Increasing soil pH reduces fertiliser derived N_2O emissions in intensively managed temperate grassland

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ABSTRACT

Soil pH is generally considered a master variable, controlling a wide range of physical, chemical and biological properties, including a significant effect on microbial processes responsible for production and consumption of nitrous oxide (N_2O), a potent greenhouse gas. Evidence of this pH impact on microbial denitrification mainly stems from observations in controlled laboratory experiments, while the results from field studies are mainly short-term, more variable and circumstantial. Soil pH is also one of the main factors controlling the availability of soil phosphorous (P), which has been also linked with N_2O emissions. Here, we utilised an existing intensive grassland liming and P trial to investigate the effect of longer-term lime and P management and their interaction on N_2O emissions and grassland productivity. The treatment plots were subject to different liming and P fertilisation strategies over 8 years and had a wide gradient of soil pH (5.1–6.9) and extractable P (2.3–8.3 mg kg^{-1}). All plots received a total of 300 kg ha^{-1} of fertiliser nitrogen (N), applied in 8 splits across the growing season. N_2O emissions, soil mineral N and grass yields were measured over 12-month period. We found a negative linear relationship between soil pH and cumulative N_2O emissions, with a decrease in N_2O emissions up to 39 % from limed plots compared to the unlimed control. The same effect was observed in relation to N_2O emission factors and yield-scaled N_2O emissions. Extractable soil P content had positive effect on yields, but no effect of P or P and pH interaction was observed in terms of direct N_2O emissions or yield-scaled N_2O emissions. We estimated that the increase in soil pH of grasslands in Ireland over the last 12 years potentially reduced national N_2O emissions by 95 Gg CO_2-eq yr^{-1}, with potential for a further reduction by up to 254 Gg CO_2-eq yr^{-1} if all the remaining acidic soils are brought up to optimal pH.

1. Introduction

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) and one of the major contributors to global warming and stratospheric ozone depletion (Stocker et al., 2013). In Ireland, agriculture is the single largest contributor to overall GHG emissions and it contributes to more than 90 % of the total N_2O emissions (Duffy et al., 2020). As a result, N_2O is a key target for GHG mitigation in agricultural systems. The main sources of N_2O from agricultural soils are direct or indirect emissions as a consequence of increased fertilisation with synthetic N or manures. Global increases in N fertiliser use is also one of the main causes of soil acidification, which is a major problem in agricultural production worldwide (Tian and Niu, 2015). Keeping soil pH at the optimum level to maintain high crop productivity in agricultural systems is usually accomplished by applying ground limestone, dolomite or other calcareous materials to

neutralise soil acidity. The extent of increase in soil pH by liming depends on the amounts of applied lime and buffer capacity of soil. The benefits of liming as an agronomic measure to ameliorate acidic soils have been known for centuries. Liming has a positive effect on the availability of plant nutrients, microbial activity and stability of soil aggregates, and therefore has a strong influence on soil fertility and crop productivity in agroecosystems (Holland et al., 2018).

Soil pH is generally considered a master variable, as it pervasively controls a wide range of physical, chemical and biological properties of soil (Rengel, 2002; Essington, 2015). Furthermore, there is increasing evidence that pH has a significant effect on microbial processes responsible for production and consumption of N_2O in soils. This evidence mainly originates from well documented observations in laboratory denitrification studies that the production of N_2O relative to dinitrogen (N_2) is higher in acidic soils (Šimek and Cooper, 2002).

Recent studies demonstrated that the $N_2O/(N_2O + N_2)$ ratio of denitrification in agricultural soils is strongly controlled by pH, where a linear decrease in $N_2O/(N_2O + N_2)$ product ratio with increasing soil pH was reported (Zaman et al., 2007; Liu et al., 2010; Raut et al., 2012; Qu et al., 2014; Russenes et al., 2016). While the exact mechanisms of pH effect on $N_2O/(N_2O + N_2)$ ratio are not fully understood, these studies hypothesised that the synthesis of the enzyme N_2O-reductase at the cellular level was hindered at low pH levels. An alternative explanation is that low soil pH indirectly effects the $N_2O/(N_2O + N_2)$ ratio in soil due to shift in the composition of denitrifying communities (Čuhel and Šimek, 2011). Regardless of the mechanism at work, N_2O-reductase is a critical enzyme of the microbial denitrification pathway, responsible for the final step of denitrification, where N_2O is reduced to inert N_2. N_2O-reductase is the only known sink for N_2O in terrestrial ecosystems (Thomson et al., 2012) and therefore has a significant N_2O mitigation potential when fully expressed and functional.

Given the significance of N_2O as one of the major GHGs and the increasing acidification of agricultural soils due to increased application of N-fertilizers and manures in intensive agricultural systems, more attention should be given to soil pH amelioration accomplished by liming in efforts to mitigate N_2O emissions. Of the few attempts that have been made to investigate the effect of liming and consequent increase in soil pH on N_2O emissions in field studies, most of them reported variable, sometimes conflicting findings (Qu et al., 2014). What is particularly lacking is more N_2O measurements from long-term liming experiments, where the replicated lime treatments and acidic control plots are uniformly managed over time within the same site and soil type. Such studies could shed more light on the influence of lime/soil pH by reducing variability in agronomic treatments caused by other factors, which could potentially mask the effect of soil pH on N_2O emissions.

Recently soil phosphorous (P) has also been linked with N_2O emissions, with some studies reporting the relationship between soil P and N_2O to be positive (Mori et al., 2013; Wei et al., 2017) and negative (O'Neill et al., 2020). Suggested mechanisms between soil P and N_2O emissions are increased soil nitrogen transformations such as mineralisation and nitrification (Mehnaz et al., 2019) and/or influencing the soil microbial community (Wei et al., 2017). Under low soil P conditions fungi, such as arbuscular mycorrhizal fungi (AMF) have been observed to be more abundant in permanent grassland soils (Randall et al., 2019). Although AMF can reduce N_2O emissions by symbiotically aiding plant N-uptake (Storer et al., 2018; Teutscherova et al., 2019), soil fungi are considered to be an important source of N_2O in grassland soils due to their lack of the nitrous oxide reductase enzyme (Maeda et al., 2015).

The main objective of this study was to stringently test the effect of soil pH under different liming strategies on N_2O emissions from intensively managed grassland and thereby assess the potential of liming as a strategy for reduction of N_2O emissions from soils. In addition to this objective, we also investigated the effects of lime in combination with P application and their interaction on N_2O emissions and grassland productivity. This is of considerable interest in agricultural systems, as liming could be a cost-effective method to achieve significant reduction in N_2O emissions, while adequate P supply can also have an impact on the on the composition of microbial community structure in terms of N_2O emissions or indirectly alleviate N_2O emission by increasing N uptake by increased crop yields in combination with liming. In order to achieve these objectives, we carried out 12-month experiment on an ongoing long-term grassland trial set in a humid temperate climate, in which different liming and phosphorus management strategies had been imposed for the last 8 years.

2. Materials and methods

2.1. Experimental site

The study was carried out at the Teagasc research farm in Johnstown Castle, Ireland (52°17′47″N 6°30′25″W; 63 m above sea level) for 12 months, between February 2019 and February 2020. Here, a liming and phosphorus field trial under perennial ryegrass (*Lolium perenne*) was established in 2011, with the aim to investigate lime, P and N dynamics in intensively managed grassland (Sheil et al., 2015). The soil is classified as moderately drained brown earth (Stagnic Cambisol, IUSS-WRB (2015)), with the pH of 5.2, total carbon content of 3.2 %, total N content of 0.3 %, bulk density 1.18 g cm^{-3} and a loamy texture with sand, silt, and clay contents of 49 %, 29 % and 22 %, respectively. Previous N_2O research has identified high N_2O emissions from this soil after application of calcium ammonium nitrate (CAN) fertiliser (Harty et al., 2016). Johnstown Castle is situated in a temperate maritime climate, allowing for pasture-based dairy and beef production with a grazing season of up to 10 months per annum. The mean annual temperature at the site is 10.4 °C and the mean annual precipitation is 1037 mm (1981–2010 reference period).

The experimental plots, 1.5×6 m each, were set in a factorial design with four rates of lime and four rates of P in a randomized block design, with four replicates per treatment. By applying different liming and phosphorus management strategies since the establishment of the trial, a wide pH and P gradient was achieved between treatments (Fox et al., 2015). Within this experiment, we selected two P treatments – P0 and P40, which have been receiving 0 and 40 kg P ha^{-1} yr^{-1}, respectively, since 2011. The average extractable P content (Morgan's extractant) for P0 and P40 was 3.0 mg kg^{-1} and 6.3 mg kg^{-1}, respectively, and corresponds to P index 1 (very low) and 3 (optimal), respectively. Each of the two P treatments had the following lime sub-treatments:

  i) C, the unlimed control
 ii) L1, where 5 t ha^{-1} lime was applied in 2011
iii) L2, 5 t ha^{-1} lime was applied in 2014
 iv) L3, 5 t ha^{-1} lime applied in 2011 and 2014

in order to further increase the pH range between lime treatments, ground limestone was applied at the rate of 1.5 t ha^{-1} and 5 t ha^{-1} to L2 and L3, respectively, a month before the commencement of the experiment. The grass on the site was desiccated and reseeded using no-till seed drill in the previous year to maintain uniform sward composition across the trial. All treatments received a total of 300 kg ha^{-1} of N in a form of calcium ammonium nitrate with sulfur (Sulfa CAN – 26 % N, 5% S), split in 8 applications after each harvest in order to mimic a typical grazing fertiliser application regime over the growing season (February-October 2019). Triple superphosphate (16 % P) was applied in March at the rate of 40 kg P ha^{-1} in P40 treatment plots, while all plots received 250 kg ha^{-1} of fertiliser K (MOP, 50 % K), applied in 2 splits (March and July).

2.2. Soil and weather measurements

Soil temperature and volumetric moisture content from a depth of $0-5$ cm were measured per block on each gas sampling date using the HH2 moisture meter equipped with the WET2 sensor probe (Delta-T Devices Ltd, UK). Daily and hourly meteorological data (temperature, precipitation, atmospheric pressure) were collected from the Met Éireann automatic weather station located in the vicinity of the field site. Soil samples were taken once during each fertilisation-harvest cycle, usually 2–3 weeks after N fertiliser application. Between 5 and 10 soil cores to a depth of 10 cm were taken by soil auger, pooled and homogenised into one composite sample per each experimental plot. Soil samples were sieved through 4 mm mesh and extracted for mineral N analysis on the day of sampling after shaking for 1 h in 2 M KCl (Carter, 1993). The filtered soil extracts were kept in the cold room (4 °C) until analysis. NH_4^+ and NO_3^- concentrations were analysed colorimetrically using the Aquakem 600 discrete analyser (Thermo Fisher Scientific, Waltham, MA, USA) and reported on a dry weight soil basis. The remaining soil was dried and analysed for pH in a 1:5 suspension of soil in water (ISO, 10390:, 2005). Macro- and micro-nutrient status in

soil samples was determined by Mehlich-3 extraction (Mehlich, 1984) followed by analysis using Agilent 5100 ICP-OES spectrometer (Agilent Technologies, Mulgrave, Australia). Soil inorganic P was determined using Morgan's extractant (Morgan, 1941) followed by analysis on Lachat QC8500 Quikchem FIA System (Hach Company, Loveland, CO, USA). Undisturbed soil cores were taken for bulk density estimation (ISO, 11272:, 2017) at the mid-point of the experiment (July 2019) and used to calculate water filled pore space (WFPS) from the volumetric soil moisture content.

2.3. Herbage measurements

Herbage was harvested 7 times during the growing season (March-October), approximately one month after each N fertiliser application. A total of 8 harvests were planned initially, but the last harvest in November was not possible due to unfavourable weather conditions and a lack of grass growth. A 6 m long x 1.25 m wide strip from each treatment plot was harvested to 4 cm above ground level using a rotary mower (Etesia UK Ltd, Warick, UK). Fresh weights per each plot were measured on site and 100 g grab sub-samples were taken to determine dry matter (DM) content. Herbage samples were dried for 5–7 days in an oven with forced air circulation at 70 °C. Dry weights were recorded and used to calculate DM yields.

2.4. N_2O flux measurements

A static chamber method (de Klein and Harvey, 2015) was used to measure N_2O fluxes. The chamber design, deployment time and gas sampling technique were carried out following the slightly modified methodology previously described by Harty et al. (2016). In brief, stainless steel frames (40 × 40 x 10 cm) were permanently installed in the plots to a depth of ≥5 cm, removed only briefly for the duration of grass harvest. The frames had open grooves on the top, which were lined with neoprene to ensure tight seals between the frames and the corresponding lids (10 cm in height). The seal between the frame and the lid was further tightened by placing 5 L plastic drums filled with gravel and water on the top of the lid during chamber deployment. Headspace samples were taken at 0, 20 and 40 min after deployment with a 20 mL polypropylene syringe (B. Braun, Melsungen, Germany). The air within the headspace was mixed by pumping the syringe plunger 3 times, after which a 10 mL headspace sample was transferred to 7 mL pre-evacuated glass vials with double-wadded PTFE/silicone septa (Labco ltd, Lampeter, UK) and kept over-pressurised prior to analysis. Frequent N_2O measurements were carried out over 12 months in order to capture the spatial and temporal variability of N_2O fluxes across the experimental period. Gas sampling was carried out four times per week for two weeks after each fertiliser application and reduced to two times per week until the next fertiliser application. The frequency of sampling was reduced to a fortnightly period during winter once N_2O fluxes returned to the background levels. Sampling took place between 9 a.m. and 12 p.m. on each occasion, as this period was reported to represent the average daily flux (Reeves and Wang, 2015).

2.5. Gas analysis and calculations of N_2O emissions

Gas samples were analysed by gas chromatography (GC), using a Bruker Scion 456 GC coupled with PAL COMBI-xt auto–sampler (CTC Analytics AG, Switzerland) and equipped with a 63Ni electron capture detector (ECD). The operating temperature of the ECD was 300 °C and argon was used as a carrier gas. N_2O fluxes were calculated from the change in headspace concentration over the deployment period, according to Eq. 1:

$$F_{N_2O} = \frac{\Delta N_2O}{\Delta t} \times \frac{M \times P}{R \times T} \times \frac{V}{A} \tag{1}$$

Where F_{N_2O} is N_2O flux (µg N_2O-N m^{-2} min^{-1}), $\Delta N_2O/ \Delta t$ is the linear rate of N_2O accumulation in the chamber headspace (ppm$_v$ min^{-1}), M is the molecular weight of N in N_2O (28 g mol^{-1}), P is atmospheric pressure (Pa), T is temperature (K) at the sampling time, R is the ideal gas constant (8.314 J K^{-1} mol^{-1}), V is volume of the chamber headspace (m^3) and A is the area covered by the chamber (m^2). The results obtained were upscaled to represent the daily N_2O flux in g N_2O-N ha^{-1} day^{-1}. Cumulative fluxes for the experimental period were calculated by linear interpolation between sampling dates (Smith and Dobbie, 2001). The emission factors (EFs) were calculated for each treatment according to Eq. 2.

$$EF\ (\%) = \frac{Cum\ N_2O\ (treatment) - Cum\ N_2O\ (background)}{N\ applied} \times 100 \tag{2}$$

Since our trial did not have zero N control plots, the background values for cumulative N_2O emissions were obtained from the grassland trial at the same site and the same time period as our trial, with the similar experimental design and the average soil pH of 5.6 (n = 5).

Yield-scaled N_2O emissions were calculated for each treatment replicate by dividing the cumulative N_2O emissions by total dry matter yield of harvested grass (Venterea et al., 2011) after 7 harvests. Since the 8th harvest after last fertilisation in October was not possible, dry matter yields of the first harvest next year, shortly after conclusion of our experiment, were added to total yields for yield-scaled N_2O emission calculation to take into account grass N uptake and N_2O emissions following the last N fertiliser application and residual soil N.

2.6. Statistical analysis

SPSS ver. 24 (IBM Corp, USA) was used for all statistical analyses in this study and all the tests were performed at the 95 % confidence interval. Cumulative N_2O emissions, EFs, yield-scaled N_2O emissions and grass yields were calculated for each individual treatment replicate, followed by calculation of arithmetic means and variances. Significant treatment effects for cumulative N_2O fluxes, NH_4^+, NO_3^- and grass yield were determined by two-way ANOVA, with lime and P as independent variables (n = 4), followed by Tukey's post hoc test. Levene's test showed that none of the dependent variables violated the homogeneity of variance assumption required for an ANOVA. To further investigate the relationship between soil pH and cumulative N_2O emissions, linear regression analysis was carried out using average soil pH values of each individual treatment plot and the cumulative N_2O fluxes of corresponding chambers across the measurement period.

3. Results

3.1. Soil chemical properties

Most of the soil chemical properties evaluated for treatments in our study were significantly influenced by long-term lime management and the resulting increase in soil pH (Table 1). There was a significant increase in pH, extractable Ca and P with the increasing amount of lime applied, while the concentrations of extractable Al, Fe, Mn, S and Zn decreased. Extractable K, Mg, Na, Co and Cu contents were not different between lime treatments. Monthly soil pH values were different between lime treatments (p < 0.001) across the duration of the experiment. The initial soil pH values dropped up to 0.3 units on average after basal fertiliser application in March, but increased gradually for the remainder of the experiment and fluctuated only slightly (± 0.1) on average (Supplementary Fig. S1). Average pH values for lime sub-treatments were almost equal between P0 and P40.

Soil mineral N ranged from 0.3 to 29.6 mg kg^{-1} and 0.3–24 mg kg^{-1} for NH_4^+ and NO3-, respectively (Fig. 1). Mineral N concentrations were mainly dependent on the timing of soil sampling, which varied between 2–4 weeks after fertiliser application. Both NH_4^+ and NO3- content declined below 10 mg kg^{-1} 3–4 weeks after fertilisation, with the

Table 1

Changes in the main soil chemical properties of treatments in our study as a result of long-term liming and P application (n = 4, SE shown in brackets).

P treatment	P0				P40			
Lime treatment	C	L1	L2	L3	C	L1	L2	L3
Soil chemical properties								
pH (H$_2$O)	5.0 (0.07)[a]	5.4 (0.08)[b]	6.2 (0.05)[c]	6.9 (0.02)[d]	5.1 (0.06)[a]	5.5 (0.04)[b]	6.2 (0.09)[c]	6.9 (0.06)[d]
SOC (%)	2.2 (0.1)[a]	2.3 (0.1)[a]	2.3 (0.1)[a]	2.3 (0.2)[a]	2.1 (0.1)[a]	2.1 (0.1)[a]	2.2 (0.0)[a]	2.3 (0.1)[a]
Al (mg kg^{-1})	867.1 (28)[c]	757.5 (27)[bc]	661.2 (45)[ab]	609.0 (7)[a]	860.5 (20)[c]	782.2 (18)[bc]	666.4 (13)[ab]	572.2 (51)[a]
Ca (mg kg^{-1})	816.3 (100)[a]	1158.7 (83)[a]	1897.7 (96)[b]	2983.6 (97)[c]	907.0 (40)[a]	1300.7 (31)[a]	2115.1 (138)[b]	2702.3 (189)[c]
Co (mg kg^{-1})	0.2 (0.0)[a]	0.1 (0.0)[a]	0.1 (0.0)[a]	0.1 (0.0)[a]	0.2 (0.0)[a]	0.1 (0.0)[a]	0.1 (0.0)[a]	0.1 (0.0)[a]
Cu (mg kg^{-1})	4.3 (0.5)[a]	4.5 (0.4)[a]	4.5 (0.4)[a]	4.3 (0.3)[a]	4.2 (0.4)[a]	4.6 (0.5)[a]	4.6 (0.4)[a]	4.7 (0.2)[a]
Fe (mg kg^{-1})	306.7 (10)[e]	256.2 (7)[cd]	216.6 (10)[bc]	173.7 (2)[a]	319.4 (8)[e]	281.1 (4)[de]	230.7 (14)[bc]	201.3 (5)[ab]
K (mg kg^{-1})	109.3 (7)[a]	83.5 (8)[a]	92.2 (12)[a]	106.1 (15)[a]	107.0 (8)[a]	103.8 (12)[a]	124.7 (24)[a]	89.3 (6)[a]
Mg (mg kg^{-1})	94.4 (11)[a]	82.8 (7)[a]	93.2 (18)[a]	73.6 (6)[a]	76.1 (6)[a]	79.9 (8)[a]	88.9 (15)[a]	70.7 (6)[a]
Mn (mg kg^{-1})	53.2 (3)[bc]	51.9 (3)[bc]	43.6 (2)[ab]	40.8 (2)[a]	55.6 (3)[c]	50.4 (2)[ac]	40.7 (1)[a]	46.7 (2)[ac]
Na (mg kg^{-1})	14.4 (1.5)[a]	14.8 (1.9)[a]	17.2 (1.9)[a]	17.4 (0.3)[a]	12.6 (1.3)[a]	15.2 (1.6)[a]	14.7 (1.6)[a]	16.4 (1.0)[a]
P (mg kg^{-1})	2.3 (0.1)[a]	2.4 (0.3)[a]	3.7 (0.5)[ab]	3.6 (0.2)[ab]	4.3 (0.1)[ab]	5.0 (0.5)[b]	7.4 (0.6)[c]	8.3 (0.9)[c]
S (mg kg^{-1})	37.3 (3.3)[b]	27.5 (5.0)[ab]	19.6 (1.3)[a]	20.9 (1.2)[a]	23.8 (1.4)[ab]	26.6 (4.2)[ab]	20.8 (1.6)[a]	25.1 (4.3)[ab]
Zn (mg kg^{-1})	2.3 (0.3)[c]	1.6 (0.2)[ac]	1.4 (0.3)[ac]	0.8 (0.1)[a]	1.9 (0.1)[bc]	1.7 (0.1)[ac]	1.3 (0.2)[ab]	1.2 (0.1)[ab]

Values with different letters (a–d) within a row indicate significant differences between treatments (p < 0.05).
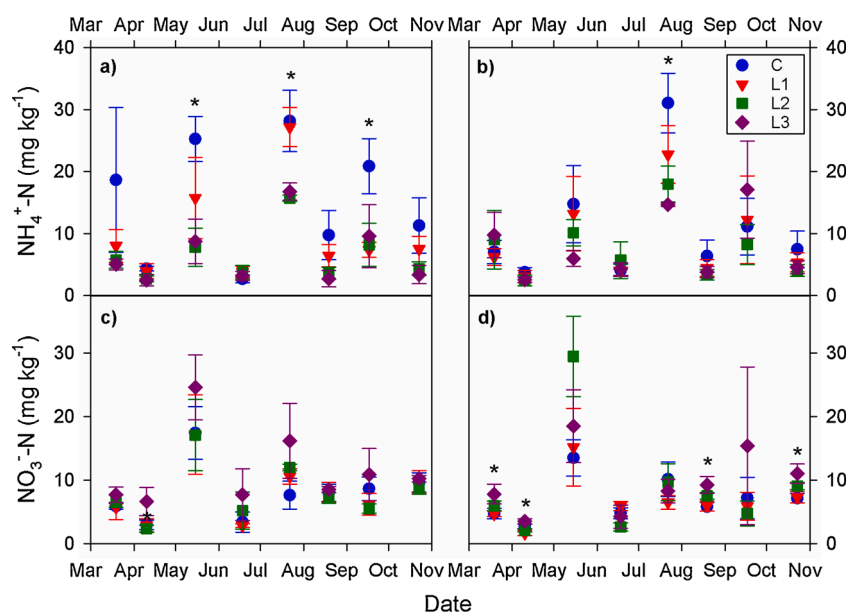
Fig. 1. Soil mineral N content for lime treatments at sampling dates; NH$_4^+$ content for **a)** P0 and **b)** P40; NO$_3^-$ content for **c)** P0 and **d)** P40. Bars represent standard errors (n = 4). Asterisks indicate significant differences (p < 0.05).

exception of predominantly dry months. NH$_4^+$ content was higher in C and decreasing in the order from lowest to highest lime treatment on most of sampling occasions, while the opposite trend was noted in case of NO$_3$- content (Fig. 1). P treatment had no effect on soil mineral N content, although the differences in NH$_4^+$ content were more pronounced between lime treatments in P0 and NO$_3$- in P40.

3.2. Temporal N$_2$O emissions

All treatments demonstrated a similar N$_2$O emission dynamic, characterised by transient emission peaks shortly after N fertilisation events when the soil moisture was high (Fig. 2). The highest N$_2$O fluxes for all treatments were observed between the spring and early summer period (March-June). All emission peaks during this period coincided with high WFPS, most notably between March and early May, when WFPS was constantly within the 70–80 % range. The maximum WFPS observed during the study period was 83 %.

The highest daily N$_2$O fluxes in all treatments happened in May, shortly after application of 50 kg N ha^{-1}, when particularly high average N$_2$O fluxes up to 1164 g N$_2$O-N ha^{-1} day^{-1} were recorded. A notable

response to N fertilisation in terms of N$_2$O emission peaks was recorded on 7 out of 8 fertilisation events. The only exception is July, the driest month of the study period. N$_2$O emissions in July remained low throughout the month, increasing up to 7 g N$_2$O-N ha^{-1} after occasional light rainfall events.

The lime treatment effect was notable irrespective of P treatment, with C plots having the highest fluxes when the N$_2$O emission peaks occurred on most occasions. This was especially evident in the first six months (March-August) of the trial (excluding July), where the daily N$_2$O fluxes were usually in the order of C > L1 > L2 > L3. The fluxes were more variable and less pronounced between lime treatments for the remainder of the research period (September-February).

3.3. Cumulative N$_2$O emissions

The cumulative N$_2$O emissions ranged from 4 to 6.6 kg N$_2$O-N ha^{-1} for L3 and C, respectively (Table 2). The effect of liming was significant (p < 0.05) but soil P and the interaction between soil pH and P were not significant. Cumulative N$_2$O emissions decreased with increasing soil pH in the order of C > L1 > L2 > L3 (Fig. 3). This order was highly
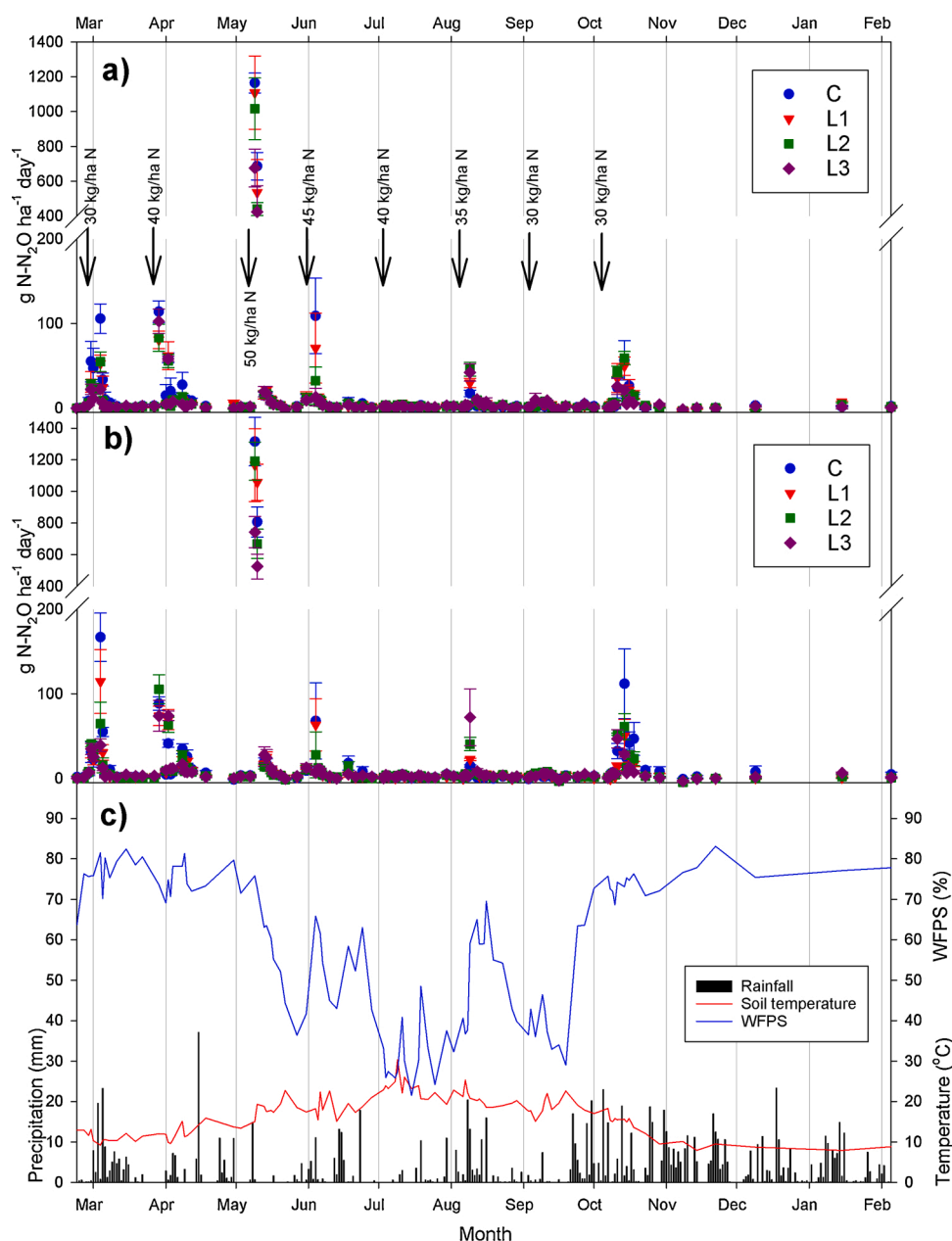
Fig. 2. a) P40 plots – average daily N$_2$O emissions for different lime treatments, **b)** P0 plots – average daily N$_2$O emissions for different lime treatments, **c)** Water-filled pore space, soil temperature and precipitation. Bars represent standard errors (n = 4).

pronounced in the first 4 fertilisation-harvest periods (March-June). Extremely high N$_2$O fluxes in May (Fig. 2) account for 32–39 % of the total emissions during the observed period. We found a negative linear relationship (p < 0.001) between soil pH and cumulative N$_2$O emissions when the average soil pH value was plotted against the corresponding cumulative N$_2$O emissions for each treatment plot (Fig. 4).

The N$_2$O EFs for the observed period ranged from 1.2 to 2% (Table 2). Similar to the cumulative N$_2$O emissions, the soil pH effect was significant (p < 0.05) and the EFs decreased in the same order.

3.4. Grass yield and yield-scaled N$_2$O emission

Grass yields and average dry matter content are shown in Table 2. P treatment had a significant effect on DM yield production (P < 0.01), with yields from P40 plots being higher compared to P0. Lime did not have an overall effect on yield, but the differences were found within P40 treatment. Lime and P interaction was not significant. No

differences were found in terms of average dry matter content of herbage across lime and P treatments.

Yield-scaled N$_2$O emissions ranged between 314.6 and 536.6 g N$_2$O-N t DM yield^{-1} (Table 2). Liming had a significant effect (p < 0.01) on yield-scaled N$_2$O emissions, with C and L1 being higher than L3. No differences were found in relation to soil P content.

4. Discussion

4.1. N$_2$O emissions in relation to main soil physico-chemical properties

Temporal N$_2$O emission patterns across the experimental period resembled each other irrespective of the treatment, characterised by transient emission peaks shortly after N fertilisation events. The highest N$_2$O emission peaks shortly after fertilisation occurred when WFPS was between 60–80%, indicating that denitrification was the dominant source of N$_2$O (Skiba and Smith, 2000; Liu et al., 2007). In contrast, little

Table 2
Average values for dry matter content and grass yields, cumulative N_2O emissions, N_2O emission factors and yield-scaled N_2O emissions (n = 4, SE shown in brackets).
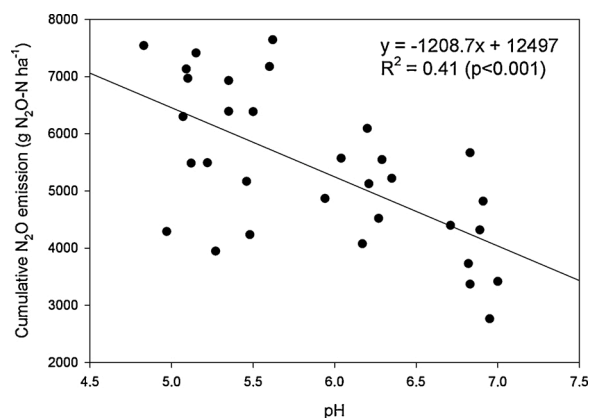
Lime treatments*	P treatments**	
	P0	P40
Herbage dry matter content (%)		
C	20.6 (0.4)[a]	20.3 (0.3)[a]
L1	20.3 (0.4)[a]	20.0 (0.2)[a]
L2	20.4 (0.2)[a]	20.2 (0.2)[a]
L3	20.3 (0.0)[a]	20.0 (0.2)[a]
Grass yield (t DM ha^{-1})		
C	[y]11.0 (0.3)[a]	[z]12.3 (0.2)[a]
L1	[y]11.0 (0.2)[a]	[z]11.9 (0.1)[ab]
L2	[y]10.7 (0.1)[a]	[z]12.1 (0.2)[a]
L3	[y]10.6 (0.2)[a]	[z]11.5 (0.2)[b]
Cumulative N_2O emissions (g N_2O-N ha^{-1} yr^{-1})		
C	6385.4 (752)[a]	6628.7 (384)[a]
L1	5751.2 (693)[ab]	5857.4 (741)[a]
L2	5080.5 (350)[ab]	5175.1 (338)[ab]
L3	4058.8 (321)[b]	4061.2 (632)[b]
N_2O emission factor (%)		
C	1.9 (0.3)[a]	2.0 (0.1)[a]
L1	1.7 (0.2)[ab]	1.8 (0.2)[a]
L2	1.5 (0.1)[ab]	1.5 (0.1)[ab]
L3	1.2 (0.1)[b]	1.2 (0.2)[b]
Yield-scaled N_2O emission (g N_2O-N t DM yield^{-1})		
C	536.6 (67)[a]	495.0 (36)[a]
L1	479.9 (57)[ab]	445.1 (58)[ab]
L2	430.0 (29)[ab]	381.2 (21)[ab]
L3	347.3 (29)[b]	314.6 (47)[b]

* Values with different letters (a,b) within a column indicate significant differences between lime treatments (p < 0.05).

** For grass yields, values with different letters (y,z) within a row indicate significant differences between P treatments (p < 0.05).

or no N_2O emission response to N fertilisation was observed during the driest periods of the experiment (July and September). The soil moisture conditions in these relatively dry months were favourable for nitrification (WFPS around 40 %), but no significant response was recorded in terms of N_2O emissions on occasional dry-rewetting periods during 4 weeks post-fertilisation. Lower emissions in dry periods when CAN was applied were previously reported in temperate grasslands of Ireland (Burchill et al., 2014; Harty et al., 2016) and the UK (Smith et al., 2012; Bell et al., 2016). The average cumulative N_2O emissions of the measurement period ranged from 4 to 6.6 kg N_2O-N ha^{-1}. These values were within range of the values reported in intensively managed grasslands across humid temperate climates (Flechard et al., 2007; Cardenas et al., 2019), including Ireland (Hyde et al., 2006; Burchill et al., 2014).

The soil mineral N pool (NH_4^+ and NO_3^-) usually decreased to values below 10 mg kg^{-1} 3–4 weeks after fertilisation. Generally, temperate grasslands are highly responsive to N input (Cameron et al., 2013; Forrestal et al., 2017), with the particularly high N fertiliser recovery rate (up to 70 %) reported 4 weeks after CAN application in intensively managed perennial ryegrass swards (Murphy et al., 2013). The soil NH_4^+

$$y = -1208.7x + 12497$$
$$R^2 = 0.41 \ (p < 0.001)$$

Fig. 4. Relationship between cumulative N_2O emissions and average soil pH for each lime treatment plot, including the equation and R^2 of the linear regression.
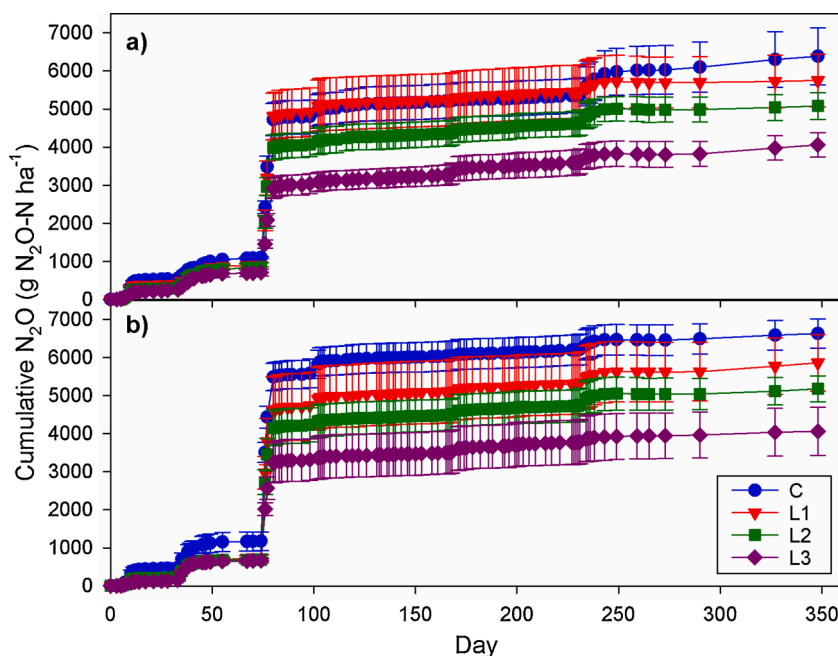
Fig. 3. Cumulative N_2O emissions for lime treatments in **a)** P0 and **b)** P40. Values in brackets next to treatment name represent average soil pH values across the measurement period. Bars represent standard errors (n = 4).

content was generally higher in low soil pH plots. This may indicate increased nitrification at higher soil pH levels. Although nitrification is reported to take place in highly acidic (pH = 4.5) soils (Robertson, 1989), it is generally accepted that the rate of nitrification is positively correlated with soil pH, with cultured nitrifiers exhibiting an optimum at pH 7.5–8 (Robertson and Groffman, 2007).

Long-term lime application resulted in strong differentiation between lime treatments in terms of chemical soil properties in our study. Increased input of $CaCO_3$ displaces hydrogen (H^+), aluminium (Al^{3+}) and manganese (Mn^{2+}) ions from the exchange sites of soil colloids. This increases soil pH and precipitation of Al^{3+} and Mn^{2+} in soil solution, leading to alleviated toxicity of these elements associated to soil acidity (Filipek, 2011). The increase in soil pH has a positive effect on the availability of most plant macro- and micro-nutrients, resulting in increased plant growth and productivity (Holland et al., 2018). Some elements, like Cu and Zn, have been shown to influence microbial communities and impact soil biochemical processes, hence denitrification and N_2O production (Bollag and Barabasz, 1979; Shen et al., 2020). However, this effect occurs at much higher concentrations than measured in our soils.

4.2. Soil pH effect on N_2O emissions

There was a significant effect of liming management, and its subsequent increase in soil pH, on N_2O emissions in our study, with the cumulative emissions in low pH treatments (C and L1) being significantly higher compared to the highest pH treatment (L3). Furthermore, soil pH and N_2O emissions had a negative linear relationship, with soil pH as a significant predictor (p < 0.001), explaining 41 % of total variation in cumulative N_2O fluxes. The partially or predominantly anaerobic soil environment, together with the non-limiting supply of NO_3^- due to high rates of CAN application, indicate that denitrification was most likely the dominating process when the emission peaks occurred and that soil pH was the main regulator of N_2O losses via denitrification between lime treatments in our study. This is in line with the number of previous laboratory studies on the effect of liming on N_2O emissions, showing a decrease in N_2O emissions with the increasing application of different liming materials (Zaman and Nguyen, 2010; Shaaban et al., 2015; Hénault et al., 2019). Soil pH may act as both distal and proximal regulator of denitrifying communities in soils (Wallenstein et al., 2006; Čuhel and Šimek, 2011; Samad et al., 2016a). The evidence of a proximal effect of soil pH N_2O production comes from studies of gene transcription and enzyme activities in microbial denitrifier communities or in model organisms, such as *Paracoccus denitrificans* (Bergaust et al., 2010; Bakken et al., 2012). These studies showed that the synthesis of the enzyme N_2O-reductase at the cellular level was hindered at low pH levels. Soil pH may also regulate denitrifying communities in a distal manner by playing a critical role in shaping soil microbial community composition and diversity (Zheng et al., 2019). There is evidence that low soil pH indirectly effects the $N_2O/(N_2O + N_2)$ ratio in soil due to a shift in the composition and abundance of denitrifying communities (Čuhel and Šimek, 2011). This includes a finding that soil pH is positively correlated with nitrite reductase (*nir*) and nitrous oxide reductase (*NosZ*) gene abundance, and with overall microbial community diversity (Samad et al., 2016a).

In contrast to laboratory studies, variable findings on the effect of liming on N_2O emissions were reported from field experiments, with increased (Khan et al., 2011), decreased (Mkhabela et al., 2006; Barton et al., 2013; Hénault et al., 2019) and no effect (Galbally et al., 2010) on N_2O emissions after liming. This variability in results across different ecosystems, soil types and climatic conditions comes as no surprise, since N_2O emissions under field conditions are context specific and notoriously variable in response to fluctuating soil moisture, temperature, mineral N, carbon substrate availability and the underlying biogeochemical processes. One of the reasons which could possibly obscure the effect of soil pH on N_2O emissions is that most experiments

in which soil pH was manipulated have been relatively short-term and investigated the immediate effect of such manipulations. Lime application results in a transient increase in C and N mineralisation (Curtin et al., 1998; Kemmitt et al., 2006), which may consequently stimulate both nitrification and denitrification. Therefore, any observed immediate and short-term microbial responses to liming may be due to this transient increase in mineralized C and N, which can be utilised by denitrifiers as a substrate for denitrification, rather than a direct effect of soil pH on the microbial communities themselves. This is in agreement with Baggs et al. (2010), who demonstrated the differences between short- and long-term responses to soil pH adjustment in terms of N_2O emissions from both nitrification and denitrification. Long-term liming and fertilisation may enhance C sequestration or attenuate reduction in SOC stock under intensive grassland management systems, particularly in temperate climates (Egan et al., 2018; Eze et al., 2018). However, liming of acidic soils may also increase soil biological activity, which could increase soil respiration rates and organic matter (OM) mineralization, leading to decreasing SOC stocks (Kowalenko and Ihnat, 2013). There was no difference in SOC content between lime treatments in our study. This suggests that increases in plant productivity and biomass as a result of long-term liming could lead to increased returns of OM to the soil in the form of crop residues, compensating for higher soil respiration rates in limed soils (Abalos et al., 2020).

There is a lack of information from field studies regarding the long-term effect of liming on N_2O emissions, especially from agricultural ecosystems. Abalos et al. (2020) found higher N_2O emissions from unlimed acidic arable soil in a two-year period compared to the same soil where lime was applied every 5–9 years as dolomite since the establishment of the experiment in 1942. Similarly, García-Marco et al. (2016) reported lower N_2O emissions from limed arable soil under conventional tillage after 7 years. Borken and Brumme (1997) also reported that liming over more than 20 years resulted in a reduction of N_2O emissions by 9–62% in forest ecosystems. In contrast, Yamulki et al. (1997) found an increase in N_2O emissions from limed plots in a long-term liming grassland trial after application of ammonium sulphate, although the emissions were relatively low. Therefore, more long-term studies on effects of liming in intensively managed agricultural soils would be required in order to fully assess the mitigation potential of liming in terms of N_2O emissions and the overall GHG balance.

4.3. N_2O mitigation potential of liming in temperate grassland ecosystems

The N_2O EFs in our study decreased by up to 0.8 % with increasing amount of lime applied and the consequent increase in soil pH. The EFs were within the range for CAN reported by Harty et al. (2016) in Irish conditions and within the uncertainty range of the IPCC global default EF of 1%. IPCC tier I default EF of 1% for N_2O emissions in croplands is based on N fertiliser input only and does not take into account the variability in soil properties and climatic conditions, which can significantly influence the intensity and duration of N_2O emissions. The negative relationship between EFs and soil pH in our study is in line with the findings of Wang et al. (2018), who demonstrated that soil pH is the main modifier explaining regional disparities in N_2O emissions in addition to N input. They also emphasized inclusion of soil pH in regional and national GHG inventories for a more realistic assessment of the impact of N management on soil N_2O emissions. Given the linear decrease in N_2O emissions with the increase in soil pH, there is a potential that the emissions could be further reduced if the soil pH is increased above the agronomic optimum for most plants (pH above 7). Such measures should be carried out with caution, however, in respect to soil type and plant requirements, as over-liming could decrease the availability of macro- and micro-nutrients and increase susceptibility to crop diseases, which could lead to reduced yields (Holland et al., 2018). The impact of increasing soil pH to above 7 on other nitrogen loss pathways, such as ammonia volatilisation, also needs to be considered (Ernst and Massey, 1960).

Yield-scaled N_2O emissions in our experiment were within the range found in fertilised grasslands located in humid temperate climate (Bell et al., 2015; Cardenas et al., 2019; Maire et al., 2020), but were also significantly reduced by liming. According to our results, the grassland soil limed to soil pH of 6.9 emitted 36 % less N_2O per ton of DM yield under the same management and fertiliser regime compared to the same soil with the pH of 5.1.

Our findings indicate that liming of acidic soils is a promising management option for mitigating N_2O emissions in temperate areas, such as Ireland, where denitrification is the dominant pathway contributing to N_2O production. In Ireland, national lime use has decreased from over 2 m tonnes in the early 1980s to less than 1 m tonnes in recent years. The reduction in lime use led to a decrease in the number of soil samples that had optimal soil pH (Plunkett et al., 2020). Recently, there has been a concerted national research and advisory campaign in Ireland around soil fertility and in particular liming. The outcome of this campaign was a substantial increase in the number of soil samples within the optimal range (pH > 6.2), from 32 % of soils in 2007 to 62 % in 2019 (Plunkett et al., 2020). The effect of increasing soil pH on national N_2O emissions from grasslands can be estimated based on i) the change of soil pH in grasslands over time (increase in soils with optimal soil pH from 29 % to 55 % (Plunkett et al., 2020)), ii) the area occupied by intensively managed grasslands (more than 3.6 million ha (Central Statistics Office Ireland (CSO, 2019)), iii) the average rate of ammonium nitrate-based fertiliser N applied in these systems (89 kg ha^{-1} yr^{-1} according to Dillon et al. (2018)) and iv) reducing the current grassland EF for CAN by Harty et al. (2016) used for the National GHG inventory reporting (EF 1.49 %, established on acidic soils with pH 5.4–5.7, which corresponds to our L1) by 33 % (the difference in EF between L1 and L3 in our study). The full calculation method can be found in Supplementary Table S2. We estimated that the national increase in soil pH between 2007 and 2019 could have potentially reduced national N_2O emissions by between 0.26 and 0.43 Gg N_2O-N yr^{-1} (0.36 Gg N_2O-N yr^{-1} on average) or between 70 and 115 Gg CO_2-eq yr^{-1} (95 Gg CO_2-eq yr^{-1} on average). This is a significant reduction given that the agricultural sector accounts for nearly 33 % of the total GHG emissions in Ireland and inorganic N fertilisation contributes 12 % (2381 Gg CO_2-eq) of the emissions within the agricultural sector (Duffy et al., 2020). There is a potential for a further reduction in national N_2O emissions by up to 0.96 Gg N_2O-N yr^{-1} (254 Gg CO_2-eq yr^{-1}) if all the remaining acidic soils are brought up to optimal pH. This does not take into account the estimated increase in soil N supply (up to 70 kg N ha^{-1} yr^{-1}) through OM mineralisation processes by achieving optimum soil pH and the amount of fertiliser N that can be reduced accordingly (Culleton et al., 1999; Lanigan et al., 2018). The potential reductions in N_2O emissions have to be balanced against the CO_2 emissions associated with liming (De Klein et al., 2019), as well as impacts of liming on C sequestration by soils (Eze et al., 2018; Paradelo et al., 2015). The effect of soil pH on N_2O emissions from other forms of N such as different fertiliser types, dung, urine and manure should also be considered (Clough et al., 2004; Khan et al., 2011).

4.4. Phosphorus effect on N_2O emissions and grassland productivity

Despite the differences in P fertilisation management and the resulting differences in bioavailable soil P content between P0 and P40, we did not find significant differences between these two treatments in relation to N_2O emissions. While P availability plays an important role in microbial nutrient cycling and community composition in soils (Randall et al., 2019; Dai et al., 2020), its effect on microbially-mediated N transformations and losses is still poorly understood. The limited number of studies dealing with P effect on N_2O emissions show contrasting results and provide different explanations for such findings. According to Mehnaz and Dijkstra (2016), N_2O emissions increased following P addition in P-deficient soils due to changes in composition and abundance of denitrifier communities caused by removing P limitation in

such soils. Similar findings were previously reported by Mori et al. (2013). O'Neill et al. (2020) reported higher N_2O emissions from low-P soils compared to high-P soils under non-limiting C and N conditions. They hypothesised that fungal communities dominant at low-P soil could be responsible for increasing N_2O emissions due to their lack of N_2O-reductase, while bacterial denitrifiers with the potential capability to fully reduce N_2O to N_2 are dominant at high-P soil. It would be of considerable interest to further investigate C, N and P interactions in relationship to soil microbial communities in efforts to mitigate N_2O emissions and increase nutrient efficiency in agroecosystems.

Soil P content had significant effect on grassland productivity, with grass DM yields being higher in P40 compared to P0. In terms of soil pH, P availability to plants is generally maximised at soil pH close to neutral (Penn and Camberato, 2019). However, the relationship between soil pH, solubility of P and plant of P uptake is not straightforward as it depends on a wide range of soil properties, such as Al and Fe content, clay mineralogy, cation exchange capacity, content and type of OM, as well as microbial and plant preferences for certain P forms (Shen et al., 2011). This is shown by the results from our study, where lime application of 5 t ha^{-1} significantly reduced grass yields in L3 plots compared to unlimed C within P40 treatment. It is likely that high concentration of Ca on the soil surface caused precipitation and reduced dissolution of available P and applied superphosphate P (which also contains 15 % of Ca), while this form of fertiliser is readily dissolved in acidic soil (Hylander, 1995; Hinsinger and Gilkes, 1997). However, this effect is only short-term (Viadé et al., 2011; Simonsson et al., 2018) as shown by previously reported results from the same trial by Fox et al. (2015). According to their results, liming did not lead to an increase in grass yields in the first year regardless of the amount of P applied, but a positive effect of lime and P interaction on yield was found in the years following lime application. Alternatively, the extreme weather events following reseeding in the year prior to our experiment could have influenced sward establishment and therefore yields to some degree. Thus, keeping the soil pH and P at the optimum level in the long-term has potential to increase both agronomic and environmental performance of intensive grasslands by further reducing N_2O emissions due to higher grass N uptake through increased yields.

5. Conclusions

Our study indicates that long-term liming of acidic soils, in accordance with good farming practices, is a promising management option for mitigation of N_2O emissions from denitrification in temperate grassland ecosystems. The relationship between soil pH and cumulative N_2O emissions was linear and negative, corroborating previous studies where liming lead to reduced N_2O emissions. The grass yields and yield-scaled N_2O emissions from our experiment suggest that adjusting the soil pH slightly above the agronomic optimum for most crops, in combination with optimal P supply, is the most favourable option in terms of both environmental and agronomic benefits of grassland production. In case of Ireland, we estimated that the increase in liming of grasslands over the last 12 years potentially reduced national N_2O emissions by 95 Gg CO_2-eq yr^{-1}, with potential for a further reduction by up to 254 Gg CO_2-eq yr^{-1} if all the remaining grasslands on acidic soils are brought up to optimal pH or slightly above that. Furthermore, our results provide evidence that liming should be included as an option in GHG mitigation assessments and that soil pH should be considered as a significant variable in regional and national GHG inventories. However, more studies across different production systems, soil types and climates are necessary in order to comprehensively assess the overall impact of liming on GHG balance in soils and the potential trade-offs, such as increased CO_2 emissions, as well as impacts on C sequestration by soils.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.agee.2021.107319.

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