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Dairy Slurry Application to Stubble-Covered Soil: A Study on Sustainable Alternatives to Minimize Gaseous Emissions

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Abstract: The development of sustainable application practices, which do not demand incorporation into the soil, is necessary to encourage slurry use in conservation agriculture (CA). Incorporation is the most common practice to reduce nitrogen losses from the applied slurry. However, in CA, soil disturbance must be avoided. Two experiments were conducted to evaluate strategies to reduce gaseous emissions from dairy slurry applied to stubble-covered soil without incorporation. We evaluated (1) effects on ammonia (NH_3) emissions of pretreatment by acidification (ADS), irrigation (IR) and placement under the stubble (US); and (2) effects of ADS, IR, US and delayed fertilization (RDS T16) on greenhouse gases (GHG). The results of the evaluated strategies were compared to raw slurry (RDS) and ammonium sulphate (MS). Additionally, in experiment 2, the results were compared to ammonium sulphate (MB) and slurry injection (IN), both in bare soil. ADS, US and IR decreased NH_3 emissions by 66%, 60% and 32.5%, respectively, with total N emissions NH_3 emissions accounting for more than 79% of N losses in slurry-based treatments. Late application reduced N_2O emissions by 48%. GHG emissions from ADS, US and IR were similar to those from MS, MB and IN. ADS, US and IR are the most suitable strategies for slurry application in CA.

Keywords: GHG; GWP; N_2O; NH_3; CO_2; nitrogen; no tillage; conservation agriculture; crop residues; manure

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1. Introduction

The most common practice worldwide to reduce gaseous nitrogen (N) and carbon (C) emissions from applied manure/slurry is its incorporation into the soil immediately after application [1,2]. However, in conservation agriculture (CA), for which soil cover is required (e.g., no tillage, orchard row-middle sod maintenance), soil disturbance must be avoided, making incorporation an unsuitable technique for this kind of farming system [3]. On the other hand, conservation farmers may be encouraged to fertilize their land with animal slurry, reducing dependence on synthetic fertilizers, through the development of solutions that do not require soil disturbance, as long as they are capable of mitigating N gas emissions.

Insofar as agricultural intensification is needed to meet the increasing demand for food, the search for agricultural systems that are proven to reduce environmental impact but also increasing the resilience of crops to new climate patterns makes the eyes of stakeholders turn to more sustainable practices, such as slurry fertilization and CA [4–6]. Perceptible changes in climate patterns include recurrent events of intense rainfall [7], as well as long periods of drought during the rainy season in Mediterranean countries [8,9]. Soil erosion, as a consequence of heavy rains and lack of soil conservation practices, leads to soil degradation, one of the major soil threats in the Mediterranean region [10]. More frequent and intense droughts, besides their socioeconomic impact, influence plant growth, reducing carbon assimilation and affecting the greenhouse gas balance in agriculture [9].

Dairy slurry (liquid manure) production is increasing as a consequence of the geographical concentration and specialization of dairy farms, and it is widely used as organic fertilizer, providing organic C, N, phosphorus (P), potassium (K) and other nutrients to plants, and can therefore replace mineral/synthetic fertilizers [11–13]. Furthermore, manure is a local source of nutrients that does not need to be transferred on trains, ships and trucks over long distances [14].

When not properly managed, animal slurry can become an important source of NH_3 and greenhouse gases (GHG), mainly N_2O, a long-lived gas with a strong environmental impact contributing to stratospheric ozone depletion and climate change [11,15]. Emissions of reactive N into the atmosphere threaten human health and decrease fertilizer value by reducing the N available for crop nutrition [12,15,16]. Thus, acting on N fertilizer (e.g., source, application method, time and treatment) is the most practical way to reduce N gas emissions [12,17].

Conservation tillage can increase carbon retention in the soil while decreasing superficial runoff and erosion, improving the biological, chemical and physical parameters of the soil [3,13,18,19]. Otherwise, conventional tillage systems lead to significant disturbance of soil biota through soil disarrangement caused by ploughing, removal of litter layers from the land surface with consequent loss of soil organic matter and increased flux of carbon dioxide (CO_2) from soils [20], and changes in soil temperature and humidity [21]. As the maintenance of ground cover contributes to keeping the soil moist for longer, as well as protecting the soil surface against solar radiation and temperature fluctuation, CA practices can help crops thrive in challenging weather conditions during the growing season [22].

EU Member States are advised to adopt good agricultural practices to control the emission of NH_3 resulting from the application of livestock manure to soil [23]. Slurry injection is a recommended technique in most European countries. However, its adoption requires a significant investment, which, in addition to restrictions on use in small, stony or sloping areas, can impair the broad use of this technique [12]. Nevertheless, other ammonia mitigation methods appear to have the potential to be used in a wide range of croplands under CA. Irrigation, when available, allows for slurry incorporation through rapid infiltration by water downwards into the soil when watering occurs immediately after slurry application [24]. Acidification is a technique, already used at field-scale [25], that can efficiently decrease NH_3 volatilization from animal slurry applied to soil [12,26–28], although the slurry is applied on stubble-covered soil [29]. In-season slurry application (i.e., side-dressing application) may also contribute to decreasing N losses, as plants already emerged from the soil can uptake part of the available N [30]. In conservation cropping systems, when a slurry with low dry matter content is applied to crop residues, a reduction in ammonia emission may occur, as the stubble works as a barrier, protecting the slurry from wind and solar radiation [31]. Therefore, slurry placement under the stubble layer might lead to a reduction in ammonia emission rates. However, techniques that efficiently decrease ammonia emissions may, on the other hand, increase nitrous oxide (N_2O) emissions and therefore global warming potential (GWP) [32,33]. Consequently, it is important to evaluate the efficiency of a fertilization practice with respect to the occurrence of pollution swapping [11,34].

In the present work, two concomitant experiments were conducted to evaluate management strategies of dairy slurry application to stubble-covered soil with the potential to mitigate gas emissions even when the slurry is not injected or incorporated into the soil. In a first experiment (E-AM), we assessed the effects of dairy slurry acidification (ADS), irrigation (IR) and placement under the stubble (US) on ammonia emissions in the absence of plants. In a second experiment, we evaluated the effects on greenhouse gas emissions (E-GHG) of the same strategies assessed in E-AM but applied to pots grown with ryegrass, plus the in-season raw dairy slurry application (RDS T16), and we compared these effects to those of widely used and recommended practices: mineral nitrogen fertilizer application to stubble (MS) and bare soil (MB), as well as dairy slurry injection in bare soil (IN).

The main goal of this study was to determine the efficiency of the evaluated techniques to be used in CA through their effects on NH_3 and GHG emissions and GWP. We hypothesized that the strategies used in this study allow for non-incorporation of slurry into the soil due to their ability to (i) reduce NH_3 and total N gas emissions and (ii) reduce the effects caused by mineral fertilizer and slurry injection on GHG emissions and GWP.

2. Materials and Methods

2.1. Soil, Slurry and Wheat Stubble

Vertic cambisol (28.6% clay, 2% organic carbon) from an agricultural area usually cultivated with wheat at Instituto Superior de Agronomia, Lisbon, Portugal (co-ordinates: 38°42′29.786″ N; 9°11′6.18″ W) was collected to perform two concomitant experiments. For the ammonia experiment (E-AM), the soil was gathered from the 0–5 cm layer, and for the GHG experiment (E-GHG), a 5 cm top-layer soil monolith and a disrupted soil from a 5–20 cm layer were collected in the field.

The physicochemical characteristics of the soil, dairy slurry and stubble; ambient daily temperatures; and ryegrass cultivation and yield are described in detail in [35].

The dairy slurry (pH = 7.5, dry matter = 11.3%, total N = 3.2 g kg^{-1}, NH_4^+–N = 1.2 g kg^{-1}) used in both experiments was collected from a storage tank of a commercial dairy farm located in the Setubal region, Portugal.

2.2. Experimental Design

Two-pot experiments were performed simultaneously in an agricultural greenhouse to assess how ammonia emissions (E-AM) and GHG emissions (E-GHG) are impacted by strategies of dairy slurry application on stubble-covered soil relative to standard practices.

2.2.1. NH_3 Experiment (E-AM)

The treatments (three replicates) considered were: control, unfertilized soil (CS), raw dairy slurry placed on the stubble (RDS), acidified slurry placed on the stubble (ADS), irrigation immediately after dairy slurry application (IR), dairy slurry applied under the stubble (US) and mineral nitrogen (ammonium sulphate) placed on the stubble (MS). The experiment was conducted according to a completely randomized design for seven days to assess the NH_3 emissions from each treatment in uncultivated soil. Metallic trays (Ø = 300 mm, h = 70 mm) were filled with 2.6 kg of dry soil covered by wheat stubble (300 g m^{-2}).

All pots, except CS, received the equivalent to 0.5 g of total nitrogen by slurry or ammonium sulphate application. The ammonium sulphate contained 20.5% total nitrogen. For IR treatment, the irrigation rate was equivalent to 10 mm. In the US, the slurry was placed on the soil and then covered with stubble. For the ADS treatment, the dairy slurry was acidified to pH 5.5 using concentrated sulfuric acid (about 6 mL kg^{-1} of raw slurry), as described in [36]. Slurry acidification was performed one day before application. Soil moisture was adjusted to be close to 70% of soil water-holding capacity (WHC) in all pots.

Ammonia fluxes were measured by a dynamic chamber technique based on the model depicted in [37], following the methodology described in [12]. To this end, a polyvinyl chloride chamber (Ø = 210 mm, h = 200 mm, area = 0.035 m^2) was used to cover the ground surface. A constant airflow (3 L min^{-1}) produced by a suction pump was maintained inside the chamber carrying the air toward an acid trap (200 mL of H_3PO_4 0.05 M) to capture the emitted NH_3. The acid traps were replaced after 4, 8 and 12 h for the first 24 h; twice a day on the 2nd and 3rd days; and then, every 24 h until day 7. The total ammonium nitrogen (TAN) content in each acid trap at the end of each sampling period was analyzed by automated segmented-flow spectrophotometry [38]. Ammonia emission rates (E, mg N m^{-2} h^{-1}) for each sampling period were calculated according to Equation (1).

$$E = \frac{TAN \times V}{S \times t} \quad (1)$$

where TAN in the acid solution is expressed in mg L^{-1}, V is the volume of acid solution (in L), S is the surface area (in m^2) and t is the sampling period (in h).

Total NH_3–N emissions were calculated as the sum of the amount of NH_3–N emitted during each time interval and expressed as mg N pot^{-1}, % of TAN and % of the total-nitrogen applied.

2.2.2. GHG Experiment (E-GHG)

This longer experiment lasted for 108 days and was carried out to measure GHG emitted from the treatments during ryegrass growth. This study enabled the assessment of the application of dairy slurry after plant emergence and also compared the results of the tested management strategies with RDS and the widely used and recommended practices, such as the application of mineral fertilizer to stubble-covered or bare soil and slurry injection in bare soil.

A completely randomized design with three replications was used. Polyvinyl chloride pots were filled with a total of 7 kg of dry soil; a first disrupted soil layer was placed in the bottom of the pots and covered with a 5 cm undisturbed monolith.

Six treatments were implemented with soil covered by wheat stubble to simulate no-tillage conditions: control, unfertilized soil (CS), raw dairy slurry on the stubble (RDS), acidified dairy slurry on the stubble (ADS), irrigation immediately after dairy slurry application (IR), mineral nitrogen on the stubble (MS), dairy slurry applied under the stubble (US), all applied on the sowing day, and dairy slurry applied 16 days after sowing (RDS T16). Furthermore, to allow for comparisons between the results obtained under no-tillage conditions and the standard practices in conventional tillage systems, three treatments were installed in bare soil on the sowing day: dairy slurry injection (IN), surface application of mineral fertilizer (MB) and an unfertilized control (CB).

Annual ryegrass (*Lolium multiflorum*) was sown on the first day in all pots. A total of 16 seeds were sown in two parallel rows to provide 10 plants in each pot (surface area = 0.049 m^2). In RDS T16, the slurry was applied only at the ryegrass tillering stage, nine days after plant emergence (sixteen days after sowing). For IN, the slurry was injected at 5 cm depth in two grooves parallel to seed lines. RDS, ADS, IR, MS and US were implemented as in E-AM. The soil moisture in the pots during the whole experiment was maintained close to 70% WHC by the periodic addition of deionized water. No leachate was produced, and consequently, no nutrients were lost via leaching. P and K were added to equalize their content in all treatments that received slurry or ammonium sulphate. More details can be found in [35].

The total nitrogen supply was 1.5 g per pot, that is, 0.5 g (155 g dairy slurry or 2.4 g ammonium sulphate, depending on the treatment) immediately after sowing (16 days later for RDS T16) and 0.5 g (2.4 g ammonium sulphate) after each of the following two harvests performed 66 and 94 days after ryegrass sowing, respectively. Therefore, after the first harvest, topdressing was performed only with ammonium sulphate for all treatments, except CS and CB (controls).

Nitrous oxide, carbon dioxide and methane fluxes from each pot were measured following the method described by [12]. Briefly, a PVC chamber (Ø = 220 mm, h = 200 mm) fitted with a Teflon tube (Ø = 4 mm; length = 300 mm) was used to allow for air sampling from each pot. After closure of the chamber, a gas sample of 20 mL was immediately collected (T0) from the headspace air (5.8 dm^3) using a 60 mL syringe. A similar sampling of each pot was then performed at 30 (T1) and 60 (T2) minutes of closure. The concentration of N_2O, CH_4 and CO_2 in air samples was then measured by gas chromatography. The temperature was recorded at each sampling point. Gas measurements were carried out on days 2, 6, 9, 15, 17, 21, 24, 29, 34, 44, 52, 58, 63, 73, 77, 85, 99 and 108 after the start of the experiment.

Gas fluxes were calculated by fitting linear regressions through the data collected at T0, T1 and T2 of closure. The N_2O, CH_4 and CO_2 emission fluxes (F, $m^3\ m^{-3}\ min^{-1}$) were calculated as described in [39]. The GHG emission rates (ER, g C or N $m^{-2}\ d^{-1}$) for each sampling period were calculated using Equation (2).

$$ER = \frac{F \times M}{V \times \left(\frac{273+T}{273}\right)} \times h \times k \quad (2)$$

where F ($m^3\ m^{-3}\ min^{-1}$) is the gas emission flux obtained by fitting linear regression, M is the gas molecular weight (44 g mol^{-1} for CO_2 or N_2O and 16 g mol^{-1} for CH_4), V is the volume of an ideal gas (0.0224 $m^3\ mol^{-1}$), T is the temperature during the sampling period (in °C), h is the height of the chamber (in m) and k is the time corrected for a 1–day duration (1440 min).

Cumulative emissions were estimated by averaging the ER between two samplings and multiplying by the time interval [39].

The global warming potential of the treatments considered here was compared based on the total amount of greenhouse gas (GHG) emitted during the experiment. Therefore, accumulated GHG emissions were expressed as CO_2 equivalent using the conversion factors of 265 and 28 for N_2O and CH_4, respectively, based on a 100-year time frame [40] and using Equation (3) [41]:

$$GWP = Cum\ CO_2 + (Cum\ N_2O \times 265) + (Cum\ CH_4 \times 28) \quad (3)$$

where Cum X refers to cumulative emission of gas X (g pot^{-1}).

The yield-scaled GWP (ys-GWP) represents the GWP emitted by each unit of ryegrass harvested calculated with Equation (4):

$$ys - GWP = \frac{GWP}{yield} \quad (4)$$

where yield is the sum of the ryegrass yields (dry matter) after three harvests, as reported in [35], expressed in g CO_2-eq g^{-1}.

2.3. Statistical Analysis

All results were analyzed using Statistix 9 software (Analytical Software, Tallahassee, FL, USA). For both experiments, the effects of the different treatments on gaseous emissions were tested by analysis of variance (one-way ANOVA). When significant, differences between treatments were identified at a 0.05 probability level of significance using a Tukey test. To ensure the normality and homogeneity of the variances, log transformations were performed when necessary.

3. Results

3.1. Ammonia Emissions

The highest cumulative ammonia emissions were observed in the RDS treatment. All the strategies studied as NH_3 mitigating solutions (ADS, US and IR), led to a significant reduction in NH_3 emissions. Cumulative NH_3 emissions from ADS, US and IR treatments were 66%, 60% and 32.5% lower than those observed in raw dairy slurry, respectively. Ammonia emissions from MS were as low as with CS treatment (Table 1).

Table 1. Cumulative NH_3 emissions (mg N pot^{-1}) as a percentage of total N and NH_4–N applied (excluded control emission). Values followed by different letters in the same column are significantly different ($p < 0.05$) based on the Tukey test. Standard error values are displayed in parentheses (mean, n = 3).

Treatment	NH_3 mg N pot^{-1}	N Lost as NH_3	
		% of Applied Total N	% of Applied NH4–N
CS	3.32 (0.2) [d]	-	-
MS	3.98 (0.2) [d]	0.13 (<0.1) [d]	0.13 (<0.1) [d]
RDS	170.19 (3.3) [a]	33.82 (0.7) [a]	90.75 (1.8) [a]
ADS	57.84 (12) [c]	11.05 (3.7) [c]	29.65 (9.9) [c]
IR	114.97 (5.2) [b]	22.63 (1.0) [b]	60.72 (2.8) [b]
US	68.44 (8.7) [c]	13.20 (1.8) [c]	35.41 (4.7) [c]

Notes: Unfertilized stubble-covered soil (CS), raw dairy slurry on the stubble (RDS), acidified dairy slurry on the stubble (ADS), irrigation immediately after RDS (IR), mineral nitrogen on the stubble (MS), raw dairy slurry applied under the stubble (US). Different lowercase letters within the same column indicate significant difference at $p < 0.05$.

Ammonia emissions represent important nitrogen losses from slurry applied to stubble-covered soil. In RDS, 34% of total N and 91% of NH_4-N was lost through NH_3 volatilization. Compared to RDS, ADS decreased N loss by 3 times, whereas in US and IR, the reductions were 2.5 and 1.5 times, respectively (Table 1). Ammonium sulphate presented insignificant nitrogen losses.

Daily rates of ammonia emissions, expressed in mg NH_3-N h^{-1} pot^{-1}, of CS, MS and slurry-based treatments during the experiment are shown in Figure 1. The ammonia emissions peaked on the first day for all treatments fertilized with slurry, following a decreasing trend until presenting negligible values from the fifth day on. On day 1, RDS led to the greatest ammonia emissions, followed by IR, whereas emissions from ADS and US represented less than half of those observed in RDS and IR on this same day. Daily ammonia emission rates from MS remained residual, as in CS, over the whole measurement period.

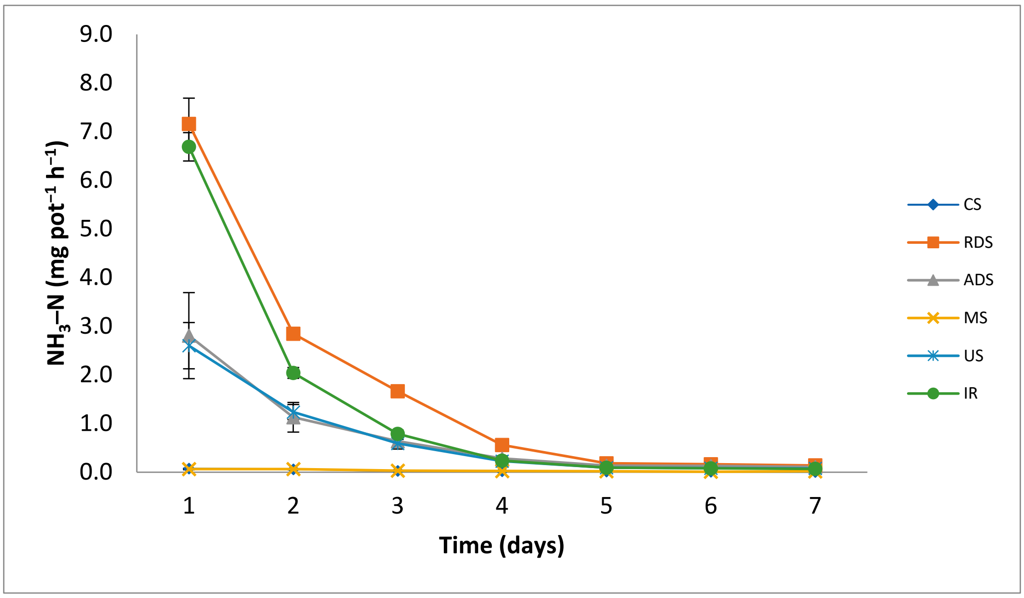


Figure 1. Daily ammonia emission rates (mg NH_3–N pot^{-1} h^{-1}). Vertical bars represent the standard error of the mean (mean, n = 3). Unfertilized stubble-covered soil (CS), raw dairy slurry on the stubble (RDS), acidified dairy slurry on the stubble (ADS), irrigation immediately after RDS (IR), mineral nitrogen on the stubble (MS), raw dairy slurry applied under the stubble (US).

The ammonia emission dynamics, presenting the intensity of daily emissions from each treatment (total emission = 100%), can be found in Figure 2. Most ammonia emissions took place on the first day, except for MS and CS. The treatments containing slurry emitted more than 50% of their total emissions on the first day, with emphasis on IR (67%).

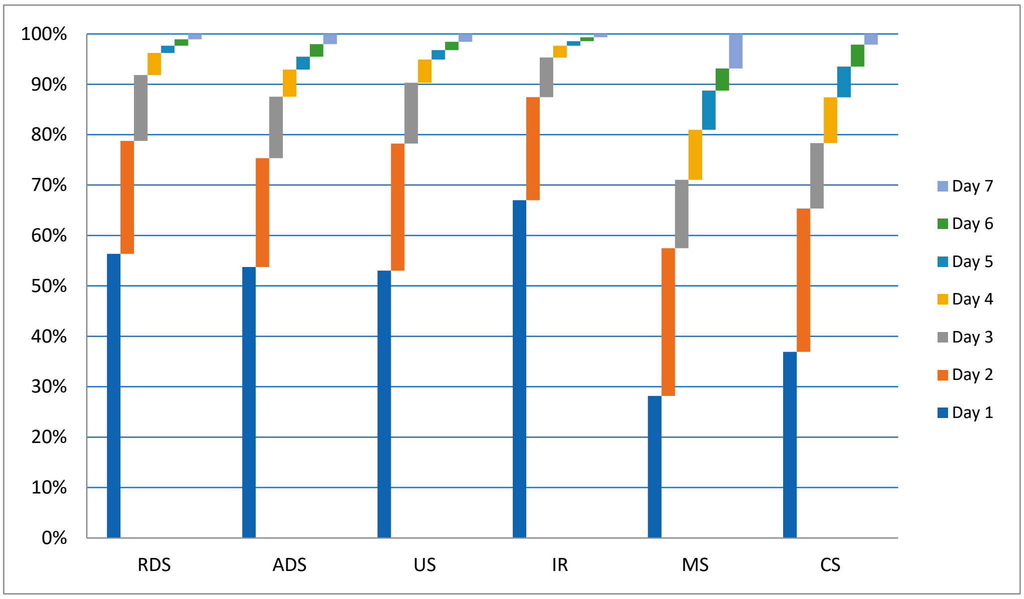


Figure 2. Ammonia emission dynamics. Intensity of daily emission rates as a percentage of the total emissions (100%). Unfertilized stubble-covered soil (CS), raw dairy slurry on the stubble (RDS), acidified dairy slurry on the stubble (ADS), irrigation immediately after RDS (IR), mineral nitrogen on the stubble (MS), raw dairy slurry applied under the stubble (US).

3.2. Nitrous Oxide Emissions

The cumulative N_2O emissions varied significantly ($p < 0.05$) among treatments (Table 2). MS treatment led to the highest value of total N_2O emissions, both until the first harvest (66 days) and for the total GHG sampling period (108 days)—significantly greater than that of RDS, RDS T16 and controls but similar to that of MB, IN, ADS, US and IR. RDS T16 was the strategy that led to the lowest N_2O cumulated emissions, similar to controls (CB and CS).

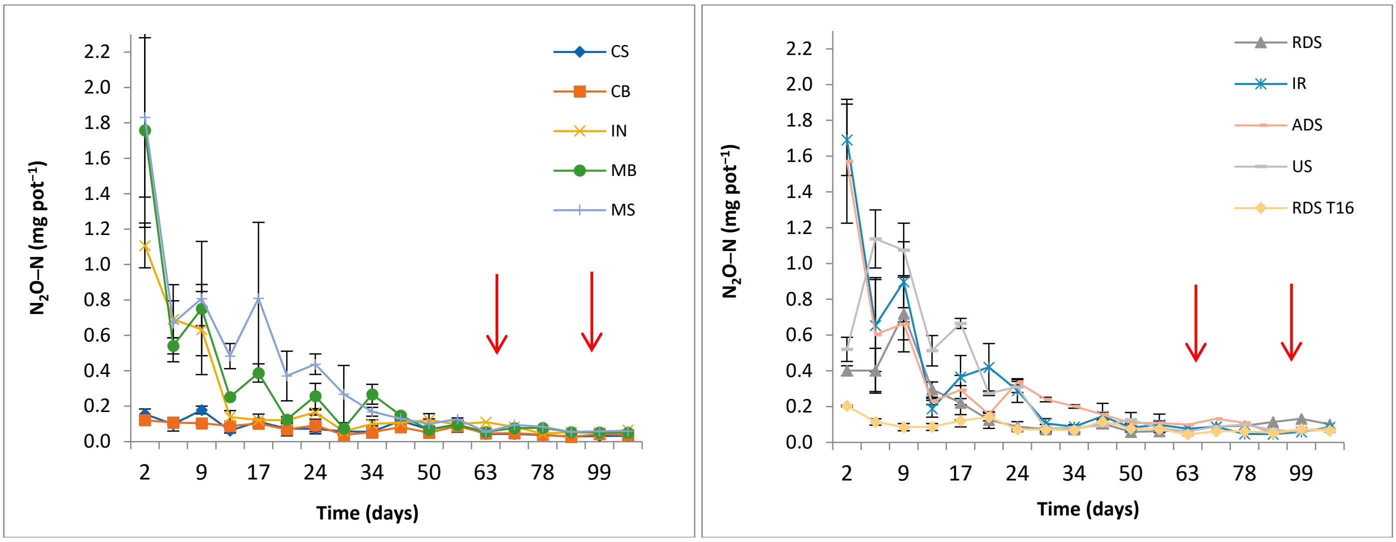
Our results showed that most nitrous oxide emissions were due to basal N fertilization. Between 68% and 89% of the total emissions occurred within the first 66 days after the start of the experiment, corresponding to the interval between sowing and the first harvest. The two subsequent N topdressings had a low impact on nitrous oxide emissions. MS led to the greatest total N_2O-N loss, although not significantly greater than that of ADS, US, IR, MB and IN. On the other hand, the smallest loss was observed in RDS T16, statistically similar to that of RDS (Table 2).

In all treatments, except RDS T16, US and RDS, a peak of N_2O emission was detected immediately after the application of basal fertilization, followed by a downward trend throughout the remaining gas sampling period, despite the two topdressing fertilizations (Figure 3a,b). In contrast, US and RDS emissions peaked on the sixth and ninth days, respectively. the RDS T16 treatment led to the most surprising results, with N_2O emissions similar to those of the control treatment. The highest N_2O emissions peaks were observed in MS, MB, IR and ADS treatments.

Table 2. Cumulative N_2O–N emissions before the first harvest (effect of basal fertilization), total cumulative emissions (effect of basal + two topdressing fertilization) and percentage of total nitrogen applied (basal + two topdressing fertilization) lost through N_2O–N emissions (excluding control emissions). Values followed by different letters in the same column are significantly different (p < 0.05) based on the Tukey test. Standard error values are displayed in parentheses (mean, n = 3).

Treatment	Cumulative N_2O Emissions at First Harvest (mg N pot^{-1})	Total Cumulative N_2O Emissions (mg N pot^{-1})	% of Total N Applied Lost as N_2O (%)
CB	4.82 (0.3) ^{c}	6.57 (0.4) ^{c}	-
CS	5.66 (0.4) ^{c}	7.21 (0.4) ^{c}	-
IN	14.82 (1.7) ^{ab}	17.67 (1.8) ^{ab}	0.74 (0.1) ^{abc}
MB	19.86 (2.9) ^{a}	22.55 (3.2) ^{ab}	1.07 (0.2) ^{ab}
MS	25.08 (4.7) ^{a}	28.08 (4.4) ^{a}	1.39 (0.3) ^{a}
RDS	11.45 (1.7) ^{b}	16.17 (1.9) ^{b}	0.60 (0.1) ^{bc}
ADS	19.98 (1.4) ^{a}	23.79 (1.8) ^{ab}	1.11 (0.1) ^{ab}
IR	20.51 (1.6) ^{a}	23.36 (1.7) ^{ab}	1.08 (0.1) ^{ab}
US	20.16 (1.0) ^{a}	23.50 (1.0) ^{ab}	1.09 (0.1) ^{ab}
RDS T16	5.91($\pm$0.2) ^{c}	8.68 (0.2) ^{c}	0.10 (0.1) ^{c}

Notes: unfertilized bare soil (CB), unfertilized stubble-covered soil (CS), injected slurry on bare soil (IN), mineral fertilizer applied on bare soil (MB), mineral fertilizer on the stubble (MS), raw dairy slurry on the stubble (RDS), acidified dairy slurry on the stubble (ADS), irrigation immediately after RDS (IR), raw dairy slurry applied under the stubble (US), application of raw dairy slurry on the stubble 16 days later (RDS T16). Different lowercase letters within the same column indicate significant difference at p < 0.05.



(**a**) (**b**)

Figure 3. N_2O–N daily fluxes (mg N_2O–N pot^{-1}). (**a**) Daily fluxes from CS, CB, IN, MB and MS. (**b**) Daily fluxes from RDS, IR, ADS, US and RDS T16. Arrows indicate the topdressing applications. Vertical bars represent the standard error of the mean (mean, n = 3). Unfertilized bare soil (CB), unfertilized stubble-covered soil (CS), injected slurry on bare soil (IN), mineral fertilizer applied on bare soil (MB), mineral fertilizer on the stubble (MS), raw dairy slurry on the stubble (RDS), acidified dairy slurry on the stubble (ADS), irrigation immediately after RDS (IR), raw dairy slurry applied under the stubble (US), application of raw dairy slurry on the stubble 16 days later (RDS T16).

3.3. Total Nitrogen Emissions

The total N gaseous emissions (NH_3–N + N_2O–N) from the treatments carried out in stubble-covered soil, except RDS T16, were accessed by using data of the two concomitant experiments (Figure 4). All fertilizers emitted more N gases than CS. RDS led to the greatest N loss, although similar to that of IR (p > 0.05). N gaseous emissions from RDS were halved by ADS and US. Ammonium sulphate (MS) emitted three times more N gases than CS, whereas among fertilized treatments MS lost the least nitrogen by gas emissions.

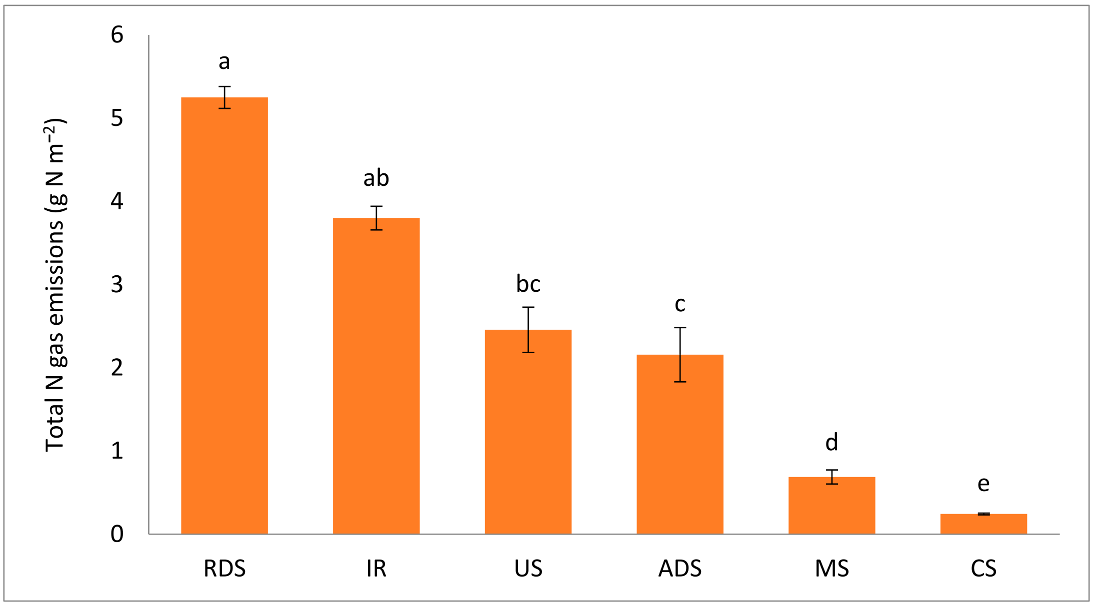


Figure 4. Total N lost via gas emissions (NH_3–N + N_2O–N) in g N m^{-2}. Different letters on the columns indicate significant differences among treatments ($p < 0.05$) based on the Tukey test. Vertical bars represent the standard error of the mean (mean, n = 3).

Figure 5 presents the influence of NH_3 and N_2O on total N losses to the atmosphere. N loss by N_2O emissions from MS (~83%) was higher than N loss by NH_3 emission, as well as in CS. In the slurry-based treatments, on the contrary, ammonia emission accounted for as main cause of N losses: 94%, 87%, 80% and 79%, respectively, for RDS, IR, US and ADS.

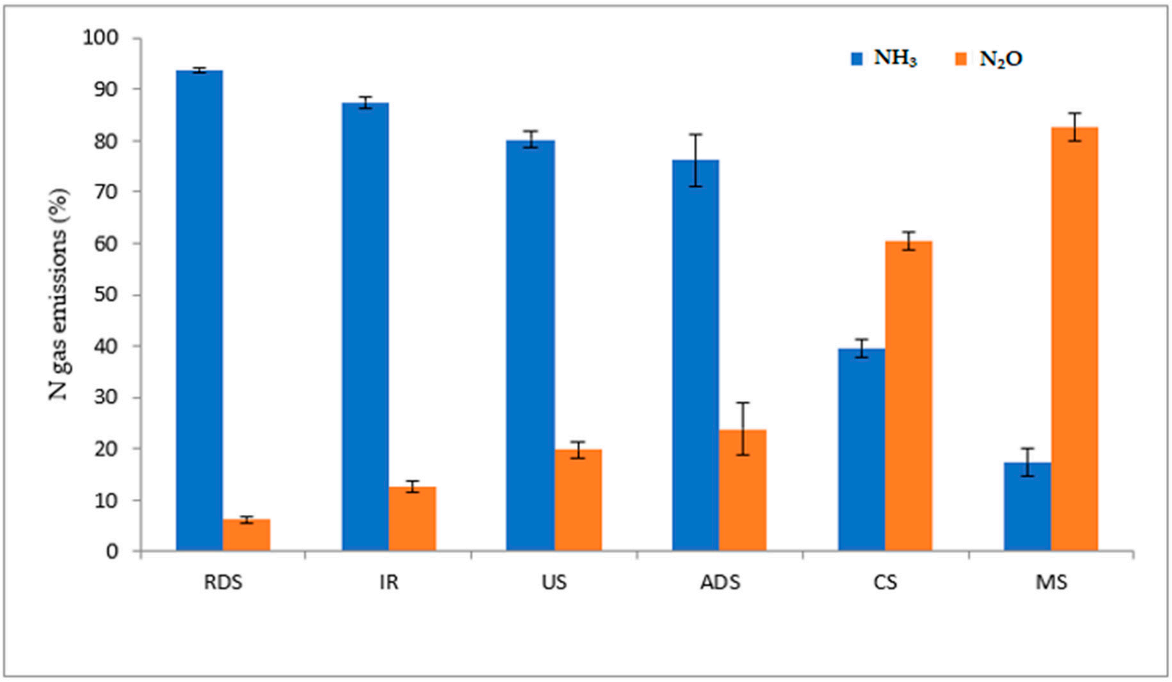


Figure 5. Contribution of NH_3 and N_2O to total N gas emissions (%). Vertical bars represent the standard error of the mean (mean = 3).

3.4. Carbon Dioxide and Methane Emissions

Carbon dioxide was responsible for more than 99% of GHG emissions from the treatments. The cumulative CO_2 and CH_4 emissions are presented in Table 3. The amount of CO_2 emitted from ADS, IR, US, RDS and RDS T16 were similar to that emitted by IN, MS and MB, indicating that mineral and organic sources performed similarly with respect to carbon emissions. However, ADS, IR, MS and US emitted more CO_2 than the controls ($p < 0.05$).

Table 3. Cumulative carbon dioxide and methane emissions from treatments, as well as total C emission (CO_2–C + CH_4–C) and total C emitted as a percentage of initial C content in each treatment (soil, soil + stubble, soil + fertilizer or soil + stubble + fertilizer). Global warming potential (GWP) and yield-scaled GWP (ys-GWP). Values followed by different letters in the same column are significantly different ($p < 0.05$) based on the Tukey test. Standard error values are displayed in parentheses (mean, n = 3). The absence of letters in the same column = not significant (^{NS}).

Treatment	CO_2 Emissions (g C pot^{-1})	CH_4 Emissions (mg C pot^{-1})	CO_2 + CH_4 Emissions (g C pot^{-1})	% of Initial C Lost as C Emissions (%)	GWP (g CO_2–eq pot^{-1})	ys-GWP (g CO_2–eq g^{-1})
CB	7.19 (0.4) ^{c}	2.44 (0.4) ^{NS}	7.19 (0.4) ^{c}	4.47 (0.3) ^{c}	29.20 (1.7) ^{c}	9.64 (2.4) ^{a}
CS	8.32 (0.5) ^{bc}	2.59 (0.1)	8.33 (0.5) ^{bc}	5.00 (0.3)^{bc}	33.62 (1.6) ^{bc}	7.76 (0.9) ^{ab}
IN	11.38 (0.8) ^{ab}	3.08 (0.5)	11.38 (0.8) ^{ab}	6.84 (0.2)^{a}	49.20 (3.4) ^{a}	3.77 (0.3) ^{b}
MB	9.75 (0.2) ^{abc}	2.68 (0.3)	9.76 (0.2) ^{abc}	6.06 (0.1)^{abc}	45.26 (1.3) ^{ab}	3.48 (0.3) ^{b}
MS	11.93 (0.9) ^{a}	2.59 (0.1)	11.94 (0.9) ^{a}	7.17 (0.5)^{a}	55.57 (2.7) ^{a}	3.85 (0.1) ^{b}
RDS	11.28 (0.4) ^{ab}	2.61 (0.2)	11.29 (0.4) ^{ab}	6.56 (0.2)^{ab}	48.20 (2.0) ^{a}	4.24 (0.4) ^{b}
ADS	12.55 (0.8) ^{a}	2.88 (0.5)	12.55 (0.8) ^{a}	7.30 (0.4)^{a}	56.04 (0.3) ^{a}	3.73 (1.7) ^{b}
IR	12.10 (1.0) ^{a}	2.57 (0.2)	12.10 (1.0) ^{a}	7.04 (0.6)^{a}	54.18 (4.3) ^{a}	4.31 (0.3) ^{b}
US	11.52 (0.2) ^{a}	3.02 (0.1)	11.52 (0.2) ^{a}	6.70 (0.1)^{ab}	52.12 (0.5) ^{a}	4.46 (0.4) ^{b}
RDS T16	10.84 (0.6) ^{ab}	2.22 (0.1)	10.85 (0.6) ^{ab}	6.31 (0.3)^{ab}	43.45 (2.2) ^{ab}	4.92 (0.6) ^{b}

Notes: unfertilized bare soil (CB), unfertilized stubble-covered soil (CS), injected slurry on bare soil (IN), mineral fertilizer applied on bare soil (MB), mineral nitrogen on the stubble (MS), raw dairy slurry on the stubble (RDS), acidified dairy slurry on the stubble (ADS), irrigation immediately after RDS (IR), raw dairy slurry applied under the stubble (US), application of raw slurry on the stubble 16 days later (RDS T16). Different lowercase letters within the same column indicate significant difference at $p < 0.05$.

The cumulative CH_4 emissions did not differ significantly among treatments. In summary, the cumulative CO_2 and CH_4 emissions from slurry applied to stubble were equivalent to the emissions from IN or ammonium sulphate.

3.5. Global Warming Potential and Yield-Scaled Global Warming Potential

The impacts of fertilized treatments (dairy-slurry-based or mineral fertilizer) on GWP were similar, with no significant differences observed between treatments (Table 3). CO_2 was the biggest contributor to the GWP of fertilized treatments (from 79% to 91%). The contribution of N_2O, as CO_2-eq, to GWP was more significant in MB and MS (~21%). Dairy slurry applied to stubble without injection or incorporation into the soil impacted the GWP at the same level as MS, MB and IN. CB presented the lowest GWP, although not significantly different from that of CS.

When considering the yield-scaled GWP, the highest value was also obtained by CB, significantly higher than all other treatments, except CS. All the fertilized treatments led to similar values of ys-GWP in a range of 3.48–4.92 g CO_2–eq g^{-1}. It is noteworthy that among the fertilized treatments, RDS T16 presented the highest ys-GWP and the lowest GWP, despite not showing a significant difference relative to the other treatments.

4. Discussion

4.1. Ammonia Emissions

The strategies for ammonia emission mitigation assessed in this work were all reduced emissions compared to raw dairy slurry applied to stubble (Table 1).

Compared to RDS, acidified slurry application to stubble-covered soil decreased NH_3 emissions by 66%, a value within the range reported in different studies where acidified slurry was applied to bare soil and grassland [12,25,27,42]. Additionally, [29] reported reduced emissions from acidified pig slurry applied to crop residues, reinforcing the ability of acidification to mitigate NH_3 emissions under different field conditions. This ammonia abatement occurred because slurry acidification acts on NH_4^+/NH_3 balance, reducing NH_3 emissions [28,39]. The stubble cover on the slurry in US probably acted as a protective layer against abiotic factors that significantly influence ammonia volatilization (i.e., air flow and solar radiation), efficiently reducing NH_3 emissions, as described in [43]. Irrigation, such as in the IR treatment, or rain events soon after slurry application may reduce ammonia emissions by rapidly driving TAN down into the soil [24,43] but can also lead to nitrate leaching if the amount of irrigation or precipitation is too high. The contribution of IR to the reduction in NH_3 emission, with respect to RDS, was lower than ADS and US (Table 1), likely due to the high DM content (11.3%) and the viscosity of the applied slurry, hindering the efficiency of TAN transport by the water downwards through the stubble layer and into the soil. As expected, cumulative ammonia emissions from MS were the lowest among the fertilizers, similar to the control. Ammonium sulphate generally has no significant N loss via ammonia emission when applied to the surface of acidic or neutral soils. The acid reaction of ammonium sulphate induces a decrease in the soil pH, maintaining NH_3 emissions at low levels [44–46]. Despite its efficiency, ammonium sulphate is not usually the farmer's first choice due to its low N concentration (compared to other mineral N sources) and consequent high cost per unit of nitrogen [47,48].

The greatest nitrogen loss by ammonia volatilization took place in RDS (34% and 90% of applied total N and NH_4–N, respectively). Compared to RDS, as previously described, ADS, US and IR significantly reduced ammonia emissions and therefore N losses (Table 1). These results are relevant because the reduction in N losses helps to improve crop productivity and farm profitability, in addition to protecting the environment.

ADS, US, MS and CS treatments allowed for a decrease in the high emissions rates observed in RDS on the first days (Figure 1). The decreasing trend in daily emission rates from slurry-based treatments throughout the trial period is in line with the results reported in [49]. Despite having reduced cumulative emission with respect to RDS emission, IR presented the most intense emissions on the first day (67% of its cumulative emissions) among all treatments (Figure 2). Such intensity might be initially motivated by the spread effect promoted by irrigation water applied to the slurry, expanding the exposed surface area and promoting intense ammonia emission soon after watering. The strategy of decreasing the surface area where ammonia emissions can occur is recognized as a major solution to reduce emissions from manure applied to soil [24]. Then, as the liquid phase penetrated the stubble layer (sometimes slowly due to the high DM content) as a consequence of the irrigation, ammonia emissions decreased, probably due to the protective effect of the stubble, similarly to the US treatment but also due to the adsorption of slurry–NH_4^+ to the soil negative charges.

4.2. Greenhouse Gas Emissions

Nitrogen additions to croplands are a major contributor to human-induced N_2O emissions, which increased by 30% over the past forty years. N is the crucial limiting nutrient in crop production; therefore, new fertilization strategies should be focused on stabilizing or reducing N_2O emissions [15].

Most of N_2O emissions (68% to 89%) from fertilized treatments took place from basal fertilization to the 66th day, when ryegrass was first harvested (Table 2). Similarly, [50] reported that 69% to 90% of seasonal N_2O fluxes were detected in the first 40 days following manure (liquid and solid) and synthetic fertilizer applications. As the nitrous oxide emissions in cultivated soils are derived from the processes of nitrification and denitrification [46], the initial fertilization probably boosted the microbial activity, accelerating the nitrification and denitrification processes. The initial absence of plants when basal fertilization was performed, except for RDS T16, allowed a considerable portion of the nitrogen in the soil solution to be available for nitrification or denitrification processes, generating an important amount of N_2O emissions (Figure 3a,b). Although CB and CS were not fertilized, most of their N_2O emissions also occurred within the first 66 days, mainly as an effect of the increase in soil moisture, stimulating the activity of micro-organisms [46,51]. Then, new N_2O fluxes were possibly generated following soil organic N mineralization [46]. After topdressing fertilization, the plants were ready to immediately uptake nutrients from the soil, diminishing the N content available for nitrification/denitrification processes and maintaining N_2O emissions at low levels.

The cumulative nitrous oxide emissions (Table 2) of IR, US and ADS were similar to those of mineral fertilizer applied to stubble or bare soil and slurry injection (IN), the widely recommended practice for soil slurry application. The absence of differences between dairy-slurry-based treatments and mineral fertilizers on N_2O emissions is in agreement with the results reported in [52]. RDS cumulative emissions were lower than those associated with the above-mentioned strategies, although the reason is probably the previously high N loss through ammonia volatilization, as seen in Table 1. Therefore, as a significant amount of N was lost through ammonia emissions, little NH_4^+ was available for nitrification and subsequent denitrification, decreasing N_2O emissions in RDS, in addition to explaining the initial N_2O peak delay (Figure 3b). Ammonia emissions also justify the high N_2O emissions from mineral fertilizer (MB and MS); on contrary, in this case, the maintenance of higher TAN content in the soil due to low NH_3 emissions provided a large amount of substrate for N_2O production. The delay in the initial N_2O peak observed in US might be due to the slower gas diffusion process from the soil surface throughout the stubble layer to the atmosphere. The lowest N_2O emissions among fertilized treatments occurred in RDS T16 (48% lower than RDS), probably because slurry application occurred after plants emerged. Thus, plants were able to uptake most of the available nitrogen, reducing the substrate needed for nitrification denitrification [30,46]. Additionally, the fertilizer source in RDS T16 was raw dairy slurry, and consequently, some N was surely lost through ammonia emission, as occurred in RDS. These two points, in addition to the fact that it had 16 fewer days of emissions derived from fertilization than the other treatments, might explain the residual N_2O–N fluxes from RDS T16 throughout the experimental period (Figure 3b).

The total amount of reactive nitrogen lost to the atmosphere was accessed by the sum of NH_3–N and N_2O–N emissions, reflecting the efficiency of a fertilizer or a strategy of slurry application. The highest N gaseous emissions were observed in RDS (Figure 4) due to the influence of the high NH_3 volatilization. For slurry-based treatments, ammonia emissions had a more considerable impact on total N loss than nitrous oxide (Figure 5). On the other hand, despite being highly efficient in mitigating ammonia volatilization, MS treatment led to the highest proportional N_2O emissions (Figure 5), as discussed previously. Thus, higher ammonia mitigation efficiency leads to higher nitrous oxide emissions and vice versa. Conditions that contribute to reducing the concentration of available nitrogen in the soil could help to overcome this paradigm.

The CH_4 cumulative emissions, possibly due to the controlled soil moisture, were low when compared to other GHGs and similar among the treatments. CH_4 emissions are promoted by soil conditions that allow for organic matter decomposition in the absence of oxygen, in additions emission and consumption of methane, which can occur at the same time in soils [40,53].

No significant differences were observed with respect to cumulative CO_2 emissions among the studied slurry application strategies and injected slurry or mineral fertilizers (Table 3). Unexpectedly, the CO_2 emissions from mineral fertilizers (MS and MB) were similar to those of slurry-based treatments, despite being in line with the results reported in [54], possibly influenced by the high organic carbon content in the soil, the low rate of initial fertilization and the short duration of the experiment. Carbon dioxide emissions from raw manure are markedly greater than emissions from mineral fertilizers in long-term experiments with high manure application rates [55–57]. Despite the absence of significant differences, the effect of stubble cover on soil moisture maintenance, in the short-term, might have influenced CO_2 emissions, as the increased water-filled pore space leads to an increase in CO_2 emissions [58]. Moreover, some studies reported an increase in CO_2 emissions when mineral N fertilizer was applied to stubble [55,59]. Soil disturbance caused by slurry injection in bare soil might have contributed to an increase in CO_2 emissions from IN. Carbon dioxide emissions, especially in the first days, result from the decomposition of organic matter promoted by the stimulus of fertilization, moisture and soil disturbance on soil microbial activity [60]. Ultimately, similar C emissions between slurry-based and mineral (without C input) fertilizers may indicate an accumulation of carbon in the soil promoted by slurry-based fertilizers (although it was not possible to detect in this 108-day experiment), as observed in [35,57]. Results reported in [61] complement this information, with an increase in soil organic carbon promoted by the long-term application of straw and manure.

Most of the C emitted to the atmosphere occurred through CO_2 emissions (~99%) due to the low methane emissions in all treatments. The percentage of total carbon emitted relative to the carbon supply (soil, slurry and/or stubble) was largely determined by the C content in the soil and was similar among fertilized treatments, justifying the values of C emissions from CS and CB.

4.3. Global Warming Potential and Yield-Scaled Global Warming Potential

The absence of differences for GWP and ys-GWP among the fertilized treatments indicates that dairy slurry applied to stubble-covered soil with no incorporation or injection does not represent an increased environmental hazard with respect to its contribution to global warming potential, relative to ammonium sulphate (MS or MB) or dairy slurry injection in bare soil. Among fertilized treatments, ADS and RDS T16 presented the highest and the lowest values for GWP, respectively; however, when the effect of those strategies on ryegrass yield was considered, the relative contribution of each to GWP was reversed (Table 3). Thus, high GWP may not necessarily imply high ys-GWP and vice versa [62]. For instance, the ryegrass yield [35] and GWP of ADS were 2.98 and 1.66 times greater than CS, respectively. Therefore, to compensate for the lower CS yield, it would be necessary to grow an area 2.98 times larger, which means that the new GWP of CS would be 100.19 g CO_2–eq pot^{-1} (2.98×33.62), or 1.79 times greater than ADS.

5. Conclusions

ADS, US and IR applied to stubble-covered soil without mechanical incorporation reduced NH_3 emissions and total N emissions. However, these strategies affected GHG emissions and GWP similarly to slurry injection and N mineral fertilizer. NH_3 emissions were the main cause of N loss in slurry-based treatments. ADS, US and IR reduced cumulative NH_3 emissions by 66%, 60% and 32.5%, respectively, compared to RDS. ADS and US halved N gaseous emissions from RDS. The evaluated strategies did not lead to increased GHG emissions or GWP relative to MS, MB or IN. Between 68% and 89% of cumulative N_2O emissions occurred under the influence of basal fertilization. The N_2O emissions from RDS were possibly limited by the significant loss of N that occurred through NH_3 emissions. The effects of RDS T16 on N_2O and GHG emissions, as well as on GWP, showed the potential of in-season application as a strategy to reduce the fertilization impacts on climate change. However, the ys-GWP of RDS T16 seems to indicate that shorter delays are suitable, in addition to potentially reducing plant damage. Ammonium sulphate maintained NH_3 emissions and total N emissions at a low level, although it was unable to decrease N_2O emissions compared to dairy-slurry-based treatments.

In summary, based on the ability to decrease NH_3 and total N emissions, in addition to their effects on GHG emissions and GWP, ADS, US and IR have proven to be sustainable options to replace synthetic fertilizers, as well as slurry injection, contributing to promotion of animal slurry fertilization in CA by obviating incorporation into the soil. Furthermore, the improved sustainability of slurry-fertilized conservation systems can help to promote the adoption of CA, increasing the resilience of food production, especially in regions that face more frequent droughts or that are highly susceptibility to erosion.

Such results may support decision makers as a reference for future regulations with respect to the application of animal slurry in conservation agriculture. Confirmation of our findings in field studies is still necessary before farm-scale application.

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