Emissions of nitrous oxide and methane after field application of liquid organic fertilizers and biochar

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ABSTRACT

The use of anaerobic digestates as fertilizer is proposed as a means to close agricultural nutrient cycles. However, digestates have higher inorganic nitrogen contents than raw manures, which could translate into increased emissions of potent greenhouse gases such as nitrous oxide (N_2O) and methane (CH_4). To mitigate these emissions, the addition of biochar with high nutrient absorption capacity is suggested. To quantify the effects of anaerobic digestion and biochar amendment on N_2O and CH_4 emissions, we conducted a study over 33 months with four different crops (silage maize, winter wheat, winter barley, and forage grass). We measured soil parameters such as mineral nitrogen, moisture, and temperature. The N_2O emissions after application of digestates were generally similar to those observed after cattle slurry or mineral fertilizer application. The highest N_2O emissions were observed in the first year of the experiment during maize cultivation and were strongly influenced by high soil nitrate concentrations, which were likely linked to enhanced soil organic N mineralization after ley termination. The CH_4 emissions were mostly negative. The addition of biochar to co-digested manure before application at an annual rate of 2 t ha^{-1} had no effect on N_2O emissions but led to short-lived CH_4 peaks from organic fertilizers directly after spreading. We conclude that digestates do not promote larger N_2O emissions than mineral fertilizers or cattle slurry, and that biochar addition to digestates in small application quantities does not reduce N_2O emissions but bears the risk of CH_4 release.

1. Introduction

Reducing nitrous oxide (N_2O) emissions is a crucial part of optimizing agricultural management. Agricultural soils currently account for more than 50% of all human-generated N_2O emissions, making them the largest anthropogenic source of this potent greenhouse gas (GHG) (Tian et al., 2020). Research shows that nitrogen (N) fertilization is the main cause of high N_2O emissions from soils (Reay et al., 2012). However, N supply is vital for crop productivity. Organic fertilizers such as manures, if available, support long-term maintenance of soil organic carbon levels by supplying organic matter and can generate energy if subjected to anaerobic digestion (AD).

AD facilitates the recycling of organic materials and is therefore proposed as an option to close nutrient cycles while generating energy (Dahlin et al., 2015). In Switzerland, agricultural and non-agricultural

organic wastes are processed via AD (Brändli et al., 2005). Agricultural digestates, derived from AD of about 80% liquid and solid animal manure, and around 20% non-agricultural co-substrate, such as food processing waste, have been extensively studied. In contrast, non-agricultural digestates, produced from municipal and industry waste such as organic household waste, food processing waste and green waste from gardens and public green areas, have received less attention in the literature (Nicholson et al., 2017). Due to the variation in feedstock materials and production methods applied in AD, digestate properties can be highly variable, resulting in different dynamics of soil mineral N (N_{min}) (Alburquerque et al., 2012) and affecting N_2O-producing soil microorganisms (Lazcano et al., 2021). Consequently, estimating N_2O emissions from digestate application is inherently complex. The higher ammonium (NH_4^+) content of digestates may allow the replacement of synthetic N fertilizers with digestates with a minimal

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yield penalty (Gutser et al., 2005). But this could potentially increase N_2O emissions due to higher substrate availability for the N_2O-producing microbial community. However, digestates have lower concentrations of easily degradable carbon (C) after AD (Nkoa, 2014), which can be used by denitrifiers as an energy source for the denitrification process and to produce N_2O, potentially reducing N_2O emissions (Stuchiner and von Fischer, 2022). Because of these complexities, prior studies have shown variable effects of AD on N_2O emissions. Some reported lower emissions compared to undigested manure (Sänger at al, 2010, Senbayram et al., 2009, Möller and Stinner, 2009), while others reported higher emissions (Eickenscheidt et al., 2014).

Biochar, a porous, C-rich end product of the pyrolysis of organic materials, has gained popularity as its application can improve soil properties and increase yields (Jeffery et al., 2017), potentially reduce both nitrate (NO_3^-) leaching and N_2O emissions (Borchard et al., 2018), as well as enhancing C- sequestration (Schmidt et al., 2021). At present, we do not have a full picture of the mechanisms by which biochar reduces N_2O emissions (Kammann et al., 2017), but several mechanisms have been proposed. Increased gas entrapment of N_2O in water-saturated soil pores may stimulate microbial N_2O reduction (Harter et al., 2016). The outer and inner (pore) surface of biochar can adsorb negatively charged functional groups such as NO_3^- (Hagemann et al., 2017) and the resulting N immobilization is a potential pathway which could result in lower N_2O emissions. This process might be more effective when biochar is combined with NH_4^+-rich digestates compared to raw manure. The mitigating effect of biochar on N_2O emissions was shown in two meta-analyses, with overall reductions of 54% (Cayuela et al., 2014) and 38% (Borchard et al., 2018) recorded. Yet, when evaluating field studies only, the potential of emissions reduction by biochar decreased to an average of 12% (Verhoeven et al., 2017). The effectiveness of biochar for reducing N_2O emissions further varies with soil type, application amount, feedstock used for production and pyrolysis conditions during production (Kammann et al., 2017). Moreover, biochar weathers in soil and thus changes its properties and functionality over time (Joseph et al., 2010), further complicating the prediction of its effects on N_2O emissions.

The magnitude of N_2O emissions from agricultural soils is influenced by various factors, including fertilizer N input, microbial community composition and functioning, soil properties, weather conditions, and agronomic management practices, such as tillage (Butterbach-Bahl et al., 2013; Oertel et al., 2016; Six et al., 2004). Therefore, the ability to reliably predict N_2O emissions in field studies will require long-term measurement campaigns and will not be a trivial task due to the temporal and spatial variability of abiotic conditions. However, these studies are critical due to the fact that the global warming potential of N_2O is 273 times that of CO_2. (IPCC, 2021).

Conversely, CH_4 emissions from well-aerated agricultural soils are generally small or negative (Hütsch, 2001). However, short-term CH_4 emission peaks after application of cattle slurry have been reported in Krauss et al. (2017). So far AD does not show a clear trend towards increasing or mitigating soil CH_4 emissions (Eickenscheidt et al., 2014; Wulf et al., 2002), which are also highly relevant given that the global warming potential of methane (CH_4) is 27 times that of CO_2 (IPCC, 2021).

The objective of this study was to evaluate the effects of agricultural and non-agricultural digestates, and small doses of biochar added to agricultural digestate, on N_2O and CH_4 emissions in organic agriculture. The study quantified N_2O and CH_4 emissions and associated soil and weather parameters during four consecutive cropping periods. The hypotheses were that (i) N_2O emissions from digestates are greater than from cattle slurry due to higher NH_4^+ contents in digestates, and (ii) adding biochar to agricultural digestate reduces N_2O emissions compared to digestate alone. Further, we expected (iii) smaller CH_4 emissions from digestates compared to cattle slurry, due to lower contents of readily degradable organic C compounds in digestates.

2. Material and methods

2.1. Study site, crop rotation and experimental setup

The study was conducted between March 2018 and December 2020 on an organic farm in the northwest of Switzerland (47°33′44.3″N 7°53′15.7″E, 330 m a.s.l.). The region has a temperate climate with an average annual rainfall of 1104 mm and a mean annual temperature of 10.8 °C (2004–2017) (data source: weather station, 47°34′10.8″N 7°53′54.4″E, Agrometeo, MeteoSwiss). The soil is a Haplic Luvisol with a silt-loam texture and an average pH ($CaCl_2$) of 5.6 (Table 1). Prior to establishing the trial in March 2018, a grass-clover ley was grown on the field, followed by a crop rotation of silage maize (*Zea mays L.*), winter wheat (*Triticum aestivum L.*) and winter barley (*Hordeum vulgare L.*). Cultivation measures are listed in Supplementary: Table S1. White mustard (*Sinapis alba L.*) was planted as an intercrop in between wheat harvest and barley sowing. Upon the harvest of the barley, a legume-grass mixture would traditionally follow, but was replaced by a forage grass mixture (*Lolium hybridum, Lolium perenne, Festuca perennis* and *Festuca pratensis*) in this experiment to avoid N inputs from symbiotic N fixation. The field was plowed to 20 cm depth, shortly before sowing of maize, wheat and barley. A cultivator was used to prepare the field before planting the forage grass mixture. Manual weeding (combining harrow/star cultivator) and seedbed preparations (rotary harrow) were conducted as needed.

The treatments consisted of an unfertilized control (NON), a mineral fertilized control (MIN, ammonium sulphate) and four liquid organic fertilizers: cattle slurry (SLU), agricultural slurry from an on-farm biogas plant (SLA), SLA amended with biochar (SLA+) and liquid digestate from a non-agricultural biogas plant (LID). The same amount of total N was applied in all treatments except NON in order to supply 140 kg N ha-1 to maize, 140 kg N ha-1 to winter wheat, 120 kg N ha-1 to winter barley and 50 kg N ha-1 to fodder grass. Plots of 9 m x 18 m were arranged in a split-plot design, and each treatment was replicated four times (Supplementary: Figure S2).

2.1.1. Environmental conditions

Average annual air temperature and rainfall over the measurement period of 33 months were 12.4 °C and 605 mm, respectively (weather station, 47°34′10.8″N 7°53′54.4″E, Agrometeo, Meteoschweiz). Due to drought conditions, maize plants received artificial irrigation of 54 mm water once in August 2018.

2.2. Fertilizers and biochar

The characteristics of the liquid fertilizers are presented in Table 2. SLU originated from two organic farms (Aemethof, Densbüren, Switzerland and Kiesholzhof, Wallbach, Switzerland) for the applications in maize, wheat and forage grass, but were highly diluted with rain water in spring 2020 and therefore sourced from a conventional farm (Paul Frey, Asp, Switzerland) for application in barley. SLA was produced in an agricultural biogas plant (Aemethof, Densbüren, Switzerland) using cattle slurry, and solid cattle and horse manure as the

Table 1
Selected soil characteristics (0–20 cm) before the start of the field experiment (February 2018). Means±standard deviations of all initial plots ($n = 32$).

Parameter	Unit	Mean±SD
Sand	%	23±13
Silt	%	47±8
Clay	%	28±5
pH$_{CaCl2}$		5.6±1
Total organic C	g kg^{-1}	15.3±1
Total N	g kg^{-1}	1.6±0.1
Microbial C	mg kg^{-1}	403±5
Microbial N	mg kg^{-1}	70±7

Table 2
Chemical characteristics of the liquid organic fertilizers and total volume added to a given crop.

Crop	Treatment	Volume	DM	C_{org}	N_{tot}	NH_4^+-N	NH_4^+-N:N_{tot}	C:N	pH
		[m^3]	[%]	[g (kg DM)$^{-1}$]	[g (kg DM)$^{-1}$]	[g (kg DM)$^{-1}$]			
Silage maize	SLU	74.1	4.4	433.2	41.0	20.0	0.49	10.6	7.3
	SLA	36.3	5.4	370.4	65.5	38.2	0.58	5.7	7.9
	SLA+	40.7	8.0	411.7	45.4	24.3	0.54	9.2	7.8
	LID	24.8	13.0	273.3	40.1	22.3	0.56	6.9	7.8
Winter wheat	SLU	91.5	3.4	425.2	47.9	23.2	0.48	8.9	7.2
	SLA	39.3	5.2	384.6	76.6	46.6	0.61	5.0	7.9
	SLA+	39.9	7.9	442.2	49.8	28.7	0.58	8.9	8.0
	LID	25.9	8.8	351.8	56.6	32.3	0.57	6.2	7.8
Winter barley	SLU	45.6	6.1	434.9	38.3	19.6	0.51	11.4	7.0
	SLA	22.0	6.0	362.8	85.2	57.5	0.67	4.3	8.1
	SLA+	22.5	9.3	362.8	52.2	27.5	0.53	7.3	8.2
	LID	23.4	8.7	364.7	56.5	33.2	0.59	6.5	7.8
Forage grass	SLU	64.6	3.1	390.3	43.5	19.7	0.45	9.0	7.8
	SLA	19.8	5.2	382.9	82.5	54.2	0.66	4.6	8.2
	SLA+	19.8	8.5	331.4	47.5	31.8	0.67	8.9	8.1
	LID	14.6	11.2	413.4	49.5	27.4	0.55	6.7	8.0

SLU: cattle slurry; SLA: agricultural slurry (from an on-farm biogas plant); SLA+ : agricultural slurry (from an on-farm biogas plant) and biochar (2 t ha-1 year-1); LID: non-agricultural digestate; DM: dry matter.

main feedstock and various food-processing wastes as co-substrates (perished cereals, residues from coffee capsule production, cocoa residues and remainders of herbs after extraction). SLA is the liquid fraction from solid-liquid separation after a 60-day digestion process at thermophilic (53 °C) conditions. For SLA+ , we added biochar to SLA to apply approximately 2 t ha^{-1} year^{-1}. LID was produced in a non-agricultural biogas plant (Biopower, Pratteln, Switzerland) from urban green cuttings and various organic wastes (from households, grocery shops, gastronomy and food processing). The mean residence time for AD was 15 days and the reaction was thermophilic (55 °C). LID refers to the liquid phase of the digested material. The certified biochar (European Biochar Certificate EBC) was obtained from tree and shrub cuttings (Verora AG, Edlibach, Switzerland) and characterized by on average 57–81% C, 0.65–0.75% N and an H/Corg ratio between 0.29 and 0.44. From the second application onwards, biochar was milled before application to slurry to allow homogeneous mixing.

Liquid organic fertilizers were stored in non-corrosive containers on the field site for about two weeks before fertilizer application. Fertilizers were analyzed for total N contents and batch-specific volumes needed to apply similar amounts of total N in each treatment were calculated. Granular ammonium sulphate was used as mineral fertilizer in the MIN treatment. The chosen N fertilization levels were 140 kg N ha^{-1} for maize and wheat, 120 kg N ha^{-1} for barley, and 80 kg N ha^{-1} for the establishment of forage grass. Applications were split into two equal applications, except for forage grass, where the first application was 50 kg N ha^{-1}, followed by an autumn application of 30 kg N ha^{-1}. Liquid fertilizers were applied by hand using watering cans to mimic drag hose spreading. To prevent crop limitation of P and potassium (K), NON and MIN received 20 kg P ha^{-1} (triple superphosphate in 2018; rock phosphate in 2019 & 2020) and 130 kg K ha^{-1} (potassium sulphate) annually. LID was lower in K compared to the agricultural fertilizers SLU, SLA and SLA+ , and therefore received an additional 70 kg K ha^{-1} (potassium sulphate; permitted in organic farming) applied to barley.

2.3. N₂O and CH₄ flux measurements

We quantified N_2O and CH_4 emissions over 33 months. Sampling took place weekly during the vegetation period, bi-weekly during winter, and daily or every second day for 7–14 days after fertilizer applications. Additional samples directly after spreading fertilizers were taken in barley and forage grass. Gas samples were collected with the static chambers method (two chambers per plot to allow for technical replication, resulting in 48 chambers in total). Chambers were designed according to international guidelines (Clough et al., 2020). Each circular

chamber covered a basal area of 0.07 m^2 with a volume of 14 dm^3 (chamber height: 0.2 m, chamber diameter: 0.3 m). PVC rings were permanently inserted at 0.1 m soil depth and removed only during soil cultivation activities (Supplementary: Figure S1). Chambers were placed between crop rows during maize cultivation and included the crop for wheat, barley and grass. Gas samples were collected with a three-way-syringe system in pre-evacuated headspace vials with a volume of 12 ml (Labco Limited, Lampeter, United Kingdom), and closed with a double rubber septum. Samples were taken at 0, 10, 20 and 30 min after closing the chambers. Soil surface temperatures and chamber temperatures were recorded at the beginning and end of each sampling round. Gas samples were analyzed with a gas chromatograph (7890 A, Agilent Technologies, California, USA) equipped with an electron capture detector (µECD) to measure N_2O concentration and a flame ionization detector (FID) for CH_4 determination.

2.3.1. Calculations for N₂O and CH₄ emissions

Fluxes of N_2O and CH_4 were determined by taking into account the mean gas con- centrations (ppm), chamber air temperature (°C), as well as the area (m^2) and volume (L) of the chambers. Fluxes were then calculated for each chamber with the R package gasfluxes (Fuß, 2016). The *kappa.max* selection algorithm was used to select the method for flux trajectories (linear, robust-linear, Hutchinson- Mosier regression) for each flux individually based on the flux size and the measurement uncertainty (Hüppi et al., 2018, 2022). Fluxes were averaged between the two technical replicates per plot.

Cumulative N_2O and CH_4 emissions per hectare (area-scaled) were calculated for each cropping period (from tillage to tillage). Additional measurements taken directly after fertilizer applications, as displayed in Fig. 4 and Supplementary: Figure S2, were not included in the calculations of cumulative emissions. Due to different growing periods, the number of observations varied between crops, with 34 data points per treatment and replicate used to calculate the cumulative emissions from maize, 40 for wheat, 37 for barley, and 20 for forage grass.

Area-scaled N_2O emissions from NON (N_2O-$N_{control}$) were subtracted from fertilizer treatment emissions and divided by the corresponding amount of total N (N_{tot}) per fertilizer application to obtain fertilizer-based emission factors (EFs) as follows:

$$N_2O \quad EF1[\%] = \frac{N_2ON_{treatment} - N_2ON_{control}}{Fertilizer \quad N \quad input}$$

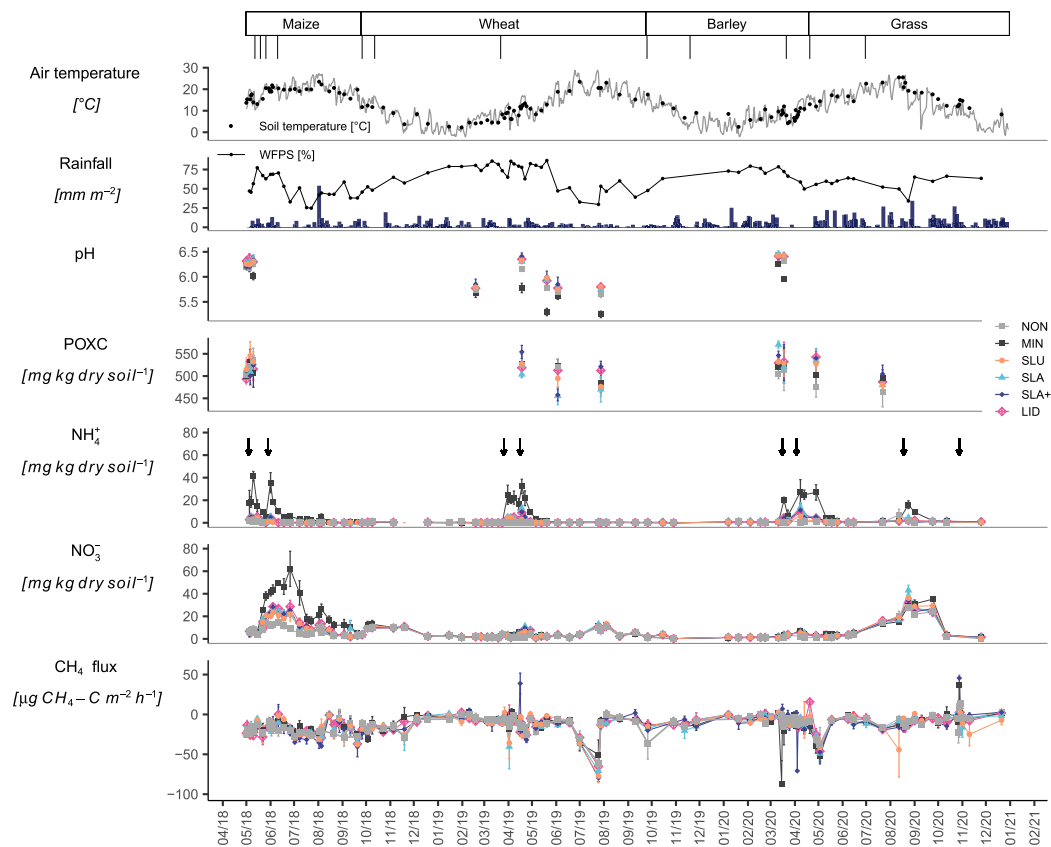$$N_2O \quad EF2[\%] = \frac{N_2ON_{treatment}}{Fertilizer \quad N \quad input}$$

Fig. 1. Time series measurements of air temperature and rainfall (data Source: weather station, 47°34'10.8"N 7°53'54.4"E, Agrometeo, MeteoSwiss), averages across all treatments for soil temperature (−7 cm soil depth) and WFPS (0–20 cm) and treatment means fpr pH, POXC, NH_4^+, NO_3 and soil-borne CH_4 emissions during a 33-month period with a crop rotation of silage maize, winter wheat, winter barley and forage grass (April 2018 to December 2020). Values represent treatment mean ±SEM (*n* = 4). For soil temperature and WFPS, values represent daily averages. Treatments: unfertilized control (NON); mineral fertilized control (MIN); cattle slurry (SLU); agricultural slurry from an on-farm biogas plant (SLA) and amended with biochar (SLA+) and liquid digestate from a non-agricultural biogas plant (LID). The arrows in the NH_4^+ panel represent fertilization events. Vertical lines above the first panel indicate soil cultivation measures

Data for EF2 and crop yields are listed in Supplementary: Table S3 and S1. By dividing area-scaled emission by grain yield (wheat, barley) or dry biomass yield (maize, grass), yield-scaled N_2O emission (g N_2O- N t^{-1} dry biomass for maize or grain in the case of cereals) were calculated (Venterea et al., 2011):

$$Yield-scaled \quad N_2O \quad emissions \quad \left[g \quad t^{-1} \right]$$
$$= \frac{Area \quad scaled \quad N_2ON[kg \quad N_2ON \quad ha^{-1}]}{Yield/grain \quad yield \quad dry \quad matter[t \quad ha^{-1}]}$$

We did not calculate yield-scaled N_2O emission for forage grass because the growing period was not complete when the last measurement was taken. CO_2- equivalents for N_2O (Table 3) and CH_4 (Supplementary: Table S6) emissions were calculated according to the IPCC guidelines (IPCC, 2021).

2.4. Soil sampling

N_2O and CH_4 samplings were regularly accompanied by plot-specific soil sampling. Composite soil samples of eight cores (∅=2 cm) were taken from each plot to a depth of 20 cm and stored in cooling boxes for transport. Samples were passed through a 2 mm sieve and N_{min} was extracted from the fresh soil with a 0.01 M $CaCl_2$ solution (1:4 v/w), followed by filtration (pore size < 2 μm) after shaking for 60 min. Contents of N_{min} were determined with a spectrophotometer (Smartchem450, AMS Alliance, Rome, Italy) according to Keeney and Nelson (1982) for NH_4^+ and using the method of Krom (1980) for NO_3.

Gravimetric soil moisture was determined by drying the soil at 105 °C.
Soil WFPS was calculated as:

$$WFPS \quad [\%] = \frac{GWC \quad x \quad BD}{PO} \quad x100$$

with GWC = gravimetric water content [%], BD = soil bulk density [g cm^{-3}] and PO = soil porosity [%].

On selected dates, portions of the sieved soil were air-dried to measure the pH in $CaCl_2$ (1:2.5 $CaCl_2$). Bulk density was determined plot-wise before establishing the field trial and before sowing barley. Permanganate oxidizable C (POXC), which has been shown to represent a management-sensitive labile soil C fraction (Culman et al., 2012), was measured according to the method described by Weil et al. (2003) at ten time points in air-dried soil samples using a 0.2 M $KMnO_4$ solution.

2.5. Statistical analysis

Data analysis and production of graphs were conducted using R version 4.0.2 (R Development Core Team, 2021). The significance threshold was $p < 0.05$ for all statistical analyses. A linear mixed effects model was applied on log-transformed data using R-package *nlme* (Pinheiro et al., 2022). Negative N_2O fluxes were negligible and replaced by zeros. The time courses of N_2O fluxes (μg N_2O-N m^2 h^{-1}) were examined separately for each crop and combined across all crops for correlations with soil temperature (°C), WFPS (%) and contents of NO_3 (mg kg^{-1}) and NH_4^+ (mg kg^{-1}) as fixed effects co-variates. Obtained model estimates (Table 4) represented the estimated increase of N_2O
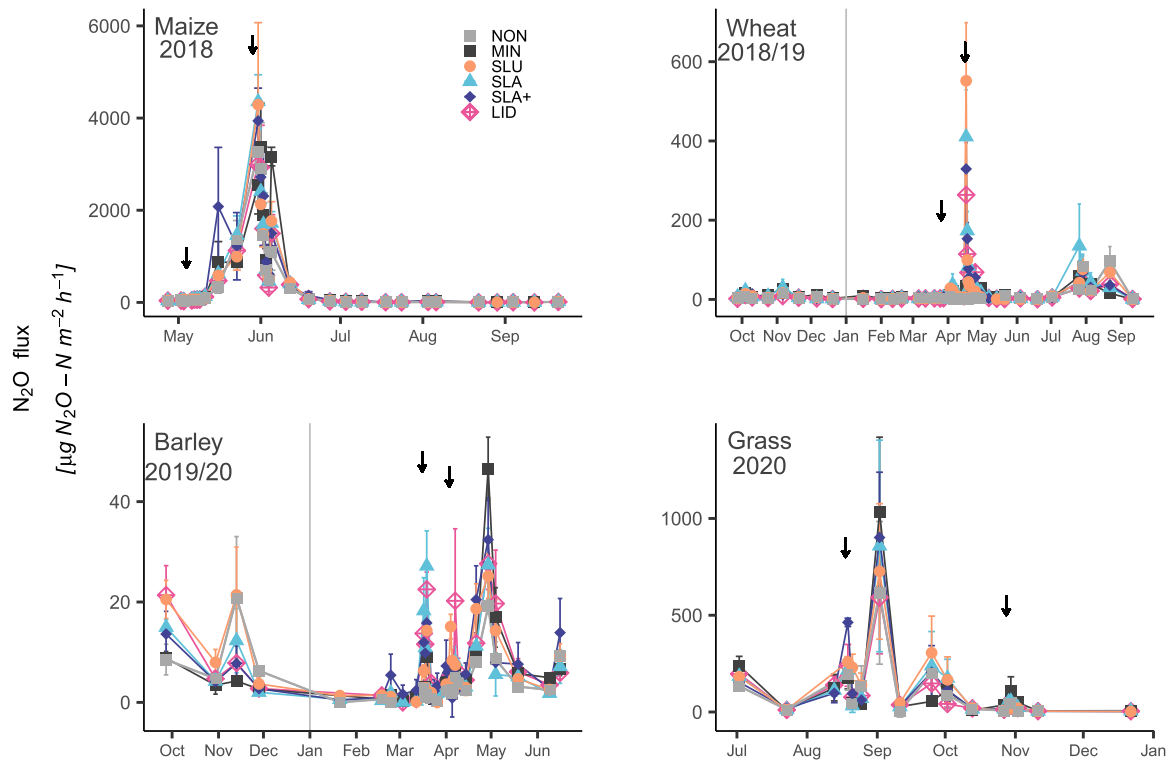
Fig. 2. Time series measurements of N_2O emissions from silage maize, winter wheat, winter barley, and forage grass. Values represent treatment mean ±SEM ($n = 4$). Scaling of the y-axis differs between panels. Arrows indicate the time points of fertilizer applications. Treatments: unfertilized control (NON); mineral fertilized control (MIN); cattle slurry (SLU); agricultural slurry from an on-farm biogas plant (SLA) and amended with biochar (SLA+) and liquid digestate from a non-agricultural biogas plant (LID).

fluxes (µg N_2O-N $m^2\,h^{-1}$) by an increment of one unit of the explanatory variables (Soil temperature, WFPS, NO_3^- and NH_4^+ contents). For example, an estimate value of 1.5 for WFPS is to be interpreted as an increase of N_2O fluxes of 1.5 µg N_2O-N $m^2\,h^{-1}$ by an increase of 1% WFPS. The model accounted for treatments nested in split-plots and within replicated blocks as random factors in the analysis. Split-plots and blocks did not have a statistically significant impact on the data. Temporal correlation was included in the model. Soil pH and POXC were not included in this analysis because both parameters were sampled only on a few occasions.

We performed a linear mixed model followed by Tukey's Post Hoc test accounting for split plots nested in four replicates as random factors to examine differences between cumulative area-scaled N_2O and CH_4 emissions, yield- scaled N_2O emissions, EFs and CO_2-equivalents, firstly between crops and secondly between treatments within crops (Fig. 3; Table 3; Supplementary: Table S4 and Table S5). Data from cumulative area-scaled N_2O emission in barley was log-transformed to meet the criteria of normal distribution, while data from maize, wheat and barley was normally distributed. Statistical differences in wheat for area- and yield-scaled N_2O emission, EFs and CO_2-equivalents were further investigated with specified contrasts for comparison between SLU-MIN, SLU-NON, SLA-MIN and SLA-NON using the R-package *stats* (R Development Core Team, 2021).

Differences between snapshots of CH_4 (Fig. 4) and N_2O emissions (Supplementary: Figure S2) directly after fertilizer application were examined by a non-parametric test (Kruskal-Wallis test + pairwise Wilcoxon test) because the data did not fulfill the requirement of normal distribution despite log- transformation. Treatment differences and differences between sampling time points for soil pH and POXC were examined with an ANCOVA with split plots nested in four replicates as random factor (Supplementary: Table S3).

3. Results

3.1. Soil parameters

Soil temperature followed a seasonal pattern, and the overall highest value (25.5 °C) was recorded in maize in August 2018 and the lowest value (2.2 °C) in wheat in early February 2019 (Fig. 1). WFPS ranged between 25% and 86% and was not significantly different between treatments.

Soil pH ranged between 5.7 and 6.4 and was significantly lower in the MIN treatment compared to the organic fertilizers and NON (Fig. 1; Supplementary: Table S3). No consistent pattern was found for POXC contents, which ranged between 474 and 533 mg (kg dry soil)$^{-1}$.

Across all crops, soil NH_4^+ contents increased immediately following N input and showed a clear treatment distinction, with the highest concentrations in MIN. Much lower concentrations occurred in SLU, SLA, SLA+ and LID, and the lowest NH_4^+ contents were measured in NON after fertilizer application (Fig. 1).

Soil NO_3^- contents after fertilizer applications varied strongly over time, with the highest values of more than 50 mg (kg dry soil)$^{-1}$ measured in maize after the second application, and the lowest contents (< 20 mg (kg dry soil)$^{-1}$) in barley after the second application (Fig. 1). Clear treatment differences occurred in maize, where NO_3^- contents were about twice as high in MIN than in SLU, SLA, SLA+ and LID, and about three times as high as in NON. Fertilizer applications in wheat and barley induced much smaller NO_3^- peaks compared to maize. Increasing NO_3^- contents were also observed after management operations such as plowing, harrowing or sowing and also during fertilizer application in forage grass.
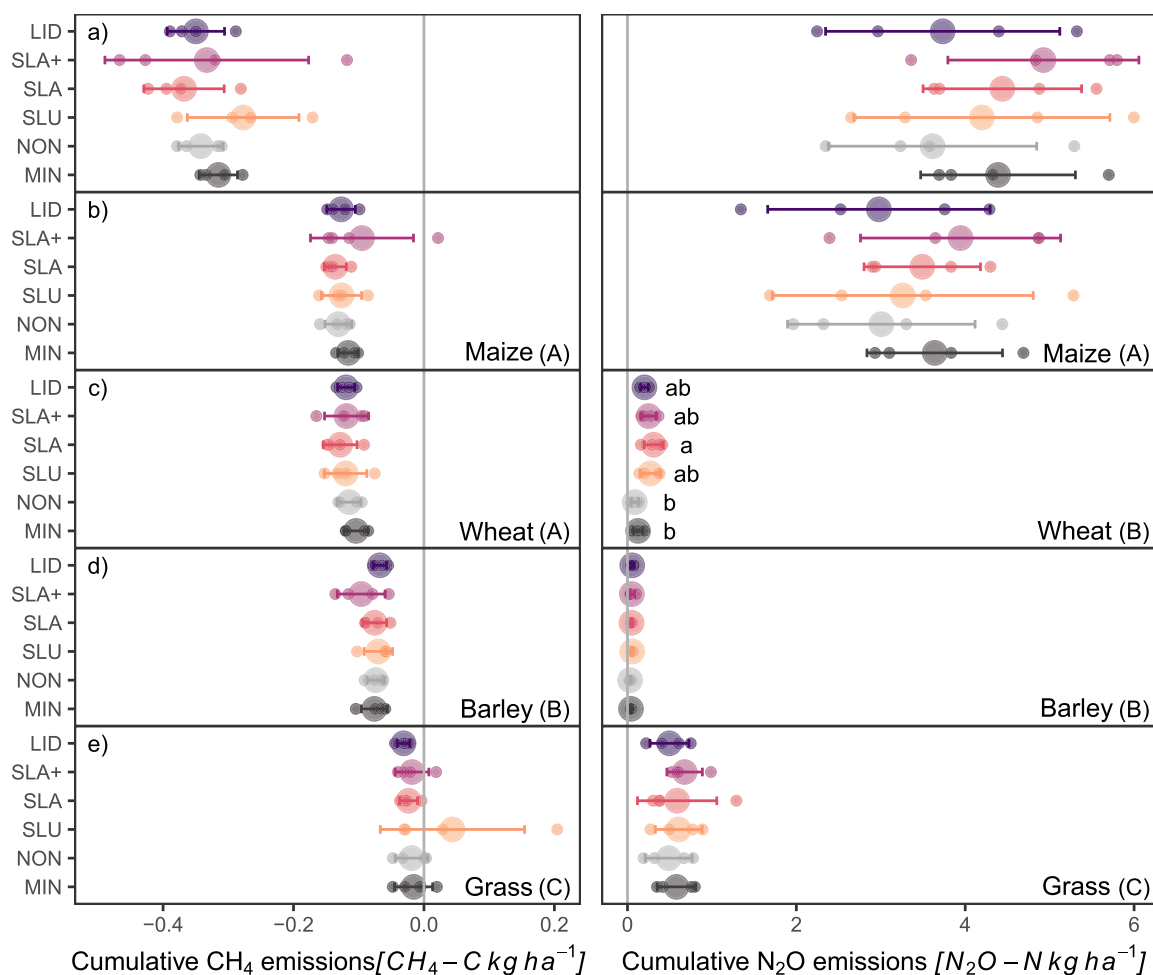
Fig. 3. Average cumulative CH_4 (left) and N_2O (right) emissions (big circles represent treatment means, small circles indicate replicates ($n = 4$)±SEM across 33 months ($n = 131$; upper panel) from silage maize ($n = 34$), winter wheat ($n = 40$), winter barley ($n = 37$) and forage grass ($n = 20$). Small letters indicate results from a linear mixed model and specified contrasts of N_2O emissions from winter wheat for comparison between SLU-MIN, SLU-NON, SLA-MIN and SLA-NON (Supplementary: Table S4). Capital letters express differences between crops (Supplementary: S4). Treatments: unfertilized control (NON); mineral fertilized control (MIN); cattle slurry (SLU); agricultural slurry from an on-farm biogas plant (SLA) and amended with biochar (SLA+) and liquid digestate from a non-agricultural biogas plant (LID).

3.2. N_2O fluxes

Fluxes of N_2O increased after fertilizer applications and management operations in combination with rainfall and heat, but were highly variable in magnitude between crops (Fig. 2). The N_2O emissions did not correspond well with N application amounts, and treatment differences were mostly small. N_2O emission from freezing and thawing in winter was negligible. Peak emissions of N_2O occurred after fertilizer applications and were remarkably high in maize (up to 4000 µg N_2O-N m^{-2} h^{-1}) compared to emission peaks from wheat, barley and grass, which were 10, 100 and five times lower, respectively (Fig. 2). N_2O emissions from maize rose after ley termination followed by fertilizer application under high soil temperature and moisture and after peaks did not return to the baseline flux in between fertilizer applications. Emissions during maize cultivation were at similar levels for all treatments.

The N_2O emissions peaked shortly after fertilizer application in wheat, decreased rapidly and peaked a second time immediately after the second fertilizer application (Fig. 2). Only the second N_2O peak showed a treatment effect, with higher emissions in SLU, SLA, SLA+ and LID compared to MIN and NON.

Two short-term N_2O peaks characterized emissions from barley immediately after fertilizer applications, which were followed by a larger peak about two weeks after the second fertilizer application

(Fig. 2). After about 45 days, in early May 2020, N_2O emissions increased again in all treatments. During this time, soil temperatures rose significantly and rainfall occurred after prolonged drought (Fig. 1).

In forage grass, N_2O emissions already increased before fertilizer application (Fig. 2). Soil temperature and moisture were high in autumn 2020 (Fig. 1). With a time lag of about 10 days, N_2O emissions increased in forage grass after the first fertilizer application following a precipitation event (34 mm m^{-2}), while only a small increase was measured after the second fertilizer application. Soil temperatures were already lower during the second application at the end of October 2020.

3.3. Area-scaled and yield-scaled N_2O emission, emission factors and CO_2-equivalents

Area-scaled cumulative N_2O emissions throughout the experiment ranged from 0.03 kg N_2O-N ha^{-1} $crop^{-1}$ (NON treatment in barley) to 3.9 kg N_2O-N ha^{-1} $crop^{-1}$ (SLA+ treatment in maize) (Fig. 3; Supplementary B: Table S3). For maize, the emissions per area averaged across all treatments were 10 times higher (3.4±1.1 kg N_2O-N ha^{-1} $crop^{-1}$) and significantly different from wheat (0.2±0.1 kg N_2O-N ha^{-1} $crop^{-1}$) and forage grass (0.5±0.2 kg N_2O-N ha^{-1} $crop^{-1}$). Emissions from barley (0.04±0.02 kg N_2O-N ha^{-1} $crop^{-1}$) were significantly lower compared to the other crops.
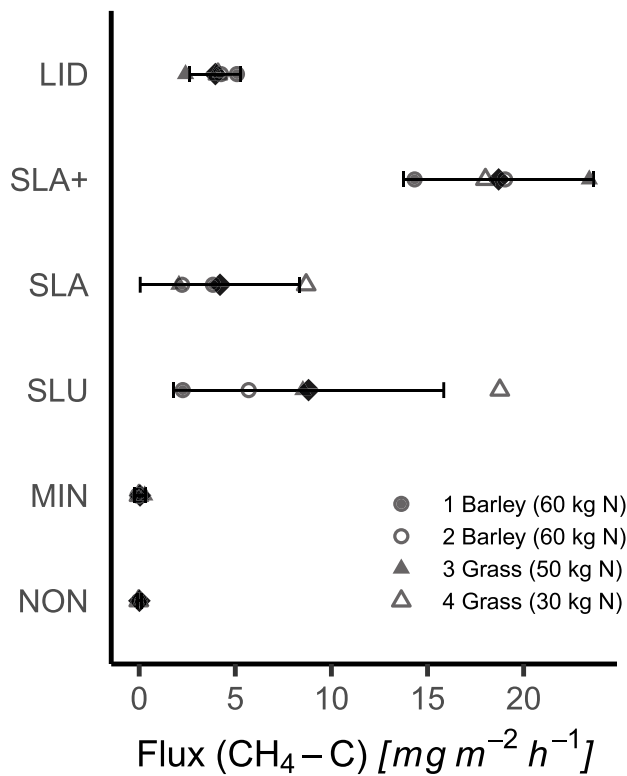
Fig. 4. Snapshot of CH₄ fluxes (mg CH₄-C m² h⁻¹) from measurements immediately after fertilizer applications at two time points in winter barley and two time points in forage grass. Black diamond shapes show treatment means ±SD ($n = 4$). Grey symbols represent individual values per sampling time point ($n = 4$). Letters indicate significant treatment differences (*Kruskal-Wallis chi-squared*=19.34, df=5, p = 0.002). NON: unfertilized control; MIN: mineral fertilizer; SLU: cattle slurry; SLA: agricultural digestate; SLA+ : agricultural digestate and biochar (2 t ha⁻¹ year⁻¹); LID: non-agricultural digestate.

Fertilizer treatment affected N₂O emissions only during wheat (p=0.011), where area-scaled N₂O emissions in SLA+ were significantly higher than in MIN (p=0.098) (Fig. 3; Supplementary: Table S4). The EF1 for MIN in wheat was on average about four times lower than for SLU, SLA and SLA+ and three times lower than for LID (0.08%) (Table 3). Forage grass had an average EF1 of 0.12%. LID had the lowest treatment mean across the crops (0.01%). The average annual EF1 across all treatments was 0.13%. EFs that were additionally calculated without subtracting the emissions of the control (EF2) ranged between 2.20 and 2.65 for maize, 0.09–0.19 for wheat, 0.03–0.05 for barley and 0.57–0.82 for forage grass (Supplementary: Table S4).

Yield-scaled N₂O emissions based on aboveground biomass were highest from maize (177 g N₂O-N t⁻¹) (Table 3). Yield-scaled N₂O emissions based on grain yield were higher from wheat (59 g N₂O-N t⁻¹) compared to barley (12 g N₂O- N t⁻¹) (Supplementary: Table S5). We found treatment differences only in wheat, where yield-scaled N₂O emissions from SLA (83 g N₂O-N t⁻¹) were significantly higher than from MIN (32 g N₂O-N t⁻¹).

Annual averages of CO₂-equivalents did not significantly differ between fertilizer treatments and ranged between 0.58 t CO₂-equivalents ha⁻¹ (LID) and 0.77 t CO₂-equivalents ha⁻¹ (SLA+) (Table 3). Maize cropping produced on average 1 t CO₂-equivalents ha⁻¹ more than the annual average.

3.4. Mixed effects model of drivers of N₂O emissions

Results from the linear mixed effects model across all crops showed that the most significant factor for increasing N₂O fluxes was soil temperature, followed by soil NO₃ and NH₄⁺ contents and soil WFPS

Table 3
Fertilizer-based emission factor (mean±SD), yield-scaled N₂O emissions (mean ±SD) for aboveground biomass (silage maize) and marketable grain yield of cereals (winter wheat and winter barley), and CO₂-equivalents (IPCC, 2021) (mean±SD). Small letters indicate results from a linear mixed model (n=4; p<0.05) and Tukey Post-Hoc test. Specified contrasts were applied in winter wheat for comparison between SLU-MIN, SLU-NON, SLA-MIN and SLA-NON.

Crop	Treatment	Fertilizer-based emission factors [%]	Yield-scaled N₂O emissions [g N₂O-N t⁻¹]	N₂O-CO₂-eq. emissions [t CO₂-eq. ha⁻¹]
Silage maize	NON	Not applicable	186±61a	1.29±0.4a
	MIN	0.45±0.50a	169±31a	1.56±0.3a
	SLU	0.19±1.00a	164±64a	1.40±0.6a
	SLA	0.37±0.45a	185±34a	1.50±0.3a
	SLA+	0.62±0.68a	207±61a	1.69±0.4a
	LID	<0	153±55a	1.28±0.5a
		F=0.3; p=0.84	F=0.4; p=0.84	F=0.4; p=0.82
Winter wheat	NON	Not applicable	34±17ab	0.04±0b
	MIN	0.03±0.04a	32±13b	0.05±0b
	SLU	0.13±0.07a	78±28ab	0.12±0ab
	SLA	0.14±0.06a	83±24a	0.13±0a
	SLA+	0.10±0.05a	67±23ab	0.11±0ab
	LID	0.08±0.03a	58±13ab	0.09±0ab
		F=2.2; p=0.12	F=3.3; p=0.03	F=4.3; p=0.01
Winter barley	NON	Not applicable	11±3a	0.01±0.01a
	MIN	0.01±0.01a	9±2a	0.02±0.00a
	SLU	0.02±0.01a	15±2a	0.02±0.00a
	SLA	0.02±0.01a	12±2a	0.02±0.00a
	SLA+	0.02±0.03a	11±6a	0.02±0.01a
	LID	0.02±0.01a	14±4a	0.03±01a
		F=0.5; p=0.71	F=0.94; p=0.48	F=1.2; p=0.35
Forage grass	NON	Not applicable	Not applicable	0.21±0.1a
	MIN	0.11±0.25a	Not applicable	0.25±0.1a
	SLU	0.13±0.27a	Not applicable	0.26±0.1a
	SLA	0.11±0.47a	Not applicable	0.25±0.2a
	SLA+	0.23±0.22a	Not applicable	0.29±0.1a
	LID	0.01±0.23a	Not applicable	0.21±0.1a
		F=0.2; p=0.93	Not applicable	F=0.2; p=0.94
Annual average	NON	Not applicable	Not applicable	0.56±0.2a
	MIN	0.15±0.14a	Not applicable	0.68±0.1a
	SLU	0.11±0.22a	Not applicable	0.65±0.2a
	SLA	0.15±0.17a	Not applicable	0.69±0.1a
	SLA+	0.22±0.15a	Not applicable	0.77±0.2a
	LID	0.02±0.21a	Not applicable	0.58±0.2a
		F=0.5; p=0.74	Not applicable	F=0.7; p=0.67

SLU: cattle slurry; SLA: agricultural slurry (from an on-farm biogas plant); SLA+: agricultural slurry (from an on-farm biogas plant) and biochar (2 t ha-1); LID: non-agricultural digestate.

(Table 4). In barley, N₂O fluxes correlated positively with soil temperature and NH₄⁺ contents, but the effect of WFPS was significantly weaker compared to maize, wheat and forage grass. Barley was the only crop where soil NO₃ contents did not correlate significantly positively with N₂O fluxes as there were no major N₂O emissions. Fluxes from forage grass were only significantly affected by rising soil NO₃ contents. In maize, the influence of soil temperature, WFPS and NO₃ but not NH₄⁺ contents on N₂O was significant, however the effect for NO₃ contents was smaller compared to the other crops. No significant relationships between N₂O emissions and fertilizer characteristics could be detected (Table 4; Supplementary: Table S7).

Table 4

Linear mixed effects model of log-transformed N$_2$O fluxes [µg N$_2$O-N m^2 h^{-1}] and soil properties for all crops combined and for each crop separately (silage maize, winter wheat, winter barley, and forage grass). Soil properties comprise soil water-filled pore space [WFPS, %], soil temperature [°C] and nitrate and ammonium contents [mg kg^{-1}]. Estimates (E), 95%-confidence intervals and p values are shown. Replicates were included as random factors and temporal correlation was considered in the model.

	All crops			Maize			Wheat			Barley			Grass		
Predictors	E	CI	p	E	CI	p	E	CI	p	E	CI	p	E	CI	p
(Intercept)	0.26	0.09 – 0.73	0.01	0.86	0.30 – 2.46	0.782	0.07	0.03 – 0.17	< 0.001	12.38	3.18 – 48.19	< 0.001	10.37	1.93 – 55.76	0.007
WFPS	1.04	1.03 – 1.04	< 0.001	1.04	1.04 – 1.05	< 0.001	1.03	1.02 – 1.04	< 0.001	0.96	0.94 – 0.97	< 0.001	1	0.99 – 1.02	0.517
Soil temp	1.12	1.10 – 1.15	< 0.001	1.07	1.02 – 1.11	0.005	1.13	1.11 – 1.16	< 0.001	1.11	1.07 – 1.15	< 0.001	1	0.94 – 1.07	0.947
Nitrate	1.05	1.04 – 1.06	< 0.001	1.03	1.01 – 1.04	< 0.001	1.14	1.11 – 1.18	< 0.001	1.07	0.97 – 1.18	0.163	1.07	1.05 – 1.10	< 0.001
Ammonium	1.05	1.03 – 1.06	< 0.001	1.01	0.99 – 1.02	0.254	1.05	1.03 – 1.07	< 0.001	1.03	1.01 – 1.06	0.005	0.99	0.92 – 1.08	0.898

3.5. CH$_4$ fluxes

Daily CH$_4$ fluxes were mostly negative throughout the study period, except for a few peaks of up to 50 µg CH$_4$-C m^{-2} h^{-1} in SLA+ one day after fertilizer application (Fig. 1). However, when fluxes were quantified immediately after applying fertilizer in barley and forage grass, highly elevated CH$_4$ fluxes were recorded, especially in SLA+ but also in SLU, SLA and LID (Fig. 4). This was not observed for N$_2$O fluxes (Supplementary: Figure S2).

The sum of average cumulative CH$_4$ uptake excluding the peaks directly after fertilizer application was between − 0.28 kg CH$_4$-C ha^{-1} (SLU) and − 0.37 kg CH$_4$- C ha^{-1} (SLA) after 33 months of monitoring fluxes (Fig. 3). The CH$_4$ uptake was significantly higher in maize and wheat compared to barley ($p<0.001$), and lowest in forage grass ($p<0.001$) (Supplementary: Table S5). No significant treatment differences were observed. There was a trend for higher cumulative emissions in SLA compared to MIN ($p=0.059$) and SLU compared to NON ($p=0.058$) excluding the additional measurements directly after fertilizer applications (Fig. 3).

4. Discussion

This study was designed to quantify parameters related to N dynamics after fertilizer applications. Fertilization with digestates did not produce markedly different emissions in N$_2$O compared to cattle slurry (Fig. 3). This is supported by the absence of significant correlations of cumulative N$_2$O emissions with digestate composition (Supplementary: Table S7). As similar emissions were observed for all fertilizer treatments while applying a similar amount of N$_{tot}$, increased N availability after fertilizer application can at most only partially explain N$_2$O emission.

4.1. Management history and abiotic factors were the main drivers of N$_2$O fluxes

In April 2018, after plowing the ley mixture into the soil, maize was sown and fertilizer was applied, followed by repeated harrowing against weeds. Fertilizers were only applied when growing plants were present, e.g. 4- and 6-leaf stage in maize. The N$_2$O emissions recorded after fertilizer applications in maize were several magnitudes higher than emissions from wheat, barley and forage grass (Fig. 2; Fig. 3). A possible explanation is that soil management triggered soil microbial activity, causing mineralization of incorporated plant residues, and soil N surplus (>10 kg N ha^{-1}) prompts N$_2$O emission (Van Groenigen et al., 2010). The legacy effect of nitrogen fixing leys or green manures and associated incorporation of organic material is another driver for N$_2$O emissions in organic farming, which can explain the weak relationship between fertilizer N-input and N$_2$O emissions (Hansen et al., 2019; Skinner et al.,

2014). In addition, maize cropping leaves part of the soil bare between the rows, and N demand of seedlings is low in the early growth stages, leaving more N for microbial processes. Conditions for spiking N$_2$O production were reached when soil temperature increased from about 15–20 °C, while at the same time WFPS was already above 60% and NO$_3$ levels started rising (Fig. 1).

Forage grass cropping produced higher N$_2$O emissions compared to wheat and barley cropping due to heat and moisture, even though N-input levels were lower (Fig. 3). During barley cultivation, N$_2$O fluxes followed a distinct trajectory including peaks after fertilizer applications similar to other crops (Fig. 2). However, the magnitude of the N$_2$O fluxes from barley was much lower compared to the other crops (Fig. 3), which was attributed to a set of conditions potentially impeding N$_2$O production that occurred during barley cultivation. Baral et al. (2017) reported similarly low N$_2$O emissions from barley cultivation from the unfertilized control, which were not significantly different from treatments that had received mineral fertilizer or digestate. During fertilizer applications in barley in spring 2020, soil temperatures were very low (around 5–10 °C), and soil WFPS gradually decreased right after the first fertilizer application due to a lack of rainfall. This likely decreased soil nitrification and/or denitrification rates as shown in Fig. 1, resulting in less available substrate for N$_2$O production and subsequently lower N$_2$O emissions.

Fertilization with ammonium sulphate lowered soil pH below 6 (Supplementary Table S3), but, due to fewer data points compared to mineral N contents, soil temperature and WFPS, the possible effects on N$_2$O emissions were not resolved statistically. In most cases, WFPS, soil temperature and availability of soil N$_{min}$ contents correlated significantly positively with N$_2$O fluxes (Table 4). This agrees with the literature (Oertel et al., 2016). Hot moments of N$_2$O formation occurred for all treatments, but the magnitude of the N$_2$O emissions seemed relatively unaffected by the course of NO$_3$ contents later on. In our study, effects of fertilizer type on N$_2$O emissions were mostly masked by soil management history and abiotic factors.

4.2. N$_2$O emissions were mostly not affected by fertilizer type

We consistently observed similar N$_2$O emissions from digested and undigested organic fertilizers (Fig. 3), and hence no adverse effects of applying anaerobic digestates compared to cattle slurry could be detected. Wheat cultivation caused nearly 2.5-fold higher yield-scaled emissions for agricultural digestates compared to the unfertilized control and mineral fertilizer (Table 3). During winter wheat cultivation, low N$_2$O emissions from the mineral fertilizer treatment might stem from substrate limitation for soil microbial transformation pathways involving N cycling due to increased plant N-uptake (Supplementary: Table S2); for example, due to plant uptake of readily plant-available ammonium (Frick et al., 2022).

The effects of digested versus raw manure on N_2O emissions are inconsistent due to various chemical characteristics of digestates and soil. Various chemical characteristics of digestates and soil contribute to the complexity of N_2O responses (Oertel et al., 2016). The formation of N_2O from digestate application can be accelerated by higher NH_4^+ contents and higher pH after AD (Sänger et al., 2010; Senbayram et al., 2009; Eickenscheidt et al., 2014). On the other hand, some studies suggest that easily degradable C is critical for N_2O production (Baral et al., 2017; Köster et al., 2015; Petrova et al., 2021). Lower microbial-accessible C contents in digestates compared to raw manure can lead to increased N use efficiency and reduced N_2O emissions (Hansen et al., 2019). In a C-rich soil like the one at the experimental field site, differences in organic C contents between digestate (SLA=374 ±11 g C_{org} (kg DM) $^{-1}$) and raw manure (SLU=413±22 g C_{org} (kg DM) $^{-1}$) did not translate into statistically different POXC contents in the soil (Fig. 1; Supplementary: Table S3). The influence of degradable C in organic fertilizers may be more important when C is generally low in the soil. For example, it was observed that higher soil C_{org} contents tend to increase N_2O emissions (Eickenscheidt et al., 2014; Dietrich et al., 2020).

The values for EF1 in this study were consistently lower than the IPCC default value of 1% (Eggleston et al., 2006) and compared to the literature (Skinner et al., 2014; Walling and Vaneeckhaute, 2017). We obtained such low EFs because the calculation of EF1 foresees to subtract emissions from the control, which had not received any N. In the present study, the control, which had not received N input, produced similarly high N_2O emissions compared to the fertilized treatments. Thus, the N_2O emissions were largely unaffected by fertilizer N input and therefore, EF1 was very small. While high N_2O emissions in maize were observed, EF1 ranged from 0.01% (MIN) in barley to 0.62% (LID) in maize 3), with the annual average EF1 lowest for LID (EF1 =0.02%) but not significantly different from the other fertilizer treatments, which ranged between 0.11% and 0.15% with high variation. Since measurements in this study were carried out in a newly established field trial, substantial amounts of N may have been released during mineralization of crop residues and previously supplied manure. High N mineralization from soil organic matter can constitute a major source of N_2O emissions (Ammann et al., 2020) and consequently lower EF1. Therefore, high N_2O emissions in maize did not translate into a high EF1. Additionally, the relatively low clay content of 18% may have contributed to lower EF1 values, as clay-rich soil promotes larger EFs (van Groenigen et al., 2004).

Comparison of our results with the literature is limited because the calculation method for EFs varies between studies, often considering only fertilized plots. Therefore, we additionally calculated overall EFs (area-scaled N_2O emissions divided by fertilizer N-input; EF2) regardless of emissions from the control (NON). The overall values for EF2 in our study ranged between 0.74% and 0.91% annually and showed no fertilizer treatment effect (Supplementary: Table S4). These values are in line with Skinner et al. (2014) who reported a large range of EF2 (between 0.3% and 36%) from fields managed under organic farming. However, their calculation included emissions from crop residues and biological N fixation in addition to N from fertilizers. Walling and Vaneeckhaute (2017) reported EF2 values of applied N from synthetic fertilizers at 0.03–12.9%, from manures at 0.05–13.9% and from digestates at 0–5.1%, suggesting that digestates tend to have lower mean EF2 values, but higher variability.

Annual averages of CO_2-equivalents (Table 3) were slightly lower in our experiment (0.58–0.77 t CO_2-equivalents ha^{-1}) compared to on average 1.2 t CO_2- equivalents ha^{-1} as reported by Skinner et al. (2014) for arable land under organic farming.

4.3. Biochar amendment to digestate did not change N_2O emissions

Biochar had no significant effect on N_2O emissions in our study, likely due to the low application rate and limited interaction with the soil. A recent meta-analysis showed that reduction of N_2O emissions by biochar by 38% occurred at > 10 t ha^{-1} biochar (Borchard et al., 2018). The field site in the present study receives 2 t ha^{-1} $year^{-1}$ biochar and will therefore reach these inputs levels only 5 years after the beginning of the experiments. The results from Borchard et al. (2018) were furthermore obtained from a database consisting mainly of laboratory experiments, while our experiment was a field study. An absence of biochar effects on soil processes and properties in field experiments is not uncommon due to high (structural) heterogeneity in fields (Kammann et al., 2017) and associated large data variability (Hüppi et al., 2015; Verhoeven et al., 2017). We did not incorporate the biochar directly into the soil, but rather it was milled, added to SLA and spread onto the soil surface together with the fertilizer after a two week incubation period. Hence, the potential for biochar to interact with the soil, for example to increase the pore volume or the pH, was limited in our study. The biochar's molar $H:C_{org}$ ratio of 0.29–0.44 also suggests limited effectiveness for mitigating N_2O emissions as biochars with an $H:C_{org}$ ratio < 0.3 mitigate N_2O emissions more effectively (Cayuela et al., 2015).

4.4. Net uptake of soil-borne CH_4 contrasts CH_4-release after fertilizer application

Cumulative area-scaled CH_4 uptake (Fig. 3) did not include the additional measurements (Fig. 4) which were conducted right after fertilizer applications in barley and forage grass. This decision was based on the lack of sufficient data to fully characterize the shape and origin of the additional CH_4 peaks. Without these additional fertilizer peaks, CH_4 fluxes were mostly negative and similar for all fertilizer treatments (Fig. 1). Although some studies have observed elevated CH_4 emissions from raw manure compared to digestates (Wulf et al., 2002; Clemens et al., 2006), no effects have been observed in other studies (Eickenscheidt et al., 2014). Across all fertilizer treatments, cumulative CH_4 uptake decreased over time, i.e. from crop to crop. This could be due to decreasing availability of organic C residues from previous ley termination for methanogenes.

The two additional measurements (Fig. 4) on the days of fertilizer applications in barley and forage grass revealed increased CH_4 fluxes from SLA+ and more moderately elevated CH_4 emissions from SLA and LID. Our study was not designed to capture non soil-borne CH_4 emissions. Possibly, dissolved CH_4 in SLA+ that remained bound to the surface of the biochar during storage was released upon fertilizer application. Alternatively, methanogens in the agricultural slurry might have been stimulated by biochar addition and incubation for about two weeks in the SLA+ treatment and dissolved CH_4 might then have been released upon fertilizer application. Methanogenesis during AD is inhibited by NH_4^+-N contents above 4000 mg L^{-1} (Czatzkowska et al., 2020; Zhang et al., 2019). Fertilizer NH_4^+ was presumably trapped within or adsorbed by the porous biochar structure allowing resumption of microbial CH_4 production. More research is needed to clarify the effect of biochar addition to liquid fertilizers on CH_4 emissions.

5. Conclusions

Based on a long-term field experiment and a multi-crop N_2O measurement campaign, our study shows that N_2O emissions were controlled by soil management history and abiotic factors rather than the type of N- fertilizer applied. Digestates did not increase N_2O emissions compared to cattle slurry. N_2O emissions from organic and mineral fertilizers were mostly similar. N_2O-EFs were generally low, because of large background emissions from the unfertilized plots. With respect to N_2O mitigation, we recommend reducing fertilizer N input to crops grown directly after ley termination as NO_3^- released by mineralization of soil organic N caused considerable N_2O emissions in all treatments. Biochar did not decrease N_2O emissions because of low application amounts. Biochar-amended agricultural digestate released CH_4 right after spreading. Therefore, measurements of CH_4 emissions during

digestate storage and spreading should be included in future field studies, especially when biochar is involved.

Author contributions

EB, NE, HMK, MK, JM and JM planned the experimental work and developed the methodological approach; NE, NV and FZ carried out the measurements; JS, HMK and EB guided and supervised the work; RH and MK provided advice on gas flux calculation and data analysis; NE analyzed the data and wrote the first draft; all authors commented on drafts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper..

Data Availability

The data will be made publicly available under the following link from Zenodo: 10.5281/zenodo.7633755.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agee.2023.108642.

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