



Article Influence of Pig Slurry Application Techniques on Soil CO₂, N₂O, and NH₃ Emissions

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Abstract: Greenhouse gas (GHG) emissions from agricultural soils can accelerate climate change, therefore, different soil fertilization techniques should be assessed before application to reduce GHG emissions. Pig slurry applications can greatly influence soil carbon dioxide (CO₂), nitrous oxide (N₂O), and ammonia (NH₃) emissions of arable fields; thus, it is important to find site-specific techniques to lessen any negative environmental impacts. In this study, we examined the shortterm effect of pig slurry application techniques of spreading and injection on soil greenhouse gas and NH₃ emissions under different irrigation amounts. We used the dynamic chamber method with in-situ gas analyzers. Our study showed that there were elevated emissions during the first week after slurry application; however, the difference between GHG emissions of spreading and injection treatments were not significant. Elevated GHG emissions (213-338% and 250-594% in the case of CO₂ and N₂O emissions, respectively) were observed under dry circumstances compared to irrigated treatments, as well as significantly higher NH₃ emissions occurred for surface spreading under non-irrigated (dry) circumstances compared to other treatments. There were no statistically significant differences between the soil chemistry of different application techniques. However, pig slurry increased the available nitrogen forms (ammonium- and nitrate-nitrogen), which caused N₂O and NH₃ peaks regardless of treatment type. Leachate chemistry was more affected by irrigation strategies than application techniques. Our study highlights the importance of soil conditions at the time of application, rather than the application technique for fertilization using pig slurry.

Keywords: spreading; injection; GHG emission; NH3 emission; leachate chemistry

1. Introduction

Greenhouse gas (GHG) and ammonia (NH₃) emissions from the agricultural sector are an increasing concern for environmental issues, because of their contribution to climate change and acid deposition [1].

Carbon dioxide (CO₂) has a great role in the biosphere with an increasing atmospheric concentration due to human activities; hence, it is the most researched GHG during recent decades [1]. Nitrous oxide (N₂O) is part of the nitrogen cycle influenced by anthropogenic modifications in nutrient supply. Its concentration in the atmosphere has also increased since the industrial revolution. Besides its greenhouse effect, N₂O contributes to stratospheric ozone depletion, thus, understanding the background processes is required [2,3] to develop reducing strategies. CO₂ and N₂O emissions of agriculture can originate from land-use changes, different tillage methods, or fertilization management. The main sources of NH₃ from the agricultural sector are animal husbandry and volatilization after fertilization events [4]. Although its atmospheric concentration was not increased during the last century, NH₃ has a role in air pollution and acid deposition. It contributes to eutrophication,



Citation: Tóth, E.; Dencső, M.; Horel, Á.; Pirkó, B.; Bakacsi, Z. Influence of Pig Slurry Application Techniques on Soil CO₂, N₂O, and NH₃ Emissions. *Sustainability* **2022**, 14, 11107. https://doi.org/10.3390/ su141711107

Academic Editor: Jan Hopmans

Received: 29 July 2022 Accepted: 2 September 2022 Published: 5 September 2022

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). soil and water acidification. Moreover, it has direct toxicity to plant surfaces and after deposition it can be a source of secondary N_2O emission. Therefore, the development of reducing techniques is desirable [5,6].

There are several techniques used to examine soil-derived GHG and NH₃ emissions, which are currently not standardized. One of the most commonly used methods for such investigations is the incubation chamber technique, e.g., using a static or dynamic chamber [7–10]. In these closed system chambers, gas concentrations change during a gas-specific incubation time and air samples can be collected with airtight syringes and quantified later using gas chromatography, or immediate analysis can be performed using in situ gas-specific or multigas analyzers [11–13]. Gas emission values can be calculated using linear or quadratic equations based on the initial and final GHG concentrations [14,15].

There are several techniques used to enrich soils with nutrients providing better plant growth and higher crop yields. Mineral (calcium ammonium nitrate, urea, etc.) and organic (pig slurry, cattle slurry, manure, etc.) fertilizers are applied all over the world depending on soil types and cultivated crops. With the increasing food demand and more intensive animal husbandry occurring worldwide, the increasing amounts of secondary products such as manure must be resolved. An apparent solution is to use animal manure as a fertilizer in crop production. Organic and mineral fertilizers have different C:N ratios that can affect soil GHG emissions [16]. The organic matter of different manures, compost, and slurry has a main role in CO_2 and N_2O emissions, since higher SOC might causes higher emissions [17]. Lower C:N ratios might result in higher NH₃ emissions, while aeration is also an important factor for NH₃ and N₂O emissions [18].

Pig slurry is commonly used as an organic liquid fertilizer. The quantification of the proportion of different fertilizers in global nutrient supplies can be difficult, thus, often only estimates are available. For example, in Hungary, around 2.1–4.6% of the total nitrogen input comes from pig slurry [19]. Worldwide, pig manure is not the most common source of nitrogen; it contributes around 10% to total manure production, compared to cattle slurry which is around 44% [20]. Pig slurry enriches soils with nutrients (nitrogen and carbon supply) and promotes microbiological processes [21–24], consequently influencing CO₂, N₂O, and NH₃ emissions [25,26]. The nitrogen content of pig slurry not only ensures balanced crop production and yields but also is a danger for nitrogen losses such as NH₃ emissions and nitrate (NO₃⁻) leaching to the surface and groundwater reservoirs [27,28]. Nitrogen forms, such as ammonium (NH₄⁺), nitrite (NO₂⁻), and nitrate (NO₃⁻) leached from soils are pollutants of the environment causing eutrophication of surface waters [29–31] and acidification of soils [32,33].

Pig slurry application techniques may result in changes in the chemical properties of soil and soil water and soil GHG and NH₃ emissions [34–36], therefore, the appropriate choice of these techniques could be a form of CO_2 emission and reactive nitrogen (N_2O and NH_3) loss mitigation policy. The most common techniques of pig slurry application are surface spray/spread, trailing shoes and trailing hose, incorporation, and row injection (shallow, deep, open slot, etc.) [34,37]. Some studies report higher GHG and NH₃ emissions of soils under surface spray than injection techniques [36–38]. However, others found that utilizing slurry applications may result in mitigation of NH₃ but can cause elevated GHG emissions [39], or injection can result in elevated N₂O emissions rather than surface techniques [40]. Surface spray techniques of pig slurry can promote soil GHG and NH₃ emissions due to higher evaporation rates and higher exposure to environmental conditions, while injections may cause elevated emissions, especially N₂O because of their positive effect on the anaerobic soil environment and denitrification processes [41,42]. Environmental drivers such as air temperature (Ta) and precipitation are coupled with soil water content (SWC) and soil temperature (T_s) that alter CO₂ emissions and reactive nitrogen loss of soils [43]. In most ecosystems, higher SWC and T_s are considered as facilitating factors of GHG and NH₃ emissions, but decreases in NH₃ emissions are also reported after heavy rainfalls, especially in the case of surface applications [39].

great variability in the simulated results [44], and these techniques used by farmers can significantly affect GHG emissions [45]. Timing of slurry application regarding ideal weather conditions is a key question to minimize nitrogen losses. For example, in EU countries legislation requires the development of future emission limits, especially for NH₃ emissions (Directive (EU) 2016/2284).

There are a number of publications on the effect of slurry application techniques on GHG and NH_3 emissions but there are still uncertainties and unknown processes yet to be understood; thus, further laboratory and field studies are required. The objective of this experiment was to investigate the short-term effect of two different pig slurry applications of surface spreading and soil injection on (i) CO_2 and N_2O emissions; (ii) NH_3 emissions; and (iii) soil chemical properties and nitrogen leaching of a sandy soil. To better understand the effect of the application techniques on soil GHG and NH_3 emissions, we also used three irrigation strategies, one of which was the non-irrigated control during the experiment. We hypothesized that GHG and NH_3 emissions can be minimized based on the pig slurry application technique.

2. Materials and Methods

2.1. Experimental Setup and Pig Slurry Application Techniques

We investigated two application techniques of pig slurry of (i) the surface spread (S) and (ii) row injection (I) for a 14-day-long period after fertilization. Because the highest NH₃ emission occurs in the first week after application of pig slurry, we opted to measure the soil GHG and NH₃ emissions frequently during the first two weeks of the experiment. With this experiment, our aim was to determine the short-term response of bare sandy soil to different fertilization techniques.

For pre-conditioning, packed soil columns were set up four days before the measurements started. We used 18 pieces of plastic columns with a height of 60 cm and a diameter of 20 cm. The bottoms of the columns were closed using airtight cups with a lockable water sampling orifice (d = 22 mm). The cups were filled with small-sized (d = 5–10 mm) gravel (2500 g in each cup) as a filter layer to prevent charge leakage. Under the gravel, dense woven mesh was placed to prevent the gravel from leaving the cup. The columns were filled with less than 2 mm grain-sized and homogenized sandy soil. To simulate original soil conditions, we applied sand with higher carbon and nitrogen content for the upper 25 cm and a leaner sandy soil below 25 cm of the columns. The soil chemical parameters of organic carbon content (SOC) and the main nitrogen forms of total nitrogen (N_{tot}), ammonium (NH₄-N), and nitrate-nitrogen (NO₃-N) of the two sand layers are provided in Table 1.

| Table 1. Initial chemical parameters of the sand | y soils at the upper and | l lower parts of the soil columns |
|--|--------------------------|-----------------------------------|
|--|--------------------------|-----------------------------------|

| Coll Longer | N _{tot} | NH4 ⁺ -N | NO_3^N | SOC |
|------------------------|------------------|------------------------|-----------------------|------|
| Soli Layer | % | ${ m mg}~{ m kg}^{-1}$ | ${ m mg}{ m kg}^{-1}$ | % |
| Upper layer (0–25 cm) | 0.128 | 3.20 | 19.09 | 0.74 |
| Lower layer (25–60 cm) | 0.064 | 2.20 | 7.98 | 0.41 |

 N_{tot} refers to total nitrogen content, SOC is the soil organic carbon content, NH_4 -N is ammonium-, and NO_3 -N is nitrate-nitrogen contents.

Basic soil physical parameters such as soil texture, bulk density, and porosity of undisturbed soils are provided in Table 2. These measurements are based on former investigations of the exact experimental location that the soil in this study was collected from [46].

| Soil Layer — | Clay | Silt | Sand | Bulk Density | Porosity | VWC |
|--------------|------|-------|-------|---------------------|----------------|----------------|
| | % | % | % | g cm ⁻³ | % | % |
| Upper layer | 5.77 | 12.10 | 82.13 | 1.66 ± 0.05 | 37.5 ± 2.0 | 13.5 ± 2.3 |
| Lower layer | 6.73 | 11.57 | 81.70 | 1.67 ± 0.03 | 36.9 ± 1.5 | 13.9 ± 3.5 |

Table 2. Soil physical properties of the different soil layers used in the experiment.

VWC is the initial mean volumetric water content of the soil.

We installed these assembled soil columns under a foil tent with open sidewalls preventing natural precipitation. A meteorological station was available under the foil tent, which provided us with air temperature data.

At the beginning of the experiment, we irrigated each column until gravitational water drainage occurred, then we sealed the sampling orifices. This soil moisture condition was considered to be close to the field capacity (~16.0–18.0%) for the used soil type. The following day we applied the pig slurry using the two application techniques (i.e., spreading (S) and injection (I)) to the columns. The same amount of pig slurry as in the spreading technique was injected at the depth of 10 cm below the soil column surface. Regarding the S treatment, we poured the slurry onto the soil column surface, and waited for the liquid to infiltrate. All column setups were prepared in three replicates. The slurry dose was 150 kgN ha⁻¹ active ingredient uniformly, which was chosen as an average quantity allowed under field conditions on sandy soils. Dry matter, Ntot and total ammoniumnitrogen (N_{TAN}) content, organic matter, raw ash content, and pH of the purchased slurry were 35.4 g kg^{-1} , 3.5 g kg^{-1} , 2.2 g kg^{-1} , 26.2 g kg^{-1} , 9.2 g kg^{-1} , and 6.45, respectively. We took initial measurements of GHG and NH₃ emissions one day before fertilization application (Day 0); right after the fertilization (Day 1); and daily measurements were performed during the first week, then three times during the second week. Daily measurements lasted for 6 h and 10 measurement days were initiated in total for the two-week-long investigation time.

2.2. Irrigation Strategies

To simulate different initial soil moisture conditions, we used three irrigation strategies on S and I slurry application techniques. We regularly irrigated with normal (N) and extreme (E) levels of tap water beside a non-irrigated treatment (D). The D strategy simulated a two-week-long dry period (0 mm water added), the N strategy of 500 mL tap water simulated a wet spring period (15.9 mm during 3 h on a day), which can be regularly the case in springs, and the E strategy of 1000 mL tap water represented heavy rainfall events (31.8 mm during 3 h on a day). We irrigated the columns on Days 2, 3, 5, 8, and 10 during the experiment. Table 3 summarizes the total of six treatments with the two slurry application techniques and three different irrigation strategies.

Table 3. Description of the study treatments (irrigation strategies and slurry application techniques).

| Treatment | Irrigation Strategy | Application Technique |
|-----------|---------------------|---|
| DS | Dry (0 mm) | Spreading (150 kg ha ^{-1}) |
| NS | Normal (15.9 mm) | Spreading (150 kg ha ^{-1}) |
| ES | Extreme (31.8 mm) | Spreading (150 kg ha $^{-1}$) |
| DI | Dry (0 mm) | Injection (150 kg ha ^{-1}) |
| NI | Normal (15.9 mm) | Injection (150 kg ha ^{-1}) |
| EI | Extreme (31.8 mm) | Injection (150 kg ha ^{-1}) |

Abbreviation of the two pig slurry applications (S—surface spreading; I—soil injection) under three irrigation strategies (D—dry condition with no water additions; N—500 mL; E—1000 mL water added at given days).

2.3. CO₂, N₂O, and NH₃ Emission Measurements

We determined the CO₂ emissions of the soil columns using the EGM-5 (PPSYSTEMS, Amesbury, MA, USA) infrared analyzer [47]. The gas incubation time was 2 min per

measurement, where the CO_2 emissions of soil columns were estimated using a linear equation. The measurement range of the device was 0–5000 ppm and the accuracy was <1% of the reference gas. Auto-calibrations to the 0 ppm base concentration were initiated between measurements randomly by the instrument.

We measured the N₂O and NH₃ emissions of each soil column with a PICARRO G2508 (PICARRO, Santa Clara, CA, USA) multigas analyzer [48] based on the dynamic chamber method [49]. The gas incubation time was set at 13 min and emissions were estimated using linear equations. The measurement range of the instrument was 0.300–200 ppm for N₂O and 0–300 ppb for NH₃; measurement accuracy was <25 ppb for N₂O and <5 ppb for NH₃ measurements.

We measured soil GHG and NH₃ emissions 10 times in every column during the duration of the experiment.

2.4. Soil Chemical Property Measurements

Besides the determination of initial soil chemical properties of the arable field (representing 0–25 and 25–55 cm depths), we collected individual samples from each column at the end of the experiment. We chose sampling depths of 0–5, 15–20, 35–40, and 50–55 cm to investigate the soil carbon and nitrogen profile along soil depths. SOC, N_{tot}, NH₄-N, and NO₂⁺/NO₃-N contents of soil samples were analyzed using wet chemical methods. Before analysis, samples were sieved below 2 mm. The amount of N_{tot} was determined using the modified Kjeldahl method (ISO 11261:1995) and the SOC was measured using wet digestion using the Tyurin method [50,51]. Briefly, during the measurement process, the total nitrogen content (N_{tot}) of the samples is converted first into (NH₄)₂SO₄ and then into NH₃. After steam distillation, the soil N_{tot}-content was determined using titration using compound-specific chemicals. The Tyurin method is a wet combustion method. The SOC was oxidized using potassium dichromate solution with sulphuric acid. After oxidation, excess dichromate was calculated using titration with Mohr's salt solution.

2.5. Nitrogen Leaching Measurements

We collected leachates via water sampling orifices on Days 3, 5, 7, and 9 concurrently with irrigation events to investigate nitrogen leaching of the irrigated treatments. All water samples were immediately frozen, then analyzed for NH_4^+ , NO_2^- , and NO_3^- content using a UV-1800 UV/Visible scanning spectrophotometer (Shimadzu, Japan) based on standardized methods (ISO 7150-1, ISO 13395:1996). We used standard solutions for calibrations of each determinant. In the case of NH_4^+ , NO_3^- , and NO_2^- measurements, the spectrophotometer was set to 655, 410, and 540 nm, respectively.

2.6. Statistical Analysis

We used GraphPad Prism for Windows, version 9.0.2 (161) February 2021, (GraphPad Software, San Diego, CA, USA) to perform the statistical analyses. We used raw data to build GHG and NH₃ emission datasets and the negative emission values were filtered. We determined dataset distributions using the D'Agostino and Pearsons test. According to the dataset distributions we utilized the Kruskall–Wallis method with Dunn's multiple comparisons to compare gas emission or leachate data. Analysis of GHG and NH₃ emission dependency on air temperature were investigated using Pearson's or Spearman's correlation depending on the normality of the data distribution.

3. Results

3.1. GHG and NH₃ Emissions of Soils

 CO_2 emissions of soils increased right after fertilization on Day 1 and peaked on Day 3 in the case of DS and DI. There was a second CO_2 emission peak for these treatments on Day 14. CO_2 emission of soils showed a permanent decrease after Day 1 for all irrigated treatments (Figure 1a).

 CO_2 Emission (mg m⁻² s⁻¹)

 $N_2O~Emission~(\mu g~m^{-2}~s^{-1})$



NH₃ Emission ($\mu g m^{-2} s^{-1}$) 0.40 0.20 0.00 0 7 2 3 5 8 9 12 14 15 0 1 4 6 10 11 13 Experimental Time (days) (c)

Figure 1. (a) Daily mean CO_2 , (b) N_2O (b,c), and NH_3 emissions of soils under spreading (S) and injection (I) slurry application techniques, under dry (D), normal (N), and extreme (E) irrigation strategies. Ta represents daily average air temperature, while arrows indicate irrigation events.

The N₂O emissions of soils also increased after fertilization (Day 1) and peaked on Day 2 in the cases of NS, ES, and DI. A second N₂O peak occurred in NS, DS, NI, and DI on Day 14 (Figure 1b).

The NH₃ emissions of soils increased right after fertilization until Day 3 for NI, DS, DI, and till Day 4 in the case of NS. A permanent decrease in soil NH3 emissions occurred in ES and EI after Day 1 (Figure 1c).

The type of pig slurry application technique did not affect soil CO₂ emissions under N, E, and D (p > 0.05) irrigation strategies. Although there were differences between non-irrigated and irrigated soils in the case of the I treatments, tendencies were not clear. The CO₂ emissions of soils were significantly higher in DI compared to NI (p < 0.01) and EI (p < 0.001), but NI and EI did not differ (p > 0.05). The irrigation showed no effect on the CO₂ emissions of any S treatments (p > 0.05) (Table 4).

Treatment $CO_2 (mg m^{-2} s^{-1})$ $N_2O (\mu g m^{-2} s^{-1})$ $NH_3 (\mu g m^{-2} s^{-1})$ 0.042 ± 0.072 $^{\rm a}$ DS 0.254 ± 0.233 ab $0.361 \pm 0.349 \ ^{\rm a}$ NS 0.109 ± 0.096 bc 0.017 ± 0.024 ^{ab} 0.042 ± 0.043 ^b ES 0.113 ± 0.095 abc 0.008 ± 0.008 ^b 0.031 ± 0.046 ^b $0.055 \pm 0.105 \text{ ab}$ DI 0.294 ± 0.235 ^a 0.008 ± 0.008 ^b NI 0.111 ± 0.138 bc 0.009 ± 0.011 b 0.012 ± 0.014 ^b EI $0.087\pm0.130\ ^{c}$ $0.009 \pm 0.016^{\text{ b}}$ $0.010 \pm 0.012^{\text{ b}}$

Table 4. Mean greenhouse gas emissions of CO₂ and N₂O, and NH₃ emissions.

S: spreading application technique I: injection application technique; D: no irrigation (0 mm tap water); N: regular irrigation with 15.9 mm tap water; E: regular irrigation with 31.8 mm tap water; ^a, ^b, ^c letters indicate significant differences between treatments (rows) (p < 0.05) for each gas emission type. $n = 25 \pm SD$.

There were no significant differences in soil N₂O emissions of the two application techniques under N (p > 0.05), E (p > 0.05), and D (p > 0.05) irrigation strategies, although the emissions were almost two times higher in NS than in NI. In the case of S treatments, soils of DS had significantly higher N₂O emissions (p < 0.05) than ES. According to statistical analysis, I treatment irrigations did not affect the N₂O emissions of soils (p > 0.05), although the mean emissions were considerably higher for DI than for the other treatments (Table 4).

The pig slurry application technique affected the NH₃ emissions of soils in the case of the D irrigation strategy only. Soils of DS had significantly higher NH₃ emissions than DI (p < 0.001), however, there were no differences between the two techniques under N (p > 0.05) and E (p > 0.05) irrigations. The irrigation had no effect on NH₃ emissions of soils in the case of the I application (p > 0.05), but it promoted changes in soils with the S technique. Soils of DS had significantly higher NH₃ emissions than NS (p < 0.01) or ES (p < 0.001); still, there was no difference between NS and ES (p > 0.05) (Table 4).

3.2. Environmental Drivers of Soil GHG and NH₃ Emissions

According to the literature, T_a correlated well with T_s [52] and both of these parameters are drivers of GHG and NH₃ emissions. We consider T_a as a representation of a basic environmental driver of soil-derived emissions. All measured gases depended on this factor in some treatments. There were significant correlations between CO₂ emissions of soils and T_a in DS (p < 0.01) and DI (p < 0.001) treatments, while no significant correlations were observed in the other cases. Soil N₂O emissions significantly depended on T_a in NS (p = 0.01) and ES (p = 0.001) treatments only. The NH₃ emission dependency of soils on T_a showed similarities with CO₂ findings, as emissions in NS, DS, and DI were significantly driven by T_a (p < 0.05, p < 0.05, and p < 0.05, respectively) (Table 5).

| Correlation of Soil Emissions with T _a | | | |
|---|-----------------|------------------|-----------------|
| Treatment | CO ₂ | N ₂ O | NH ₃ |
| DS | 0.63 * | 0.22 | 0.80 * |
| NS | 0.20 | 0.56 ** | 0.50 * |
| ES | 0.11 | 0.94 *** | 0.06 |
| DI | 0.81 *** | 0.41 | 0.60 * |
| NI | 0.03 | 0.47 | 0.42 |
| EI | 0.05 | 0.67 | 0.42 |

Table 5. Correlations (r) of CO_2 , N_2O , and NH_3 emissions with daily average air temperature (T_a).

* is the level of significance at p < 0.05, ** at p < 0.01, and *** at p < 0.001; S: spreading application technique; I: injection application technique; D: without irrigation; N irrigation: 15.9 mm tap water; and E irrigation: 31.8 mm tap water per irrigation event.

3.3. Soil Chemical Properties

The soil chemical properties of the soil columns under different treatments were similar at the end of the experiment. There were no significant differences between the treatments' SOC (p > 0.05), N_{tot} (p > 0.05), NH₄-N (p > 0.05), and NO₃-N contents (p > 0.05).

Regarding the soil chemical properties of the four different depths of each experimental column, vertical heterogeneity was observed. Mean SOC and N_{tot} contents showed similarities with the initial conditions (Table 1) for all six treatments. SOC contents of soils were higher in the upper two layers (0–5 and 15–20 cm) than in the lower ones (35–40 and 50–55 cm), and the values collected at the end of the experiment were comparable with the initial conditions. The highest N_{tot} contents were found in the surface layer (0–5 cm) and decreased with depth. The different slurry application techniques did not change the values of SOC or nitrogen contents. The NH₄-N content was the highest in the second (15–20 cm) layer of the soil columns, and the NO₃-N was the highest in the surface (0–5 cm) layer with elevated values compared to the initial conditions (Figure 2).

3.4. Nitrogen Leaching from Soils

Soil water leachate was collected and analyzed after each irrigation event. The pig slurry application technique influenced the NH₄⁺ content of the leachate under the N irrigation strategy only. NH₄⁺ concentrations of water samples were significantly higher in NS than NI (p < 0.05), however, the difference was not significant between ES and EI (p > 0.05). The irrigation strategy also affected the NO₃⁻ leaching in the case of the S technique, as leachate from NS had a significantly higher (p < 0.01) NO₃⁻ content than ES. There were no significant differences between the NO₃⁻ content of NI and EI, although NI had a somewhat higher NO₃⁻ content. The pig slurry application technique did not affect the mean NO₃⁻ content of the water samples under N (p > 0.05) or E (p > 0.05) irrigation strategies (Table 6).

Table 6. Mean leachate chemistry (ammonium, nitrite, and nitrate) during the experiment.

| Mean Leachate Chemistry | | | | | |
|-------------------------|---|----------------------------------|------------------------------------|--|--|
| Treatment | $\mathrm{NH_4^+}$ (mg $\mathrm{L^{-1}}$) | NO_2^{-} (mg L ⁻¹) | NO_{3}^{-} (mg L ⁻¹) | | |
| NS | 0.29 ± 0.09 a | $0.73\pm1.65~^{\mathrm{ab}}$ | 347.45 ± 263.98 a | | |
| ES | 0.16 ± 0.11 ^b | 0.36 ± 0.32 a | $142.43 \pm 102.41 \ ^{\rm b}$ | | |
| NI | 0.15 ± 0.04 ^b | 0.13 ± 0.18 ^b | $279.38 \pm 100.53 \ ^{\rm a}$ | | |
| EI | 0.17 ± 0.08 ^b | $3.40\pm5.58~^{\mathrm{a}}$ | $148.51 \pm 150.43 \ ^{ m ab}$ | | |

S: spreading application technique; I: injection application technique; normal (N) irrigation: 15.9 mm tap water; extreme (E) irrigation: 31.8 mm tap water; ^a, ^b letters indicate significant differences between treatments (rows) (p < 0.05) for each water chemical parameter. $n = 14 \pm SD$.

The pig slurry application technique did not affect the mean NO_2^- concentration of leachate under N (p > 0.05) or E (p > 0.05) irrigation strategies. A significant difference



between NO₂⁻ contents of leachate samples was observed only in the case of NI and EI (p < 0.001; Table 6).

Figure 2. Soil chemical properties of the treatments: (**a**,**b**) total nitrogen (N_{tot}), (**c**,**d**) soil organic carbon (SOC), (**e**,**f**) NH_4^+ , and (**g**,**h**) NO_3^- content collected at four different depths in each treatment. S: spreading application technique; I: injection application technique; N irrigation: 15.9 mm tap water; E irrigation: 31.8 mm tap water per irrigation event; D: without irrigation.

4. Discussion

4.1. GHG and NH₃ Soil Emission Trends

After the pig slurry application, elevated CO_2 , N_2O , and NH_3 emissions were observed, especially during the first few days of the experiment. Rochette et al. [25] found that 50% of the total investigated CO_2 emission occurred in the first two weeks and 70% in the first 40 days after the manure application, which was longer lasting than in the case of the NH₃ emissions. Clemens et al. [53] also found peaks of soil N_2O emissions right after the slurry application, although it had a more permanent effect on the emissions, as they did not decrease even after 20 days. In our study, there was a second peak after a permanent decrease in CO_2 and N_2O emissions coinciding with other studies [54], that can be a sign of unfinished microbial processes/dynamics of denitrification [55]. The increase in air temperature may be causing elevated emissions, as temperature is one of the main drivers of CO_2 but also can be a determinant of N_2O emissions [43,56,57]. Higher storage temperatures can promote NH_3 and N_2O emissions. The differences in the underlying microbial processes of the emissions (such as nitrifier denitrification or incomplete denitrification) depending on the actual temperature can be investigated further [58]. Soil NH_3 emissions are particularly affected by T_s, while N₂O is more dependent on SWC, T_s, and NH₄-N content [59]. Thus, applying pig slurry under colder weather conditions, and the immediate incorporation into the soil, can further reduce NH₃ emissions [60,61].

Similar to our results, other researchers found that after slurry spreading soil NH_3 emissions peaked after the application, in some cases during the first 24 h, then the emissions decreased permanently [62,63].

4.2. Pig Slurry Application Techniques

During our experiment, the application techniques did not affect significantly soil CO_2 and N_2O emissions in the short-term. Observations on this topic in the current literature are not straightforward as few studies report a reducing effect of injection on soil GHG emissions [64,65], while several others found contrary results [66–70], and some concluded no difference [53,64] between spreading or injecting pig slurry to the soils. The spreading application technique may enhance N_2O emissions due to elevated evaporation, while injection techniques promote an anoxic soil environment, which is a key factor of denitrification processes that are responsible for soil N_2O emissions. Injection may reduce NH_3 emissions and promote N_2O emissions compared to the soil surface spreading, due to promoting less aerobic conditions and denitrification [54]. In treatments with no irrigation performed (D), we found a similar pattern, as DI reduced NH_3 and increased N_2O emissions.

The reduction in NH_3 emissions due to injecting pig slurry into the soil can be also dependent on slurry dry matter and NH_4 -N content [71]. The incorporation of pig slurry into the soil after the surface technique might have an additional inhibitory effect on NH_3 production [72].

4.3. Effect of Irrigation on Soil GHG and NH₃ Emissions

It is generally accepted that GHG emissions of soils depend on environmental drivers such as SWC, T_s, and T_a [73–75]. In the case of CO₂, there is an optimum SWC when elevated emissions can occur [76], and high SWC conditions promote N₂O emissions [77]. During our experiment, there was a tendency that non-irrigated treatments with lower SWC had the highest GHG emissions compared to irrigated ones. Other researchers concluded contrary results, that intensive rainfalls caused elevated CO₂ and N₂O peaks [78–80], however, too high SWC could also inhibit CO₂ emissions [80]. In our study, non-irrigated treatments might have been close to the optimum SWC condition promoting CO₂ emissions. The lower N₂O emissions of irrigated treatments compared to non-irrigated ones can be the result of nutrient leaching of topsoil or the effect of the drying and rewetting cycle. The soil environment of irrigated treatments could have promoted N₂ emission rather than N₂O [81]. Other studies also concluded that irrigation and elevated SWC enhance N₂O emissions in general, although a too high frequency of irrigation can prevent higher N_2O emissions, due to processes causing reduction of N_2O to N_2 and the disturbing effect of drying–rewetting cycles compared to lower frequency irrigations [82,83]. In our experiment, these irrigation effects could be detected only between irrigated and D strategies but there was no difference between E and N strategies as the frequency of irrigation was the same in these treatments, and only the amount of water added was different. The similarity in GHG emissions of E and N irrigation strategies can be explained by the type of the applied soil. Sandy soils are quite permeable and they cannot hold water well, thus, they are less likely to have high SWC permanently promoting N_2O emissions, especially close to the soil surface.

In our study, the S technique initiated elevated NH₃ emissions compared to I, similar to several other results [67,68,72]. Dry treatment of the spreading (DS) application technique caused elevated NH₃ emissions in the present study, while normal and extreme strategies resulted in lower soil emissions, especially in the case of I application. Sanz-Cobena et al. [39] found that heavy rainfalls may strongly influence the abating effect of the injecting technique on NH₃ emissions, compared to spreading, due to nitrogen leaching. However, irrigation strategies eliminated the effect of different application techniques on the measured emissions, which highlights that the actual weather condition is an essential factor for the emissions when the slurry application is being performed.

The rainfall pattern (or irrigation frequency) might influence soil emissions, such as interference with soil environmental characteristics (soil evaporation, temperature, or microbiology). This might be an explanation for the outstanding NH₃ emissions in nonirrigated (e.g., DS) compared to the irrigated treatments. Some studies reported similar conclusions [39], although Sänger et al. [84] found that the rainfall pattern does not influence GHG emissions on average. According to Gu et al. [85], soil type is also an influencing factor besides rainfall pattern. In the case of clay loam soil, the high precipitation scenario resulted in elevated NH₃ and N₂O emissions compared to lower precipitation amounts. In turn, reduced emissions were occurring under high precipitation on sandy soil [85], which is consistent with the findings of our experiment.

4.4. Soil Chemical Property Changes at Different Depths

Vertical heterogeneity in the soil chemical properties of the columns was examined. However, we found that the initial soil chemical parameters of the two soil layers was one of the major determinants of the soil chemical distribution pattern rather than the slurry application technique. The similarity of initial and final soil chemical properties could be caused by great NH₃ and N₂O emissions in D treatments and nitrogen leaching in irrigated treatments. The NO₃-N content of the soil columns was the highest at the surface, which may promote denitrification processes in the upper layers [86], due to available nutrient sources, explaining N₂O emissions in the non-irrigated (D) treatments [70]. The slightly higher NO₃-N content of DI could cause higher N₂O emissions compared to other treatments, but elevated emissions for DS were not the result of soil chemical properties. The elevated NH₃ emissions of DS compared to DI or other treatments could not be explained by soil chemical parameters. We consider that in this case the evaporation of the nutrient-rich surface was the main cause.

The leachate chemistry was also influenced by the simulated precipitation conditions. the NH_4^+ content of leachates was influenced by the slurry application technique in some cases, while the NO_3^- content of leachates was influenced by irrigation strategies. Daudén et al. [87] found that an increase in irrigation reduced the NO_3^- content of the leachate, which is similar to our findings. However, other researchers noted that higher water applications can result in elevated NO_3^- leaching [88,89]. Surprisingly, the $NO_3^$ content of the leachate was higher in the N than in the E irrigation treatment, although it must be noted that the variability of data within a given treatment was high.

4.5. Proposed Techniques to Mitigate NH₃ and GHG Emissions

Based on the current literature, there are conflicting results on emission mitigation methods depending on applied techniques, weather, soil conditions, etc. Dry matter content of the applied slurry, the application techniques, and weather conditions are the main factors of NH₃ losses from soils [90]. Anaerobic digestion of organic fertilizers may result in a decrease in GHG emissions, but an increase in NH₃ emissions. The separation of the solid–liquid phase can reduce the NH₃ promoting effect, concurrent with the reduction in GHG emissions [90,91]. The acidification and composting of pig manure prior to application might also reduce NH₃ and GHG emissions [92]. According to a recent meta-analysis, acidification alone can reduce both NH₃ and GHG emissions, while other techniques (different applications, separation, storage type, etc.) can negatively affect some of the GHGs [70].

5. Conclusions

The effects of pig slurry application on soil GHG and NH₃ emissions was established under different slurry application techniques and irrigation strategies in sandy soils. The pig slurry injection was proven to be more adequate compared to spreading in regard to NH₃ emissions from the investigated sandy soil under dryer soil conditions. However, under the irrigated conditions the differences were no longer significant. The pig slurry application techniques did not affect the GHG emissions of the experimental sandy soil in the short-term during our experiment.

The slurry application caused elevated NH_4 -N and NO_3 -N contents in the soils, and an increase in NO_3^- leaching was observed under lower than extreme irrigation conditions. Nitrogen leaching of soils was more dependent on precipitation amounts in the spreading application technique compared to the injection.

In our soil column experiment, we tried to simulate field conditions and we found that the pig slurry injection may be preferable under dry conditions regarding NH_3 emissions. However, we also found that under irrigation or higher precipitation occasions the time of slurry application should not be limited in terms of CO_2 and N_2O emissions.

This study was a microcosm type of investigation simulating field conditions with three replicates under a controlled environment. Therefore, this setup is a good way to better understand the field processes; however, field conditions can be more heterogenic and further studies with higher number of replications should be implemented to draw more conclusive deductions. Overall, our study showed that a controlled column experiment can be a great tool to be used prior to slurry applications. Although the current study involved sandy soil only, this type of experiment enables us to further study different soil environmental parameters, such as different soil types more relevant to a specific location.

Author Contributions: Conceptualization, E.T., Z.B. and Á.H.; methodology, E.T., Z.B. and M.D.; formal analysis, M.D.; investigation, E.T., Z.B. and M.D.; writing—original draft preparation, E.T. and M.D.; writing—review and editing, B.P., Z.B. and Á.H.; visualization, M.D.; supervision, Z.B.; project administration, E.T.; funding acquisition, E.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Agriculture, Kossuth Lajos sq. 11, 1055 Budapest, Hungary. Tasks related to the definition of agri-environmental indicators for the pig sector MgF/27-1/201. The research presented in the article was carried out within the framework of the Széchenyi Plan Plus program with the support of the RRF 2.3.1 21 2022 00008 project. This material is based upon work supported by the Hungarian National Research Fund (OTKA/NKFI) project OTKA FK-131792. The APC was funded by Á.H. and Z.B.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We would like to thank Szandra Baklanov and Emese Ujj for their support with experiment implementation and measurements. We would like to thank András Makó and Gyöngyi Barna for providing background soil physical properties of the experimental site.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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