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Irrigation Scheduling with Soil Gas Diffusivity as a Decision Tool to Mitigate N_2O Emissions from a Urine-Affected Pasture

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Abstract: Pastures require year-round access to water and in some locations rely on irrigation during dry periods. Currently, there is a dearth of knowledge about the potential for using irrigation to mitigate N_2O emissions. This study aimed to mitigate N_2O losses from intensely managed pastures by adjusting irrigation frequency using soil gas diffusivity (D_p/D_o) thresholds. Two irrigation regimes were compared; a standard irrigation treatment based on farmer practice (15 mm applied every 3 days) versus an optimised irrigation treatment where irrigation was applied when soil D_p/D_o was ≈0.033 (equivalent to 50% of plant available water). Cow urine was applied at a rate of 700 kg N ha^{-1} to simulate a ruminant urine deposition event. In addition to N_2O fluxes, soil moisture content was monitored hourly, D_p/D_o was modelled, and pasture dry matter production was measured. Standard irrigation practices resulted in higher (p = 0.09) cumulative N_2O emissions than the optimised irrigation treatment. Pasture growth rates under treatments did not differ. Denitrification during re-wetting events (irrigation and rain) contributed to soil N_2O emissions. These results warrant further modelling of irrigation management as a mitigation option for N_2O emissions from pasture soils, based on D_p/D_o thresholds, rainfall, plant water demands and evapotranspiration.

Keywords: N_2O emissions; automatic chambers; optimised irrigation; modelled D_p/D_o; pasture management

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1. Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas and is also the dominant ozone depleting substance [1,2]. Tropospheric concentrations of N_2O have increased by 23% from 271 ppb to 333 ppb from about 1750 to 2020 [3]. Since 1960 a key driver of this increase, globally, has been the increased use of synthetic nitrogen (N) fertiliser, while, before 1960, the expansion of agriculture is thought to have increased atmospheric N_2O as a result of soil N mineralisation [4]. New Zealand has not been immune to the drive to intensify agricultural systems with a 627% increase in the annual application of N fertiliser between 1990 and 2017. Moreover, within some regions of New Zealand, the amount of N fertiliser applied, predominately urea, doubled between 2002 and 2017 [5].

A major reason for this increased use of N fertiliser has been the intensification of land use resulting from the expansion of irrigation: the area of irrigated land doubled between 2002 and 2017 [5]. In New Zealand, 747,000 ha of land is irrigated with the bulk of this concentrated in Canterbury (478,000 ha; 64% of irrigated land) and Otago (94,000; 13%): intensification of irrigated land has substantially increased dairy cattle numbers in these regions [5].

In these irrigated systems, the ingestion of relatively N rich ryegrass-based pastures exceeds the metabolic N requirements of ruminants [6]. This leads to excess N being excreted predominately as urine-N [7], at rates that exceed the pasture's immediate requirements [6]. As a consequence of these elevated soil inorganic-N concentrations (nitrate and ammonium), nitrate leaching and N_2O emissions are enhanced. Consequently, research has focused on feeding alternative forages, utilisation of catch crops and nitrification inhibitors to reduce nitrate leaching and N_2O emissions [6,8–11]. While some studies have examined the effect of irrigation management on nitrate leaching [12,13], a few studies have examined the role of irrigation management on N_2O emissions.

High ammonium concentrations in pasture urine-patches stimulate ammonia oxidising bacteria (AOB) who produce N_2O as a result of both abiotic and biotic transformations of their metabolic intermediates, and through nitrifier-denitrification [14]. The process of nitrifer-denitrification is stimulated when the soil becomes hypoxic [14–16]. The denitrification of nitrate is an anaerobic process where N_2O is an obligate intermediary [17]. Hence, soil oxygen (O_2) status, a function of supply and consumption, is a key determinant of the N_2O production pathway in pasture soils.

Soil moisture content, often measured as water-filled pore space (WFPS), influences the ability of O_2 to diffuse into the soil and it is well recognised that increasing moisture leads to hypoxia and ultimately anaerobic conditions and increases in N_2O emissions [18,19]. However, at a constant WFPS, the volume fractions of air and water vary with different soil bulk densities, making comparisons of soils problematic [18]. Balaine et al. [20] showed that relative gas diffusivity (D_p/D_o; where D_p is the soil gas diffusion coefficient (m^3 soil air m^{-1} soil s^{-1}) and D_o is the gas diffusion coefficient in free air (m^2 air s^{-1})) was better than WFPS for identifying the threshold of N_2O production when comparing soils across a range of bulk densities and soil moistures. This was further confirmed using repacked soil cores, intact soil cores and in situ [21–23]. A D_p/D_o value $\leq$ 0.02 indicates the onset of anaerobic soil conditions [24], while a value of 0.006 has been shown to result in peak N_2O emissions [20]. Thus, since D_p/D_o provides a value indicative of the soil's functional gas diffusivity at a given time, it may be indicative of the propensity for a soil to generate N_2O.

Irrigation impacts the soil O_2 status displacing air from soil pores and creating hypoxic or even anoxic conditions in the soil. While the manipulation of irrigation has been shown to mitigate N_2O emissions in cropping systems [25,26], few studies have examined this concept with respect to pasture urine-patch N_2O emissions. Vogeler et al. [27] modelled the effects of irrigation frequency and intensity (with application based on soil water deficit) on N losses from pasture, across soil types, and found higher denitrification and N_2O emissions under high-frequency/low intensity irrigation regimes that resulted in a zero moisture deficit after irrigation. Mumford et al. [28] determined the effects of irrigation frequency (4, 10 or 15 day intervals, with the number of application events based on rainfall and evapotranspiration rates) on N_2O emissions from intensively managed subtropical pastures receiving urea fertiliser (381 kg N ha^{-1} yr^{-1}) and simulated grazing: this study demonstrated the potential for strategic irrigation practices to reduce N_2O emissions. The highest cumulative losses of N_2O were from the low frequency treatment (15 day interval) and were attributed to a reduced potential for dinitrogen (N_2) production (lower N_2O reductase activity in the low frequency treatment compared to high frequency treatment) and enhanced C and N supply for denitrification due to the well-recognized 'Birch effect' [29]. This current study investigated how irrigation cycles affected N_2O emissions from ruminant urine-affected soil. Thus, the objective of this experiment was to investigate the potential to manipulate N_2O emissions from ruminant urine-affected soil using irrigation but with D_p/D_o as a decision tool for irrigation timing. It was hypothesised that N_2O emissions would be higher when D_p/D_o values were <0.02.

2. Materials and Methods

2.1. Experimental Site

The field trial was conducted on a regularly mown pasture at Lincoln University, New Zealand (43°38′54.02″ S, 172°28′6.556″ E), where perennial rye grass (*Lolium perenne* L.) was the predominant pasture species. The soil was a Wakanui Mottled Immature Pallic

Silty Loam [30]. Soil texture comprised 33% sand, 48% silt and 19% clay, with an organic matter content of 5.34% and a pH of 5.25. The site was under sprinkler irrigation during the summer period (November to March) and received irregular N fertiliser inputs. A total of 8 soil cores were used to determine the soil ϱ_b that averaged 1.1 ± 0.03 (s.e.m) g cm^{-3}. The soil inorganic-N and dissolved organic carbon (DOC) concentration characteristics of the pasture soil were determined (Table 1). An automatic weather station on site logged hourly rainfall, air temperature, humidity, solar radiation, wind-speed and soil temperature (10 cm depth) data. The data were recorded on Vista Data Vision software (VDV2016). The standardized reference evapotranspiration for short grass was calculated according to Allen et al. [31]: with the Sz parameter used to select which crop reference to use for the ETsz calculation [31] a value of zero was entered, similar to clipped grass.

Table 1. Concentration of NO_3^--N, NH_4^+-N, and dissolved organic carbon (DOC) in the soil (0–7.5 cm). The values with a pink background were sampled in the spare chambers (two cores mixed in a zip bag for each/date/chamber). Data from inside the autosampling chambers at the end of the experiment (n = 4) and errors are standard error of the mean (s.e.m). Opt = optimised; Std = Standard.

Date		Urine on Opt	Urine on Std	Urine off Std	Urine on Opt	Urine on Std	Urine off Std	Urine on Opt	Urine on Std	Urine off Std
		NO_3^--N (µg/g)			NH_4^+-N (µg/g)			DOC (µg/g)		
13 February 2020	Pre-urine	4.6	0.9	2.8	19.8	22.2	14.8	301.3	188.8	229.1
16 February 2020	Before std irrigation	—	4.9	1.9	—	128.8	13.4	—	196.2	194.6
17 February 2020	Before opt irrigation	13.2	—	—	61.9	—	—	330.7	—	—
19 February 2020	Before std irrigation	—	39.5	0.7	—	311.2	3.5	—	383.5	269.9
21 February 2020	Before opt irrigation	103.8	—	—	472.1	—	—	381.3	—	—
2 March 2020	Before opt & std irrigation	218.7	133.8	3.0	74.6	34.0	3.8	275.8	190.0	214.7
24 March 2020	end	117 (±23)	39.2 (±13)	1.3 (±0.1)	11.6 (±5.9)	4.9 (±1.4)	2.2 (±0.3)	136.0	172.5	214.5
24 March 2020	End of expt.	98.2 (±8.3)	55 (±10.7)	7.6 (±3.0)	10.2 (±2.1)	2.2 (±0.5)	3.6 (±0.5)	109.1 (±5.4)	120 (±6.9)	142.9 (±5.9)

2.2. Experimental Design

A randomised experiment was conducted comprised of three treatments, replicated four times: standard irrigation–non urine (control; off_Std); standard irrigation–plus urine (on_Std); optimised irrigation–plus urine (on_Opt). An optimised irrigation–non urine treatment was not included because the objective of the study was to examine irrigation treatment effects on N_2O emissions from ruminant urine-affected soil. This also facilitated greater replication of the three chosen treatments. The treatments were applied to 0.25 m^2 plots defined by 12 pneumatically operated automated sampling chambers that were separated by 1 m buffer areas (Figure 1). Three further plots, urine treated, were included to allow soil samples to be taken during the experiment without disturbing the chamber's soil (Figure 1). Fresh bovine urine was collected from cows grazing perennial ryegrass pasture and a 2 L volume was applied to urine-receiving chambers, at a rate equivalent to 700 kg N ha^{-1} on 13 February 2020. This N rate is typical of a dairy cow urination event when grazing ryegrass pasture [6]. An equivalent volume of water was applied to non-urine treatments.

Figure 1. A schematic of the 12 chambers randomised per treatment with optimised (Opt) and standard (Std) irrigation treatments with urine applied (on) or no urine applied (off).

Standard irrigation was comprised of a 3-day irrigation interval with 3.75 L (equivalent to 15 mm) of water applied at each irrigation event. This was chosen to simulate routine irrigation application rate and frequency as used by local farmers [21]. Based on typical evapotranspiration rates and irrigation return times, farmers in Canterbury, New Zealand typically apply 12–15 mm every 3 days during the summer months [32]. The main method of pasture irrigation used by farmers is centre pivots [33]. For this experiment, irrigation was simulated by manually applying irrigation with a hand-held sprinkler.

A survey of farmers in Canterbury, to document irrigation strategy, found that 57% of farmers started irrigation in the shoulder seasons when soil contained the equivalent of 50% of plant available water (PAW) with the majority stopping irrigation at 80% of PAW [34]. Thus, optimised irrigation occurred at an irrigation trigger point (TP) equal to 50% of PAW, a soil moisture content that avoids plant stress and yield loss, and which aimed to restore soil moisture to 80% PAW. The amount of PAW is the difference between the soil moisture at field capacity (FC) and permanent wilting point (PWP). The optimised irrigation treatment was determined based on D_p/D_o with the aim to keep the soil aerobic post irrigation. First, FC was measured by taking 8 undisturbed soil cores from the field site which were then saturated and covered for 24 h until rapid drainage had ceased. Then, PWP, defined as soil volumetric moisture content at −1500 kPa, was determined.

The difference between FC less the PWP equated to PAW. Optimised irrigation aimed to replenish soil water reserves to a value equal to 80% of PAW, a moisture content less than FC. The values of volumetric soil water content (θ_v, cm^3 water cm^{-3} soil) for FC, PWP, the optimised irrigation trigger point (50% of PAW), and 80% of FC were 0.43, 0.14, 0.29, and 0.40 cm^{-3} cm^{-3}, respectively.

In situ soil moisture was logged at 1 min intervals and then averaged hourly using a series of frequency domain reflectometry (FDR) probes (Siemens and TM5) with sensors placed within the first 10 cm of the soil. Probes were calibrated using soil water characteristics identified by analysing intact soil cores from the site with output provided as θv [35]. These measurements and predetermined measures of soil bulk density (ϱ_b) and soil porosity (Φ, cm^3 pores cm^{-3} soil) over the 0–10 cm soil depth were used to determine volumetric air content (ε, m^3 air m^{-3} soil) as follows [36]:

$$\varepsilon = \Phi - \theta_v \quad (1)$$

Hourly D_p/D_o, and daily average values were then calculated using the SWLR model [37], as follows:

$$\frac{D_p}{D_o} = \varepsilon^{[1+C_m\Phi]}\left(\frac{\varepsilon}{\Phi}\right) \quad (2)$$

The measurements were taken on intact soil so the value of C_m, the media complexity factor, was set to equal to 2.1 according to Moldrup et al. [37]. Values of D_p/D_o corresponding to FC, PWP, the optimised irrigation trigger point (50% of PAW), and 80% of FC were 0.004, 0.122, 0.033 and 0.01, respectively. In the optimised irrigation treatment, the volume of water required to bring the soil back to 80% of FC, i.e., from a D_p/D_o value of 0.033 to 0.01, was 2.75 L (11 mm).

Vista Data Vision software (VDV2016) was used to visualise the daily soil data results and make decisions for the optimised irrigation. The weather forecast was also considered for the optimised irrigation treatment as part of the decision process. If the D_p/D_o was close to the irrigation TP (0.033) but significant rainfall was forecast, then irrigation was postponed. A rain simulation event was applied on 24 March (6.7 mm) prior to the end of the experiment.

2.3. Soil N_2O Flux Measurements, Soil Sample Collection and Their Analyses

Daily N_2O fluxes were measured with a pneumatically operated, automated sampling chamber [28,38]. The chambers (headspace height of 150 mm), constructed in-house, were made from stainless steel frames with Perspex® walls and lids (insulated) to enable plant growth. Chamber bases (0.25 m^2) were embedded 10 cm into the soil. During a sampling event, 4 chambers (one replicate) closed for 60 min (chambers from bloc 1 are closed while chambers from bloc 2 and 3 are open, Figure 1). Over this time, automated sampling of the chamber headspaces occurred with a sample taken every 3 min in a sequential order, followed by a reference N_2O gas sample (1 μL L^{-1} N_2O, BOC, Christchurch, New Zealand), taking a total of 15 min. The sampling sequence was repeated a further three times giving a total of four samples per chamber headspace over the 60 min period. The automated chambers were sealed airtight during the sampling procedure by two lids that closed and opened via pneumatic actuators using an air compressor.

The 4 chambers sampled were then automatically opened where upon the next set of 4 chambers closed, and the sampling sequence was repeated. All 12 chambers were sampled once every 3 h and eight times every 24 h. Gas samples were analysed using a gas chromatograph (8610, SRI Instruments, Torrance, CA, USA) interfaced to a liquid autosampler (Gilson 222XL, Middleton, WI, USA) as previously described [39]. PeakSimple™ software (version 4.90) was used to integrate the GC output in order to determine sample N_2O concentrations. Any CO_2 and H_2O contained in the gas samples was removed before N_2O was analysed via a scrubber containing sodium hydroxide and magnesium perchlorate to avoid any contamination during the GC determination of N_2O concentration. The system was calibrated using the reference N_2O standards. The slope of the change in chamber headspace N_2O concentration versus time was used to calculate the magnitude of the N_2O flux as follows:

$$F_{N_2O} = \frac{\partial C}{\partial t}\,\frac{V_c M_{mol}}{A V_{mol}} \quad (3)$$

where $\partial C/\partial t$ is the rate of change of N_2O concentration inside the chamber, A is the surface area (m^2) of the chamber, Vc is the total volume (L) of the chamber corrected for temperature and relative humidity, M_{mol} is molar mass of N_2O (g mol^{-1}) and V_{mol} is the volume of a mole of N_2O (L mol^{-1}) inside the chamber corrected for air temperature using the ideal gas law. The automated system and flux calculation details are further described in detail by Barton et al. [40]. The N_2O flux rates were calculated and corrected for air temperature, atmospheric pressure and the ratio of chamber volume to surface area and expressed on an elemental weight basis as g N_2O-N ha^{-1} day^{-1}. An automated tipping bucket to measure rainfall was also connected to the automated chamber sampling system: rainfall events exceeding 5 mm triggered the opening of all chambers until rainfall ceased.

Pasture was cut to a uniform height of 5 cm prior to treatment application and harvested twice during the experiment. Harvested grass samples were dried at 60 °C for 2 days and then weighed to determine dry matter (DM) content.

Soil inorganic-N concentrations and DOC concentrations were determined pre-urine application, and then prior to irrigation treatments on the plots (Figure 1) and at the end of the experiment inside the 12 chambers. Soil cores (2 cm diameter, 7.5 cm long) were taken inside the plots. Soil gravimetric water contents were determined prior to extracting the soil cores with 2 M KCl for one hour with a 1:10 extraction ratio of soil:KCl, and then filtering (Whatman 42; GE Healthcare UK Limited, Buckinghamshire HP7 9NA, UK). Flow injection analysis (Alpkem FS3000; OI Analytical, TX, USA.) was used to determine NO_3^--N and NH_4^+-N concentrations [41]. Finally, further soil subsamples were extracted for DOC using 5 g equivalent of dry soil and 30 mL of deionised water, which was shaken for 30 min before centrifugation (2280× g for 20 min, T = 25 °C, Megafuge 40, Thermo Scientific, Waltham, MA, USA), and filtration (Whatman 42; GE Healthcare UK Limited, Buckinghamshire, UK), with analyses performed on a Shimadzu TOC analyser (Shimadzu Oceania Ltd., Sydney, Australia). Water samples from the irrigation water were also analysed for NO_3^--N content.

2.4. Statistical Analyses

Statistical analyses were performed using Rstudio (v1.2) using the "Stats" and "bestNormalize" packages. Before any statistical analysis was made, data were tested for normality, residual repartition and the homoscedasticity. The function "shapiro.test" was used to double test the normality of the residues. If the value of the Shapiro–Wilk Test was >0.05, the data was considered normal. If the Shapiro-Wilk Test was <0.05, the data significantly deviated from a normal distribution. Then, the best fit transformation was applied using the "bestNormalize" decision tool, designed to estimate the best normalizing transformation for a vector consistently and accurately. The outliers in a linear regression model were detected by plotting the residuals vs. leverage and using Cook's distance line as an indicator of the effect of deleting a point on the combined parameter vector. A repeated measures analysis, using a two-way ANOVA, urine (2 levels: on and off), irrigation conditions (2 levels: Opt and Std), combined treatments (3 levels: off_Std, on_Std and on_Opt) and days were the explanatory variables. Tukey's post-hoc test was used to determine specific differences between means with the least significant set to 5% level.

3. Results

3.1. Soil Moisture and D_p/D_o

Standardized reference evapotranspiration and daily mean soil temperature ranged from 0.9 to 4.9 mm day^{-1} and 10 to 19 °C, respectively (Figure 2). Over the period 13 February 2020 to 24 March 2020, cumulative rainfall totalled 21 mm, lower than the average (50 mm). A significant rainfall (12.8 mm) occurred on 22 February (Figure 2). The first irrigation treatments were applied three days and five days after urine application for standard and optimised, respectively (Figure 2). Irrigation water contained an average NO_3^--N concentration of 7.11 ± 0.03 (s.e.m) mg L^{-1}.

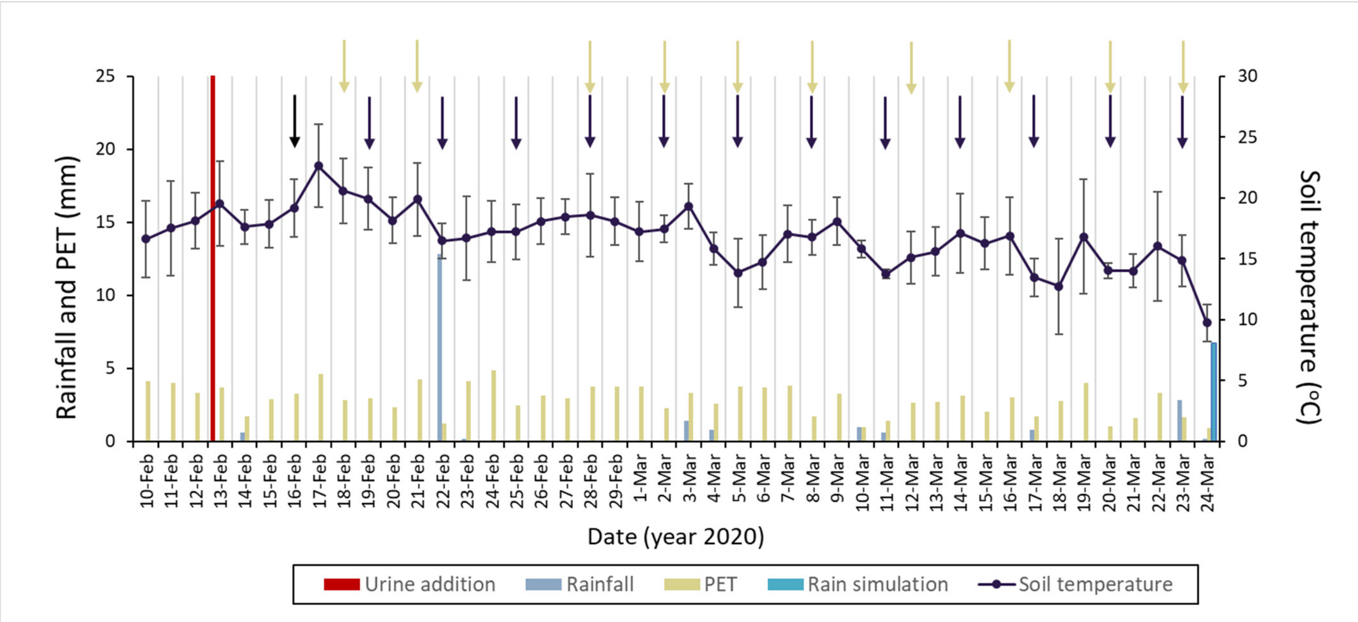

Figure 2. Daily rainfall (grey bar), standardized reference evapotranspiration (PET; yellow bar) and soil average temperature (black line) from 10 February 2020 to 24 March 2020 following ruminant urine application (red bar). Blue and yellow arrows denote standard and optimised irrigation events, respectively, and the blue bar represents the rain simulation (6.7 mm) on 24 March 2020. The error bars represent the daily temperature range.

The urine application (and water for the non-urine treatment) on 13 February increased soil WFPS as did each irrigation event (Figure 3). Despite a greater volume of water being added during an irrigation event in the standard treatment (3.75 L vs. 2.75 L for optimised), the increase in WFPS after each irrigation was not higher. Under standard irrigation, measures of WFPS were relatively consistent over time (Figure 3) with or without urine, with soil moisture restored to ~65% WFPS every three days, lower than FC (83% WFPS). However, on 16 March, the WFPS in the standard irrigation, with urine, dropped and only returned to 66% after the rain simulation on 24 March (Figure 3). For this last date, and with the same volume of water added to each chamber, WFPS values were 58 and 80% for optimised irrigation with urine and standard irrigation without urine, respectively. The WFPS in the standard irrigation treatment with urine reached its maximum (71%) after the rain event on 22 February (Figure 3).

Soil D_p/D_o values decreased after each irrigation event (Figure 4). Optimised irrigation was triggered when the D_p/D_o value increased to ~0.033 and D_p/D_o values stayed $\geq$0.01 (equal to $\leq$80% FC) over the experiment for this treatment. The lowest values for D_p/D_o were observed on 13, 14, 18 and 23 February for the optimised treatment. After urine application, the D_p/D_o values in the standard irrigation were $\leq$0.02 (Figure 4). The rainfall event on 22 February (Figure 4) resulted in standard irrigation soil D_p/D_o values being equal to a value of 0.006. This threshold was also crossed by the standard irrigation without urine treatment (D_p/D_o = 0.0025) at the end of the experiment after the rain simulation event.

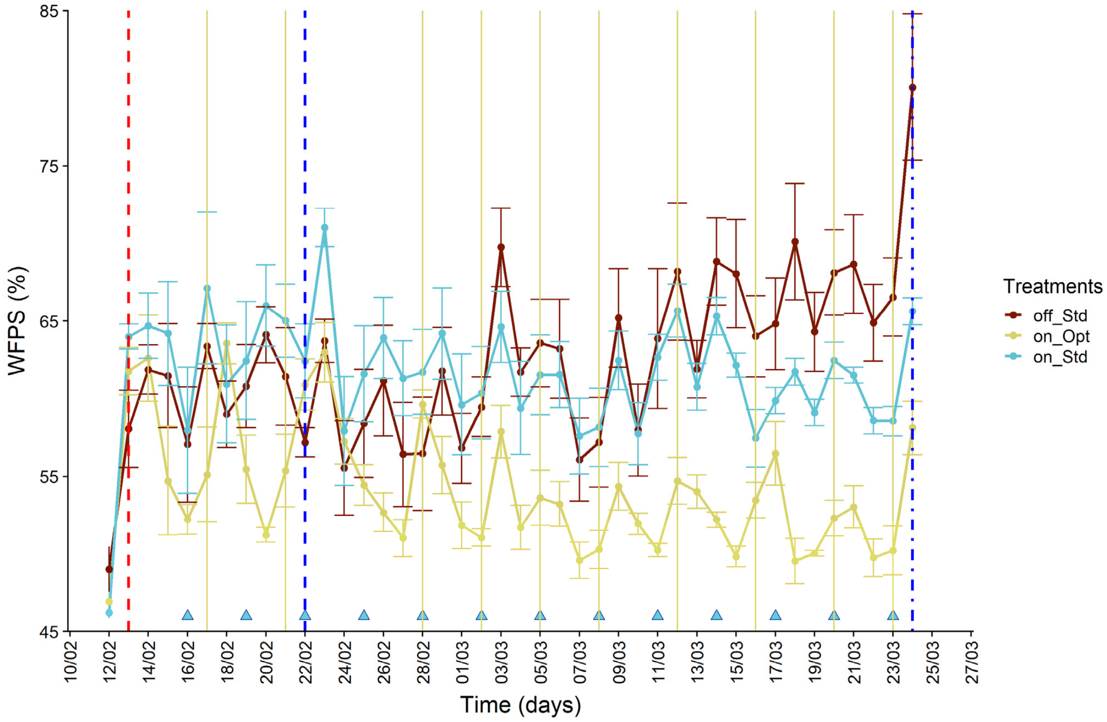

Figure 3. Daily average WFPS (%) from 12 February 2020 to 24 March 2020. The vertical red dashed line shows timing of urine application, blue triangles and yellow vertical lines denote timing of the standard (Std) and optimised (Opt) irrigation applications, respectively. Error bars = s.e.m, n = 4. Treatment with urine applied (on) or no urine applied (off). The blue vertical dashed lines on 22 February 2020 represent the rain event (12.8 mm) and a rain simulation, respectively.

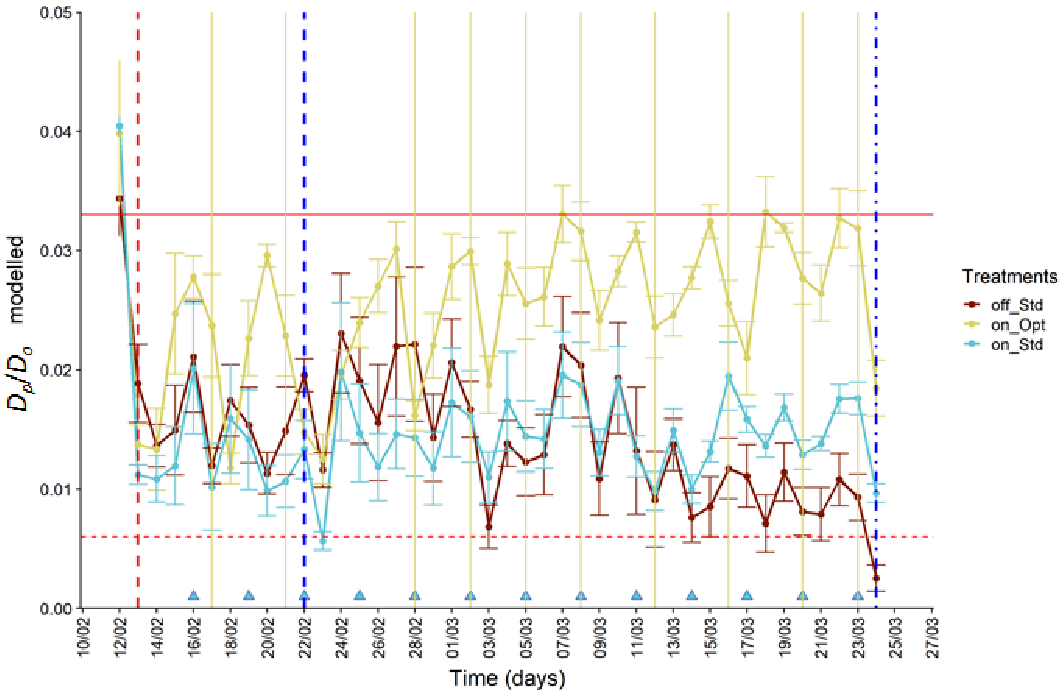

Figure 4. Modelled daily average relative gas diffusivity (D_p/D_o) from 12 February 2020 to 24 March 2020. The vertical red dashed line shows the timing of urine application, blue triangles and yellow vertical lines denote timing of the standard (Std) and optimised (Opt) irrigation applications, respectively. Error bars = s.e.m, n = 4. Treatment with urine applied (on) or no urine applied (off). The blue vertical dashed lines on the 22 February 2020 represent the rain event (12.8 mm) and a rain simulation, respectively.

3.2. *Dry Matter Production and Soil Inorganic-N, DOC and N_2O Fluxes*

Dry biomass was unaffected by irrigation or urine treatments (Figure 5). At the end of the experiment, an average of 57.3 g of cumulative dry matter was harvested from the control chambers, similar to chambers with urine under either standard or optimised irrigation, with 55.9 g and 53.5 g of cumulative dry matter, respectively (Figure 5). With urine applied, the average daily growth rates were 26.8 ± 2.0 (s.e.m) and 30.8 ± 1.3 kg DM ha^{-1} day^{-1} in the optimised and standard irrigation treatments, respectively—while, in the control (without urine and with standard irrigation), the average daily growth rate was 30.9 ± 1.5 kg DM ha^{-1} day^{-1}.

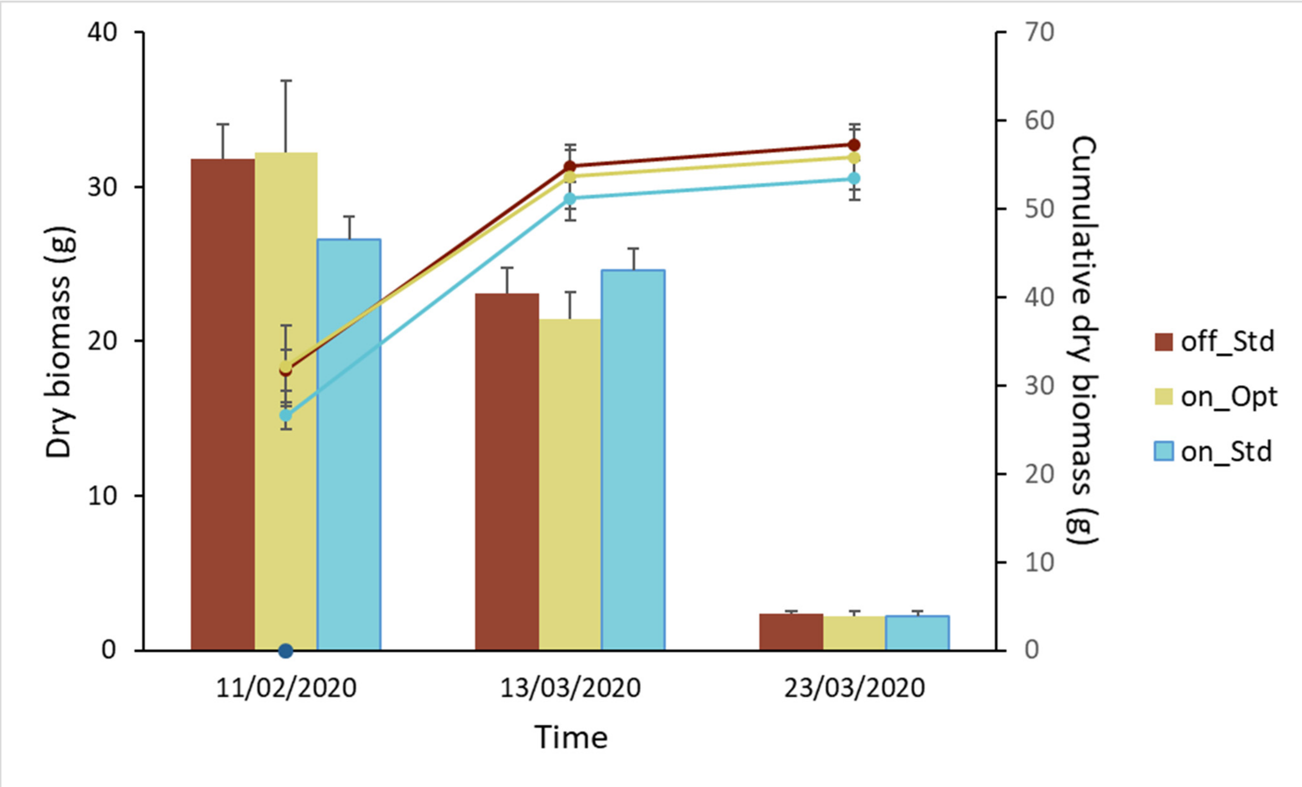

Figure 5. Dry biomass collected three times over the experiment, and cumulative dry biomass, for optimised (Opt) and Standard (Std) irrigation treatments with urine applied (on) or no urine applied (off). Data points are means of four replicates ± S.E.M.

Figure 6 shows that the average daily N_2O-N fluxes increased markedly the day of the urine application, and then gradually declined until the first irrigation event. Until 5 March, N_2O-N flux peaks were observed after every irrigation event (Figure 6). After 5 March, the N_2O fluxes were ≤9.8 ± 1.5 g N ha^{-1} day^{-1} regardless of treatment until the rain simulation (6.7 mm) on 24 March. The more regular irrigation events in the standard irrigation treatment resulted in higher N_2O-N fluxes from the urine applied until 5 March (Figure 6) and especially on the day following the rain event that occurred on 22 February. The peak emissions observed on 23 February 2020 differed significantly ($p < 0.05$) in all treatments and were, on average, equal to 235.4 ± 31.8, 60.3 ± 11.4 and 24.3 ± 19.5 g N ha^{-1} day^{-1} for standard and optimised irrigation with urine, and standard irrigation without urine, respectively. A significantly higher peak of 69.2 ± 32 g N ha^{-1} day^{-1} in the standard irrigation without urine was observed at the end of the experiment after the rain simulation when compared to the urine treatments.

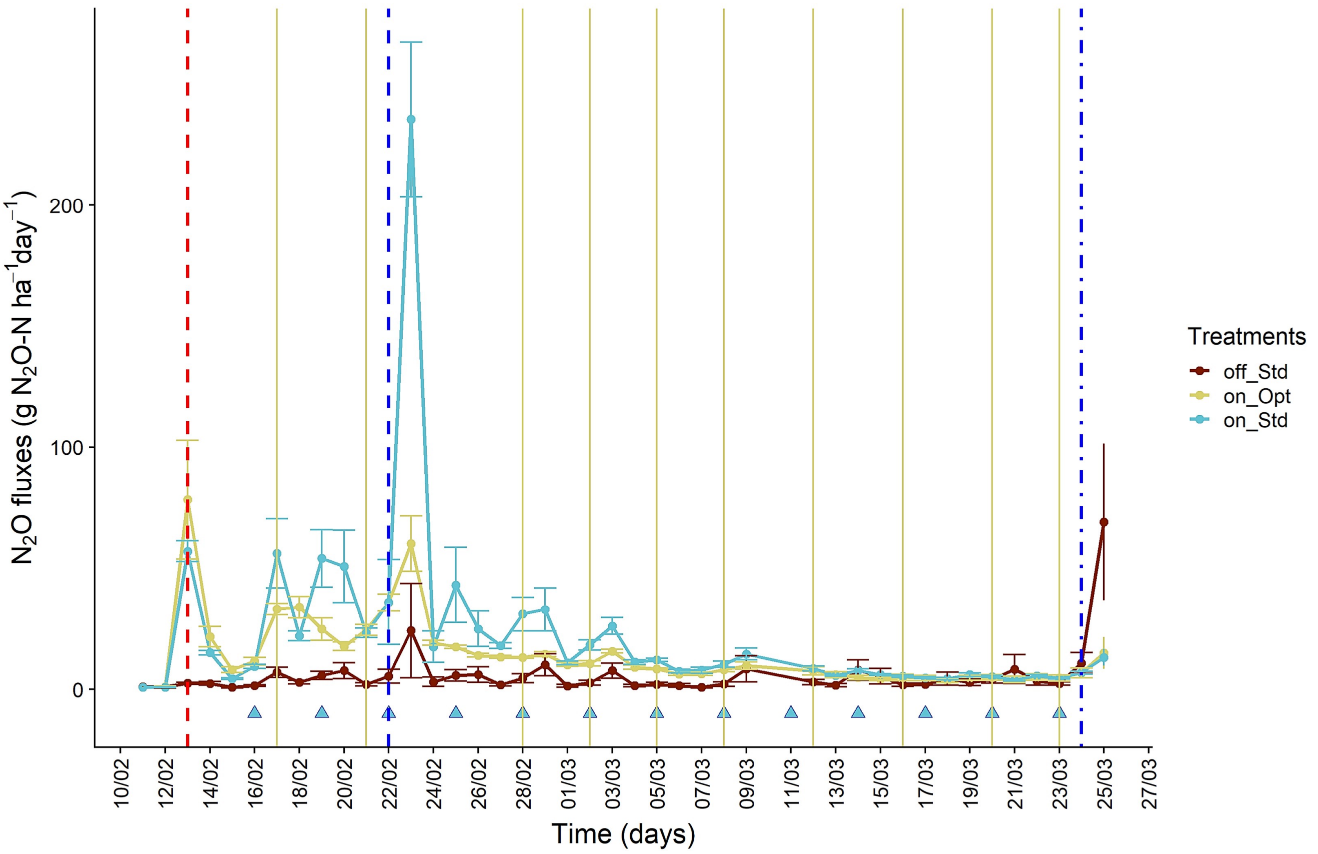

Figure 6. Daily N_2O emissions (g N ha^{-1} day^{-1}) from 11 February 2020 to 25 March 2020. The vertical red dashed line shows timing of urine application, blue triangles and yellow vertical lines denote timing of the standard (Std) and optimised (Opt) irrigation applications, respectively. Error bars = s.e.m, n = 4. Treatment with urine applied (on) or no urine applied (off). The blue vertical dashed lines on 22 February 2020 represent the rain event (12.8 mm) and a rain simulation, respectively.

These daily N_2O-N fluxes determined the trends observed in the cumulative N_2O-N fluxes (Figure 7). Total cumulative losses in the standard and optimised urine treatments differed (p = 0.09) when considering the entire experimental period and were 941 ± 136 g N ha^{-1} and 609 ± 27 g N ha^{-1}, respectively. Over the total period, the non-urine treatment emitted a significantly lower (p = 0.002) total cumulative N_2O-N flux than the urine treatments: 252 ± 100 g N ha^{-1}. Total cumulative mean N_2O-N fluxes under urine resulted in emission factors of 0.05 and 0.1% for the optimised and standard urine irrigation treatments, respectively.

Soil NH_4^+-N and NO_3^--N concentrations pre-urine application were 18.9 ± 1.8 (±s.e.m) and 2.7 ± 0.9 µg N g^{-1}, respectively (Table 1). By 2 March, the NO_3^--N concentrations had increased to equal 219 and 134 µg N g^{-1} for the optimised and standard irrigation treatments with urine, respectively. However, by the end of the experiment, the NO_3^--N concentrations had decreased (p < 0.05, Table 1). The values measured in the additional plots, that received urine, were not significantly different from the values measured in the chambers at the end of the experiment for NH_4^+-N and NO_3^--N concentrations (Table 1), except for the non-urine standard irrigation treatment where the NO_3^--N concentration in the spare chamber (1.3 ± 0.1 µg N g^{-1}) was lower than that within the chambers under similar treatment (7.6 ± 3 µg N g^{-1}). An irrigation effect with urine was observed with higher NO_3^--N concentrations in the optimised compared to the standard irrigation treatment with 98.2 ± 8.3 and 55 ± 10.7 µg N g^{-1}, respectively, at the end of the experiment.

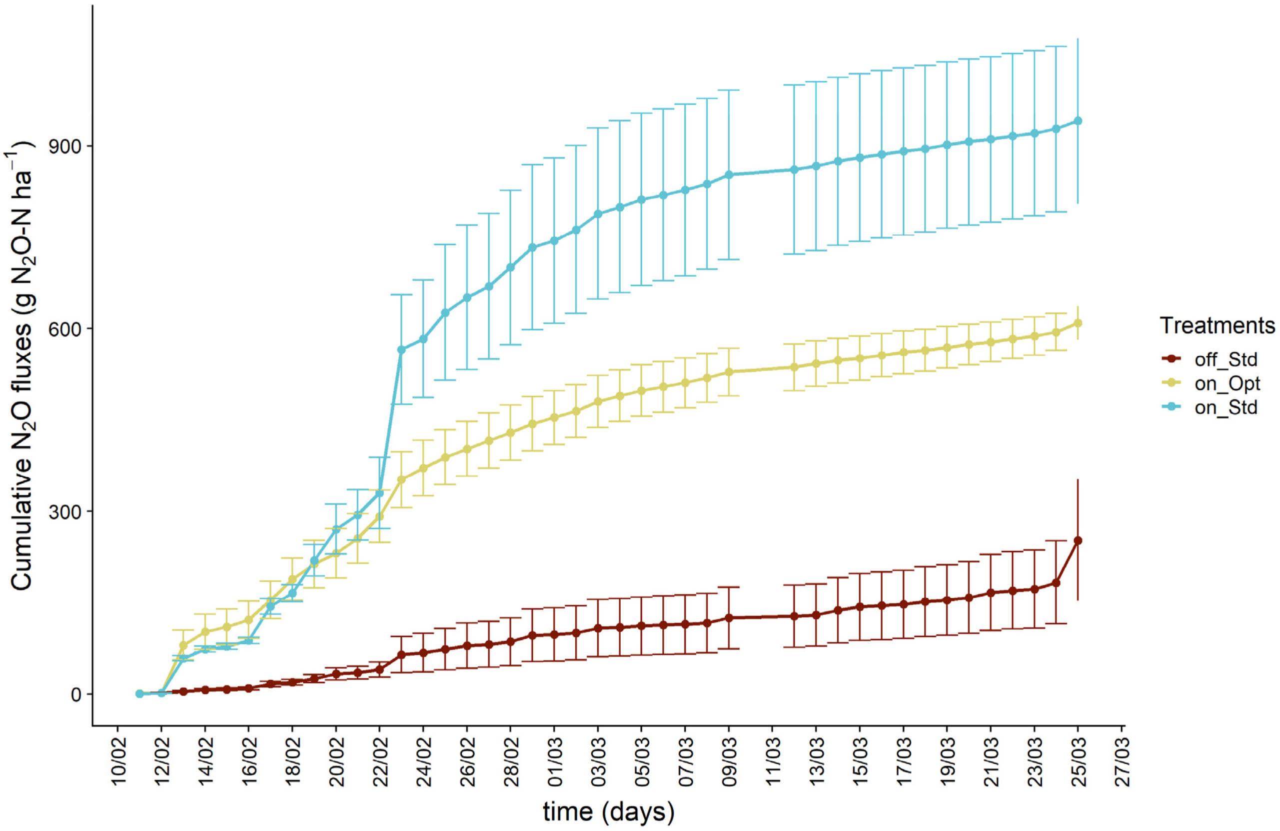

Figure 7. Cumulative N_2O emissions (g N ha^{-1}) from the 11 February 2020 to the 25 March 2020 for the optimised (Opt) and standard (Std) irrigation treatments with urine applied (on) or no urine applied (off). Data points are means of four replicates ± s.e.m.

Under urine application, soil NH_4^+-N concentrations had increased up to 21 February and then declined by the end of the experiment but no effect of irrigation was observed in the additional chambers (p = 0.25) with averages equal to 11.6 ± 5.9 and 4.9 ± 1.4 µg N g^{-1} for optimised and standard irrigation, respectively.

Inorganic-N concentrations in the non-urine control remained low with NH_4^+-N and NO_3^--N concentrations ≤ 14.8 and 7.6 ± 3 µg N g^{-1}, respectively (Table 1). The NO_3^--N concentrations were lower ($p < 0.05$) in the non-urine treatment than under urine at the end of the experiment.

Soil DOC concentrations pre-urine application averaged, across all treatments, 230 ± 27 µg g^{-1} (Table 1). At the end of the experiment, DOC concentrations had decreased in all treatments (≤143 ± 6 µg g^{-1}) when compared to pre-urine values. A treatment effect was also observed (p = 0.048) with the lowest value occurring in the optimised irrigation treatment with urine present (109 ± 5 µg g^{-1}).

4. Discussion

Evapotranspiration and soil temperatures were typical for the summer period but rainfall was below average. The soil inorganic-N concentrations following urine application were characteristic of those previously observed under ruminant urine patches [6,42] where soil NH_4^+-N concentrations are initially high, following urine deposition, but then decline over a two to three week period as soil NO_3^--N concentrations increase, before they too decline as a result of leaching, gaseous N loss or plant N uptake. The concentrations of inorganic-N measured, and which increased significantly following urine application, were sufficient for N transformation pathways that potentially generate N_2O to be present. Nitrification or nitrifier-denitrification will have potentially generated N_2O [14,15] as will the denitrification of NO_3^-, since there was adequate DOC available for denitrification to potentially occur [43,44]. The key determinant responsible for the mechanisms generating the observed N_2O fluxes is the level of O_2 in the soil.

Traditionally, WFPS has been used to describe the potential for a soil to perform nitrification or denitrification [45], with an excess of water leading to hypoxia and ultimately anaerobic conditions where N_2O emissions occur through denitrification. Linn and Doran [45] observed that nitrification dominated at soil WFPS values < 70%. However, at a constant WFPS, the volume fractions of air and water vary as soil bulk densities vary, making comparisons across soils problematic if they have varying bulk densities [18]. The observed WFPS values in the current experiment were generally <75% WFPS under standard irrigation and <65% WFPS under optimised irrigation. Based on the work of Linn and Doran [45], this would be indicative of nitrification dominating N_2O emissions' processes.

An advantage of using soil D_p/D_o values to understand irrigation effects on soil N transformation pathways is that D_p/D_o provides an indication of functional diffusivity within the soil. Previous studies have observed denitrification derived peak N_2O emissions at values ≤ 0.006 [20,23,46] or where soil conditions have commenced becoming anaerobic < 0.02 [47]. Based upon these values, the optimised irrigation treatment, with urine, where soil D_p/D_o values were >0.02, except when irrigation or heavy rainfall (22 February) caused D_p/D_o values to decrease ($\geq$0.01, equal to $\leq$80% FC), was more aerobic than the standardised irrigation treatment. This is consistent with previous research, using intact soil cores, that showed that maintaining D_p/D_o above 0.005–0.01 could improve soil aeration and minimise N_2O emissions [22]. With urine, where D_p/D_o values in the standard irrigation were $\leq$0.02, the soil can be considered as having been hypoxic or anaerobic [47]. Given the relatively high levels of DOC, and plant growth conditions that would have generated further carbon sources such as root exudates, the consumption of O_2 due to respiration could have also resulted in O_2 consumption, further lowering the aerobic nature of the soil.

The differences in D_p/D_o values are consistent with the observed N_2O flux dynamics, between 14 February and 3 March, where fluxes were generally higher under the more anaerobic/hypoxic conditions of the standard irrigation treatment, with urine, than the optimised irrigation treatment, with urine. Urine application also had the expected effect on the N_2O emissions with significantly lower emissions observed in the non-urine treatment. Notably, peak N_2O emissions in the standard irrigation treatment, with urine, occurred when D_p/D_o decreased to be <0.006, as a consequence of the heavy rainfall event on 22 February. However, the response was not as great in the optimised irrigation treatment, with urine, because the heavy rainfall event did not result in such a low value of D_p/D_o due to prior irrigation events generating a buffer in terms of the ability for the soil to take more water without dropping to such a relatively low, and significant, D_p/D_o value. The D_p/D_o values at this time are informative as to the soils ability to supply O_2, and thus their relative aerobic/anaerobic status. The WFPS values at this time, which were ca. 64–68%, are not as informative. The ability of the optimised irrigation treatment to buffer against prolonged or lower values of D_p/D_o explains the generally lower daily N_2O fluxes observed in the optimised irrigation treatment, following irrigation events, between 14 February and 3 March, and hence the difference in cumulative N_2O fluxes and the emission factors. Similar legacy effects of irrigation were also observed by Mumford et al. [28]. Another significant N_2O flux event occurred under urine, regardless of irrigation treatment, on 13 February following urine application and when D_p/D_o values were >0.01. This is most likely due to the soil O_2 concentration declining due to the combination of abiotic generation of ammonia and the biotic hydrolysis of carbonate ions generating carbon dioxide, following the hydrolysis of urea [48], and soil wet up enhancing soil respiration.

As noted above, several mechanisms are likely to be responsible for N_2O generation. For denitrification to occur, conditions must be fully anaerobic. The fact that the N_2O flux spiked upwards after D_p/D_o values fell below 0.006 (standard irrigation with urine 23 February; nil-urine 24 March) indicates that the potential for denitrification was rarely met, despite NO_3^- and DOC being available, due to conditions not being fully anaerobic. Instead, it is likely that the bulk of the N_2O resulted from nitrification or nitrifier-denitrification. Under hypoxic conditions, ammonia oxidising bacteria (AOB), but not archaea, may perform nitrifier-denitrification, where nitrite is reduced to nitric oxide and then N_2O [14]. Soil D_p/D_o values ≤ 0.02 indicate that the soil may have been hypoxic [24], but measures of soil O_2 concentrations are needed to verify such assumptions. Nitrous oxide may also have formed following abiotic reactions of nitric oxide, hydroxylamine and nitrite, either with each other or other components of the soil media [14]. The decline in soil NH_4^+-N concentrations over time supports the occurrence of nitrification, while the decline in soil NO_3^--N concentrations between 2 and 24 March could be due to leaching from the soil sample depth, or plant N uptake if conditions were not conducive for denitrification.

Daily dry matter production in all treatments was lower than the typical summer growth rates for a fertilised irrigated pasture at Lincoln University (67 kg DM ha^{-1} day^{-1}, [49]). This indicates that the conditions were not as conducive for pasture growth, potentially due to lower soil fertility or cultivar differences. It is worth noting, however, that there was a lack of significant difference in dry matter production between the standard and optimised irrigation treatments, demonstrating that irrigation can be manipulated to mitigate N_2O emissions without reducing pasture production. Based on this result, modelling of model soil water dynamics, associated gas diffusivity, and pasture production are warranted to determine the sensitivity of pasture production to irrigation when managed according to the soil's aeration status as defined by D_p/D_o. Soil D_p/D_o is readily modelled using the same parameters required to calculate WFPS. However, as this study shows, D_p/D_o can be more informative with respect to the soils' aeration status, from which the relative prevalence of denitrification or nitrification processes can be inferred.

5. Conclusions

Here, we demonstrate that, in principle, pasture irrigation frequency can be manipulated based on using soil relative gas diffusivity as a decision-making tool for irrigation. Irrigating pasture soil when soil relative gas diffusivity increased to reach 0.033, but only providing sufficient irrigation to reduce this value to 0.01 resulted in the soil being more aerobic (higher diffusivity). As a consequence, significant rainfall, and the irrigation events themselves, resulted in lower daily N_2O emissions and, as a consequence, cumulative N_2O emissions were also reduced. Pasture yields were unaffected by irrigation treatments. To determine the sensitivity of using relative soil gas diffusivity, further modelling studies integrating pasture physiology, yield, soil moisture dynamics and gas diffusivity are required.

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