Agriculture, Ecosystems and Environment 345 (2023) 108327

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Greenhouse gas balances and yield-scaled emissions for storage and field application of organic fertilizers derived from cattle manure

Xiaoyi Meng[a,*], Peter Sørensen[a], Henrik B. Møller[b], Søren O. Petersen[a]

[a] Department of Agroecology, iClimate, Aarhus University, Blichers Allé 20, 8830 Tjele, Denmark
[b] Department of Engineering, Aarhus University, Blichers Allé 20, 8830 Tjele, Denmark

A R T I C L E I N F O

Keywords:
Anaerobic digestate
Liquid separation
Greenhouse gas emission
Manure management
Fertilizer value

A B S T R A C T

Manure treatment such as anaerobic digestion and solid-liquid separation has shown a potential to abate greenhouse gas (GHG) emissions, but few studies have considered GHG emissions from both storage and field application regarding crop yield. In this study, four different organic fertilizers were studied: untreated cattle manure (CA); digestate of cattle manure anaerobically co-digested with grass-clover (DD); a liquid fraction from the separation of DD (LF); and a liquid fraction derived from a biogas desulfurization biofilter enriched with sulfur and ammonium (NS). The CH_4, N_2O and NH_3 emissions during storage of CA, DD and LF between August and November 2020 (11 weeks) were quantified. Storage continued until April 2021 when these materials, as well as the NS fertilizer and a mineral NKS fertilizer, were applied at a rate of 100 kg total N ha^{-1} to spring barley. N_2O emissions and soil mineral N content were monitored during the growing season. Overall, CH_4 emissions during storage were the main source of GHG emissions independent of treatments, accounting for 85 %, 40 % and 11 % of total GHG emissions (based on field application of 100 kg ha^{-1} total N) from treatments CA, DD and LF, respectively. Anaerobic digestion and separation significantly reduced CH_4 emissions during storage due to the diminished content of degradable organic matter available for methanogens. The N_2O emissions from treatments CA, DD, and LF during storage were not significantly different. Treatments DD and LF emitted more NH_3 than CA during storage, presumably because of higher pH and ammonium content. In the field experiment, the dilute solution of NS emitted the most N_2O, while emissions from treatments CA, DD and LF were comparable. Yield-scaled GHG emissions for treatments CA, DD, LF and NS during both periods of storage and field were 44.4, 17.1, 8.5 and 24.3 kg CO_2 eq hkg^{-1} grain yield, respectively. Anaerobic digestion with or without separation were thus effective strategies for the mitigation of GHG emissions from cattle manure in this study. Yields and nitrogen use efficiencies of the processed manure materials were not significantly different from those observed with the same N application rate as inorganic fertilizer, and hence anaerobic digestion with or without separation were promising GHG mitigation strategies.

1. Introduction

Ruminants excrete 75–95 % of the ingested N as dung and urine, and recycling the manure as an organic fertilizer is a widely used practice to supply essential nutrients for crop production (Castillo et al., 2000; Eckard et al., 2007). This is particularly needed in organic farming where synthetic N is not available to meet the N demand of plants (Chmelíková et al., 2021). Anaerobic co-digestion of livestock manure and other biomasses is a well-known strategy to produce biogas as a renewable energy source, and an additional benefit of this treatment is to increase the proportion of nutrients in plant available form compared to the untreated substrates (Holly et al., 2017). In organic farming, however, co-digestates are restricted to fiber-rich residues such as deep litter or plant biomass, and this may complicate the management of nutrients and environmental losses by significantly changing the physical and chemical properties of digestates. For example, Häfner et al. (2022) reported N fertilizer values of digestates based on food waste, manure and crop residues ranging from 18 % to 83 % across two years. Also, fiber-rich residues may increase the potential for CH_4 and N_2O emissions during storage and after field application (Wang et al., 2014; Baral et al., 2017).

Additional processing is possible to obtain new products that meet

---

* Corresponding author.
E-mail address: au657355@uni.au.dk (X. Meng).

https://doi.org/10.1016/j.agee.2022.108327
Received 25 October 2022; Received in revised form 15 December 2022; Accepted 17 December 2022

specific needs (Mata-Alvarez et al., 2000; Svensson et al., 2004; Odlare et al., 2011). For example, solid-liquid separation produces a nitrogen- and potassium-rich liquid fraction and a phosphorus-rich and dry matter-rich solid fraction (Møller et al., 2000; Baral et al., 2018). The solid fraction of a digestate can be used directly as a biofertilizer in agriculture, or it can be composted and used as a soil amendment (Dinuccio et al., 2008). Depending on separation technology, an NH_4^+-enriched liquid fertilizer with a reduced dry matter content is produced (Hjorth et al., 2011), and with physical characteristics that may promote infiltration and benefit plant N uptake (Morris and Lathwell, 2004). Further treatments of digestates and separation products are possible, such as membrane treatment, biological treatment, stripping and evaporation, but there will be a trade-off between fertilizer value, environmental effects, and the cost of processing.

Manure processing to increase crop production should not have negative environmental impacts. Gaseous losses during storage and after field application contribute significantly to greenhouse gas (GHG) emissions, with far-reaching environmental effects (Zervas and Tsiplakou, 2012). It has been reported that methane (CH_4) was the main GHG source during storage, and N_2O was the main contributor after field application (Amon et al., 2006; Baral et al., 2018). Removing degradable organic matter by manure treatment such as anaerobic digestion or separation is expected to reduce the potential for methanogenesis and CH_4 emissions during storage (Amon et al., 2006; Holly et al., 2017), and in some cases reduce N_2O emissions after field application (Petersen, 1999; Möller and Stinner, 2009; Thomsen et al., 2010).

In order to ensure high availability of manure N for crop production, it is important to minimize N losses during both storage and field application. It was reported that the anaerobic digestion of dairy manure increased the NH3 emissions during storage due to higher total ammoniacal nitrogen and pH (Sun et al., 2014; Neerackal et al., 2015). Temperature also affects NH_3 emissions especially when NH_3 level and pH are high (Clemens et al., 2006). Studies reporting N_2O emissions from digestate and untreated manure during storage were not consistent; Sommer et al. (2000) concluded that there were more N_2O emissions from digestate during storage, while other studies found insignificant differences (Amon et al., 2006; Holly et al., 2017).

A review of field studies found that field-applied organic fertilizers have a higher N_2O emission factor (1.21 ± 0.14 %) than the IPCC default emission factor of 1 % (IPCC et al., 2006; Charles et al., 2017). By comparison, N_2O emissions from inorganic fertilizers are much more variable and may be much less than 1 % depending on site conditions such as annual rainfall (Bell et al., 2015). Many studies have found that annual emissions of N_2O from well-drained arable soils occur mainly during the period in spring and early summer when N applied for crop production is available in the soil (Chirinda et al., 2010; Bell et al., 2015; Herr et al., 2020). A review by Möller (2015) concluded that the predominant response to anaerobic digestion of manure is a reduction of N_2O emissions after field application, possibly as a result of the lower availability of degradable carbon to maintain anaerobic conditions supporting denitrification (Baral et al., 2016). There is little information about the possible effect of separating digestate on soil N_2O emissions; (Meng et al., 2022) found in laboratory incubation experiments, surprisingly, higher N_2O emissions from the liquid fraction and concluded that denitrification was enhanced by the greater contact between the liquid fraction and soil.

Nitrogen use efficiency and crop yield were in some studies higher with digestates compared to untreated manure if application method, timing, and rate were optimal (Abubaker et al., 2012; Webb et al., 2013). However, other studies found that crop yields were not significantly different between undigested and digested cattle slurry (Pötsch, 2005; Möller et al., 2008). The amount and composition of organic matter in organic fertilizers may also affect crop N availability through priming effects or inorganic N immobilization (Bernal and Kirchmann, 1992; Kirchmann and Lundvall, 1993).

Greenhouse gas emissions from organic fertilizers should be held up against crop N use efficiency to evaluate yield-scaled emissions. This is best done with a system-oriented approach where the emissions from both storage and field application are determined together with N use efficiency, to suggest best strategies for low-emission crop production. In this study we investigated (i) CH_4, N_2O and NH_3 emissions during storage of untreated cattle manure, a digestate based on cattle manure, and the liquid fraction of mechanically separated digestate; (ii) N_2O emissions from these organic fertilizers, as well as an NS fertilizer and mineral fertilizer treatment after field application; and (iii) the N uptake and yield of spring barley at harvest. Our hypotheses were: (i) GHG emissions from digested organic fertilizers would be less compared to untreated cattle manure during storage; (ii) N_2O emissions from untreated and digested fertilizer materials after field application would be comparable; and (iii) digested fertilizer materials would have higher crop yields compared to undigested fertilizer.

2. Materials and methods

2.1. Organic fertilizers

Four different fertilizer materials derived from cattle manure were part of this research including (1) untreated cattle manure (CA) as a reference; (2) a digestate produced mainly from cattle manure (DD); (3) the liquid fraction of separated DD (LF); and (4) a nitrogen-sulfur (NS) concentrate produced as described below. Liquid cattle manure was obtained from the experimental farm of the research center belonging to Aarhus University; the breed of cattle was Holstein. Digestate was obtained from an experimental biogas facility where the substrate for anaerobic digestion was a mixture of 92.5 % cattle manure and 7.5 % grass-clover silage by weight. The daily load was 270 kg for a 10 m^3 digester with an active volume of 9 m^3. The operating temperature was 51 °C, and the hydraulic retention time (HRT) was 33 days. The liquid fraction of digestate was obtained after mechanical separation of digestate using a GEA Westphalia decanting centrifuge (UCD 305–00–02, Germany). Before separation, the digestate had been stored at 20 ℃ for 30 days to collect residual biogas during the cooling phase. An NS fertilizer was produced by passing the biogas over a bio-trickling desulfurization filter with a biofilm of bacteria under microaerophilic conditions, where H_2S was oxidized to elemental sulfur or H_2SO_4, and during this process, the pH was reduced from 7.9 to 2.0. The biofilter was supplied with a liquid manure fraction from a 50 μm microfiltration (Sepcom, Italy). The acid liquid was subsequently enriched with a concentrated ammonia solution (25 %) until a final pH of about 6.5. NH_3 would originate from the process of drying the separated solids. Selected physical-chemical properties of the different manure-derived products are shown in Table 1.

2.2. Storage experiment

A pilot-scale experiment was conducted in covered and partly below-ground tanks (6.5 m^3) with continuous ventilation to quantify the GHG and NH_3 emissions during storage. Detailed information about the facility is given in Petersen et al. (2009) and pictures in Fig. S1. Storage took place between 21 August and 7 November 2020 (11 weeks). The minimum, maximum, and average air temperatures during the period of the storage experiment were 0.6, 25.4, and 11.9 ℃, respectively, and the cumulative rainfall was 157 mm. The daily precipitation and air temperature during the storage period (as well as the field application period introduced below) are shown in Fig. S2. Approximately 2 m^3 portions of untreated cattle manure (CA), digestate (DD), and the liquid fraction of the digestate (LF) were stored with two replicates per treatment. The liquid volume in each tank was measured at the beginning and end of the monitoring period and the average volume was used for calculations. Forced ventilation was employed to simulate open storage; ventilation rates varied between 85 and 121 m^3 h^{-1}.

For emission measurements, a subsample was taken from the

Table 1
Chemical and physical characteristics of fertilizers used for storage and field application. CA: untreated cattle manure; DD: anaerobic digestate of cattle manure co-digested with 7.5% grass-clover; LF: liquid fraction of DD; NS: liquid fraction from biogas desulfurization filter enriched with sulfur and ammonium. VS = volatile solids; TN = Total N; TC= Total C; Appl, Rate= Application rate.

Slurry type	DM	VS	TN	TC	NH_4^+-N	pH	NH_4^+-N /TN	Appl, Rate	Appl, Rate
	kg ton^{-1}	kg ton^{-1}	kg ton^{-1}	kg ton^{-1}	kg ton^{-1}			kg TN ha^{-1}	kg NH_4^+-N ha^{-1}
	Storage, beginning (August 21, 2020)								
CA	49.0	39.2	2.3	–	1.1	7	0.48	–	
DD	37.5	25.2	3.1	–	2.1	7.8	0.68	–	
LF	27.1	19	2.8	–	1.9	7.9	0.68	–	
NS[a]	–	–	–	–	–	–	–		
	Storage, end (November 7, 2020)								
CA	51.7	40.0	2.3	–	1.2	7.4	0.53		
DD	46.7	32.3	2.8	–	1.7	7.8	0.61		
LF	32.3	23.6	2.5	–	1.7	7.8	0.66		
Field application (April 13, 2021)									
CA	51.7	–	2.5	78	1.2	7.7	0.48	107.0	51.4
DD	40.5	–	2.8	56	1.6	8	0.57	98.8	56.3
LF	27.4	–	2.5	45	1.5	8	0.60	95.1	57.0
NS	10.5	–	1.2	22	0.8	7.3	0.67	114.9	77.0

[a] Not included in storage experiment.

ventilation air with a peristaltic pump operating continuously at 15 ml min^{-1}. For the determination of NH_3 loss, acid traps with 20 mM phosphoric acid were inserted near the sampling position, and the acid was replaced every 7 days. For determination of CH_4 and N_2O in the ventilation air, the subsamples of ventilation air from each tank were led to a rack with three-way solenoid valves downstream from the pump; the valves were programmed to collect ventilation air in 3-liter aluminum foil gas sampling bags (SKC Ltd.) for 1 min in every 60 min. The gas sampling bags were also replaced weekly. Following the 11-week storage period with monitoring of emissions, a portion of each organic fertilizer was transferred to a 1 m^3 closed plastic pellet tank for storage in a shelter until the following spring.

2.3. *Field experiment*

The field site was located at Foulumgaard (56°49′N, 09°58′E) in Central Jutland, Denmark. The soil is classified as loamy sand with 9 % clay, 13 % silt, and 78 % sand. Soil bulk density after cultivation is 1.35 g cm^{-3} (0–25 cm), and the soil contains around 1.8 g kg^{-1} total N, 23 g kg^{-1} soil organic matter, 33 mg kg^{-1} Olsen-P, 120 mg kg^{-1} extractable K. It had a pH of 6.5 (0.01 M $CaCl_2$) (Li et al., 2015). The mean annual precipitation and air temperature (1996–2016) of the site were 774 mm and 8.2 ℃, respectively (Autret et al., 2020). The minimum, maximum, and average air temperatures during the experimental period from the day of fertilization (13 April 2021) to three days after harvest (13 August 2021) were − 2.6, 28.0, and 13.3 ℃, respectively, and the cumulative rainfall was 302 mm.

The field experiment included four treatments with organic fertilizers: (1) CA; (2) DD; (3) LF; (4) NS. The application rates were close to 100 kg total N ha^{-1}; specific application rates are given in Table 1. Besides, three levels of mineral fertilizer were included at application rates of (5) 100 kg ha^{-1} total N (M100) and (6) an unfertilized control (M0). The mineral fertilizer was AXAN NS 27–4 with 27 % nitrogen (equal proportions of NH_4^+ and NO_3^-) and 4 % sulfur. The experimental area was subdivided into three blocks, each with eight 15 m × 3 m plots separated by 1.5 m wide strips. The organic fertilizers were applied by direct injection (10 cm depth, 24 cm between injectors) after plowing on 13 April 2021 with except for NS fertilizer, where the application was split over two days to allow for infiltration of a large liquid volume. Hence, half of the NS fertilizer was injected before plowing, and the other half the following day after plowing. All mineral fertilizers were surface-applied on 13 April 2021. The crop was spring barley (Hordeum vulgare L) which was sown on 14 April 2021 and harvested on 13 August 2021. The field experiment was managed according to Danish organic farming rules, except for the treatments with mineral N. No pesticides were used and the barley was protected against weeds by blind-harrowing at an early stage, and by establishing the barley at 24 cm row distance combined with inter-row hoeing in May (De Notaris et al., 2019).

The first soil and gas samples were collected on 15 April 2021, that is, 2 days (1 day for a part of the NS fertilizer) after fertilizer application, as well as 6 and 9 days after fertilization. Subsequently, samples were collected once per week during week 3–11 after fertilization, and in week 13 and 19 (three days after harvest). Gas sampling was always initiated around 10:00 (mid-morning) to represent the daily average soil temperature (Reeves and Wang, 2015). Flux measurements were done using two-part static chambers (75 cm × 75 × 20 cm) supported by stainless steel frames inserted to c. 10 cm depth immediately after seeding; the chambers were equipped with a septum for gas sampling and a battery-driven fan to mix headspace gas, but no vent. Ten ml headspace gas was sampled at chamber deployment and additionally three times within a c. 2-hour period; gas samples were transferred to 6 ml pre-evacuated exetainers (Labco, Lampeter, UK) for analysis by gas chromatography.

Soil sampling took place in parallel with gas sampling. Six subsamples (0–20 cm depth) were taken using a 2 mm diameter auger and pooled. Soil samples were stored at − 20 °C before analysis of gravimetric moisture and mineral N content. The barley crop was harvested on 13 August 2021 with a combine harvester and divided into grain and straw. The above-ground dry matter was determined after drying at 60 °C for 40 h. The total N of the harvested plant material is expressed as a percentage of DM. The apparent fertilizer N use efficiency (NUE) was calculated as:

$$NUE_i = (N_{fert,i} - N_{control})/N_{applied,i}$$

where $N_{fert\ i}$ is the crop N uptake (kg N ha^{-1} in grain + straw) with fertilizer i; $N_{control}$ is the crop N uptake in the unfertilized soil (control); and $N_{applied\ i}$ is the total N application rate (kg TN ha^{-1}) with fertilizer i.

2.4. *Analytical methods*

Concentrations of N_2O and CH_4 were determined by Model 7890 gas chromatography system with dual-inlet injection (Agilent; Nærum, Denmark) configured as previously described by Petersen et al. (2012). Detection limits were 0.042 and 61 μL L^{-1} for N_2O and CO_2, respectively.

The moisture content of soil and organic fertilizers were measured by drying at 105 ℃ for 24 h, and the volatile solids (VS) of organic fertilizers after an additional 6 h at 500 ℃ after drying at 105 ℃ for 24 h. The pH and electrical conductivity were measured by a MeterLab CDM210

(Hach; Loveland, Colodaro, USA) in a 1:1 (w/v) soil:water slurry. For analysis of NH_4^+ and NO_3^- in soil samples, about 10 g fresh wt. soil was extracted in 40 ml 1 M KCl; the mixture was rotated end-over-end for 30 min and centrifuged at 1500 rpm for 5 min. The supernatant was then filtered through a microfiber filter (Filter 691, VWR Europe) and measured colorimetrically by continuous flow analysis using an Autoanalyser III (Bran+Luebbe, Germany). The Henderson-Hasselbalch equation was used to calculate concentrations of NH_3 in the manure at the beginning of storage from pH and the total ammoniacal N concentration (Hao et al., 2005); the calculation is in Supplementary information. The total N of organic fertilizers and plant materials was determined by the Kjeldahl method (Novozamsky et al., 1983).

2.5. Data analyses

In the storage experiment, weekly average gas fluxes were calculated as the product of ventilation rate, logged as 15-minute averages for the individual storage units, and gas concentrations in the time-integrated gas samples composed of hourly 15 ml subsamples. A separate gas sampling line, collecting ambient air at 1 m height in a position among the pilot-scale storage tanks, represented the background concentrations of CH_4, N_2O and NH_3. The temperature used was a 7-day moving average of air temperature. Only treatment CA was observed to form a thin crust inside the tank during storage.

In the field experiment, fluxes of N_2O were calculated by the flux estimation software HMR using new functions pfvar, pfalpha, SatPct and SatTimeMin which constrain the datasets analyzed with a nonlinear model. The parameters selected for pfvar and pfalpha represent prefiltering to avoid using a nonlinear model with low fluxes for which measurement uncertainty is high. Here, pfvar was set at 0.0001 μg N_2O l^{-1} corresponding to a coefficient of variation of 3 %, while the default significance level, $p < 0.05$, was used for pfalpha. SatPct and SatTimeMin together limit the curvilinearity of nonlinear fluxes, and here the parameter values were 90 and 2, respectively, which means that an exponential curve increasing to a maximum would not be allowed to reach 90 % of full saturation until 2 h after chamber deployment. HMR is available as an add-on package in R (R Core Team, 2014). The cumulative N_2O emissions were calculated by linear interpolation between daily fluxes.

The emissions of CH_4, N_2O and NH_3 during storage, as well as CO_2 equivalents (100-year time horizon) from CH_4 and N_2O, and indirect N_2O emissions from NH_3, were analyzed by mixed-effects models using the "lme" function from the R package "nlme". Global warming potentials of 28 and 265 were used for CH_4 and N_2O, respectively (Woodward et al., 2014). Manure type, week and their interactions were fixed effects in the mixed-effects models, and tank ID was used as a random effect. To satisfy the requirement for normality of residuals and variance homogeneity, for N_2O emissions, the residuals of the linear model with week as fixed effect were used as the dependent variable. For CH_4, NH_3 and CO_2 equivalents, the cubic root of the raw data was used as the dependent variable. Autocorrelation was taken into account all models. Sidak was used in post-hoc comparisons. To compare treatment effects on gas emissions after field application, ANOVA was used followed by the Tukey-HSD test using R 4.0.3 software. Levene's test was used to test for homogeneity of variance, and the Shapiro-Wilk test was used to test for normality. The level of significance was set to 0.05.

3. Results

3.1. Properties of organic fertilizers

Table 1 and Table S1 present the composition of organic fertilizers before and after storage. At the beginning of the storage period, dry matter (DM) and volatile solids (VS) contents in treatment DD were lower compared to treatment CA, while total N and NH_4^+-N concentrations were higher. DM and VS were further reduced in the LF treatment, whereas N concentrations were unchanged, indicating a selective removal of fibers that had low nitrogen content. During storage, the NH_4^+/TN and NH_4^+ content declined in DD and LF. Between the end of the storage experiment in November 2020 and the field application of organic fertilizers in April 2021, the trends of dry matter loss continued, and there was an increase in pH in all three treatments. Treatment NS had the lowest dry matter content, as well as NH_4^+ and total N content, while it had the highest ratio of NH_4^+-N/total N.

3.2. Temporal dynamics of emissions during storage

Transformations of C and N during storage were accompanied by gaseous emissions of CH_4, N_2O and NH_3. Treatment CA showed the highest CH_4 emissions which gradually increased and peaked after about 50 days of storage (Fig. 1a). CH_4 emissions from treatment DD were lower and dropped after the first month, while the emissions from treatment LF remained close to zero throughout the measurement period. The CH_4-C/(CH_4-C + CO_2-C) ratios showed a declining trend, varying between 11 % and 45 % (mean: 34 %) in treatment CA, between 0% and 23% (mean: 13%) in treatment DD, and between 0 % and 31 % (mean: 6 %) in treatment LF (Fig. 1b, CO_2 emission are in Fig. S3).

Treatment CA emitted the least NH_3 during most weekly periods while DD emitted the most (Fig. 1c); the largest difference in NH_3 emission between CA and other treatments occurred in the first week. Based on NH_4^+-N concentrations and pH of individual treatments, the concentrations of free NH_3 at the beginning of storage in treatments CA, DD and LF were 6, 63 and 80 mg NH_3 l^{-1}, respectively (Supplementary calculation). N_2O emissions during storage in all three treatments showed similar trends, with a decline during day 0–28 and a transient increase around day 30–50 (Fig. 1d).

3.3. Temporal dynamics of N_2O emissions after field application

From all treatments in the field experiment, N_2O emissions occurred mainly during the first 50 days (Fig. 2a). NS fertilizer stood out with extremely high emissions, and treatments CA, LF, DD, M0 and M100 were not significantly different ($p > 0.05$) (Fig. 3a). Even without including NS fertilizer, they were also not significantly different from each other ($p > 0.05$, results not shown). NS had the highest N_2O emission factor (EF) of 2.4 %, whereas treatments CA, LF and DD all had EF values lower than 1 %, and M100 had a negative EF since this treatments showed less N_2O emission than M0 (Fig. 3b). The largest emissions of N_2O from treatments CA, LF and DD occurred during day 28–42. Yield-scaled GHG emissions applied with per 100 kg TN ha^{-1} were lower in treatment LF than in CA, DD and LF during the storage and field monitoring periods (Table 2).

3.4. Soil mineral N dynamics and water content

Treatment NS and M100 had high NH_4^+ levels during day 1–42 (Fig. 2b). Treatments CA, DD, and LF had comparable NH_4^+ during the whole period and the NH_4^+ value fluctuated during day 1–25 and then diminished slowly. The soil NO_3^- concentrations of treatment M100 during day 1–42 closely followed the NH_4^+ trend, while there was a slower decline during day 28–60 (Fig. 2c). For all organic fertilizers, soil NO_3^- concentrations remained below 20 μg N g^{-1} during the whole monitoring period. There were no clear differences in soil gravimetric water content, which were averaged 20–22 % (corresponding to 50–55 % WFPS in this soil), with all manure-derived fertilizers during day 0–42 (Fig. 2d).

3.5. Cumulative GHG emissions during storage and after field application

Cumulative CH_4 emissions during storage from treatment CA were, respectively, 4 and 33 times larger than those from treatments DD and LF, whereas N_2O emissions were similar and NH_3 emissions were

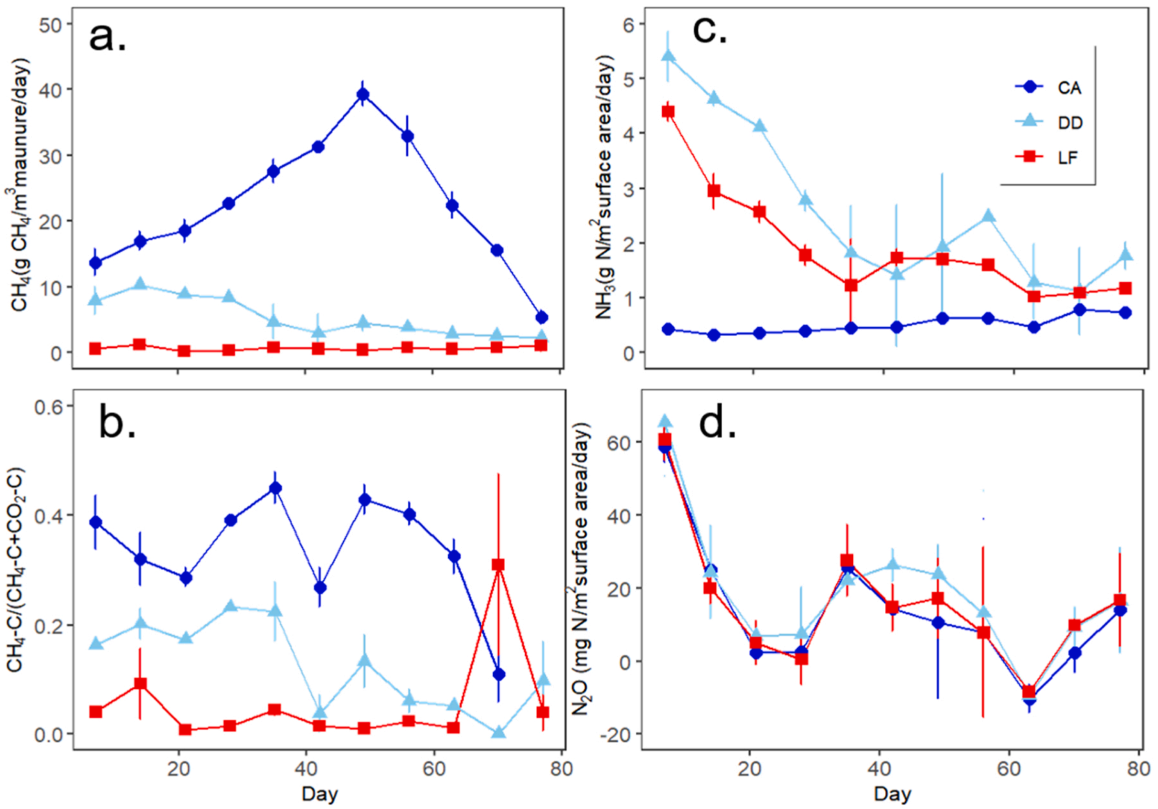

Fig. 1. Emissions of CH_4 (a), CH_4-C/(CH_4-C + CO_2-C) ratios (b), emissions of NH_3 (c) and emissions of N_2O (d) from untreated manure (CA), digestate of cattle manure co-digested with 7.5% grass-clover (DD), and the liquid fraction of digestate (LF) during storage. The error bars represent the standard deviation of the mean.

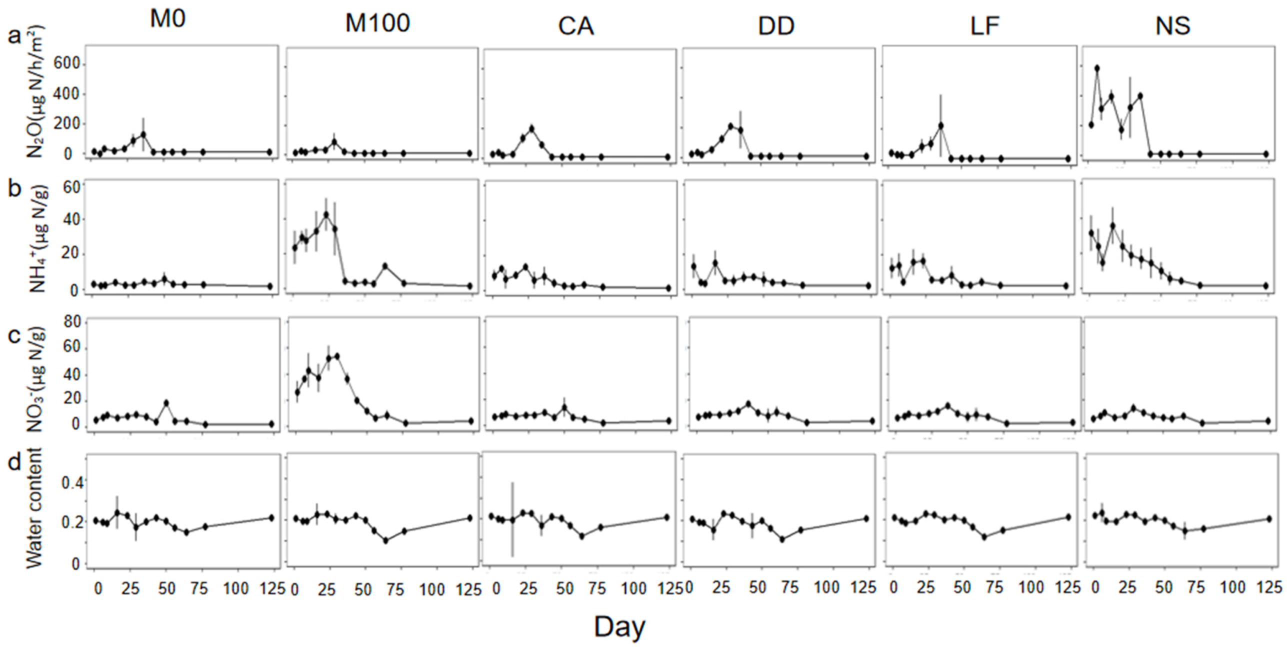

Fig. 2. N_2O emissions (a), concentration of NH_4^+ (b) and NO_3^- (c), and soil water content (d) after fertilization with different N sources. CA: untreated cattle manure; DD: anaerobic digestate of cattle manure co-digested with 7.5% grass-clover; LF: liquid fraction of DD; NS: liquid fraction from biogas desulfurization filter enriched with sulfur and ammonium; M100: mineral fertilizer with an application rate of 100 kg TN ha^{-1}; M0: unfertilized control.

4–5 times lower than from the digested fertilizers DD and LF (Table 2). The cumulative emissions of N_2O after field application were also similar in treatments CA, DD and LF ($p > 0.05$), whereas the cumulative N_2O emissions from the NS fertilizer were significantly higher. About 93 %, 94 % and 93 % of total N_2O emissions during storage and after field application came from the field for treatments CA, DD and LF, respectively (data not shown). For treatment CA, CH_4 emissions during storage constituted the main source of the overall GHG emissions during storage

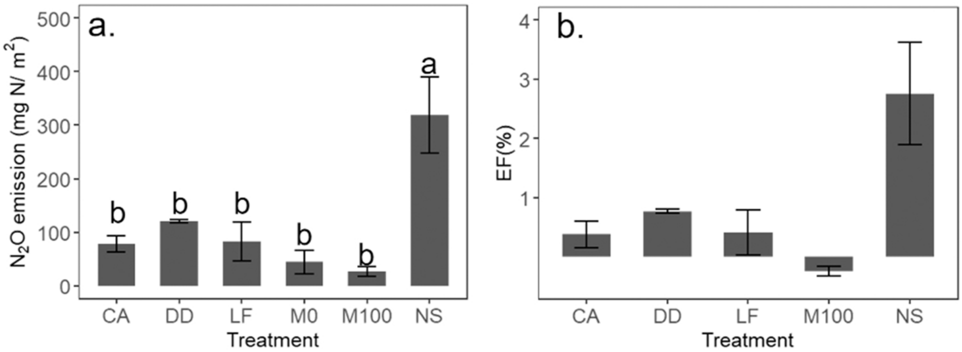

Fig. 3. Cumulative N_2O emissions (a) and N_2O emission factors (EF) (b) of the different fertilizers after field application. The letters show significant differences at $p < 0.05$. CA: untreated cattle manure; DD: anaerobic digestate of cattle manure co-digested with 7.5 % grass-clover; LF: liquid fraction of DD; NS: liquid fraction from biogas desulfurization filter enriched with sulfur and ammonium; M100: mineral fertilizer with an application rate of 100 kg TN ha^{-1}; M0: unfertilized control.

Table 2
Cumulative emissions of CH_4, NH_3 and N_2O, and overall greenhouse gas (GHG) emissions during storage and after field application. Only N_2O was considered in the GHG calculation during the field period. Different letters within columns indicate a significant difference at $p < 0.05$. The grain yield indicates the dry matter (DM) of spring barley grain yield. CA: untreated cattle manure; DD: anaerobic digestate of cattle manure co-digested with 7.5% grass-clover; LF: liquid fraction of DD; NS: liquid fraction from biogas desulfurization filter enriched with sulfur and ammonium. The yield-scaled GHG emission indicated the total GHG kg^{-1} grain DM yield during storage and field application, except that there was no measurement of emissions from NS during storage.

Slurry type	Storage				Field application		
	CH_4	N_2O	NH_3	GHG§	N_2O	GHG	Yield-scaled GHG emission
	g C m^{-3}	g N m^{-2}	g N m^{-2}	kg CO_2 eq 100 kg^{-1} TN	kg N ha^{-1}	kg CO_2 eq 100 kg^{-1} TN	kg CO_2 eq hkg^{-1} grain yield
CA	1249a	1.1a	39.7a	2128a	0.78b	326b	44.4
DD	309ab	1.4a	201a	500ab	1.20b	501b	17.1
LF	37.4b	1.2a	148a	140b	0.83b	345b	8.5
NS	–	–	–	–	3.20a	1331a	24.3

§GWP(N_2O) = 265; GWP(CH_4) = 28; NH_3 contributed as an indirect source of N_2O assuming an emission factor of 1 %.

and after field application, and the N_2O emissions after field application constituted the second source (Fig. 4). In contrast, N_2O emissions after field application were more important for treatments DD and LF. Adding up all measured emissions, the anaerobically digested fertilizers in treatments CA had the highest, and treatment LF the lowest overall GHG emissions.

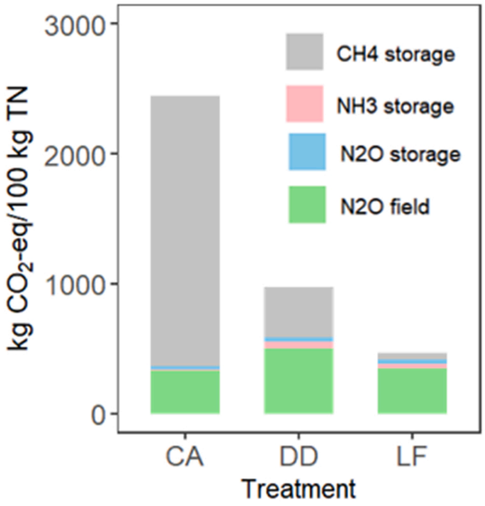

Fig. 4. Total GHG emissions from organic fertilizer treatments during storage and after field application. The application rate for these three treatments was approximately 100 kg TN ha^{-1}. CA: untreated cattle manure; DD: anaerobic digestate of cattle manure co-digested with 7.5 % grass-clover; LF: liquid fraction of DD.

3.6. *Spring barley yields*

Treatments were not significantly different ($p > 0.05$) except that the yield of M0 was lower than those of all other treatments (Fig. 5). The nitrogen use efficiency (NUE) was 48 % for M100 and not different from NUE of organic fertilizers ($p > 0.05$). (Fig. S4). Only considering N_2O in the GHG calculation during the field period, treatment NS had the highest GHG emission per hkg of grain yield ($p < 0.05$), while CA, DD and LF were not significantly different ($p > 0.05$) (Table 2). NS also had higher yield-scaled N_2O emissions (0.58 g N_2O-N kg^{-1} grain yield) compared to the other treatments ($p < 0.05$), which were not significantly different ($p > 0.05$) (Table 3). Considering both storage and field

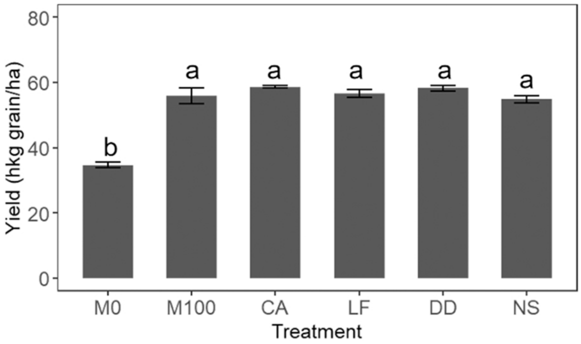

Fig. 5. The grain dry matter yields of spring barley after the application of different fertilizers. The letters show significant differences at $p < 0.05$. CA: untreated cattle manure; DD: anaerobic digestate of cattle manure co-digested with 7.5% grass-clover; LF: liquid fraction of DD; NS: liquid fraction from biogas desulfurization filter enriched with sulfur and ammonium; M100: mineral fertilizer with an application rate of 100 kg TN ha^{-1}; M0: unfertilized control.

Table 3

Cumulative emissions of N_2O per kg grain dry matter yield after field application to spring barley. Different letters within columns indicate a significant difference at $p < 0.05$. CA: untreated cattle manure; DD: anaerobic digestate of cattle manure co-digested with 7.5% grass-clover; LF: liquid fraction of DD; NS: liquid fraction from biogas desulfurization filter enriched with sulfur and ammonium; M0 and M100 indicate the mineral fertilizer with an application rate of 0 and 100 kg TN ha^{-1}, respectively.

(g N_2O-N kg^{-1} grain yield)					
CA	DD	LF	NS	M0	M100
0.13b	0.21b	0.15b	0.58a	0.13b	0.05b

periods, the yield-scaled GHG emissions were 44.4, 17.1, 8.5 and 24.3 kg CO_2 eq hkg^{-1} grain yield, respectively (Table 2).

4. Discussion

4.1. GHG and NH_3 emissions during storage

CH_4 emissions from untreated cattle manure (treatment CA) were on average 0.90 g CH_4 m^3 h^{-1} during the 11-week autumn storage period, which is higher than the average emission of 0.58 g CH_4 m^3 h^{-1} given by Kupper et al. (2020) in a literature review of results from pilot-scale and full-scale studies. Early autumn is the period where CH_4 emissions from liquid manure storage are typically highest (Maldaner et al., 2018), and this may explain the relatively high level observed. In accordance with this, the CH_4-C/(CH_4-C + CO_2-C) ratio was initially around 0.4 in treatment CA, indicating a highly active methanogenic community.

Treatments DD and LF had much lower CH_4 emissions during storage corresponding to 25 % and 3 % of those from treatment CA. Methanogenesis depends on abundant labile C and neutral pH (El-Mashad et al., 2004). The reduction of VS content from digestate (treatment DD) compared to CA was 61 % (based on initial VS), which is comparable to the reduction of 66% reported by Maldaner et al. (2018) for full-scale storage tanks, although the CA and DD treatments in this study were derived from the anaerobic co-digestion of cattle slurry and 7.5 % grass-clover silage, which is not a widely used co-digestion substrate. The LF fertilizer was more directly comparable with the digestate of treatment DD as it was produced by decanter centrifugation of the digestate. Surprisingly, the liquid fraction of digestate (treatment LF) showed an 8-fold reduction of CH_4 emissions during storage compared to treatment DD although the VS content was only 20 % lower; presumably, the fraction of VS removed was important as a source of substrates for fermentation and methanogenesis. The average CH_4-C/(CH_4-C + CO_2-C) ratios of 34 % and 13 % in untreated manure and digestate are in reasonable agreement with the values of 25 % and 10 % assumed in a recent analysis of biogas scenarios (Møller et al., 2022). Anaerobic digestion thus appears to be an effective method to reduce CH_4 emissions during manure storage, although it must be stressed that an effective digestion process and collection of biogas during the cooling phase have to be ensured (Sommer et al., 2000). The climate impact of separating the digestate depends on the management of the solids removed (Hansen et al., 2006).

Inhibition by ammonia potentially contributes to suppressing methanogenesis in manure during storage. Yenigün and Demirel (2013) reviewed ammonia inhibition in anaerobic digestion of organic wastes, and the potential roles of both total ammoniacal N (TAN) and free NH_3 were discussed. Varel et al. (1977) concluded that the production of CH_4 was inhibited when the liquid contained above 1700 mg total ammonia nitrogen (TAN) per liter and pH 7.8. Koster and Lettinga (1984) reported that acetotrophs were more negatively affected above 1700 mg TAN per liter, and it is noteworthy that Methanosarcina, reported by Habtewold et al. (2018) to dominate CH_4 production in dairy cattle manure, is characterized by acetotrophic methanogenesis. The role of free NH_3 in manure is not clear; Yenigün and Demirel (2013) cited inhibitory effects with different organic wastes that ranged from 40 to several hundred mg l^{-1} free NH_3. It is, therefore, possible that the concentrations of total ammoniacal N in treatments DD and LF at the time of storage, which were 2100 and 1900 mg TAN l^{-1}, respectively, or/and the concentrations of free NH_3, which were 63 and 80 mg l^{-1}, respectively, were involved in suppressing methanogenesis.

The emissions of N_2O during storage were comparable in treatments CA, DD and LF, and lower than the average rate of 0.002 g N_2O m^{-2} h^{-1} reported by Kupper et al. (2020). N_2O emissions during liquid manure storage depend on the N availability, oxygen content, pH, and redox status (Chadwick et al., 2011), and N_2O production occurs at the manure-air interface since nitrification requires oxygen. Reported effects of biogas treatment on N_2O emissions from stored digestate and untreated manure are not consistent; Sommer et al. (2000) observed higher N_2O emissions from digestate during storage compared to untreated manure, while other studies found no significant differences (Amon et al., 2006; Holly et al., 2017). N_2O emissions are mainly produced in well-developed surface crusts (Kupper et al., 2020), but in the present study, only treatment CA formed a thin crust, which indicates that the small amounts of N_2O observed came from the liquid phase.

NH_3 is not a greenhouse gas, but NH_3 emitted from manure is an indirect source of N_2O formed elsewhere following re-deposition. It is assumed that 1% of NH_3-N will be re-emitted as N_2O-N (Houghton et al., 1996). The pH in CA, DD and LF was 7, 7.8 and 7.9, respectively. Based on NH_4^+-N concentrations and pH of individual treatments, the concentrations of free NH_3 at the beginning of storage in treatments CA, DD and LF were 6, 63 and 80 mg NH_3 l^{-1}, respectively (see Supplementary information). Much higher free NH_3 in treatments DD and LF led to higher NH_3 emissions from treatments DD and LF than from treatment CA during storage. The emission of NH_3 is affected by many factors for example the homogeneity of manures, aeration, and NH_4^+ immobilization. The reason why DD emitted slightly more NH_3 than LF is unknown. Also, the thin crust forming in treatment CA may have delayed emissions of NH_3 (Baldé et al., 2018). These trends are consistent with the decreases observed in concentrations of TN, NH_4^+ and NH_4^+/TN of treatments DD and LF, but not CA, during storage. There is also a possibility that more organic N was mineralized during the storage of the cattle slurry compared to the digested fertilizers.

4.2. N_2O emissions after field application

With one exception (treatment NS), N_2O emissions during the growing season were moderate from both organic and mineral fertilizers and not significantly different from the unfertilized control. Half of the NS fertilizer was injected after plowing and therefore not disturbed by tillage, and this could be a reason why NS emitted much higher N_2O than other treatments. There was no evidence for stimulation of N_2O emissions in treatment M100 receiving 100 kg N ha^{-1} mineral fertilizer, indicating that bulk soil conditions in this experiment did not support N_2O emissions even with the higher concentrations of NO_3^- or NH_4^+. Li et al. (2015) investigated the drivers of N_2O emissions from the same soil by laboratory incubation experiments and found a positive interaction between CO_2 emissions (an indicator of O_2 demand in the soil) and concentration of NO_3, which suggested the availability of degradable organic matter in organic fertilizers was important. There was limited accumulation of soil NO_3^- in treatments with organic fertilizers in this study, possibly because of effective plant uptake, and hence NO_3^- availability may have been a limiting factor. Except for treatment NS, high N_2O emissions from other treatments occurred with rainfall in May 2021, at this period, oxygen depletion in the soil probably activated denitrifiers (Sexstone et al., 1988). A similar response to rainfall was not observed in June 2021. However, the NH_4^+ and NO_3^- content in the soil were low in all treatments by this time, indicating that soil NO_3^- availability limited N_2O emissions. There were no clear differences in soil gravimetric water content, which averaged 20–22 % in soil samples from all manure-derived fertilizers during the first six weeks, corresponding to 50–55 % WFPS in this soil (Li et al., 2015). A recent laboratory study concluded that the interactions between liquid organic fertilizers and the soil are critical for N_2O emissions (Meng et al., 2022), and greater redistribution of N and labile C with infiltrating water may trigger higher N_2O emissions.

Pools of NH_4^+ and NO_3^- in treatments with mineral fertilizer remained at the same high level until the time when N uptake by spring barley was expected, indicating that dissolution of inorganic N and subsequent nitrification were slow. The content of soil NH_4^+-N with organic fertilizers remained much lower than in soil with mineral fertilizer, the reasons could be microbial immobilization, plant uptake, or environmental losses. The crop yield of the control treatment M0 was significantly lower than that of fertilized treatments ($p < 0.05$), but there were no significant differences in crop yields among fertilized treatments, thus environmental losses were generally independent of fertilizer type or composition. Nitrification has been considered the main source of N_2O emissions from the soil below 60% WFPS (Davidson (1993), but Meng et al. (2022) used ^{15}N to study sources of N_2O with the same organic fertilizers and soil as this study at 55% WFPS, and the results showed that denitrification was the main source of N_2O; thus coupled nitrification-denitrification may have contributed to N_2O emissions (Petersen et al., 1991). Since crop N uptake was similar to mineral and organic fertilizers, any N immobilization was probably re-mineralized during the spring period.

Except for treatment NS, the N_2O emission factors (EF) for the growing season were below 1 %, which is the default annual emission factor proposed by IPCC et al. (2006). This is consistent with previous studies on this soil type (Chirinda et al., 2010; Mutegi et al., 2010; Brozyna et al., 2013). In a meta-analysis of N_2O emissions from organic fertilizers, Charles et al. (2017) reported the average EF was 1.12 ± 0.18 %, and the EF was 2.8 times higher in fine-textured compared to coarse-textured soils. Therefore, the sandy soil type in this study may explain the lower EF. In the present study, treatments CA, DD, and LF emitted similar amounts of N_2O, indicating that characteristics of the soils, i.e., environmental controls, were more important than the composition of the organic fertilizers as driver for N_2O emissions.

4.3. Yield-scaled emissions

The DM yield and NUE of spring barley in all fertilized treatments were similar. The fact that the NUE of treatment NS was similar to other fertilizer treatments indicates that the higher N_2O emissions were not an indicator of much higher total gaseous losses, but also that the NS fertilizer with this application did not have particular benefits over the other organic fertilizers despite a higher NH_4^+-N/TN ratio.

4.4. GHG balances

Greenhouse gas balances were calculated and expressed as CO_2 equivalents (CO_2 eq); CO_2 itself was not considered due to the recent offset by the C fixation of crops used for cattle feed (IPCC et al., 2006). Anaerobic digestion with or without separation was effective to mitigate CH_4 emissions as well as total GHG emissions in this study, which was in accordance with Amon et al. (2006), who found that GHG emissions during storage and field periods were reduced by 60% by the digestion of cattle manure and the main contributor to this reduction was CH_4. Holly et al. (2017) found that anaerobic digestion and separation of dairy cattle slurry reduced total GHG emissions during storage and after field application by 25 % and 31 %, respectively, with most of the reduction coming from CH_4 emissions during storage. However, in their studies, N_2O emissions during the storage of digestate after separation increased and therefore did not result in further GHG reduction.

The monitoring of emissions during storage was terminated in mid-November, 2020. Methane emissions were close to zero by this time, but there were still low emissions of NH_3 (about 0–2 g N m^{-2} d^{-1}) and N_2O (about 20 mg N m^{-2} d^{-1}), and the total GHG emissions could therefore have been underestimated. However, Baral et al. (2018) in a study conducted using the same pilot-scale storage facility showed that CH_4 and other emissions from cattle slurry remained low from winter to April. Husted (1994) also, in an annual study of full-scale storage tanks in Western Denmark, found that CH_4 emissions from cattle slurry were negligible during winter and early spring. Both of these studies thus took place under the same climatic conditions as this study. NH_3 emissions from stored manure highly depend on the temperature, and losses during winter were expected to be low (Sommer, 1997). N_2O emissions increased during early November, indicating some crust formation in the absence of rainfall (Sommer et al., 2000), but both NH_3 and N_2O emissions were expected to be low during winter as observed previously (Clemens et al., 2006; Petersen et al., 2013). The air temperature between mid-November and April was always below 10 °C and with occasional episodes of freezing temperatures, except that Clemens et al. (2006) did not specify temperature conditions.

From a system perspective, effective measures are required to curb the NH_3 and N_2O emissions from the solid fraction after separation (Hansen et al., 2006). Amon et al. (1998) reported that the solid fraction of the anaerobic digestate emitted more N_2O than compost. For treatment CA, CH_4 during storage was the main source of GHG emission, whereas, for treatments DD and LF, the main source of GHG was N_2O emissions after field application. This highlights that GHG mitigation efforts should consider all stages of manure management, and that manure treatment may change the emissions substantially.

In this study, CH_4 and NH_3 emissions after field application were not considered. CH_4 production in manure after field application is considered to be minor because the soil oxygen status does not support methanogenesis (Dämmgen et al., 2012), and CH_4 released immediately after manure application is probably a result of degassing (Sommer et al., 2013). In one study on well-drained arable soil in Germany, CH_4 emissions were minor after manure application in spring, and the observed emission was believed to result from dissolved CH_4 (Wulf et al., 2002). NH_3 losses highly depend on the application method, it was reported that 20–40% of NH_4^+-N was lost after broadcast application (Thompson et al., 1990; Sanz et al., 2010). Following the legislation in Denmark, the organic fertilizers were surface applied and immediately incorporated, or injected; immediate incorporation is the most effective way to reduce NH_3 emissions and may achieve a 90% abatement of NH_3 emissions compared to a surface application (Sommer and Hutchings, 2001; Webb et al., 2013).

The yield-scaled N_2O emissions ranging from 0.13 to 0.21 g N_2O-N kg^{-1} grain yield for the organic fertilizers did not show effects of manure treatment. The driving factors of N_2O after fertilizer application include the amount of easily degradable C, available N as well as the water content in soils. The effect of digestion on yield-scaled N_2O emissions in this experiment is in contrast to a previous study with the application of 100 kg NH_4^+-N ha^{-1} on the same soil type (Baral et al., 2017); in that study the yield-scaled N_2O emissions were 0.26 and 0.04 g N_2O-N kg^{-1} spring barley grain yield for cattle manure and digestate, respectively. In another experiment where spring barley was fertilized with inorganic fertilizers at a rate of 120 kg TN ha^{-1}, the yield-scaled N_2O emissions were about 0.4 and 0.3 g N_2O-N kg^{-1} grain yield for ammonium nitrate or urea, respectively (Hinton et al., 2015). Considering both storage and field emissions, the yield-scaled GHG emissions were 44.4, 17.1, 8.5 and 24.3 kg CO_2 eq hkg^{-1} grain yield for treatments CA, DD, LF and NS, respectively, which was not surprising since the DM yield of spring barley in all fertilized treatments were similar.

5. Conclusions

Anaerobic digestion and separation were effective methods to mitigate total GHG emissions from storage and field application in this study, and the main effect was the reduction of CH_4 emissions during storage resulting from the lower degradability and content of residual volatile solids and a pH above neutral in digestate. For untreated cattle slurry, the CH_4 emitted during storage was the largest component of the total GHG emissions, while for treatments with digestate and a liquid fraction of the digestate, the N_2O emissions after field application were the main source, and this difference should be considered in GHG mitigation strategies. The treatment with liquid manure from biogas desulfurization containing a proportion of ammonium and sulfur, but at low concentrations, had much higher N_2O emissions than other treatments during the growing season, and the mechanism behind this should be investigated. The DM yields of processed organic fertilizers were similar, and yield-scaled GHG emissions were lower, compared to untreated cattle manure when considering emissions during storage and after field application. Therefore, we recommend anaerobic co-digestion of manure and grass with or without post-processing as a viable GHG mitigation strategy. Since anaerobic digestion also produces biogas, and post-processing requires energy, further environmental assessments are needed to evaluate the full potential of these organic fertilizers.

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

Data will be made available on request.

Acknowledgments

The study was funded by the Green Growth and Development program (GUDP) from the Danish Ministry of Environment and Food, coordinated by the International Center for Research in Organic Food Systems (ICROFS). We thank technicians Bodil Stensgaard, Marianne Ahrenfeldt M Stevenson, Karin Dyrberg and Margit Paulsen for their assistance with gas analysis and chemical analysis in the laboratory. We thank Helle Baadsgaard Sørensen for her assistance with the fieldwork. We thank Maarit Mäenpää for her assistance with the statistics.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agee.2022.108327.

References

Abubaker, J., Risberg, K., Pell, M., 2012. Biogas residues as fertilisers – effects on wheat growth and soil microbial activities. Appl. Energy 99, 126–134. https://doi.org/10.1016/j.apenergy.2012.04.050.

Amon, B., Kryvoruchko, V., Amon, T., Zechmeister-Boltenstern, S., 2006. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. Agric. Ecosyst. Environ. 112, 153–162. https://doi.org/10.1016/j.agee.2005.08.030.

Amon, B., Amon, T., Boxberger, J., Pollinger, A., 1998. Emissions of NH3, N2O and CH4 from composted and anaerobically stored farmyard manure. In: Proceedings of the 8th International Conference on Management Strategies for Organic Waste Use in Agriculture, Rennes, France, p. 1999. https://doi.org/10.1023/A:1012649028772.

Autret, B., Mary, B., Strullu, L., Chlebowski, F., Mäder, P., Mayer, J., Olesen, J.E., Beaudoin, N., 2020. Long-term modelling of crop yield, nitrogen losses and GHG balance in organic cropping systems. Sci. Total Environ. 710, 134597 https://doi.org/10.1016/j.scitotenv.2019.134597.

Baldé, H., VanderZaag, A.C., Burtt, S.D., Wagner-Riddle, C., Evans, L., Gordon, R., Desjardins, R.L., MacDonald, J.D., 2018. Ammonia emissions from liquid manure storages are affected by anaerobic digestion and solid-liquid separation. Agric. For. Meteorol. 258, 80–88. https://doi.org/10.1016/j.agrformet.2018.01.036.

Baral, K.R., Arthur, E., Olesen, J.E., Petersen, S.O., 2016. Predicting nitrous oxide emissions from manure properties and soil moisture: an incubation experiment. Soil. Biol. Biochem. 97, 112–120. https://doi.org/10.1016/j.soilbio.2016.03.005.

Baral, K.R., Labouriau, R., Olesen, J.E., Petersen, S.O., 2017. Nitrous oxide emissions and nitrogen use efficiency of manure and digestates applied to spring barley. Agric. Ecosyst. Environ. 239, 188–198. https://doi.org/10.1016/j.agee.2017.01.012.

Baral, K.R., Jégo, G., Amon, B., Bol, R., Chantigny, M.H., Olesen, J.E., Petersen, S.O., 2018. Greenhouse gas emissions during storage of manure and digestates: key role of methane for prediction and mitigation. J. Agric. Syst. 166, 26–35. https://doi.org/10.1016/j.agsy.2018.07.009.

Bell, M.J., Hinton, N., Cloy, J.M., Topp, C.F.E., Rees, R.M., Cardenas, L., Scott, T., Webster, C., Ashton, R.W., Whitmore, A.P., 2015. Nitrous oxide emissions from fertilised UK arable soils: fluxes, emission factors and mitigation. Agric. Ecosyst. Environ. 212, 134–147. https://doi.org/10.1016/j.agee.2015.07.003.

Bernal, M.P., Kirchmann, H., 1992. Carbon and nitrogen mineralization and ammonia volatilization from fresh, aerobically and anaerobically treated pig manure during incubation with soil. Biol. Fertil. Soils 13, 135–141. https://doi.org/10.1007/BF00336268.

Brozyna, M.A., Petersen, S.O., Chirinda, N., Olesen, J.E., 2013. Effects of grass-clover management and cover crops on nitrogen cycling and nitrous oxide emissions in a stockless organic crop rotation. Agric. Ecosyst. Environ. 181, 115–126. https://doi.org/10.1016/j.agee.2013.09.013.

Castillo, A.R., Kebreab, E., Beever, D.E., France, J., 2000. A review of efficiency of nitrogen utilisation in lactating dairy cows and its relationship with environmental pollution. J. Anim. Feed. Sci. 9, 1–32. https://doi.org/10.22358/jafs/68025/2000.

Chadwick, D., Sommer, S., Thorman, R., Fangueiro, D., Cardenas, L., Amon, B., Misselbrook, T., 2011. Manure management: implications for greenhouse gas emissions. Anim. Feed. Sci. Technol. 166, 514–531. https://doi.org/10.1016/j.anifeedsci.2011.04.036.

Charles, A., Rochette, P., Whalen, J.K., Angers, D.A., Chantigny, M.H., Bertrand, N., 2017. Global nitrous oxide emission factors from agricultural soils after addition of organic amendments: a meta-analysis. Agric. Ecosyst. Environ. 236, 88–98. https://doi.org/10.1016/j.agee.2016.11.021.

Chirinda, N., Carter, M.S., Albert, K.R., Ambus, P., Olesen, J.E., Porter, J.R., Petersen, S.O., 2010. Emissions of nitrous oxide from arable organic and conventional cropping systems on two soil types. Agric. Ecosyst. Environ. 136, 199–208. https://doi.org/10.1016/j.agee.2009.11.012.

Chmelíková, L., Schmid, H., Anke, S., Hülsbergen, K.J., 2021. Nitrogen-use efficiency of organic and conventional arable and dairy farming systems in Germany. Nutr. Cycl. Agroecosyst. 119, 337–354. https://doi.org/10.1007/s10705-021-10126-9.

Clemens, J., Trimborn, M., Weiland, P., Amon, B., 2006. Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. Agric. Ecosyst. Environ. 112, 171–177. https://doi.org/10.1016/j.agee.2005.08.016.

Dämmgen, U., Amon, B., Hutchings, N.J., Haenel, H.-D., Roesemann, C., 2012. Data sets to assess methane emissions from untreated cattle and pig slurry and solid manure storage systems in the German and Austrian emission inventories. Landbauforsch. Völkenrode. 62, 1–19.

Davidson, E.A., 1993. Soil water content and the ratio of nitrous oxide to nitric oxide emitted from soil. In: Oremland, R.S. (Ed.), Biogeochemistry of Global Change. Springer, New York, NY, pp. 369–386. https://doi.org/10.1007/978-1-4615-2812-8.

De Notaris, C., Rasmussen, J., Sørensen, P., Melander, B., Olesen, J.E., 2019. Manipulating cover crop growth by adjusting sowing time and cereal inter-row spacing to enhance residual nitrogen effects. Field Crops Res. 234, 15–25. https://doi.org/10.1016/j.fcr.2019.02.008.

Dinuccio, E., Berg, W., Balsari, P., 2008. Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. Atmos. Environ. 42, 2448–2459. https://doi.org/10.1016/j.atmosenv.2007.12.022.

Eckard, R., Chapman, D., White, R., 2007. Nitrogen balances in temperate perennial grass and clover dairy pastures in south-eastern Australia. Austral. J. Agric. Res. 58, 1167–1173. https://doi.org/10.1071/AR07022.

El-Mashad, H.M., Zeeman, G., Van Loon, W.K., Bot, G.P., Lettinga, G., 2004. Effect of temperature and temperature fluctuation on thermophilic anaerobic digestion of cattle manure. Biores. Technol. 95, 191–201. https://doi.org/10.1016/j.biortech.2003.07.013.

Habtewold, J., Gordon, R., Sokolov, V., VanderZaag, A., Wagner-Riddle, C., Dunfield, K., 2018. Targeting bacteria and methanogens to understand the role of residual slurry as an inoculant in stored liquid dairy manure. Appl. Environ. Microbiol. 84, 17–30. https://doi.org/10.1128/AEM.02830-17.

Häfner, F., Hartung, J., Möller, K., 2022. Digestate composition affecting N fertiliser value and C mineralisation. Waste Biomass Valoriz. 3445–3462. https://doi.org/10.1007/s12649-022-01723-y.

Hansen, J., Sato, M., Ruedy, R., Lo, K., Lea, D.W., Medina-Elizade, M., 2006. Global temperature change. Proc. Natl. Acad. Sci. USA 103, 14288–14293. https://doi.org/10.1073/pnas.0606291103.

Hao, X., Mir, P.S., Shah, M.A., Travis, G.R., 2005. Influence of canola and sunflower diet amendments on cattle feedlot manure. J. Environ. Qual. 34, 1439–1445. https://doi.org/10.2134/jeq2004.0455.

Herr, C., Mannheim, T., Müller, T., Ruser, R., 2020. Effect of nitrification inhibitors on N_2O emissions after cattle slurry application. Agronomy 10, 1174. https://doi.org/10.3390/agronomy10081174.

Hinton, N.J., Cloy, J.M., Bell, M.J., Chadwick, D.R., Topp, C.F.E., Rees, R.M., 2015. Managing fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities from a cultivated Cambisol in Scotland. Geoder. Reg. 4, 55–65. https://doi.org/10.1016/j.geodrs.2014.12.002.

Hjorth, M., Christensen, K.V., Christensen, M.L., Sommer, S.G., 2011. Solid–liquid separation of animal slurry in theory and practice. Sust. Agric. 2, 953–986. https://doi.org/10.1007/978-94-007-0394-0_43.

Holly, M.A., Larson, R.A., Powell, J.M., Ruark, M.D., Aguirre-Villegas, H., 2017. Greenhouse gas and ammonia emissions from digested and separated dairy manure during storage and after land application. Agric. Ecosyst. Environ. 239, 410–419. https://doi.org/10.1016/j.agee.2017.02.007.

Houghton, J., Meira Filho, L., Lim, B., Treanton, K., Mamaty, I., Bonduki, Y., Griggs, D., 1996. Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories, Vol. 3. OECD/IEA/UK Meteorological Office, Bracknell.

Husted, S., 1994. Seasonal variation in methane emission from stored slurry and solid manures. J. Environ. Qual. 585–592. https://doi.org/10.2134/jeq1994.00472425002300030026x.

IPCC, 2006. IPCC Guidelines for National Greenhouse Gas Inventories. In: Eggleston, H. S., Buendia, L., Miwa, K., Ngara, T., Tanabe, K. (Eds.). Institute for Global Environmental Strategies.

Kirchmann, H., Lundvall, A., 1993. Relationship between N immobilization and volatile fatty acids in soil after application of pig and cattle slurry. Biol. Fertil. Soils 15, 161–164. https://doi.org/10.1007/bf00361605.

Koster, I.W., Lettinga, G., 1984. The influence of ammonium-nitrogen on the specific activity of pelletized methanogenic sludge. Agric. Waste 9, 205–216. https://doi.org/10.1016/0141-4607(84)90080-5.

Kupper, T., Häni, C., Neftel, A., Kincaid, C., Bühler, M., Amon, B., VanderZaag, A., 2020. Ammonia and greenhouse gas emissions from slurry storage – a review. Agric. Ecosyst. Environ. 300, 106963 https://doi.org/10.1016/j.agee.2020.106963.

Li, X., Petersen, S.O., Sørensen, P., Olesen, J.E., 2015. Effects of contrasting catch crops on nitrogen availability and nitrous oxide emissions in an organic cropping system. Agric. Ecosyst. Environ. 199, 382–393. https://doi.org/10.1016/j.agee.2014.10.016.

Maldaner, L., Wagner-Riddle, C., VanderZaag, A.C., Gordon, R., Duke, C., 2018. Methane emissions from storage of digestate at a dairy manure biogas facility. Agric. For. Meteorol. 258, 96–107. https://doi.org/10.1016/j.agrformet.2017.12.184.

Mata-Alvarez, J., Macé, S., Llabres, P., 2000. Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. Biores. Technol. 74, 3–16. https://doi.org/10.1016/S0960-8524(00)00023-7.

Meng, X., Ma, C., Petersen, S.O., 2022. Sensitive control of N_2O emissions and microbial community dynamics by organic fertilizer and soil interactions. Biol. Fertil. Soils 58, 771–788. https://doi.org/10.1007/s00374-022-01662-9.

Möller, K., 2015. Effects of anaerobic digestion on soil carbon and nitrogen turnover, N emissions, and soil biological activity. A review. Agron. Sust. Dev. 35, 1021–1041. https://doi.org/10.1007/s13593-015-0284-3.

Möller, K., Stinner, W., 2009. Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and on gaseous nitrogen losses (ammonia, nitrous oxides). Eur. J. Agron. 30, 1–16. https://doi.org/10.1016/j.eja.2008.06.003.

Möller, K., Stinner, W., Deuker, A., Leithold, G., 2008. Effects of different manuring systems with and without biogas digestion on nitrogen cycle and crop yield in mixed organic dairy farming systems. Nutr. Cycl. Agroecosyst. 82, 209–232. https://doi.org/10.1016/j.eja.2008.06.003.

Møller, H.B., Lund, I., Sommer, S.G., 2000. Solid–liquid separation of livestock slurry: efficiency and cost. Biores. Technol. 74, 223–229. https://doi.org/10.1016/S0960-8524(00)00016-X.

Møller, H.B., Sørensen, P., Olesen, J.E., Petersen, S.O., Nyord, T., Sommer, S.G., 2022. Agricultural biogas production – climate and environmental impacts. Sustainability 14, 1849. https://doi.org/10.3390/su14031849.

Morris, D., Lathwell, D., 2004. Anaerobically digested dairy manure as fertilizer for maize in acid and alkaline soils. Commun. Soi. Sci. Plant. Anal. 35, 1757–1771. https://doi.org/10.1081/CSS-120038567.

Mutegi, J.K., Munkholm, L.J., Petersen, B.M., Hansen, E.M., Petersen, S.O., 2010. Nitrous oxide emissions and controls as influenced by tillage and crop residue management strategy. Soil. Biol. Biochem. 42, 1701–1711. https://doi.org/10.1016/j.soilbio.2010.06.004.

Neerackal, G., Ndegwa, P., Joo, H., Wang, X., Harrison, J., Heber, A., Ni, J.-Q., Frear, C., 2015. Effects of anaerobic digestion and solids separation on ammonia emissions from stored and land applied dairy manure. Water Air Soil Pollut. 226, 301. https://doi.org/10.1007/s11270-015-2561-9.

Novozamsky, I., Houba, V., Van Eck, R., Van Vark, W., 1983. A novel digestion technique for multi-element plant analysis. Commun. Soi. Sci. Plant. Anal. 14, 239–248. https://doi.org/10.1080/00103628309367359.

Odlare, M., Arthurson, V., Pell, M., Svensson, K., Nehrenheim, E., Abubaker, J., 2011. Land application of organic waste–effects on the soil ecosystem. Appl. Energy 88, 2210–2218. https://doi.org/10.1016/j.apenergy.2010.12.043.

Petersen, S.O., 1999. Nitrous oxide emissions from manure and inorganic fertilizers applied to spring barley. J. Environ. Qual. 28, 1610–1618. https://doi.org/10.2134/jeq1999.00472425002800050027x.

Petersen, S.O., Henriksen, K., Blackburn, T.H., 1991. Coupled nitrification-denitrification associated with liquid manure in a gel-stabilized model system. Biol. Fertil. Soils 12, 19–27. https://doi.org/10.1007/bf00369383.

Petersen, S.O., Skov, M., Drøscher, P., Adamsen, A.P., 2009. Pilot scale facility to determine gaseous emissions from livestock slurry during storage. J. Environ. Qual. 38, 1560–1568. https://doi.org/10.2134/jeq2008.0376.

Petersen, S.O., Hoffmann, C.C., Schäfer, C.-M., Blicher-Mathiesen, G., Elsgaard, L., Kristensen, K., Larsen, S., Torp, S., Greve, M., 2012. Annual emissions of CH_4 and N_2O, and ecosystem respiration, from eight organic soils in Western Denmark managed by agriculture. Biogeosci 9, 403–422. https://doi.org/10.5194/bg-9-403-2012.

Petersen, S.O., Dorno, N., Lindholst, S., Feilberg, A., Eriksen, J., 2013. Emissions of CH_4, N_2O, NH_3 and odorants from pig slurry during winter and summer storage. Nutr. Cycl. Agroecosyst. 95, 103–113. https://doi.org/10.1007/s10705-013-9551-3.

Pötsch, E., 2005. Nutrient content of fermentation residues from agricultural biogas systems and their utilization on permanent grassland. In: Proceedings of the 20th EGF-Meeting "Land Use Systems in Grassland Dominated Regions, Luzern, Switzerland, p. 32.

R Core Team, 2014. R: a language and environment for statistical computing. http://www.R-project.org.

Reeves, S., Wang, W., 2015. Optimum sampling time and frequency for measuring N_2O emissions from a rain-fed cereal cropping system. Sci. Total Environ. 530, 219–226. https://doi.org/10.1016/j.scitotenv.2015.05.117.

Sanz, A., Misselbrook, T., Sanz, M.J., Vallejo, A., 2010. Use of an inverse dispersion technique for estimating ammonia emission from surface-applied slurry. Atmos. Environ. 44, 999–1002. https://doi.org/10.1016/j.atmosenv.2009.08.044.

Sexstone, A.J., Parkin, T.B., Tiedje, J.M., 1988. Denitrification response to soil wetting in aggregated and unaggregated soil. Soil. Biol. Biochem. 20, 767–769. https://doi.org/10.1016/0038-0717(88)90165-4.

Sommer, S.G., 1997. Ammonia volatilization from farm tanks containing anaerobically digested animal slurry. Atmos. Environ. 31, 863–868. https://doi.org/10.1016/S1352-2310(96)00250-6.

Sommer, S.G., Hutchings, N.J., 2001. Ammonia emission from field applied manure and its reduction. Eur. J. Agron. 15, 1–15. https://doi.org/10.1016/S1161-0301(01)00112-5.

Sommer, S.G., Petersen, S.O., Søgaard, H.T., 2000. Greenhouse gas emission from stored livestock slurry. J. Environ. Qual. 29, 744–751. https://doi.org/10.2134/jeq2000.00472425002900030009x.

Sommer, S.G., Clough, T.J., Chadwick, D., Petersen, S.O., 2013. Greenhouse gas emissions from animal manures and technologies for their reduction. Anim. Manure Recycl. 177–194. https://doi.org/10.1002/9781118676677.ch10.

Sun, F., Harrison, J.H., Ndegwa, P.M., Johnson, K., 2014. Effect of manure treatment on ammonia emission during storage under ambient environment. Water Air Soil Pollut. 225, 1–13. https://doi.org/10.1007/s11270-014-2094-7.

Svensson, K., Odlare, M., Pell, M., 2004. The fertilizing effect of compost and biogas residues from source separated household waste. J. Agric. Sci. 142, 461–467. https://doi.org/10.1017/S0021859604004514.

Thompson, R.B., Pain, B.F., Rees, Y.J., 1990. Ammonia volatilization from cattle slurry following surface application to grassland. Plant. Soil. 125, 119–128. https://doi.org/10.1016/j.atmosenv.2013.08.005.

Thomsen, I.K., Pedersen, A.R., Nyord, T., Petersen, S.O., 2010. Effects of slurry pre-treatment and application technique on short-term N_2O emissions as determined by a new non-linear approach. Agric. Ecosyst. Environ. 136, 227–235. https://doi.org/10.1016/j.agee.2009.12.001.

Varel, V.H., Isaacson, H.R., Bryant, M.P., 1977. Thermophilic methane production from cattle waste. Appl. Environ. Microbiol. 33, 298–307. https://doi.org/10.1128/aem.33.2.298-307.1977.

Wang, Y., Dong, H., Zhu, Z., Liu, C., Xin, H., 2014. Comparison of air emissions from raw liquid pig manure and biogas digester effluent storages. Trans. ASABE 57, 635–645. https://doi.org/10.13031/trans.57.10292.

Webb, J., Sørensen, P., Velthof, G., Amon, B., Pinto, M., Rodhe, L., Salomon, E., Hutchings, N., Burczyk, P., Reid, J., 2013. An assessment of the variation of manure nitrogen efficiency throughout Europe and an appraisal of means to increase manure-N efficiency. Adv. Agron. 119, 371–442. https://doi.org/10.1016/B978-0-12-407247-3.00007-X.

Woodward, A., Smith, K.R., Campbell-Lendrum, D., Chadee, D.D., Honda, Y., Liu, Q., Olwoch, J., Revich, B., Sauerborn, R., Chafe, Z., 2014. Climate change and health: on the latest IPCC report. Lancet 383, 1185–1189. https://doi.org/10.1016/S0140-6736(14)60576-6.

Wulf, S., Maeting, M., Clemens, J., 2002. Application technique and slurry co-fermentation effects on ammonia, nitrous oxide, and methane emissions after spreading: II. Greenhouse gas emissions. J. Environ. Qual. 31, 1795–1801. https://doi.org/10.2134/jeq2002.1795.

Yenigün, O., Demirel, B., 2013. Ammonia inhibition in anaerobic digestion: a review. Proc. Biochem. 48, 901–911. https://doi.org/10.1016/j.procbio.2013.04.012.

Zervas, G., Tsiplakou, E., 2012. An assessment of GHG emissions from small ruminants in comparison with GHG emissions from large ruminants and monogastric livestock. Atmos. Environ. 49, 13–23. https://doi.org/10.1016/j.atmosenv.2011.11.039.