381, doi: <https://doi.org/10.5194/acp-14-10363-2014>.
44. B. N. Makarov, Release of nitrogen dioxide from the soil, *Pochvovedeniye* **1** (1969) 49–53.
45. F. Shepherd, S. Barzetti, D. R. Hastie, The production of atmospheric NO_x and N₂O from a fertilized agricultural soil, *Atmosph. Environ.* **25** (1991) 1961–1969, doi: [https://doi.org/10.1016/0960-1686\(91\)90277-E](https://doi.org/10.1016/0960-1686(91)90277-E).
46. M. Almaraz, E. Bai., C. Wang, J. Trousdell, S. Conley, I. Falooona, B. Z. Houlton, Agriculture is a major source of NO_x pollution in California, *Sci. Adv.* **4** (2018) 3477, doi: <https://doi.org/10.1126/sciadv.aar3477>.

- org/10.1126/sciadv.aao3477.
47. M. K. Firestone, E. A. Davidson, Microbiological basis of NO and N₂O production and consumption in soil, in M. O. Andreae, D. S. Schimel (ed.), *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*. Vol. 47, Wiley, 1989, pp. 7–21.
 48. NRC, Rethinking the Ozone Problem in Urban and Regional Air Pollution. Washington, DC: The National Academies Press, 1991, doi: <https://doi.org/10.17226/1889>.
 49. L. P. S. Cruz, V. P. Campos, A. M. C. Silva, T. M. Tavares, A Field Evaluation of a SO₂ Passive Sampler in Tropical Industrial and Urban Air, *Atmos. Environ.* **38** (2004) 6425–6429, doi: <https://doi.org/10.1016/j.atmosenv.2004.07.022>.
 50. V. P. Campos, L. P. S. Cruz, R. H. M. Godoi, A. F. L. Godoi, T. M. Tavares, Development and validation of passive samplers for atmospheric monitoring of SO₂, NO₂, O₃ and H₂S in tropical areas, *Microchem. J.* **96** (2010) 132–138, doi: <https://doi.org/10.1016/j.microc.2010.02.015>.
 51. S. V. Krupa, Passive sampling of ambient, gaseous air pollutants: a review, in A. H. Legge, L. L. Jones (Ed.), *Proceedings of the Int. Spec. Conf., Emerging Air Issues for the 21st Century: The Need for Multidisciplinary Management*, VIP-78. Air and Waste Management Association, Pittsburgh, 1998, pp. 485–505.
 52. C. K. Varshney, A. P. Singh, Passive Samplers for NO_x Monitoring: A Critical Review, *The Environmentalist* **23** (2003) 127–136, doi: <https://doi.org/10.1023/A:1024883620408>.
 53. D. J. Moschandreas, S. M. Relwani, K. C. Taylor, A Laboratory Evaluation of Nitrogen Dioxide Personal Sampling Device, *Atmosph. Environ.* **24** (1990) 2807–2811, doi: [https://doi.org/10.1016/0960-1686\(90\)90167-L](https://doi.org/10.1016/0960-1686(90)90167-L).
 54. T. S. Hansen, M. Kruse, H. Nissen, M. Glasius, C. Lohse, Measurements of Nitrogen Dioxide in Greenland Using Palmes Diffusion Tubes, *J. Environ. Mon.* **3** (2001) 139–145, doi: <https://doi.org/10.1039/B008325I>.
 55. J. S. M. Boleij, E. Lebret, F. Hoek, D. Noy, B. Brunekreef, The Use of Palmes Diffusion Tubes for Measuring NO₂ in Homes, *Atmosph. Environ.* **20** (1986) 597–600, doi: [https://doi.org/10.1016/0004-6981\(86\)90103-4](https://doi.org/10.1016/0004-6981(86)90103-4).
 56. D. Krochmal, L. Gorski, Determination of Nitrogen Dioxide in Ambient Air by Use of a Passive Sampling Technique and Triethanolamine as Absorbent, *Environ. Sci. Tech.* **25** (1991) 531–535, doi: <https://doi.org/10.1021/es00015a023>.
 57. J. D. Mulik, R. G. Lewis, W. A. McClenny, D. D. Williams, Modification of a high-efficiency passive sampler to determine nitrogen dioxide or formaldehyde in air, *Anal. Chem.* **61** (1989) 187–190, doi: <https://doi.org/10.1021/ac00177a022>.
 58. K. Stevenson, T. Bush, D. Mooney, Five years of nitrogen dioxide measurement with diffusion tube samplers at over 1000 sites in the UK, *Atmosph. Environ.* **35** (2001) 281–287, doi: [https://doi.org/10.1016/S1352-2310\(00\)00171-0](https://doi.org/10.1016/S1352-2310(00)00171-0).
 59. D. Noij, E. Lebret, H. Willers, A. Winkes, J. S. M. Boleij, B. Brunekreef, Estimating Human Exposures to Nitrogen Dioxide: Results from a Personal Monitoring Study Among Housewives, *Environ. Intern.* **12** (1986) 407–411, doi: [https://doi.org/10.1016/0160-4120\(86\)90055-3](https://doi.org/10.1016/0160-4120(86)90055-3).
 60. I. Colbeck, Nitrogen Dioxide in the Workplace Environment, *Environ. Monit. Assess.* **52** (1998) 123–130, doi: <https://doi.org/10.1023/A:1005887007663>.
 61. D. E. Rolston, Gases flux, in: A. Klute, editor, *Methods of soil analysis. Part 1. Physical and mineralogical methods*. SSSA Book Ser. 5. SSSA, Madison, WI. p. 1986, 1103–1119.
 62. W. Powers, M. Capelari, Analytical methods for quantifying greenhouse gas flux in animal production systems, *J. Anim. Sci.* **94** (2016) 3139–3146, <https://doi.org/10.2527/jas2015-0017>.
 63. K. Yu, A. Hiscox, R. D. DeLaune, R. D. DeLaune, K. R., Reddy, C. J. Richardson, J. P. Megonigal, *Greenhouse Gas Emission by Static Chamber and Eddy Flux Methods*, SSSA Book Series, 2013, doi: <https://doi.org/10.2136/sssabookser10.c22>.
 64. M. Reich, *Metode mjerenja ugljikovog dioksida iz tla*, Diplomski rad, Zagreb, 2012.
 65. M. Pavelka, M. Acosta, R. Kiese, N. Altimir, C. Brümmer, P. Crill, E. Darenova, R. Fuß, B. Gielen, A. Graf, L. Klemmedtsson, A. Lohila, B. Longdoz, A. Lindroth, M. Nilsson, S. Marañón Jiménez, L. Merbold, L. Montagnani, M. Peichl, M. Pihlatie, J. Pumpanen, P. Serrano Ortiz, H. Silvennoinen, U. Skiba, P. Vestin, P. Weslien, D. Janous, W. Kutsch, Standardisation of chamber technique for CO₂, N₂O and CH₄ fluxes measurements from terrestrial ecosystems, *Int. Agrophys.* **32** (2018) 569–587, doi: <https://doi.org/10.1515/intag-2017-0045>.
 66. P. Rochette, G. L. Hutchinson, *Measurement of Soil Respiration in situ: Chamber techniques*, 2005.

SAŽETAK

Mjerenje emisija dušikovih oksida iz tla primjenom metode pasivnih sakupljača i statičkih komora

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Dušikovi oksidi imaju glavnu ulogu u kemiji atmosfere kao primarne onečišćujuće tvari, sudjelovanjem u stvaranju sekundarnih onečišćujućih tvari ili kao staklenički plinovi. Istraživanje je provedeno u zapadno panonskoj podregiji Hrvatske, s ciljem utvrđivanja prikladnosti vlastite metode pasivnih sakupljača i statičkih komora u svrhu mjerenja koncentracije N-NO₂. Cilj je također bio utvrditi utjecaj mineralne gnojidbe na N-NO₂ fluks tijekom vegetacije tritikale. Istraživanje je pokazalo prikladnost primijenjene metode za mjerenje N-NO₂ fluksa. Prosječni dnevni fluks N-NO₂ kretao se u rasponu od 2,78 do 5,09 mg ha⁻¹ dan⁻¹, ovisno o fenofazi i tretmanu. Statistički značajne razlike u emisiji N-NO₂ između dvaju istraživanih tretmana (300 kg N ha⁻¹ i 0 kg N ha⁻¹) nisu zabilježene, kao niti između dviju istraživanih fenofaza.

Ključne riječi

Hrvatska, N-NO₂ fluks, gnojidba, vegetacija tritikale, agroekosustav

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