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. 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 NOx represent primary pollutants. According to Duxbury and Isemann, 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 (NOx) have an effect on the formation of ozone (O3), which is a common greenhouse gas responsible for a non-negligible part of radiative forcing, 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. However, soil microbial emissions are also of high interest, especially since microorganisms as diffusive sources affect the atmospheric chemistry over large areas. Soil NO emissions from agricultural soils are estimated to represent 40% of the total NO emission from all sectors. According to Hall and Matson, 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. Accordingly, in the research of Troy and Tang, 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 NOx in agricultural systems indicate that the application of nitrogen fertilizers results in elevated NOx emissions as compared with background levels, regardless of the type of fertilizer used. A few studies have observed increased fluxes of NOx from soil with clipped vegetation, as well as from cleared or plant-less soil, compared to undisturbed, vegetated sites.

With the population increase and rapid industrialization and urbanization growth in recent decades, air pollution has been recognized as a global problem. Thus, together with air quality guidelines, air quality standards have been established in many countries around the world. Accordingly, WHO 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.

In this research, the main goal was to determine the suitability of the passive sampler method for N-NOx 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-NOx emission (two treatments with 0 and 300 kg N ha−1). Also, the intention was to compare N-NOx emission between two sets of measurements in phenophases (tillering and jointing) of triticale.
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-CO\(_2\) flux measurements due to the climate change issues (carbon balance). The total area of the experiment was 39 000 m\(^2\). 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 NO\(_2\) measurements in this research, applied were treatment without mineral nitrogen fertilization (N\(_0\) + P + K), and treatment with a high dose of nitrogen fertilization (N\(_{300}\) + 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 m\(^2\) 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/m\(^2\) 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 NO\(_2\) concentration and agro-ecological factors

During the vegetation period, soil-emitted NO\(_2\) 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 NO\(_2\) 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 cm\(^3\) 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 NO\(_2\) 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
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, 28

2.4.2 Sample analysis

Sample analysis was performed according to Paukovic27 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:

\[
y(\text{NO}_2) = m \cdot k / t \tag{1}
\]

where: \(y(\text{NO}_2)\) – mass concentration of NO₂ in air (in µg m⁻³), \(m\) – mass of NO₂ (in µg), \(k\) – mass of NO₂ collected on filter during sampling (in µg), \(t\) – 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:

\[
F = \left( \frac{V}{A} \right) \left( \frac{p M c_2 - c_1}{RT t_j - t_i} \right) \tag{2}
\]

where: \(F\) – NO₂ flux or NO₂ emission [gm⁻² s⁻¹], \(M\) – NO₂ molecular mass [g mol⁻¹] (46 g mol⁻¹), \(V\) – chamber volume [m³] (\(V = 0.002955\) m³), \(A\) – chamber surface [m²] (\(A = 0.0314\) m²), \(c_1\) – NO₂ concentration at the beginning of measurement [10⁻³ mol m⁻³], \(c_2\) – NO₂ concentration at the end of measurement [10⁻³ mol m⁻³], \(T\) – air temperature 273 + \(T\)/°C, \(R\) – gas constant (8,314 J mol⁻¹ K⁻¹), \(P\) – air pressure [Nm⁻²], \(t\) – 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-
ised as a humid climate \( (L_i = 112) \). 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-NO\(_2\) flux

According to Schindlbacher and Zechmeister-Boltenstern\(^{28}\), 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\(_2\) emissions\(^{29,30,28}\), there are also contrasting results concerning high-temperature responses of soil NO\(_2\) emissions.\(^{31,32}\) In this research, average daily N-NO\(_2\) flux increased with temperature (Fig. 5), showing linear dependence. However, temperature was considered as one of the reasons why a statistical difference between N-NO\(_2\) 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-Boltenstern\(^{29}\), each soil has specific soil moisture which optimises soil NO emissions. In Troy and Tang\(^{34}\) 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-NO\(_2\) flux was inversely proportional to soil moisture (Fig. 6). In Medinet\(_{\text{et al.}}\)^{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 changes in moisture and temperature.

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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\textsubscript{x} emissions.\textsuperscript{10} Around a quarter of global NO\textsubscript{x} production derives from soils, mainly from fertilized agriculture.\textsuperscript{40} However, estimates of global soil NO\textsubscript{x} emissions vary widely from 9 to 27 Tg per year.\textsuperscript{41,42,43} The first data on field measurements of NO\textsubscript{x} emissions were published by Makarov.\textsuperscript{44} His experiments with mineral fertilizers showed that 0.2 % of the applied nitrogen was lost as NO\textsubscript{2} to the atmosphere, demonstrating that the increased application of mineral fertilizer may have an effect on the atmospheric NO\textsubscript{x} budget. In this research, there was no significant difference in N-NO\textsubscript{2} flux between treatments with mineral nitrogen fertilizer (300 kg N ha\textsuperscript{-1}) and treatment without nitrogen fertilizer (0 kg N ha\textsuperscript{-1}) in the tillering and jointing phases (Figs. 7a and 7b). Although there was no significant difference between investigated treatments, in both phenophases, N-NO\textsubscript{2} flux was higher in treatment where 300 kg N ha\textsuperscript{-1} was applied. Depending on treatment and phenophase, daily values in this research ranged from 1.66 mg ha\textsuperscript{-1} day\textsuperscript{-1} to 7.18 mg ha\textsuperscript{-1} day\textsuperscript{-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-
tation, (iii) high data variability – high RSD in the range 3–55 %), (iv) soil temperature inversion. In a research conducted in California, soil NO \(_2\) emissions varied non-linearly 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.,\(^{25}\) the fluxes increased linearly with fertilizer application, where 11 % of the nitrogen in the fertilizer converted to NO\(_2\) and 5 % to \(\text{N}_2\text{O}\). In Almaraz et al.,\(^{46}\) study, NO\(_2\) emissions were greatest from agricultural soils where N fertilizer applications can reach > 600 kg N ha\(^{-1}\) year\(^{-1}\). The importance of N inputs through fertilizer in accelerating NO\(_2\) emissions from soil microbial communities is presented by Firestone\(^{27}\) through the comparison of high mean efflux from agricultural soils (average of 19.8 kg N ha\(^{-1}\) year\(^{-1}\)) compared to much lower NO\(_2\) emissions from natural ecosystems (average of 1.0 kg N ha\(^{-1}\) year\(^{-1}\)). In this research, average annual cumulative N-NO\(_2\) flux was 1.15 g ha\(^{-1}\) year\(^{-1}\) on treatment without nitrogen fertilizer (0 kg N ha\(^{-1}\)) and 1.55 g ha\(^{-1}\) 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\(_2\) emissions at concentrations below parts per billion\(^{48}\). 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.,\(^{59}\) 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.\(^{57}\) used four different types of passive samplers in a tropical urban environment to measure soil NO\(_2\) emissions, including: (i) ogawa samplers, (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\(_2\) emissions. Furthermore, Mukl et al.\(^{57}\) compared the results from passive (triethanolamine, TEA absorbent) and continuous (tunable diode laser) measurement methods for soil NO\(_2\) 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\(_2\) 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\(_2\) 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\(_2\) emissions.\(^{59,60}\) In his research, Campos et al.\(^{61}\) 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.\(^{61,62}\) 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.\(^{63}\) 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\(^{69}\), 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\(^{66}\), 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 NO$_2$ 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-NO$_2$ 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-NO$_2$ 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 NO$_2$ concentrations at observed N-NO$_2$ fluxes.

List of abbreviations

Popis kratica

- GHG – greenhouse gas
- NO – nitrogen(I) oxide
- O$_3$ – ozone
- NO$_3$ – nitrogen oxide
- N$_2$O – nitrogen(IV) oxide
- CH$_4$ – methane
- CO$_2$ – carbon dioxide
- NH$_3$ – ammonia
- WHO – World Health Organization
- P – phosphorus
- K – potassium
- KAN – nitrogen fertilizer
- N – nitrogen
- W1 – Whatman 1

L$_r$ – Lang’s rain factor
RSD – relative standard deviation

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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 fluksu tijekom vegetacije tritikale. Istraživanje je pokazalo prikladnost primijenjene metode za mjerenje N-NO₂ fluksa. Prosječni dnevni flukus 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 fluksu, gnojidba, vegetacija tritikale, agroekosustav

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