N₂O and CO₂ Emissions from Bare Soil: Effect of Fertilizer Management

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Abstract: The paper presents the results of a laboratory experiment focused on the assessment of the effect of different methods of application of ammonium nitrate (TD—top dressing and DP—deep placement) on N₂O and CO₂ emissions from soil without crop cover. Nitrogen application increased soil N₂O–N fluxes by 24.3–46.4%, compared to untreated soil (NIL). N₂O–N emissions from TD treatment were higher by 12.7%, compared to DP treatment. Soil CO₂–C fluxes from DP treatment were significantly higher by 17.2%, compared to those from NIL treatment. Nonetheless, the differences between soil CO₂–C fluxes from DP and TD treatments, as well as from TD and NIL treatments, were of no statistical significance. The cumulative greenhouse gas (GHG) emissions (a sum of cumulative soil emissions of CO₂–C and N₂O–N after conversion to the equivalent of CO₂–C) from both N-fertilized soils were similar, and higher by 20% than from untreated soil. The obtained data show that the effect of reduction of N₂O–N soil emissions gained by deep placement of nitrogen fertilizer was completely lost through an increase in CO₂–C emissions from the soil. This suggests that deep placement of nitrogen fertilizers in sandy soil without crop cover might not lead to a mitigation of soil GHG emissions.

Keywords: greenhouse gas emission; nitrogen fertilization; arable soils

1. Introduction

Compared to conventional fertilization and cultivation, a deep placement of nitrogen fertilizers provides an alternative method of fertilization, allowing for effective plant nutrition in a later growth stage of plants [1]. Deep placement of nitrogen fertilizers seems to be a promising method of mitigation of N₂O–N soil emission [2,3]. Gaihre et al. [4] showed that N₂O–N emissions from soil with deep-placed urea were lower by up to 80% than from top-dressed soil. Chatterjee et al. [5] argued that deep placement of nitrogen could reduce N₂O–N emissions, since a larger fraction of fertilizer nitrogen can be maintained in the soil for a longer period. According to Chapuis-Lardy et al. [6], a reduction of soil N₂O–N emission results from N₂O microbial consumption. Rutkowska et al. [7] evaluated the effect of deep nitrogen placement on N₂O–N soil emissions from C-poor light sandy soils on four experiments conducted in different regions of Poland. In this study, deep fertilizer placement mitigated the soil emission of N₂O–N, although the reductions of soil N₂O emission were lower than those described in the literature. Adviento-Borbe and Linquist [8] observed no significant differences in N₂O–N soil emissions between broadcasting and deep placement of nitrogen in the soil, whereas Linquist et al. [9] reported that nitrogen deep placement promoted N₂O–N emissions. These inconsistent results may be explained by differences in the source and amount of N fertilizer and interactions between...
the soil and weather conditions [10]. N₂O–N is formed as a result of microbiological processes: denitrification and nitrification, as well as abiotic chemodenitrification. Denitrification is carried out by heterotrophic bacteria that use nitrate (NO₃⁻) or nitrite (NO₂⁻) as alternative electron acceptors. Although denitrification is one of the sources of N₂O–N in the soil, Ruser et al. [11] explained a decrease in N₂O–N emissions by a switch to N₂ at high soil moisture conditions. On the other hand, denitrification is limited in well-drained sandy soils. Nitrification is performed under aerobic conditions by chemoautotrophy, using NH₃–N as an energy source which can produce N₂O–N by nitrifier nitrification, nitrifier denitrification, or nitrification-coupled denitrification [12,13]. According to Sánchez-Martín et al. [14], in C-poor and C-rich soils, respectively, the nitrifier denitrification and coupled nitrification–denitrification constitute the principal sources of N₂O–N. Generally, optimum conditions for N₂O–N emissions via denitrification occur at water-filled pore space (WFPS) of 70–90%, whereas N₂O–N emissions at lower WFPS are caused by nitrification [13].

The divergent assessments of the influence of different ways of nitrogen application on N₂O–N soil emissions are probably shaped by extreme weather conditions. Atypical meteorological conditions (long-term and short-term drought/flood) occurring during the growing season constitute manifestations of the global climate change. Floods resulting from heavy rainfall were observed in Central Poland at the turn of May and June 2013 [15], contrary to drought in 2012 [16]. The level of precipitation influences the N cycle in the environment through impacting on the intensity of nitrogen leach from the soil. Prior evaluation evidenced a two-fold elevation of the nitrogen leaching in the year of heavy rainfall, compared to a year with rainfall and multi-year average, notwithstanding the fertilization system [17]. In 2015, the Institute of Soil Science and Plant Cultivation—State Research Institute (IUNG-PIB) reported very low values of climatic water balance in three Polish voivodeships (Mazowieckie, Podlaskie, and Lubelskie—Central and Eastern Poland). However, in 2019, such conditions were found on 57.2% of the arable land in all sixteen Polish voivodeships [18]. In 2020, a long-term drought occurred over the spring. Despite favorable meteorological conditions prior to, or after, the atypical meteorological phenomena, the latter can result in a reduction of yields by up to 40% [18], or even in crop loss. Under these conditions, the soils may be left without plant cover, or low-yielding plants might be unable to uptake the fertilizer nitrogen applied in doses adjusted to a high yielding potential. Therefore, even a large amount of fertilizing nitrogen may remain in the soil during the growing season unused by the plants. It can lead to oversize N₂O–N soil emissions or N leaching. Fertilization leads to an increase in CO₂–C soil respiration [19,20]. Microbial N cycling processes are associated with enhanced microbial carbon metabolism in the soil [21]; therefore, excessive content of mineral N in the soil could result in elevated CO₂–C soil emissions. On the other hand, it could be expected that, in conditions of entire or partial yield loss, soil respiration would be reduced because of reduced root respiration. Relatively low CO₂–C soil fluxes over the growing season are observed at the emergence stage, as a consequence of absence of roots [22,23], and over plant maturing and senescence, due to a decrease in plant physiological activity [24].

Atypical weather conditions, which affect the plant growth and yielding, are expected to occur more frequently in the future. Nonetheless, insufficient evidence is published to characterize the impact of different methods of N application on the N₂O–N and CO₂–C emissions from the soil without crop cover. We hypothesized that deep placement of nitrogen fertilizers might decrease the N₂O–N and CO₂–C emissions from the soil without crop cover. The aim of this study was to evaluate the effects of deep placement of N-fertilizer on N₂O–N and CO₂–C soil emissions under the conditions of lacking plant cultivation.

2. Materials and Methods

2.1. Laboratory Experiment

The laboratory experiment was carried out over 51 days in an air-conditioned laboratory at a temperature of 22 °C at the Warsaw University of Life Sciences—SGGW. The soil was collected
up to 25 cm depth (ploughing soil layer) from five replications of the experimental treatment of a long-term experiment in Skierniewice (51°96′60″ N, 20°16′63″ E). In the treatment, mineral fertilizers were applied annually at the following rates: 90 kg N ha\(^{-1}\) (ammonium nitrate); 26 kg P ha\(^{-1}\) (triple superphosphate); 91 kg K ha\(^{-1}\) (potassium chloride 50%). In the long-term experiment, since 1923, plants have been cultivated in a five-crop rotation: potatoes (30 t manure ha\(^{-1}\)), spring barley, yellow lupine, winter wheat, and rye (the soil was collected in the autumn, after rye). In the long-term experiment, a conventional ploughing soil tillage was used. The soil was loamy sand with the following fractions in the 0–25 cm layer: 87% sand (>0.05 mm), 5% silt (0.002–0.05 mm), and 7% clay (<0.02 mm). The content of soil organic carbon and total nitrogen was as follows: 7.35 g C kg\(^{-1}\) ± 0.15 standard deviation (SD) and 0.71 g N kg\(^{-1}\) ± 0.02 SD, respectively, and soil NO\(_3\)\(^-\)–N content was 8.50 mg NO\(_3\)\(^-\)–N kg\(^{-1}\) ± 0.55 SD (the average from five replications). The soil pH in 1 M KCl was 5.8 (with the range between 5.7 and 6.0 pH).

After air-drying and sieving through a mesh of 5 mm, 8 kg of the soil was placed in polyvinyl chloride (PVC) pots. The pots used for the experiment were 20 cm in height with an inside top and bottom diameter of 22 cm and 19 cm, respectively. The pot experiment was conducted in three repetitions, in a fully random system. No plants were cultivated. Over the study period, each pot was weighed daily, and any lost moisture replenished with distilled water to maintain soil moisture content at 60% WFPS. Two days after the first irrigation, the non-fertilized treatment (NIL) and N-fertilized treatments were established. Nitrogen was applied in the fertilized treatments at a dose of 1 g N per pot, in the form of ammonium nitrate (34% N). As we decided to test the nitrogen fertilizer that is most prevalent in Poland, we evaluated the effects of the application of ammonium nitrate, which remains the fertilizer used the most in our agrotechnical and soil conditions, irrespective of a noticeable increase in the urea consumption [25]. The fertilizer was scattered on the surface of soil (top dressing—TD treatment) or applied at a depth of 10 cm (deep placement—DP treatment), which can be extrapolated to 26.31 g N m\(^{-2}\) and 263 kg N ha\(^{-1}\) in field conditions. The extrapolation of the experimental dose of nitrogen to the area of 1 m\(^2\) and 1 ha was made assuming that 1 g of N was applied to the pot area of 0.038 m\(^2\). Such doses of nitrogen are currently applied in the cultivation of maize on the Polish soil and agricultural conditions. Therefore, we decided to use similarly high nitrogen doses in the laboratory experiment.

2.2. \(N_2O\)–N and \(CO_2\)–C Emissions

\(N_2O\)–N and \(CO_2\)–C emissions from the soil were measured in situ by means of infrared spectroscopy using a portable FTIR spectrometer, model Alpha (Bruker, Optic GmbH, Ettlingen, Germany). The measurements of \(N_2O\)–N and \(CO_2\)–C emission was taken before, and a day after, soil nitrogen fertilization, and were continued weekly for the next 51 days (nine test dates) in all replications of the experimental treatments. The emission of \(N_2O\)–N and \(CO_2\)–C \((F)\) from the soil was calculated as an increase in the amount of \(N_2O\)–N and \(CO_2\)–C in the measurement chamber (\(\phi = 16\) cm, \(h = 18.5\) cm) after 10 min exposure to the soil surface according to the equation presented by Burton et al. [26]:

\[
F = \frac{\Delta C}{\Delta t} = \frac{V_c \cdot M}{A \cdot V_mol}
\]

where: \(\Delta C/\Delta t\) is the rate of change in \(N_2O\)–N or \(CO_2\)–C concentration inside the chamber, \(A\) is the surface area of the chamber, \(V_c\) is the total volume of the chamber corrected by temperature, \(M\) is molar mass of \(N_2O\)–N or \(CO_2\)–C, and \(V_mol\) is the molar volume of \(N_2O\)–N or \(CO_2\)–C inside the chamber, corrected by air temperature using the ideal gas law. \(N_2O\)–N and \(CO_2\)–C emissions from soil were expressed in \(\mu g\) \(N_2O\)–N m\(^{-2}\) h\(^{-1}\) and \(mg\) \(CO_2\)–C m\(^{-2}\) h\(^{-1}\), respectively. Cumulative emissions of \(N_2O\)–N and \(CO_2\)–C (i.e., \(mg\) \(N_2O\)–N m\(^{-2}\) and \(g\) \(CO_2\)–C m\(^{-2}\)) were calculated by linear interpolation between two close sampling dates and the numerical integration of the function over time, assuming that fluxes changed linearly among sampling days [27]. The correction for background cumulative \(N_2O\)–N emissions from nitrogen fertilized treatments were calculated as the difference between the
cumulative emissions from the TD or DP and NIL treatments: i.e., cumulative $\text{N}_2\text{O}–\text{N}$ emissions from TD—cumulative $\text{N}_2\text{O}–\text{N}$ emissions from NIL, and cumulative $\text{N}_2\text{O}–\text{N}$ emissions from DP – cumulative $\text{N}_2\text{O}–\text{N}$ emissions from NIL.

Carbon dioxide equivalent (CO$_2$eq) for $\text{N}_2\text{O}$ emission was calculated from Global Warming Potential [28], according to the formula: CO$_2$eq = N$_2$O · 298.

2.3. Soil Analysis

Soil NO$_3^−$–N content was measured at the beginning and (separately in the soil layers: 0–10 cm and 10–20 cm) at the end of the experiment, by means of the Skalar San Plus analyzer (Skalar Analytical BV, Breda, Netherlands), after fresh soil extraction in 0.01 mol CaCl$_2$ dm$^{-3}$ with a soil/extractant weight ratio of 1:10. The same soil samples were subject to extraction of dissolved organic carbon (DOC) in accordance with the methodologies described by Zsolnay [29]. The soil samples were extracted in 0.01 mol CaCl$_2$ dm$^{-3}$. The weight ratio of soil to extraction solution was 1:2, and the extraction time was 10 min. Total organic carbon (TOC) content in the soil and soil DOC content were measured by means of the Thermo Electron-C TOC-500 (Shimadzu, Kyoto, Japan). Soil total nitrogen (TN) content was measured using a Vapodest VAP 30 analyzer (Gerhardt, Bonn, Germany).

2.4. Statistical Analysis

To determine statistically significant differences between treatments (at $p < 0.05$), one-way analysis of variance (ANOVA) was carried out. Homogeneous groups for the examined treatments were determined by Tukey’s (HSD) multiple-comparison test. Data had been previously tested for normality distribution by a Shapiro–Wilk’s test, and for homoscedasticity by Levene’s test. Statistical analyses were carried out with the application of the Statistica PL 13.3 software (Tulsa, OKLA, USA).

3. Results and Discussion

3.1. Soil $\text{N}_2\text{O}–\text{N}$ Fluxes

The measured soil $\text{N}_2\text{O}–\text{N}$ fluxes over the study period are presented in Figure 1. Soil $\text{N}_2\text{O}–\text{N}$ fluxes from all treatments before ammonium nitrate application on the first day (D1) of study were similar. Differences in measured fluxes became noticeable on D2. Compared to NIL treatment and DP treatment, scattering of ammonia nitrate on the soil (TD treatment) resulted in a significant ($p < 0.05$) increase in the measured soil $\text{N}_2\text{O}–\text{N}$ flux as early as on D2. On D9, the measured $\text{N}_2\text{O}–\text{N}$ soil flux from TD treatment was more than twofold higher than from NIL treatment, and approximately 76% higher than from DP treatment. A substantial impact of NH$_4$NO$_3$ top dressing on the measured $\text{N}_2\text{O}–\text{N}$ soil fluxes was also observed on D16, when soil $\text{N}_2\text{O}–\text{N}$ emissions from TD treatment reached a maximum. Soil $\text{N}_2\text{O}–\text{N}$ emissions from NIL and DP treatments peaked one week later (D23). That suggests that deep N-fertilizer placement may delay and reduce the $\text{N}_2\text{O}–\text{N}$ emissions from the soil. After the peak of $\text{N}_2\text{O}–\text{N}$ emissions, the amount of nitrous oxide emitted from both N-fertilized soils showed a decreasing pattern until D30, followed by an increase, which resulted in second, smaller peaks reached by DP and TD treatments on D37 and D44, respectively. The $\text{N}_2\text{O}–\text{N}$ emissions from NIL treatment followed a pattern similar to those from TD treatment; however, the measured fluxes from NIL were significantly lower. The observed changes in $\text{N}_2\text{O}–\text{N}$ emissions from the tested soils could be caused by an increase in the microbial activity of the soil and, also, to some extent, by changes in natural soil compaction during the experiment.
Measured N₂O–N fluxes over the study periods showed a high variability, with a range of 30.2–254.8 µg N m⁻² h⁻¹ from TD treatment, 29.5–200.2 µg N m⁻² h⁻¹ from DP treatment, and 33.0–206.7 µg N m⁻² h⁻¹ from NIL treatment (Table 1). The determined high variability of soil N₂O–N emission patterns over the study period seems to be typical of this process [30]. Measured N₂O–N fluxes from the soil treated with ammonium nitrate significantly (p < 0.05) exceeded (approximately by 24.3 and 46.4% on the DP and TD treatments, respectively) those from NIL (Table 1). The cumulative soil N₂O–N emissions from soils under TD and DP treatments were significantly (p < 0.05) higher, by 26.9% and 42.9%, than those from NIL treatment (Table 1). Several authors indicated that N-fertilization increased N₂O–N emissions of the soil [6,31–33]. The significant (p < 0.05) impact of ammonium nitrate application on N₂O–N emission evidenced in our study is similar to experimental results obtained by Bouwman et al. [34], van Groenigen et al. [35], and Meng et al. [36], who observed a significant increase in N₂O–N emissions from the soil, particularly at high doses of nitrogen (200–300 kg N ha⁻¹).

![Figure 1](image-url)  
**Figure 1.** N₂O–N and CO₂–C emissions from non-fertilized soil (NIL) and soils fertilized with ammonium nitrate: top dressing (TD) and deep placement (DP).

| Treatment | N₂O–N Emissions | Daily µg N m⁻² h⁻¹ | Cumulative From: | Cumulative From: mg N m⁻² | NH₄NO₃ |
|-----------|-----------------|------------------|-----------------|--------------------------|--------|
| NIL       | mean            | 94.0 ± 5.6       | Soil            | 133.5 ± 6.7              | -      |
|           | median          | 93.3             |                 | 137.4                    | -      |
|           | min–max         | 33.0–206.7       |                 | 125.7–137.4              | -      |
| TD        | mean            | 137.5 ± 3.3      | Soil            | 190.8 ± 5.6              | 57.3 ± 7.3 |
|           | median          | 125.9            |                 | 188.8                    | 59.8   |
|           | min–max         | 30.2–254.8       |                 | 186.4–197.2              | 49.0–63.1 |
| DP        | mean            | 116.8 ± 4.7      | Soil            | 169.4 ± 20.2             | 35.9 ± 26.7 |
|           | median          | 123.5            |                 | 164.7                    | 27.3   |
|           | min–max         | 29.5–200.2       |                 | 151.9–191.5              | 14.5–65.8 |

Values followed by the same letters (a–c) in the column are not statistically different (p < 0.05).

We observed a limited transformation of the fertilizer nitrogen into N₂O–N. Corrected for background cumulative soil, N₂O–N emissions from TD and DP treatments were low, and accounted for 0.22% and 0.14% of applied N, respectively. In several studies, differing in the soil and atmospheric
conditions, plant cover, nitrogen fertilizers, or nitrogen leaching, N$_2$O–N emissions from agricultural soils were found to vary between 0.05% and 15.54% of applied nitrogen [37–40]. Upon the TD and DP treatments, the measured N$_2$O–N losses from the estimated load of 263 kg N ha$^{-1}$ equaled, respectively, 0.58 kg and 0.37 kg N ha$^{-1}$. Our experiment, however, lasted only 51 days, a fraction of the growing period in Central Poland. The emission of N$_2$O–N from TD and DP treatments extrapolated to the full growing period (March to November, i.e., approximately 210–220 days) reached 2.50 kg and 1.59 kg per ha (i.e., 0.6–0.95% of nitrogen applied per ha). Our earlier laboratory experiment showed that N$_2$O–N emission from soil without mineral fertilization was 0.77 kg N$_2$O–N ha$^{-1}$ [41]. Therefore, it can be expected that the total soil N$_2$O–N emission from the TD and DP treatments during the growing period would reach a maximum of 3.27 kg and 2.36 kg N$_2$O–N ha$^{-1}$, respectively.

According to Zhu et al. [13], in soils where nitrifier denitrification is the dominant pathway of N$_2$O–N production, application of ammoniacal fertilizer results in higher N$_2$O–N emissions, compared with acidic-forming fertilizers (e.g., NH$_4$NO$_3$). In the experimental conditions of the soil, i.e., soil texture, low content of soil carbon, and moisture at level of 60%, promoted the nitrifier denitrification, rather than denitrification, as the dominant pathway of N$_2$O–N production, resulting in a preferential use of the ammonium ion and retention of nitrate in the soil. Most of the NO$_3^-$–N remained accumulated in the soil (Table 2). In comparison to the NIL treatment, the application of ammonium nitrate as part of the TD treatment increased the content of NO$_3^-$–N in the 0–10 cm and 10–20 cm soil layers 23.8-fold and 2.3-fold, respectively. Under the conditions of deep N-fertilizer placement (DP treatment), the nitrate contents in the 0–10 cm and 10–20 cm soil layers were 1.6-fold and 25.6-fold higher, respectively, than on NIL treatments.

Table 2. Effect of different NH$_4$NO$_3$ applications: top dressing (TD) and deep placement (DP) on the content of NO$_3^-$–N and dissolved organic carbon (DOC) in the soil at the end of study period.

| Treatment | Soil Content | NO$_3^-$–N | DOC |
|-----------|--------------|------------|------|
|           | 0–10 cm      | 10–20 cm   | 0–10 cm | 10–20 cm |
| NIL       | mean 6.84 ± 1.6 | 6.27 ± 1.6 | 9.12 ± 0.7 | 8.03 ± 0.9 |
|           | median 5.93 | 5.59 | 8.99 | 8.04 |
|           | min–max 5.90–8.69 | 5.13–5.59 | 8.52–9.86 | 7.15–8.90 |
| TD        | mean 163.13 ± 22.5 | 14.55 ± 1.9 | 9.54 ± 1.4 | 11.81 ± 1.3 |
|           | median 174.2 | 14.46 | 9.56 | 11.51 |
|           | min–max 137.2–178.0 | 12.74–16.46 | 8.18–10.88 | 10.69–13.23 |
| DP        | mean 10.03 ± 0.8 | 160.63 ± 20.4 | 12.64 ± 2.3 | 9.78 ± 0.9 |
|           | median 9.76 | 167.2 | 13.61 | 10.30 |
|           | min–max 9.45–10.89 | 127.8–176.9 | 10.04–14.26 | 8.73–10.32 |

Values followed by the same letters ($^{a,b}$) in the column are not statistically different ($p < 0.05$).

The share of N$_2$O–N emitted from NH$_4$NO$_3$ applied in the DP and TD fertilization systems reached merely 21.2% and 30.0% of total cumulative nitrous oxide emissions from the soil (Table 1). This finding is explained by relatively high emissions of N$_2$O–N from the NIL treatment. Prior nitrogen fertilization, as part of the long-term experiment in Skierniewice, which led to an accumulation of various forms of organic and mineral nitrogen in the soil and, possibly, their transformation to N$_2$O–N during the study period, can partly explain the small differences in N$_2$O–N emissions from experimental (fertilized) treatments (TD and DP) and the NIL treatment.

Further consideration needs to be given to the soil reaction. In different soil conditions (soil texture, low content of soil carbon, and moisture), several studies showed that optimum values of soil pH for N$_2$O–N production ranged between pH 3.9 and 7.0 [42–45]. Although Russow et al. [46] showed that high NH$_4^+$–N concentration could facilitate N$_2$O–N emissions in limed soils with pH 7.0–8.1, in this type of soil under aerobic conditions, nitrification is the main pathway of soil N$_2$O–N
production [47,48]. In acid soils, approximately 80% of the N2O–N flux results from denitrification. Soil pH of the tested soils (pH 5.8) should be favorable for denitrification. However, we maintained non-variable soil moisture at the level of 60% WFPS, which is unfavorable for denitrification. That was probably the cause of the relatively low N2O–N emissions from the soil treated with NH4NO3 (DP and TD treatments).

Several authors evidenced a reduction of N2O–N emissions from soil after deep N-fertilizer placement [9,49,50]. Liu et al. [3] reported mitigation of N2O–N emission after an application of liquid urea–ammonium-nitrate fertilizer at soil depths of both 10 cm and 15 cm. However, the authors observed no significant differences between N2O–N emissions from soil fertilized on the topsoil and at a depth of 5 cm. Hosen et al. [51] showed that the deep application of urea neither to the 0–10 cm soil layer nor to the 10–20 cm soil layer did reduce the N2O–N emissions. In their opinion, N2O–N emission is more dependent on soil conditions than on the depth of fertilizer application. The level of mitigation of N2O–N emissions recorded in our study was lower than that recorded by Gaihre et al. [4] in field conditions under rice cultivation. Cumulative N2O–N emissions from the soil with top dressing of NH4NO3 application were higher by 12.7%, compared to N2O–N emission from the soil with deep N-fertilizer placement (Table 1). Our results were similar to data obtained by Rutkowski et al. [7]. According to the authors, in the majority of experimental locations, in a year with lower precipitation, deep placement of nitrogen fertilizer in maize cultivation resulted in lower than a 17% reduction of N2O–N soil emissions. However, on numerous measurement dates, N2O–N emissions from soils with deep N-fertilizer placement were similar to, or higher than, those from the conventional top-dressing system of maize fertilization [7]. Chapuis-Lardy et al. [6] hypothesized that conditions interfering with N2O–N diffusion in the soil enhanced the N2O–N consumption and decreased the N2O–N soil emissions as an effect of the longer presence of N2O–N in the soil. Our data confirm that the diffusion of N2O–N between the place of its formation and the soil surface has an important impact on the emissions from the DP treatment.

Among multifactorial impacts, the soil moisture and content of soil organic carbon act as the proximal regulator of N2O–N production in the soil. Both soil moisture and the content of organic carbon regulate the oxygen availability to soil microbes. Zhu et al. [13] showed that oxygen availability regulated pathways of N2O–N formation in the soil. N2O–N production via NH3–N oxidation increased with decreasing O2 concentration from 21% to 0.5% (vol/vol). At low O2 concentrations, the contribution of nitrifier denitrification and heterotrophic denitrification to total N2O–N production ranged between 34% and 66% and between 34% and 50%, respectively. Heterotrophic denitrification was responsible for all N2O–N production at 0% O2. Bateman and Baggs [52] showed that N2O–N was formed during denitrification at 70% WFPS. According to Butterbach-Bahl et al. [12], N2 as the end product of denitrification is formed in the soil at soil moisture higher than 80–90% WFPS. The available organic carbon is also a critical factor in controlling denitrification [53]. Its availability promotes the microsite anaerobiosis as a result of increased respiratory demand for oxygen. Therefore, an increase in the availability of labile carbon would favor complete denitrification to N2. In our study, soil moisture was constantly maintained at 60% WFPS, and the content of dissolved organic carbon (DOC) in the soil at the end of the study period was low (Table 2). Therefore, the possibility of reducing the soil N2O–N emissions from DP treatment as a result of denitrification was limited. The difference in N2O soil emissions between DP and TD treatments shows that, at soil moisture of 60% WFPS and low DOC soil content, there is a limited possibility of higher N2O microbial consumption via denitrification, as an effect of a longer presence of N2O in the light sandy soil.

3.2. Soil CO2–C Fluxes

Measured soil CO2–C fluxes are presented in Figure 1. Soil CO2–C fluxes from all treatments before ammonium nitrate application on D1 were similar. Differences in measured fluxes became perceptible on D2. A gradual increase in the emission of CO2–C from the soil was recorded for all treatments leading to the first (and the least elevated) peak on D9. Subsequently, we observed a drop
in the measured CO₂-C fluxes, with a first nadir noted for all treatments on D16. This was followed by a substantial rise in the measured CO₂-C fluxes resulting, for all treatments, in the second (and the most elevated) peak on D23. Similar emission patterns, with a peak on D23, may have resulted from the short period between the soil irrigation and measurement date, and the soil compaction change. Before the experiment, the soil was dried and sieved. During the experiment, irrigation could have resulted in a change in the soil density. Hence, the observed changes could, to some extent, be driven by factors not evaluated in the experiment. Successively, an extensive decline in the measured CO₂-C fluxes occurred under all treatments, with the second nadir seen on D30 for NIL treatment and on D37 for TD and DP treatments. The third peak and third nadir were observed under all treatments on D44 and D51, respectively. Except for D2 and D30, the differences in measured CO₂-C fluxes from the studied treatments were not significantly different. On D2, the fluxes for both NIL and DP treatments were significantly higher, as compared with TD treatment. On D30, the measured CO₂-C flux from DP was significantly higher than those from TD and NIL treatments, whereas the flux from TD was significantly higher, as compared with NIL treatment. As a consequence of daily fluxes, significantly (p < 0.05) higher cumulative CO₂-C soil emissions were recorded from DP treatment than from NIL treatments (Table 3).

Table 3. Daily CO₂-C soil emissions and total cumulative CO₂-C soil emissions from the soil treated with NH₄NO₃ in the top dressing (TD) and deep placement (DP) fertilization systems.

| Treatment | CO₂-C Emissions | Daily | Cumulative |
|-----------|-----------------|-------|------------|
|           |                 | mg C m⁻² h⁻¹ | g C m⁻²   |
| NIL       | mean            | 47.0 ± 25.0 | 64.0 ± 4.0 |
|           | median          | 40.7   | 64.7       |
|           | min–max         | 14.1–100.5 | 59.8–67.6  |
| TD        | mean            | 50.4 ± 27.5 | 68.4 ± 2.6 |
|           | median          | 46.4   | 68.0       |
|           | min–max         | 12.7–109.2 | 66.0–71.1  |
| DP        | mean            | 55.1 ± 25.8 | 75.4 ± 2.6 |
|           | median          | 52.9   | 75.1       |
|           | min–max         | 12.9–102.5 | 71.5–79.42 |

Values followed by the same letters (a,b) in the column are not statistically different (p < 0.05). Measured soil CO₂-C daily fluxes over the study period showed a high variability with a range of 12.7–109.2 mg C m⁻² h⁻¹ from TD treatment, 12.9–102.5 mg C m⁻² h⁻¹ from DP treatment, and 14.1–100.5 mg C m⁻² h⁻¹ from NIL treatment (Table 3).

Depending on the way of experimental fertilization, soil CO₂-C fluxes from DP treatment were significantly (p < 0.05) higher by approximately 17.2%, compared to those from NIL treatment. We observed differences between the measured soil CO₂-C fluxes from DP and TD treatments, as well as from TD and NIL treatments; however, they were of no statistical significance. CO₂-C fluxes recorded over the study period were relatively low, compared to those occurring on sandy light soils in the climatic conditions of Poland [54–56]. The relatively low soil CO₂-C fluxes recorded in our study with no crop cover were expected. It is generally acknowledged that CO₂-C is formed in the soil via both autotrophic and heterotrophic respiration. Adviento-Borbe et al. [23] estimated that autotrophic respiration could account for 36% of total soil respiration in high-yielding maize systems. Rochette et al. [57] evidenced that up to 50% of soil respiration resulted from root respiration and decomposition of root exudates. Amos et al. [24] reported that soil flux of CO₂ decreased as plants reached physiological maturity and senescence, due to the absence of root respiration.

The study data suggest that nitrogen fertilization, and the different methods of its application, has an impact on the CO₂-C emissions from the soil. Several studies indicated that N-fertilization
increased CO₂–C emissions from the soil [19,20]. Song and Zhang [20] reported, however, that nitrogen fertilization with 250 kg N ha⁻¹ suppressed soil respiration. In addition, Ding et al. [58] revealed that nitrogen fertilization resulted in a reduction of soil CO₂–C flux. The dose of nitrogen applied in our study could result in no differences in CO₂–C soil emissions, as exemplified by the lack of differences between the fluxes from TD and NIL treatments (Table 3). DeForest et al. [59] evidenced that CO₂–C fluxes could decrease when using high N rates, as a consequence of lower activity of enzymes in the soil. In our study, deep placement of ammonium nitrate resulted in a significant increase in CO₂–C emission from the soil, compared to NIL treatment. Our results are consistent with data presented by Pareja-Sánchez et al. [22]. The authors demonstrated that nitrogen fertilization increased the CO₂–C soil emissions as a result of different availability of soil nitrogen for decomposers. At the end of our study, the content of NO₃⁻–N in the topsoil layer was substantially higher under TD treatment than under DP treatment, which could reduce the soil enzymatic activity. On the other hand, the content of nitrates in the topsoil layer under DP treatment was insignificantly higher than on NIL treatment. Diffusion of NO₃⁻–N from deeper soil layers to the topsoil layer on DP treatment probably increased the amount of nitrogen available for decomposers, and resulted in higher CO₂–C soil emissions. This may be supported by a higher DOC content in the topsoil layer under DP treatment than NIL treatment (Table 2), a difference which, however, did not reach statistical significance.

Adviento-Borbe et al. [23] showed that seasonal fluctuations in soil CO₂–C fluxes depended on soil NO₃⁻–N, though to a lesser extent than on the air temperature and soil moisture. Total cumulative soil CO₂–C emissions recorded over the study period were correlated only with soil DOC content (Table 4).

**Table 4.** Correlation coefficients between cumulative N₂O–N and CO₂–C (total between 1st and 22nd and 23rd–51st day of experiment) emissions of the soil, and soil content of NO₃⁻–N and DOC on 51st day of experiment.

| Parameter | N₂O–N | NO₃⁻–N | DOC  |
|-----------|--------|---------|------|
| N₂O–N     | 1.00   | 0.55 *  | 0.57 *|
| CO₂–C     | 0.24   | 0.34    | 0.44 *|
| NO₃⁻–N    | 0.55 * | 1.00    | 0.03  |
| DOC       | 0.57 * | 0.03    | 1.00  |

* p < 0.05.

### 3.3. Cumulative Greenhouse Gas (GHG) Emissions from the Soil

Cumulative greenhouse gas (GHG) emissions from the soil, calculated as a sum of cumulative soil emissions of CO₂–C and N₂O–N converted to the equivalent of CO₂–C, are presented in Figure 2. Irrespective of the method of nitrogen application, the cumulative GHG emissions from TD and DP treated soil (125.82 g CO₂eq–C m⁻² and 126.40 g CO₂eq–C m⁻², respectively) were significantly (p < 0.05) higher, by approximately 20%, than from NIL treatment (104.40 CO₂eq–C m⁻²). No significant differences in soil GHG emissions were found between the two systems of N-fertilizer application. Our data demonstrate that an increase in CO₂–C emissions from the soil without crop cover counterbalances the reduction of N₂O–N soil emissions gained by deep placement of nitrogen fertilizer, leading to the conclusion that deep placement of nitrogen fertilizer in light sandy soils without crop cover might not mitigate the GHG emissions from the soil. Due to a greater energy input required for deep placement of the fertilizer into the soil, the total soil GHG emissions may exceed the GHG emissions from the traditional fertilization and cultivation systems.
4. Conclusions

Nitrogen fertilization increases the \( \text{N}_2\text{O}-\text{N} \) emissions from the soil. High soil emission of \( \text{N}_2\text{O}-\text{N} \) from topsoil dressed with ammonium nitrate occurs right after fertilizer application. Deep placement of ammonium nitrate at a depth of 10 cm decreases the soil nitrous oxide emissions by 12.7% and increases the soil \( \text{CO}_2-\text{C} \) emissions by 17.2%. The relatively low difference in \( \text{N}_2\text{O}-\text{N} \) soil emissions between DP and TD treatments shows that, at soil moisture of 60% WFPS and low DOC content in the soil, there is a limited possibility of higher \( \text{N}_2\text{O} \) microbial consumption via denitrification as an effect of a longer presence of \( \text{N}_2\text{O}-\text{N} \) in the light sandy soil.

However, \( \text{N}_2\text{O}-\text{N} \) diffusion from a deeper soil layer delays and decreases the intensity of soil surface nitrous oxide emissions. An increase in \( \text{CO}_2-\text{C} \) emissions from the soil without crop cover counterbalances the reduction of \( \text{N}_2\text{O}-\text{N} \) soil emissions gained by deep placement of nitrogen. This suggests that deep placement of nitrogen fertilizers in light sandy soils might not lead to the mitigation of GHG emissions from the soil without crop cover. The deep N-fertilizer placement method, however, will be required for better plant nutrition, rather than the possibility of reducing GHG emissions from soil.

This study bridges a notable gap in the published evidence to characterize the impact of different methods of N application on the \( \text{N}_2\text{O}-\text{N} \) and \( \text{CO}_2-\text{C} \) emissions from the soil without crop cover. Such conditions, albeit currently unusual, are expected to occur more frequently in the future as a result of atypical weather conditions, which affect plant growth and yielding loss.

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Abbreviations

NIL non-fertilized treatment
TD top dressing
DP deep placement

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