



Short-term effects of biogas digestate and cattle slurry application on greenhouse gas emissions affected by N availability from grasslands on drained fen peatlands and associated organic soils

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Abstract. A change in German energy policy has resulted in a strong increase in the number of biogas plants in Germany. As a consequence, huge amounts of nutrient-rich residues, the by-products of the fermentative process, are used as organic fertilizers. Drained peatlands are increasingly used to satisfy the huge demand for fermentative substrates (e.g., energy crops, grass silage) and the digestate is returned to the peatlands. However, drained organic soils are considered as hot spots for nitrous oxide (N₂O) emissions and organic fertilization is additionally known to increase N₂O emissions from managed grasslands. Our study addressed the questions (a) to what extent biogas digestate and cattle slurry application increase N₂O and methane (CH₄) fluxes as well as the mineral nitrogen use efficiency (NUE_{min}) and grass yield, and (b) how different soil organic matter contents (SOMs) and nitrogen contents promote the production of N₂O. In addition NH₃ volatilization was determined at one application event to obtain first clues with respect to the effects of soil and fertilizer types. The study was conducted at two sites within a grassland parcel, which differed in their soil organic carbon (SOC) and N contents. At each site (named C_{org}-medium and C_{org}-high) three plots were established: one was fertilized five times with biogas digestate, one with cattle slurry, and the third served as control plot. On each plot, fluxes of N₂O and CH₄ were measured on three replicates over 2 years using the closed chamber method. For NH₃ measurements we used the calibrated dynamic chamber method. On an annual basis, the application of biogas digestate significantly enhanced the N₂O fluxes compared to the application of cattle slurry and additionally increased the plant

N-uptake and NUE_{min}. Furthermore, N₂O fluxes from the C_{org}-high treatments significantly exceeded N₂O fluxes from the C_{org}-medium treatments. Annual cumulative emissions ranged from 0.91 ± 0.49 to 3.14 ± 0.91 kg N ha⁻¹ yr⁻¹. Significantly different CH₄ fluxes between the investigated treatments or the different soil types were not observed. Cumulative annual CH₄ exchange rates varied between -0.21 ± 0.19 and -1.06 ± 0.46 kg C ha⁻¹ yr⁻¹. Significantly higher NH₃ losses, NUE_{min} and grass yields from treatments fertilized with biogas digestate compared to those fertilized with cattle slurry were observed. The total NH₃ losses following the splash plate application were 18.17 kg N ha⁻¹ for the digestate treatments and 3.48 kg N ha⁻¹ for the slurry treatments (36 and 15 % of applied NH₄⁺-N). The observed linear increase of 16 days' cumulative N₂O-N exchange or annual N₂O emissions, with mean groundwater level and ammonium application rate, reveals the importance of site-adapted N fertilization and the avoidance of N surpluses in C_{org}-rich grasslands.

1 Introduction

Germany has become the largest biogas producing country in the world since a change in German energy policy and the enactment of the German Renewable Energy Act (Weiland, 2010). At the end of 2012, more than 7500 agricultural biogas plants were operating in Germany (Fachverband Biogas, 2014). Heat and power from biogas substitute for fossil fuels and therefore can reduce greenhouse gas (GHG) emissions

(Weiland, 2010; Don et al., 2012). The strong increase in the number of biogas plants caused a land-use change towards agro-biomass production and additionally raised land-use intensity to satisfy the huge demand for fermentative substrates (Don et al., 2012). In 2011, grass silage accounted for 9 % of the total renewable resources for biogas production (DBFZ, 2012) and was the second most important fermentation substrate after maize silage.

During the fermentative process high amounts of nutrient-rich residues are produced as a by-product. Today, this new form of organic fertilizer is used instead of mineral fertilizers or animal slurries to maintain soil fertility and productivity. Several studies reported a significant increase in nitrous oxide (N₂O) emissions due to the application of nitrogen fertilizers (e.g., Bouwman, 1996; Chadwick et al., 2000; Rodhe et al., 2006; Ruser, 2010). Liquid organic fertilizers such as animal slurry add easily degradable organic carbon (Christensen, 1983) and moisture, both further favoring N₂O losses through denitrification (Clayton et al., 1997). Enhanced N₂O emissions are of major concern due to the fact that N₂O acts as a radiative forcing GHG (IPCC, 2007) and contributes to the chemical destruction of stratospheric ozone (Crutzen, 1979). In Germany, about 78 % of N₂O emissions originate from the agricultural sector (Umweltbundesamt, 2014). In particular, organic soils (e.g., drained peat soils and soils developed in wet conditions) are considered as hotspots of GHG emissions including N₂O, due to the very high mineralization rates of degrading peat (Kasimir-Klemmedtsson et al., 1997; Freibauer et al., 2004; Klemmedtsson et al., 2005; Goldberg et al., 2010) and to soil moisture conditions that favor anaerobic microsites. According to Maljanen et al. (2010), N₂O emissions from drained organic soils under agricultural use were on average four times as high as those from mineral soils. The few field studies of organic fertilization effects on annual N₂O emissions from drained organic grassland soils revealed very high N₂O emissions of up to 41.0 kg N ha⁻¹ yr⁻¹ (Velthof et al., 1996).

In Germany, 50 % of the drained peatlands are used as grasslands (Drösler et al., 2011), particularly in the smallholder structure of south Germany. Grassland soils in Europe and Germany produce more N₂O per unit of fertilizer-N than croplands, and emission factors further increase with soil organic carbon (SOC) and nitrogen content (Freibauer and Kaltschmitt, 2003; Dechow and Freibauer, 2011). Moreover, agricultural soils in the southern part of Germany emit about three times as much of the applied N as N₂O as soils in the rest of Germany, which is attributed to the more frequent frost–thaw cycles and enhanced precipitation rates (Jungkunst et al., 2006; Dechow and Freibauer, 2011). Thus, grasslands on organic soils in South Germany represent a widespread high-risk situation for high N₂O emissions after cattle slurry or biogas digestate application, which has not, to our knowledge, been studied before.

Biogas digestate is depleted in easily degradable C compounds and in organic dry matter content compared to fresh

slurry due to anaerobic digestion (Möller and Stinner, 2009). The pH value and the ammonium (NH₄⁺) content as well the NH₄⁺ : N_{org} ratio are higher than in fresh slurry (Wulf et al., 2002b; Möller and Stinner, 2009). Since digested products are more recalcitrant than fresh slurry it could be assumed that microbial degradation is slow, resulting in fewer anoxic microsites and reduced N₂O emissions compared with fresh slurry application (Clemens and Huschka, 2001; Oenema et al., 2005; Möller and Stinner, 2009). However, the few available field and laboratory experiments are contradictory regarding the effect of biogas digestate application on N₂O emissions (e.g., Clemens and Huschka, 2001; Wulf et al., 2002b; Clemens et al., 2006; Senbayram et al., 2009; Sängner et al., 2010), and very few studies exist for grasslands (e.g., Wulf et al., 2002b; Clemens et al., 2006).

The different properties of biogas digestate and cattle slurry (e.g., higher NH₄⁺-N concentrations, narrower C : N ratio, higher pH values) directly affect N transformation processes, plant N availability, and thus grass yield. Furthermore it can be assumed that the plant N-uptake and the N₂O emissions are closely interconnected since N-uptake can be considered as a proxy for N availability, affecting N gaseous losses as well. Currently, the effect of anaerobic digestates on crop growth after surface application under field conditions is contradictory, since some authors reported higher crop yields compared to undigested slurries (e.g., Odlare, 2005 cited in Möller and Müller, 2012) whereas others found no effects (e.g., Möller et al., 2008). Only a few studies exist for grassland but it seems that fertilization with biogas digestates positively affects grass yields, but only in single years (Elsässer et al., 1995; Rubæk et al., 1996; Möller et al., 2008; Möller and Müller, 2012).

As well as N₂O, slurry application leads to short-term methane (CH₄) and ammonia (NH₃) emissions. Methane acts as a strong GHG, whereas NH₃ is considered an indirect GHG through ammonia deposition which could promote the formation of N₂O (Moiser, 2001). Moreover, NH₃ deposition causes soil acidification and eutrophication of ecosystems (e.g., Fangmeier et al., 1994; Galloway, 1995, 2001; Smith et al., 1999). In Germany, agriculture is responsible for 95.3 % of anthropogenic NH₃ emissions (Haanel et al., 2010). Particularly high NH₄⁺ contents and high pH values, which are typically for the biogas digestate, promote accelerated NH₃ volatilization (Quakernack et al., 2011). High NH₃ emissions particularly occur after splash plate application on grassland (Rubæk et al., 1996; Wulf et al., 2002a), which is still common practice in the smallholder farms of South Germany.

The objective of this study was to quantify short-term N₂O and CH₄ emissions after application of biogas digestate and cattle slurry on grassland on two types of organic soils in South Germany, which differed in their SOC and N contents. Additionally, to what extent biogas digestate and cattle slurry application affect N availability and grass yield should

Table 1. Summary of the grassland management for both vegetation periods.

Date	Management event
26 Mar 2010	leveling
7 Apr 2010	rolling
24 May 2010	mowing
14 Jun 2010	manuring [20 m ³ ha ⁻¹]
20 Aug 2010	mowing
25 Aug 2010	manuring [20 m ³ ha ⁻¹]
23 Sep 2010	herbicide against common sorrel (<i>Rumex acetosa</i>)
16 Mar 2011	leveling
23 May 2011	mowing
27 May 2011	manuring [25 m ³ ha ⁻¹]
1 Aug 2011	mowing
13 Sep 2011	mowing
22 Sep 2011	manuring [20 m ³ ha ⁻¹]
4 Nov 2011	manuring [25 m ³ ha ⁻¹]

be tested. Furthermore, NH₃ volatilization was determined at one application event to obtain first clues with respect to the effects of soil and fertilizer types. We hypothesize the following: (a) more N₂O is emitted after biogas digestate than after slurry application because of higher NH₄⁺-N concentrations in the substrate and, thus, higher NH₄⁺-N amounts when using equal volumetric application rates. The more recalcitrant nature of the carbon in the biogas digestate does not matter for GHG formation in high organic carbon soils. (b) N₂O emissions increase with increasing soil C_{org} and N content due to more favorable conditions for denitrification after organic fertilizer application. (c) Biogas digestate leads to a significantly higher grass yield and N-use efficiency compared to cattle slurry due to the higher N availability of the digestate.

2 Materials and methods

2.1 Study site

The study was conducted on a permanent grassland at a drained fen peatland 30 km northeast of Munich (Freisinger Moos, 48°21' N, 11°41' E; 450 m a.s.l.). The dominant species were *Poa trivialis*, *Poa pratensis*, *Festuca pratensis*, *Dactylis glomerata*, and *Alopecurus pratensis*. The grassland was mown two and three times in 2010 and 2011 respectively, as is the usual practice in this region. A summary of the complete grassland management over both vegetation periods can be found in Table 1. The grass was used as silage or hay for cattle or as substrate for biogas plants. According to the climate station in Weißenstephan, located 10 km northeast of the site, the 30-year mean annual temperature was 7.5 °C and the mean annual precipitation was 787 mm (1961–1990). Annual atmospheric N deposition amounted to 6.22 and 7.20 kg N ha⁻¹ yr⁻¹, with NH₄⁺-N:NO₃⁻-N ra-

tios of 46:54 and 49:51 in 2010 and 2011. Data of N deposition were collected by the Bavarian State Institute of Forestry at a German Level II monitoring area (Forest Intensive Monitoring Programme of the UNECE), located at 7 km distance from the investigated grassland. In October 2009 we selected two sites within the grassland parcel, which differed in their SOC contents in the topsoil (Table 2). According to the WRB (2006), soil types were classified as mollic Gleysol (named C_{org}-medium) and as sapric Histosol (named C_{org}-high; N. Roßkopf, personal communication, 2013).

2.2 Experimental design

At each site of the grassland parcel, three adjacent plots (plot dimension 12 × 12 m) were selected. At one plot biogas digestate and at another plot cattle slurry were applied; the third plot served as a control (without fertilization). Centrally at each plot, three PVC-collars for GHG measurements (inside dimension 75 × 75 cm; 0.5625 m²) were permanently inserted 10 cm into the soil with a distance of 1.5 m to each other. To prevent oscillations of the peat through movements during the measurements, boardwalks were installed. At each site a climate station was set up in March 2010 for the continuous recording (every 0.5 h; CR200X Datalogger, Campbell Scientific) of air temperature and humidity at 20 cm above soil surface (CS215-L, Campbell Scientific) and soil temperatures at depths of -2, -5 and -10 cm (109-L, Campbell Scientific). For NH₃ measurements, sensors for wind speed and wind direction (Kleinwindsensor, Thies Clima) in 2 m height were additionally integrated from May to July 2011, with a logging frequency of 5 s (GP1, Delta-T Devices). For measuring the groundwater table, plastic perforated tubes (JK-casings DN 50, 60 mm diameter, 1 m length) were inserted close to each collar to obtain individual groundwater tables for all repetitions during each gas flux measurement. In April 2010, we equipped one tube per plot with a water level logger (Type MiniDiver, Schlumberger water services), which logged the water tables every 15 min. Additionally to the recorded data, plot-specific soil temperatures at three soil depths (-2, -5 and -10 cm) were determined with penetration thermometers at the beginning and end of each gas flux measurement.

In 2010 and 2011, organic fertilizers were applied via splash plate (swiveling slurry spreader for biogas digestate; gooseneck scatterer for cattle slurry) on 14 June 2010, 25 August 2010, 27 May 2011, 22 September 2011, and 4 November 2011 by the landowners (see Table 1). The surface application technique via splash plate is the most common application technique in the smallholder structure of the region. The organic fertilizer was applied on the basis of equal volumetric rates per application event (20 or 25 m³ ha⁻¹). This method is typical for farming practices, but produces diverging N application rates per event between slurry and digestate based on NH₄⁺ or N_{tot} applications. It is known that the splash plate application technique can result in very uneven

Table 2. Soil properties of the study site.

	Sampling depth	C _{Org} -medium	C _{Org} -high	<i>n</i>
Soil type (WRB, 2006) ¹		mollic Gleysol	sapric Histosol	
Soil type (German classification KA5)		GMq	KV-KM	
Peat depth [cm] ¹		80	70	1
pH value ²		4.1	4.2	
Total nitrogen [%] ²		1.0	1.5	
Organic carbon [%]	0–10 cm	10.3 ± 0.2	17.0 ± 0.1	9
	10–20 cm	9.3 ± 0.2	16.3 ± 0.2	9
Bulk density [g cm ⁻³]	0–10 cm	0.79 ± 0.02	0.54 ± 0.02	18
	10–20 cm	0.90 ± 0.01	0.64 ± 0.01	18
Porosity [%]	0–10 cm	71 ± 1	78 ± 1	18
	10–20 cm	67 ± 1	72 ± 0	18

Values present means ± SE. ¹ World Reference Base for Soil Resources. ² Relative to the upper horizon (C_{Org}-medium 0–20 cm; C_{Org}-high 0–15 cm); N. Roßkopf, personal communication, 2013.

spreading regarding the application rate and/or the evenness. Both chosen spreading devices are known for the higher precision in their application evenness compared to conventional splash plates (approximately 15 and 18–27 % application variability for swiveling slurry spreader and gooseneck scatterer and up to 47 % for conventional splash plate; Frick, 1999). In the present study, the application of an equal volumetric slurry rate was controlled via the barrel content and the tractor speed. At all plots, the tractor lane was 1 m in front of the collars, which were placed in a row with a distance of 1.5 m to each other. Both spreading systems had a spreading width of 12 m and no overlapping zones occurred. Nevertheless we cannot give any estimation of the precision of application evenness that was actually achieved.

The physical and chemical composition of the slurries and digestates varied between the four application events (Table 3). Composition of organic fertilizers was analyzed from 1 L samples which were taken from the slurry tank in the field. Slurries were immediately frozen at –20 °C until analysis was conducted by the AGROLAB Labor GmbH (Bruckberg, Germany). Due to technical problems at the first application event, cattle slurry was applied by watering cans on the ground of the collars and on a 120 m² adjacent area. To ensure an equal volumetric amount of organic fertilizer a 1 × 1 m grid, fabricated from cords, was previously installed. The same method was used at the fourth application event for the digestate.

2.3 N₂O and CH₄ flux measurements

As a background, we measured fluxes of N₂O and CH₄ every second week from January 2010 to January 2012 using the static manual chamber method (volume 309 L) (Livingston

and Hutchinson; 1995). We removed, however, the gas fluxes measured in 2010 from the data set due to errors in the gas chromatography analysis and due to long vial storage. Intensive measurement campaigns were performed after the four fertilization events on 14 June 2010, 25 August 2010, 27 May 2011, and 22 September 2011. Immediately after fertilization flux measurements were carried out daily for a week and on every second day for another 8–9 days. To minimize diurnal variation in the flux pattern, sampling was always carried out between 09.00 and 11.30 a.m. A detailed description of chamber dimensions and configuration is given in Drösler (2005). Four gas samples were taken at regular time intervals after chamber closure (enclosure time 60 min). The samples were collected in 20 mL glass vials, each sealed with a butyl rubber septum. The vials were flushed with chamber air for 30 s using a portable micro pump (KNF Neuberger GmbH, NMP015B), so that the air in the vials was exchanged 32 times. In addition the pump was used to build up an overpressure of approximately 550 mbar to protect the sample against fluctuations in atmospheric pressure during storage. Gas analyses were carried out with a gas chromatograph (Perkin and Elmer, Clarus 400 GC respectively Clarus 480 GC) equipped with a headspace auto sampler (Perkin & Elmer, TurboMatrix 110), a PoraPack 80/100 mesh column, an electron capture detector (ECD) for N₂O (ECD temperature 380 °C) and a flame ionization detector (FID) for CH₄ analyses (FID temperature 310 °C). Gas samples from the first fertilization event (14–30 June 2010) were immediately analyzed at the Max Planck Institute for Biogeochemistry in Jena, whereas samples from the second fertilization event (25 August–10 September 2010) were analyzed at the Thünen Institute in Braunschweig with a Varian CP-3800 GC-FID/-

Table 3. Physical and chemical properties of the applied digestates and slurries.

	1. Application (14 Jun 2010)	2. Application (25 Aug 2010)	3. Application (27 May 2011)	4. Application (22 Sep 2011)	5. Application (4 Nov 2011)
Cattle slurry					
Fertilizer quantity [m ³ ha ⁻¹]	20	20	25	20	20
Total carbon [kg ha ⁻¹]	579	676	798	797	1073
Organic carbon [kg ha ⁻¹]	410	573	655	706	960
Total nitrogen [kg ha ⁻¹]	47	64	70	85	97
NO ₃ ⁻ [kg N ha ⁻¹]	0	0	0	0	0
NH ₄ ⁺ [kg N ha ⁻¹]	20	28	23	33	38
NH ₄ ⁺ : N _{tot} ratio	0.42	0.44	0.33	0.38	0.39
C : N ratio	12	11	11	9	11
pH (CaCl ₂)	–	–	6.8	7.0	7.0
Dry matter content [%]	5	7	7	9	10
Biogas digestate					
Fertilizer quantity [m ³ ha ⁻¹]	20	20	25	20	20
Total carbon [kg ha ⁻¹]	384	373	167	184	178
Organic carbon [kg ha ⁻¹]	306	337	148	161	178
Total nitrogen [kg ha ⁻¹]	49	52	78	35	61
NO ₃ ⁻ [kg N ha ⁻¹]	0	0	0	0	0
NH ₄ ⁺ [kg N ha ⁻¹]	22	28	51	17	40
NH ₄ ⁺ : N _{tot} ratio	0.45	0.53	0.65	0.49	0.66
C : N ratio	8	7	2	5	3
pH (CaCl ₂)	–	–	7.7	7.4	7.7
Dry matter content [%]	4	4	2	2	3

ECD using a headspace autosampler (QUMA Elektronik & Analytik GmbH, Germany) and similar conditions. Gas flux rates were calculated from the linear change in gas concentration over time considering chamber air temperature and atmospheric pressure. Gas fluxes were accepted when the linear regression was significant ($P \leq 0.05$). In case of small N₂O or CH₄ fluxes, fluxes were also accepted if the coefficient of determination was ≥ 0.90 and the regression slope was between -1 and 1 ppb min⁻¹. The cumulative annual mean exchange rate was calculated by linear interpolation between the measurement dates.

2.4 NH₃ flux measurements

Ammonia volatilization was measured at the third organic fertilizer application event on 27 May 2011. Measurements were performed immediately after fertilizer application and thereafter at irregular time intervals of a few hours (in total 96 measurements). For NH₃ measurements we used the calibrated dynamic chamber method (“Dräger-Tube Method”; DTM) which was described in detail by Pacholski et al. (2006). One day before application, eight stainless steel rings (104 cm²) were inserted into the upper soil (3 cm) at each plot, of which four were grouped close together. Ambient air was sucked with a defined flow rate (1 L min⁻¹) through four connected (via Teflon tubes) conical stainless

steel chambers to an ammonia indicator tube (Drägerwerk AG, Lübeck, Germany). The NH₃ volume concentration was corrected for air temperature and air pressure (Pacholski et al., 2006). To prevent overestimation of NH₃ volatilization through NH₃ enriched ambient air from surrounding area, ammonia concentration from the control treatments was subtracted from the fertilized treatments prior to NH₃ flux calculation. Different studies report a distinct underestimation of up to one order of magnitude of NH₃ fluxes determined by the DTM, mainly due to the low air exchange rate in the chambers (Roelcke et al., 2002; Pacholski et al., 2006). To avoid underestimation of cumulative NH₃-N losses determined by the DTM, Pacholski et al. (2006) developed the following calibration formula to correct the NH₃ fluxes:

$$\ln(\text{NH}_3 \text{ flux}_{\text{IHF}}) = 0.444 \cdot \ln(\text{NH}_3 \text{ flux}_{\text{DTM}}) + 0.590 \cdot \ln(v_{2\text{m}}), \quad (1)$$

where NH₃ flux_{IHF} is NH₃ flux measured by the integrated horizontal flux method (kg N ha⁻¹ h⁻¹); NH₃ flux_{DTM} is NH₃ flux measured by the DTM (kg N ha⁻¹ h⁻¹); $v_{2\text{m}}$ is wind speed at 2 m height (m s⁻¹). Quakernack et al. (2011) compared the DTM method with the frequently used micrometeorological method, concluding that the corrected DTM method also allows quantitative NH₃-loss measurements. The total cumulative NH₃ volatilization was estimated by curve fitting and integration of the area obtained by the fit-

ted curve between time zero and the time point where the NH_3 flux was zero.

2.5 Grass yield, apparent N use efficiency, and N-balances

The annual yield was determined by harvesting the grass inside the PVC-collars with a pair of scissors at each mowing event (same cutting height as the farmer, at about 5 cm; sample area = 0.5625 m²). There was no visible disturbance from trace gas measurements in the collars. The grassland parcel showed a strong spatial heterogeneity in grass yield so that only sampling inside the collars allowed grass yield and N uptake to be related with N_2O emissions. Mowing events took place on 24 May 2010, 20 August 2010, 23 May 2011, 1 August 2011, and 13 September 2011 (see Table 1). To determine the dry mass (DM), grass samples were oven dried at 60 °C for 48 h. To determine the total carbon (C_{tot}) and total nitrogen (N_{tot}) concentrations of plant biomass, dried grass samples were milled (0.5 mm) and mixed subsamples were analyzed according to DIN ISO 10694 and DIN ISO 13878 by the AGROLAB Labor GmbH (Bruckberg, Germany). The apparent N_{tot} or N_{min} use efficiency (NUE, NUE_{min}) was calculated as follows:

$$\text{NUE or } \text{NUE}_{\text{min}} = \left(\frac{N_{\text{uptake}_{\text{treatment}}} - N_{\text{uptake}_{\text{control}}}}{\text{total N applied}} \right) \cdot 100\%, \quad (2)$$

where $N_{\text{uptake}_{\text{treatment}}}$ is the amount of N taken up by the plants in the fertilized treatments, $N_{\text{uptake}_{\text{control}}}$ is the amount of N taken up by the plants in the unfertilized control, and “total N applied” is the amount of N_{tot} or N_{min} applied, corrected by NH_3 -N losses. Emission factors for NH_3 were taken from the German national GHG inventory (see Haenel et al., 2014, Table 4.6 – broadcast, grassland, emission factor (EF) of 0.60 kg kg⁻¹ related to applied NH_4^+ -N), whereas for the third application event our own estimated values based on our measurements were used.

Based on the measured gaseous N fluxes and the N uptake by plants and soil N_{min} contents, a simple N balance was calculated:

$$\text{N balance} = (\text{N applied} + (\text{N min}_{t_2} - \text{N min}_{t_1}) + N_{\text{dep}}) - (\text{N uptake} + \text{N}_2\text{O}_{\text{cum}} + \text{NH}_3_{\text{cum}}), \quad (3)$$

where “N applied” is the amount of N_{tot} applied, N min_{t_1} and N min_{t_2} are the amounts of N_{min} at time 1 (6 April 2011; early April represents the beginning of the vegetation period in 2011) and time 2 (18 October 2011; end of October represents the end of the vegetation period in 2011) for the soil depth 0–20 cm, N_{dep} is the annual atmospheric N deposition, “N uptake” is the amount of N taken up by the plants (quantified in harvested biomass), $\text{N}_2\text{O}_{\text{cum}}$ is the amount of the annual cumulative N_2O -N losses, and NH_3_{cum} is the amount of the annual cumulative NH_3 -N losses.

2.6 Soil sampling and laboratory analyses

For the determination of mineral N ($N_{\text{min}} = \text{NH}_4^+ - \text{N} + \text{NO}_3^- - \text{N}$) contents, one mixed soil sample consisting of nine individual samples was collected at two soil depths (0–10, 10–20 cm) at each plot during every gas flux measurement. Samples were immediately cooled and stored in an ice box before analyses. Mineral N was extracted after shaking 40 g of fresh soil with 160 mL CaCl_2 (0.0125 M) for 1 hour. The extracts were filtered through a 4–7 μm filter paper (Whatman 595 1/2) and the first 20 mL of the extract were discarded. The solution was frozen at –20 °C until analysis, which was conducted by the AGROLAB Labor GmbH (Bruckberg, Germany). A subsample of 20–30 g was used to determine the gravimetric water content, which was taken into account for the calculation of mineral N concentrations. For determination of C_{tot} and organic carbon (C_{org}) a mixed soil sample of nine individual samples was collected close to each collar at two soil depths (0–10, 10–20 cm) using a 3 cm diameter auger. After drying for 72 h at 40 °C, soil samples were sieved to 2 mm to remove stones and living roots. Analyses were conducted at the Division of Soil Science and Site Science (Humboldt Universität zu Berlin, Germany). For the determination of bulk density and porosity, three undisturbed core cutter samples (100 cm³) were randomly taken at four depths (0–5, 5–10, 10–15, 15–20 cm) for each plot.

2.7 Statistical analysis

Statistical analyses were conducted using R 2.12.1 (R Development Core Team, 2010). We used analysis of variance (ANOVA; for grass yield, 16 days’ cumulative N_2O emissions and treatment NO_3^- comparison) or the nonparametric Kruskal–Wallis rank sum test (for GW level) to compare means of samples. In case of significant differences among the means, we used Tukey’s honest significant differences (Tukey HSD) or the non-parametric pairwise Wilcoxon rank sum test with Bonferroni correction for multiple comparisons. For testing two independent sample means, we use the Welch two-sample *t* test (for soil type NO_3^- comparison in 2010) or the nonparametric Mann–Whitney *U* test (for soil type NO_3^- comparison in 2011). For time series data (N_2O , CH_4 field measurements) we applied linear mixed effects models (Crawley, 2007; Eickenscheidt et al., 2011; Hahn-Schöfl et al., 2011). We set up a basic model with soil type and fertilizer treatment as fixed effects and the spatial replication (individual collar) nested in time as random effect. Non-significant terms were removed from the fixed structure. We extended the basic model by a variance function when heteroscedasticity was observed. In case of significant serial correlation in data, a moving average or a first-order temporal autoregressive function was included in the model. Autocorrelation was tested using the Durbin–Watson test and by plotting the empirical autocorrelation structure. The model extension was proved by the Akaike information criterion

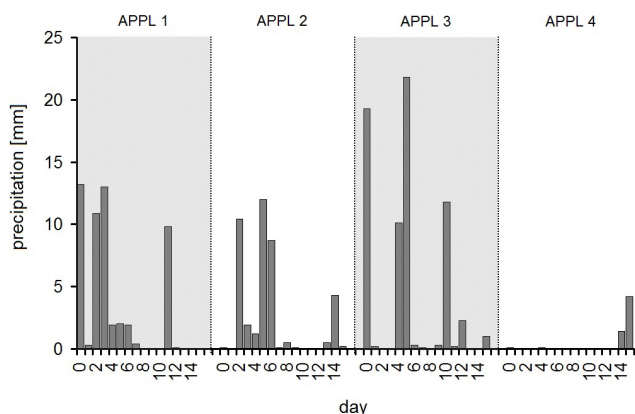


Figure 1. Daily sums of precipitation following the organic fertilizer application events (APPL).

(AIC). For multiple comparisons we conducted Tukey contrasts using the General Linear Hypotheses function from the “multcomp” package (Hothorn et al., 2013).

The assumption of normality of residuals was tested using the Lilliefors or Shapiro–Wilk test and the quantile–quantile plots. Homogeneity of variances of residuals was checked using the Levene or Breusch–Pagan test and by plotting the residuals against the fitted values. Where necessary, data were box-cox transformed prior to analyses. We used simple and multiple linear or non-linear regression models to explain N_2O , CH_4 and NH_3 fluxes. We accepted significant differences if $P \leq 0.05$. Results in the text are given as means ± 1 SD.

3 Results

3.1 Environmental drivers

Temperatures between the two investigated soil types did not differ. In 2010 and 2011, air temperature at 20 cm height ranged from -17.5 to 39.5 °C, with an annual mean of 8.6 °C in 2011 at both investigated areas. Soil temperature in -2 cm soil depth averaged 10.3 °C at the C_{org} -medium site and was slightly higher with 10.5 °C at the C_{org} -high site in 2011. Air temperature at 20 cm height 15 or 16 days after fertilization averaged 16.0 , 13.1 , 15.4 , and 11.5 °C for application events 1 to 4 at both investigated soil types. Soil temperature in -2 cm soil depth was approximately 2 °C above the mean air temperature in the same periods at both soil types. In 2010 and 2011 annual precipitation was 850 and 841 mm, which was slightly above the 30-year mean of the period 1961–1990. Figure 1 shows the precipitation following the fertilizer application. With the exception of the third application event, no rainfall occurred during the application of the organic fertilizers. However, precipitation during and after the third application event was weak and amounted to 3 mm in the time span between 16:00 and 00:00 LT.

All treatments showed similar dynamics in their annual hydrographs (Fig. 2a), but mean annual groundwater levels of the C_{org} -high treatments were significantly higher (all $P < 0.001$) compared to the C_{org} -medium treatments in 2010 and 2011 (Table 4). Mean groundwater levels following the fertilizer applications are shown in Table 4.

3.2 N input and N availability

The amount of N applied was 111 and 252 kg N ha^{-1} for slurry treatments and 101 and 174 kg N ha^{-1} for digestate treatments in 2010 and 2011, respectively. However, due to the distinctly higher $\text{NH}_4^+ - \text{N} : \text{N}_{\text{tot}}$ ratio of the biogas digestate, total $\text{NH}_4^+ - \text{N}$ input was comparable to (2010) or slightly higher than (15 % more $\text{NH}_4^+ - \text{N}$; 2011) that for the slurry treatments (Table 3). Additional physical and chemical properties of the slurry and digestate are shown in Table 3.

The extractable N_{min} contents of the soils were dominated by NO_3^- whereas NH_4^+ was only of minor importance, especially at the C_{org} -medium treatments (Fig. 2b and c). The NO_3^- content was significantly higher ($P < 0.001$) at the C_{org} -high treatments than at the C_{org} -medium treatments in 0–10 cm soil depth in both years and in 10–20 cm soil depth in 2010 ($P < 0.01$) (Table 4). With the exception of the first application event, all fertilization events increased the NO_3^- contents of the soil for a short period (Fig. 2c, Table 4). However, only in 2011 did the fertilized sites show significantly ($P < 0.01$) higher NO_3^- contents compared to the control treatments, but differences between digestate and slurry were generally not significant (except for 0–10 cm soil depth at the C_{org} -medium site; Table 4).

3.3 N_2O emissions

N_2O fluxes were generally low for all treatments (Fig. 2d). Background emissions rarely exceeded 50 $\mu\text{g N m}^{-2} \text{h}^{-1}$. Highest N_2O fluxes were found immediately after fertilizer application (Figs. 2d and 3), sometimes followed by a second phase of higher emissions after 6 to 12 days. In the case of the C_{org} -medium treatments N_2O fluxes returned to background emission level within 3 to 7 days, whereas the C_{org} -high treatments had longer lasting increased N_2O emissions, particularly for the digestate treatment.

Short-term (16 days) N_2O fluxes of fertilized treatments significantly ($P < 0.01$) exceeded N_2O fluxes of control treatments at all fertilization events. However, only in one out of four fertilization events were short-term N_2O fluxes significantly ($P < 0.001$) higher for the digestate treatments compared to the slurry treatments. Additionally, significantly ($P < 0.001$) higher short-term N_2O fluxes were observed at the C_{org} -high treatments compared to the C_{org} -medium treatments in 2011, but the opposite was observed at the second fertilization event in 2010.

However, due to the high variability and the partially fast return to the background emission level, short-term (16 days)

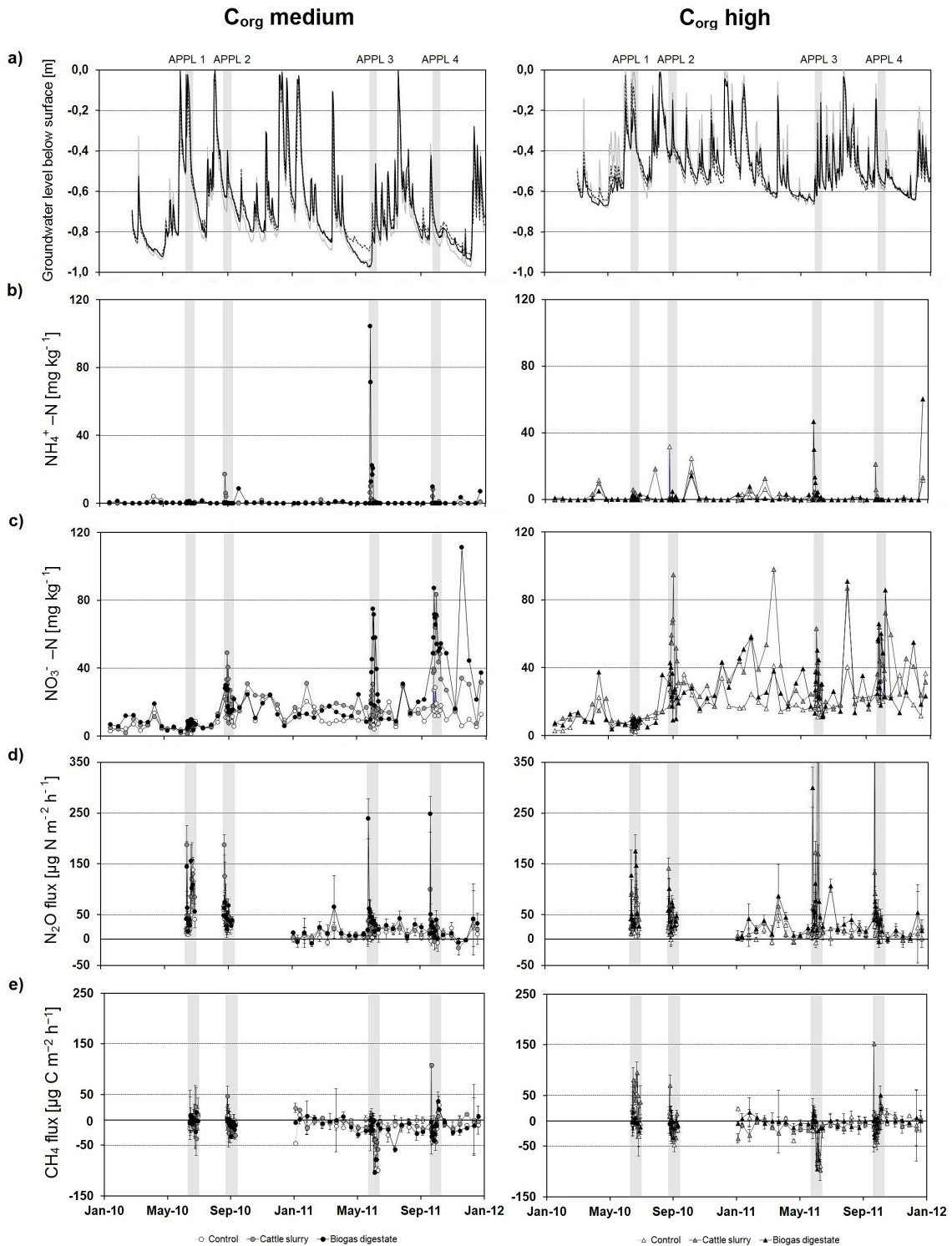


Figure 2. Variation in groundwater level (a), extractable NH_4^+ (b) and NO_3^- (c) contents for the soil depth 0–10 cm, N_2O (d) and CH_4 fluxes (e) (mean \pm SD, $n = 3$) of the C_{org} -medium and C_{org} -high sites from January 2010 to January 2012. Gray bars mark the 15 or 16 days period of intensive gas flux measurements following organic fertilizer application.

Table 4. Mean (minimum/maximum) groundwater level (GW), NO₃⁻ and NH₄⁺ content in the soil following organic fertilizer application and for the investigated years 2010 and 2011.

Sampling depth [cm]	C _{org} -medium			C _{org} -high			n
	Control	Cattle slurry	Biogas digestate	Control	Cattle slurry	Biogas digestate	
1 Application (14 Jun–30 Jun 2010)							
GW level [cm]	-32 (-62/-2)	-39 (-60/-5)	-31 (-58/-2)	-21 (-46/-1)	-26 (-45/-7)	-33 (-45/-19)	
NO ₃ ⁻ [mg N kg ⁻¹]	0–10	5 (1/9)	5 (1/7)	7 (3/10)	6 (1/12)	8 (3/11)	8 (5/10) 12
	10–20	9 (6/12)	9 (5/13)	11 (8/15)	11 (8/15)	12 (7/15)	14 (6/19) 12
NH ₄ ⁺ [mg N kg ⁻¹]	0–10	0 (0/1)	0 (0/1)	0 (0/1)	1 (0/2)	1 (0/6)	1 (0/3) 12
	10–20	0 (0/1)	0 (0/1)	0 (0/1)	0 (0/2)	1 (0/11)	1 (0/2) 12
2 Application (25 Aug–10 Sep 2010)							
GW level [cm]	-64 (-70/-49)	-58 (-63/-42)	-57 (-63/-40)	-36 (-40/-37)	-40 (-46/-22)	-37 (-43/-15)	
NO ₃ ⁻ [mg N kg ⁻¹]	0–10	13 (6/23)	27 (7/49)	21 (14/30)	25 (17/37)	50 (17/95)	25 (9/43) 12
	10–20	22 (17/28)	28 (19/37)	27 (17/38)	31 (26/35)	34 (11/45)	31 (12/48) 12
NH ₄ ⁺ [mg N kg ⁻¹]	0–10	0 (0/0)	2 (0/17)	0 (0/0)	3 (0/32)	0 (0/1)	1 (0/5) 12
	10–20	1 (0/10)	0 (0/0)	0 (0/1)		0 (0/1)	1 (0/3) 12
3 Application (27 May–11 Jun 2011)							
GW level [cm]	-82 (-94/-57)	-76 (-89/-52)	-80 (-97/-46)	-41 (-60/-11)	-47 (-62/-16)	-49 (-62/-16)	
NO ₃ ⁻ [mg N kg ⁻¹]	0–10	9 (4/17)	17 (5/30)	40 (10/75)	17 (11/26)	29 (12/63)	29 (11/50) 12
	10–20	17 (11/22)	31 (18/44)	45 (18/75)	24 (18/30)	28 (18/40)	45 (21/148) 12
NH ₄ ⁺ [mg N kg ⁻¹]	0–10	0 (0/2)	2 (0/10)	21 (0/104)	0 (0/1)	1 (0/5)	10 (0/47) 12
	10–20	0 (0/1)	1 (0/2)	6 (0/26)	1 (0/2)	1 (0/3)	4 (0/12) 12
4 Application (22 Sep–7 Oct 2011)							
GW level [cm]	-83 (-87/-72)	-77 (-81/-70)	-76 (-83/-58)	-54 (-60/-33)	-55 (-58/-46)	-53 (-57/-41)	
NO ₃ ⁻ [mg N kg ⁻¹]	0–10	18 (12/28)	48 (18/83)	62 (49/87)	23 (20/34)	43 (28/73)	45 (18/86) 12
	10–20	32 (18/46)	50 (21/79)	53 (35/66)	24 (20/30)	30 (22/39)	38 (23/86) 12
NH ₄ ⁺ [mg N kg ⁻¹]	0–10	0 (0/0)	1 (0/8)	1 (0/10)	0 (0/0)	3 (0/21)	0 (0/0) 12
	10–20	0 (0/0)	0 (0/0)	0 (0/1)	0 (0/1)	1 (0/3)	0 (0/0) 12
2010							
GW level [cm]*	-67 (-94/-2)	-65 (-91/-2)	-63 (-92/0)	-41 (-68/2)	-45 (-64/-1)	-45 (-67/-1)	
NO ₃ ⁻ [mg N kg ⁻¹]	0–10	9 (1/26)	14 (1/49)	12 (3/30)	15 (1/37)	24 (3/95)	17 (4/43) 45
	10–20	14 (5/34)	17 (5/38)	17 (4/38)	19 (7/47)	23 (6/64)	21 (6/49) 45
NH ₄ ⁺ [mg N kg ⁻¹]	0–10	0 (0/4)	1 (0/17)	0 (0/9)	2 (0/32)	2 (0/19)	1 (0/14) 45
	10–20	0 (0/10)	0 (0/1)	0 (0/1)	0 (0/8)	1 (0/11)	1 (0/5) 45
2011							
GW level [cm]	-76 (-98/-3)	-72 (-92/0)	-72 (-97/0)	-47 (-67/1)	-52 (-66/-3)	-50 (-65/-3)	
NO ₃ ⁻ [mg N kg ⁻¹]	0–10	13 (4/31)	25 (5/83)	36 (8/111)	21 (11/41)	36 (12/98)	34 (11/91) 47
	10–20	24 (9/46)	34 (15/79)	40 (18/120)	27(14/52)	33 (18/78)	37 (10/148) 47
NH ₄ ⁺ [mg N kg ⁻¹]	0–10	0 (0/2)	1 (0/10)	6 (0/104)	1 (0/12)	2 (0/21)	4 (0/60) 47
	10–20	0 (0/3)	0 (0/4)	2 (0/26)	1 (0/7)	1 (0/27)	2 (0/12) 47

cumulative N₂O emissions were not significantly different from the control treatments in 2010 (Fig. 4), but for 2011 short-term cumulative N₂O emissions had a clear trend in the order digestate > slurry > control (although not significant in one case).

On an annual basis organic fertilization led to significantly ($P < 0.001$) higher N₂O fluxes compared to unfertilized treatments. Additionally, the application of biogas digestate significantly ($P < 0.01$) enhanced the N₂O fluxes compared to the application of cattle slurry. Furthermore, N₂O fluxes from the C_{org}-high treatments significantly ($P < 0.001$) exceeded N₂O fluxes from the C_{org}-medium treat-

ments. Annual cumulative emissions ranged from $0.91 \pm 0.49 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (control treatment, C_{org}-medium site) to $3.14 \pm 0.91 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (digestate treatment, C_{org}-high site; Table 5). Calculated EFs based on the amount of N_{tot} ranged from 0.12 to 0.23 for the slurry treatments and from 0.55 to 1.13 for the digestate treatments (Table 5).

Observed collar-specific cumulative annual N₂O fluxes were strongly related to collar-specific annual plant N-uptake (Fig. 5a and b). Of the temporal and spatial variation in the 16 days' cumulative N₂O–N exchange rates, 53 % was explained by the amounts of applied NH₄⁺-N and the mean groundwater levels below surface during the same time

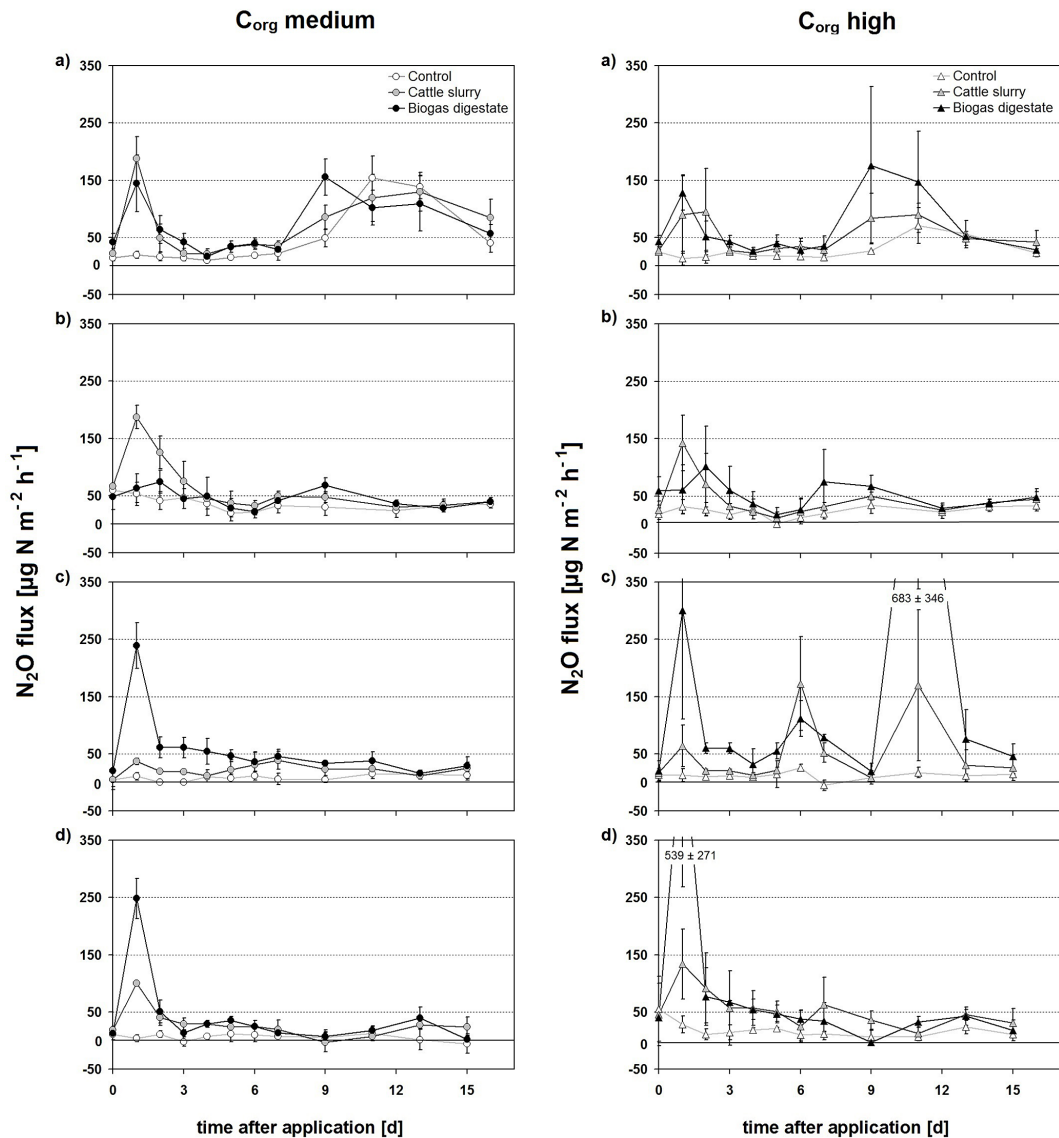


Figure 3. Mean (\pm SD, $n = 3$) N_2O fluxes following organic fertilizer application events (a) 14–30 June 2010; (b) 25 August–10 September 2010; (c) 27 May–11 June 2011 and (d) 22 September–7 October 2011.

(Fig. 6). A similar trend was observed for the annual cumulative N_2O emissions, but regression analysis was not possible due to the small sample size ($n = 6$).

3.4 CH_4 emissions

Most of the time, CH_4 emissions could not be detected (Fig. 2e). Occasionally CH_4 peaks were only found immediately after cattle slurry application. However, with the exception of the slurry treatment of the C_{org} -high site at the first application event, the organic fertilization did not result in significantly different short-term (15 or 16 days) CH_4 fluxes between the treatments or the investigated soil types. The observed weak CH_4 emissions or uptakes amounted to cumulative annual CH_4 exchange rates of -0.21 ± 0.19

to $-1.06 \pm 0.46 \text{ kg C ha}^{-1} \text{ yr}^{-1}$. Significantly different CH_4 fluxes between the investigated treatments or the different soil types could not be observed regarding the annual fluxes in 2011.

3.5 NH_3 volatilization

Highest NH_3 losses were observed immediately after fertilization (Fig. 7). During the first 24 h, 64 and 100 % of total NH_3 losses occurred at the digestate and slurry treatments, respectively. Since differences in the response of NH_3 volatilization were not significant, treatment data were pooled by soil type prior to regression analysis. The total NH_3 loss following application was $18.17 \text{ kg N ha}^{-1}$ for the digestate treatments and $3.48 \text{ kg N ha}^{-1}$ for the slurry

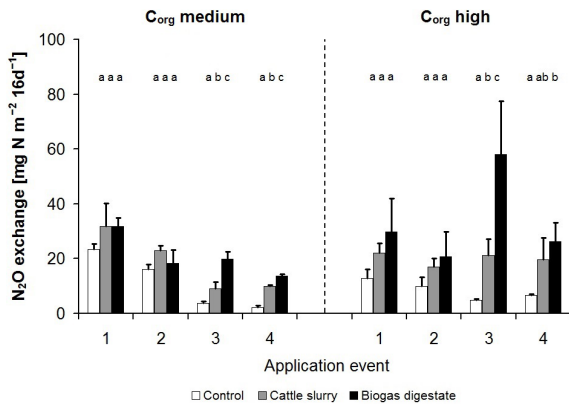


Figure 4. Cumulative N₂O exchange during 16 days following organic fertilizer application. Bars indicate mean values + SD (*n* = 3). Means with the same letter indicated no significant differences between treatments at a single application event for sites C_{Org}-medium and C_{Org}-high respectively (ANOVA, Tukey HSD test at *P* < 0.05).

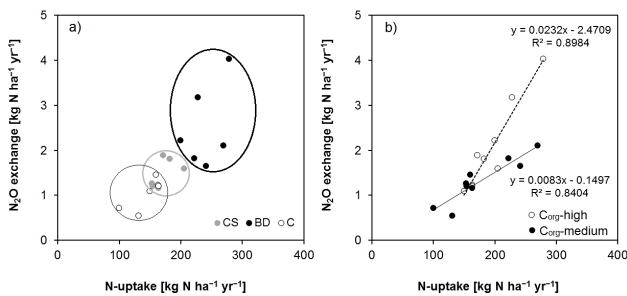


Figure 5. Relationship between cumulative annual N₂O emissions and annual plant N uptake for the treatments (a) and for the investigated soil types (b). Dots represent mean annual values of each PVC collar; CS, cattle slurry; BD, biogas digestate; C, control.

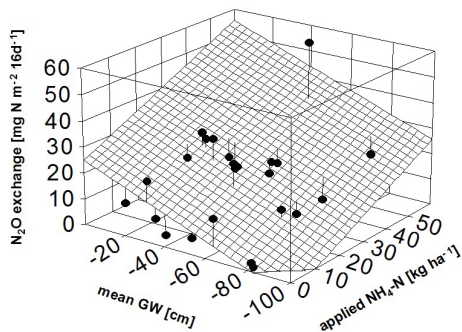


Figure 6. Relationship of plot-wise mean 16 days' cumulative N₂O-N emissions of the four application events (*y*) to mean groundwater level (*x*₁) and the amount of applied NH₄-N (*x*₂). The regression equation is $y = 24.98 (\pm 4.98) + x_1 \cdot 0.30 (\pm 0.09) + x_2 \cdot 0.51 (\pm 0.11)$; R^2 adj. = 0.53, *P* < 0.001, *df* = 21. Solid lines indicate the deviation of measured data from the model surface.

Table 5. Calculated EFs for the year 2011 and for single application events (16 days; Appl. 1–Appl. 4). The EF is based on the amount of total nitrogen (N_{tot}) without consideration of NH₃-N losses.

	Control	Cattle slurry	Biogas digestate
C_{Org}-medium			
N ₂ O exchange [kg N ha ⁻¹ yr ⁻¹]	0.91 ± 0.49	1.21 ± 0.05	1.86 ± 0.23
Annual EF		0.12	0.55
EF Appl. 1		0.18	0.17
EF Appl. 2		0.11	0.05
EF Appl. 3		0.08	0.21
EF Appl. 4		0.09	0.33
C_{Org}-high			
N ₂ O exchange [kg N ha ⁻¹ yr ⁻¹]	1.18 ± 0.07	1.77 ± 0.15	3.14 ± 0.91
Annual EF		0.23	1.13
EF Appl. 1		0.20	0.35
EF Appl. 2		0.11	0.21
EF Appl. 3		0.23	0.68
EF Appl. 4		0.15	0.56

treatments. The relative N loss was 36 and 15 % of applied NH₄⁺-N, or 23 and 5 % of total applied N for the digestate and slurry treatments, respectively.

3.6 Grass yield, apparent N use efficiency and estimated N balances

In 2010 and 2011, the mean annual grass yield ranged from 4.5 (control C_{Org}-medium) to 13.1 t DM ha⁻¹ yr⁻¹ (digestate C_{Org}-high; Table 6). In both years the mean annual grass yield from the digestate treatments was significantly (*P* < 0.05) higher compared to the slurry treatments. This pattern was also found in the annual plant N-uptake, which showed a clear partitioning between the treatments investigated (Fig. 5a). Additionally, the mean annual grass yield from the C_{Org}-high treatments exceeded yields from the C_{Org}-medium treatments of both years, but differences were not significant.

The application of biogas digestate markedly increased apparent NUE and NUE_{min} compared to cattle slurry treatments (Table 6). NUE values were on average 115 ± 136 % for biogas digestate treatments and 24 ± 23 % for cattle slurry. NUE_{min} values were always > 100 % for biogas digestate treatments, whereas for cattle slurry NUE_{min} values averaged 74 ± 68 % in 2011 but were > 100 % in 2010. Besides fertilizer type effects, higher NUE and NUE_{min} were observed at the C_{Org}-medium treatments compared to the C_{Org}-high treatments.

The estimated N balances revealed N surpluses of up to 70 kg N ha⁻¹ yr⁻¹ for cattle slurry treatments but deficits of

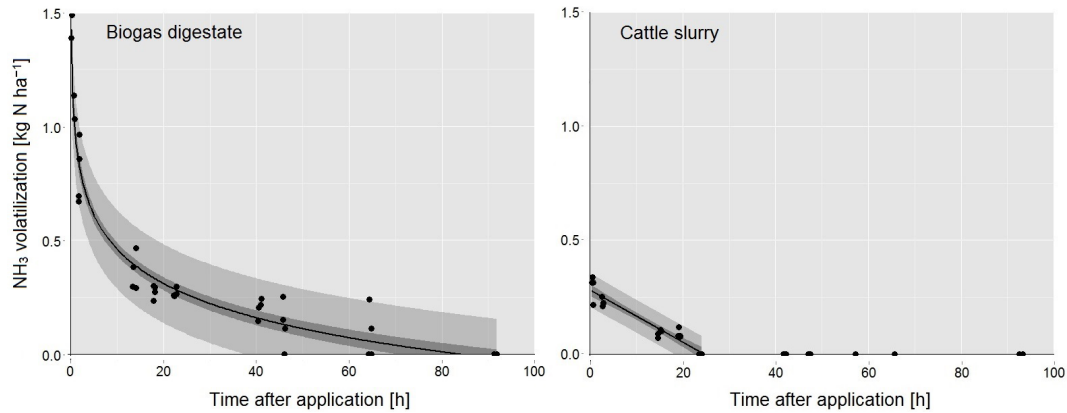


Figure 7. Ammonia (NH_3) volatilization following organic fertilizer application at event 3 (27 May 2011). Dots present single NH_3 measurements for a time period of 94 h. Black lines show the estimated NH_3 volatilization with 95 % confidence band (dark gray) and 95 % prediction band (light gray). The model function for biogas digestate is $y = -0.2619 (\pm 0.025) \cdot \ln(x) + 0.9605 (\pm 0.008)$; $r^2 = 0.96$; $P < 0.0001$; the model function for cattle slurry is $y = 0.2818 (\pm 0.012) - 0.0114(x) (\pm 0.001)$; $r^2 = 0.92$; $P < 0.0001$.

Table 6. Grass yields, N uptake and N use efficiency for the years 2010 and 2011.

Treatment	Cutting date	Fertilization date	N content plant [%]	DM [$\text{t ha}^{-1} \text{ yr}^{-1}$]	N uptake [kg N ha^{-1}]	N applied [kg N ha^{-1}] ^b	N_{\min} applied [kg N ha^{-1}] ^b	N use efficiency [%]	N_{\min} use efficiency [%]
Control C_{org} -medium	24 May 2010	–	2.04 ^a	2.52	51	–	–	–	–
Control C_{org} -high	24 May 2010	–	2.14	2.93	63	–	–	–	–
Cattle slurry C_{org} -medium	24 May 2010	N.A.	2.37	3.19	76	–	–	–	–
Cattle slurry C_{org} -high	24 May 2010	N.A.	2.14	3.58	77	–	–	–	–
Biogas digestate C_{org} -medium	24 May 2010	N.A.	2.04	4.17	85	–	–	–	–
Biogas digestate C_{org} -high	24 May 2010	N.A.	2.27	4.39	100	–	–	–	–
Control C_{org} -medium	20 Aug 2010	–	2.03	2.02	41	–	–	–	–
Control C_{org} -high	20 Aug 2010	–	2.00	2.63	53	–	–	–	–
Cattle slurry C_{org} -medium	20 Aug 2010	14 Jun 2010	2.19	3.06	67	45	17	58	153
Cattle slurry C_{org} -high	20 Aug 2010	14 Jun 2010	1.93	3.23	62	45	17	22	57
Biogas digestate C_{org} -medium	20 Aug 2010	14 Jun 2010	2.03	2.99	61	38	14	52	140
Biogas digestate C_{org} -high	20 Aug 2010	14 Jun 2010	2.00	3.51	70	38	14	47	125
Control C_{org} -medium	23 May 2011	–	1.96	2.66	52	–	–	–	–
Control C_{org} -high	23 May 2011	–	1.70	3.82	65	–	–	–	–
Cattle slurry C_{org} -medium	23 May 2011	25 Aug 2010	2.01	2.58	52	61	24	0	0
Cattle slurry C_{org} -high	23 May 2011	25 Aug 2010	1.70	4.20	71	61	24	11	27
Biogas digestate C_{org} -medium	23 May 2011	25 Aug 2010	1.96	3.97	78	40	18	64	144
Biogas digestate C_{org} -high	23 May 2011	25 Aug 2010	1.83	4.54	83	40	18	45	101
Control C_{org} -medium	1 Aug 2011	–	1.71	2.06	35	–	–	–	–
Control C_{org} -high	1 Aug 2011	–	1.48	2.88	43	–	–	–	–
Cattle slurry C_{org} -medium	1 Aug 2011	27 May 2011	1.71	2.73	47	67	20	17	58
Cattle slurry C_{org} -high	1 Aug 2011	27 May 2011	1.51	3.19	48	67	20	8	28
Biogas digestate C_{org} -medium	1 Aug 2011	27 May 2011	1.78	4.88	87	60	33	86	158
Biogas digestate C_{org} -high	1 Aug 2011	27 May 2011	1.48	5.34	79	60	33	61	112
Control C_{org} -medium	13 Sep 2011	–	2.53	1.71	43	–	–	–	–
Control C_{org} -high	13 Sep 2011	–	2.26	2.27	51	–	–	–	–
Cattle slurry C_{org} -medium	13 Sep 2011	27 May 2011	2.57	2.28	59	(55) ^c	(8) ^c	28	189
Cattle slurry C_{org} -high	13 Sep 2011	27 May 2011	2.53	2.64	67	(61) ^c	(14) ^c	25	110
Biogas digestate C_{org} -medium	13 Sep 2011	27 May 2011	2.53	3.15	80	(8) ^c	(0) ^c	436	–
Biogas digestate C_{org} -high	13 Sep 2011	27 May 2011	2.26	3.25	74	(24) ^c	(0) ^c	94	–

^a N contents from control treatments were estimated from fertilized treatments. ^b Applied N_{tot} and N_{\min} were corrected by NH_3 -N losses (23 and 5 % from N_{tot} , or 36 and 15 % from N_{\min} for biogas digestate and cattle slurry, respectively). ^c Hypothetically remaining N_{tot} and N_{\min} from the application event 3 (27 May 2011). N.A. = not available.

Table 7. Estimated nitrogen balance for the year 2011.

Treatment	N applied [kg N ha ⁻¹ yr ⁻¹]	N _{min} t ₁ ^a [kg N ha ⁻¹]	N _{min} t ₂ ^a [kg N ha ⁻¹]	N deposition [kg N ha ⁻¹ yr ⁻¹]	N uptake [kg N ha ⁻¹ yr ⁻¹]	N ₂ O [kg N ha ⁻¹ yr ⁻¹]	NH ₃ ^b [kg N ha ⁻¹ yr ⁻¹]	N balance [kg N ha ⁻¹ yr ⁻¹]
Control C _{org} -medium	0	27.5	29.4	7.2	130	0.9	0.0	-122.4
Control C _{org} -high	0	22.8	27.7	7.2	159	1.2	0.0	-148.0
Cattle slurry C _{org} -medium	252	35.7	51.2	7.2	157	1.2	46.1	70.4
Cattle slurry C _{org} -high	252	27.3	68.1	7.2	186	1.8	46.1	66.1
Biogas digestate C _{org} -medium	174	29.8	83.3	7.2	244	1.9	52.4	-64.1
Biogas digestate C _{org} -high	174	26.2	28.4	7.2	236	3.1	52.4	-108.1

^a Reference date for t₁ is 6 April 2011 and for t₂ 18 October 2011. ^b NH₃-N losses at the fourth and fifth application event were estimated based on EF taken from the German national greenhouse gas inventory (EF = 0.6 related to applied NH₄⁺; Haenel et al., 2014).

up to 108 kg N ha⁻¹ yr⁻¹ for biogas digestate treatments, for the year 2011 (Table 7).

4 Discussion

4.1 Drainage and fertilizer effects on N-availability and N-transformation

Mineral nitrogen contents were consistently higher at the C_{org}-high treatments than at the C_{org}-medium treatments, in line with the considerably higher amount of SOC and N at this site. It is well known that drainage enhances the degradation of soil organic matter (SOM) and thus stimulates net nitrogen mineralization and N transformation processes (Kasimir Klemetsson et al., 1997; Freibauer et al., 2004; Klemetsson et al., 2005; Goldberg et al., 2010). Various studies reported an annual N supply through peat mineralization of 70 to 292 kg N ha⁻¹ yr⁻¹ (Schothorst, 1977; Flessa et al., 1998; Sonneveld and Lantinga, 2011). It can be assumed that at a comparable aeration status and temperature, mineralization processes are more intensive at peatlands that were recently drained (Hacin et al., 2001; Renger et al., 2002; Sonneveld and Lantinga, 2011) or contain higher amounts of SOM.

As expected from the literature, the biogas digestates differed in their physical and chemical properties from the cattle slurries. In the present study, the biogas digestates had narrower C : N ratios (see also, e.g., Tambone et al., 2009), higher pH values (see also Wulf et al., 2002b and Quakernack et al., 2011), wider NH₄⁺ : N_{tot} ratios and thus relatively higher NH₄⁺ contents than the cattle slurries (see also Möller and Stinner 2009). The amounts of NH₄⁺-N were not distinctly different between the applied organic fertilizers but in 2011 biogas treatments received 15 % more NH₄⁺-N compared to cattle slurry treatments.

We observed an unexpected small change in the NH₄⁺ content of the soil immediately after fertilizer application, which can be attributed to different reasons. Firstly, the fertilizers partly remained on the plant canopy after splash plate application and therefore soil contact and infiltration were limited (Quakernack et al., 2011). Secondly, a significant fraction of NH₄⁺ from the organic fertilizer was lost in a few hours after splash plate application via NH₃ volatilization. Thirdly,

and probably most importantly, in well aerated soils applied NH₄⁺ underwent rapid nitrification, as was indicated by the increasing soil NO₃⁻ contents in the upper soil layer after fertilizer application. In general, the continuously observed absent or low NH₄⁺ contents with simultaneously high extractable NO₃⁻ in the soil indicate that net nitrification entirely controlled net nitrogen mineralization at all treatments of the investigated study sites. Nitrification requires sufficient oxygen (O₂) availability in the soil (Davidson et al., 1986), hence we can assume well aerated soil conditions, at least in the upper soil layer, for most of the time at the study sites.

Several studies (e.g., Gutser et al., 2005; Jones et al., 2007) reported that the infiltration of organic fertilizer may enhance the soil N pool and further stimulates SOM mineralization, leading to additional N_{min}. This becomes evident in the observed significantly higher NO₃⁻ contents of the fertilized treatments compared to the unfertilized control treatments, especially in the 0–10 cm soil layer. However, significant differences in the N_{min} contents between the two investigated organic fertilizers were not found in 2010 and 2011. This may be due to the fact that the N uptake by plants at the digestate treatments was on average 27 % higher and that marked differences in the amount of N_{tot} and NH₄⁺ of the applied organic fertilizers were only observed in the second study year.

To maintain soil fertility and yield and to reduce harmful side effects (e.g., N₂O losses, NO₃⁻ leaching), site-adapted fertilization is necessary. The estimated negative N balances for biogas treatments are in line with Andres et al. (2013), who reported that positive N balances could only be achieved when the amount of applied digestate contains more than 200 kg N ha⁻¹ yr⁻¹. However, the strong negative N balances of the control treatments reveal that large amounts of up to 148 kg N ha⁻¹ yr⁻¹ originate from peat mineralization, demonstrating the unsustainable agricultural use of drained peatlands. Assuming that the fertilized treatments received equal amounts of N from peat mineralization, all N balances of these treatments were strongly positive. N surpluses as estimated for the cattle slurry treatments enhance the soil N pool, but the gradual release of N at a non-predictable stage from the soil N pool carries the risk of leaching or gaseous losses (Amon et al., 2006). Particularly in wintertime, high amounts of available NO₃⁻ in the soil, as observed especially at the fertilized treatments of the C_{org}-high sites, carry the

risk of N leaching due to the reduced N demand by plant uptake and by the microbial community during this period (Merino et al., 2002; Sanger et al., 2010).

4.2 Fertilizer effect on N-use efficiency and grass yield

In line with investigations from Schils et al. (2008) most of the applied and produced N_{\min} was probably rapidly absorbed by the grassland as the soil N_{\min} content usually decreased within a few days after fertilizer application (Fig. 2b and c). This becomes evident also in the apparent NUE_{\min} , especially from biogas digestate treatments. A significant effect of biogas digestate on crop yields and apparent NUE_{\min} as observed in the present study was also reported from pot experiments (e.g., de Boer, 2008; Moller and Muller, 2012), but not for field applications without incorporation of the digestate into the soil (Moller and Muller, 2012). According to de Boer (2008), the higher NUE_{\min} at digestate treatments can be attributed to the wider NH_4^+/N_{tot} ratio as well as to the narrower C/N ratio of the applied digestate. Thus more N was immediately available for plant growth after fertilization (Amon et al., 2006; Sanger et al., 2010), whereas the lower C/N ratio reduced the potential for microbial immobilization of applied N (Velthof et al., 2003, de Boer, 2008). We hypothesized that the application of biogas digestate leads to a significantly higher grass yield and N-use efficiency compared to the application of cattle slurry due to the higher N availability of the digestate. This could partly be confirmed, but the much higher grass yields from biogas digestate treatments cannot solely be explained by differences in applied NH_4^+ , since differences were small. However, the much higher N-uptake at the digestate treatments (Fig. 5a) indicated that much more N must have been available at these treatments. Many studies have shown that the utilization of N derived from organic fertilizer is relatively small in the year of application, due to the slow release of organically bound N (Jensen et al., 2000; Sorensen and Amato, 2002; Gutser et al., 2005). The consistently higher NUE_{\min} of > 100 % at the digestate treatments indicates that some organic N derived from the fertilizer or from the SOM pool has been mineralized (Gunnarsson et al., 2010). Since the digestate is considered as more recalcitrant (Clemens and Huschka, 2001; Oenema et al., 2005; Moller and Stinner, 2009), it can be assumed that the digestate enhanced SOM mineralization more than cattle slurry, or that N mineralized from SOM or fertilizer had a larger share in the uptake by the plants due to lower competition of microbial immobilization as was reported by Gutser et al. (2010). Probably the assumed higher SOM mineralization at the digestate treatments could partly be related to a priming effect since the higher biomass production probably caused a higher release of root exudates, containing easily available C and N that enhanced microbial activity (Mounier et al., 2004; Henry et al., 2008), promoting SOM mineralization. However, further investigations

are needed to prove this explanation. The lower NUE at the C_{org} -high treatments compared to C_{org} -medium treatments reveals that plants are more independent of N input by fertilizer with increasing SOM at drained fen peatlands due to the extra N_{\min} derived from enhanced mineralization processes, as mentioned above.

4.3 Fertilizer- and site-induced N_2O emissions

The observed annual N_2O emissions were markedly lower than the actual default emission factor from the Tier 1 approach for temperate, deep drained, nutrient-rich grassland of $8.2 \text{ kg } N_2O\text{-N ha}^{-1} \text{ yr}^{-1}$ (IPCC, 2014) and at the lower end of literature values from other organic soils. Studies from Germany reported much higher N_2O emissions, ranging from 1.15 to $19.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Flessa et al., 1997; Augustin et al., 1998; Flessa et al., 1998; Beetz et al., 2013). Also investigations from other European countries showed that much higher N_2O emissions can be released from grasslands on drained peatlands. For example, Velthof et al. (1996) and van Beek et al. (2010, 2011) reported N_2O emissions ranging from 4.2 to $41.0 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for the Netherlands, whereas at boreal regions N_2O emissions of up to $9 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ were measured (Nykanen et al., 1995; Maljanen et al., 2004; Regina et al., 2004). The observed N_2O emissions were also in the range of those reported from grasslands on mineral soils in Germany, summarized by Jungkunst et al. (2006). In line with our results, Flessa et al. (1998) also found that N_2O losses from peat soils are not always larger than from nearby mineral soils, but in contrast, Maljanen et al. (2010) found on average four times higher N_2O emissions from cultivated organic soils than from mineral soils. The N_2O emissions from the C_{org} -high site significantly exceeded those from the C_{org} -medium site in all treatments, which was in line with higher N_{\min} contents and higher groundwater levels. Additionally, the observed markedly stronger increase of cumulative annual N_2O emissions with increasing N-uptake by plants (Fig. 5b) reveals that with increasing N availability a higher proportion is lost as N_2O at the C_{org} -high treatments compared to the C_{org} -medium treatments. This probably could be attributed to the more favorable soil conditions for denitrification, due to higher C and N mineralization rates and alternating groundwater levels, promoting anaerobicity (Koops et al., 1996). Moreover, as mentioned above, net nitrification entirely controls net nitrogen mineralization, promoting also N_2O losses, but probably to a lesser extent. However, the source of N_2O production in soils is often uncertain because aerobic and anaerobic microsites can occur within close proximity and thus nitrification and denitrification as well as other abiotic processes producing N_2O (e.g., nitrifier–denitrification, coupled nitrification–denitrification) can run simultaneously (Davidson et al., 1986; Butterbach-Bahl et al., 2013). Despite surprisingly low N_2O emission levels, we confirmed our hypothesis that N_2O emissions increase with increasing

soil C_{org} content, probably due to more favorable conditions for denitrification.

The observed background emissions on the two organic soils correspond well to those on mineral agricultural soils (Bouwman, 1996). However, calculated emission factors as a percentage of applied N without consideration of the NH_3 losses were lower for all treatments than the IPCC default value. Several other studies also reported emission factors < 1 % of applied N (Chadwick et al., 2000; Velthof et al., 2003; Clemens et al., 2006; Jones et al., 2007; Möller and Stinner, 2009), but so far not for organic soils. Indeed, N_2O studies on organic soils rarely differentiate between fertilizer and soil derived N sources by unfertilized control plots as we do in this study. In line with Möller and Stinner (2009), the application of biogas digestate resulted in a markedly higher percentage of N_2O produced from applied N compared to cattle slurry, yet at a low level.

One reason of generally low N_2O emissions observed in the present study could be the small number of frost–thaw cycles in 2011. In general frost–thaw cycles are considered to favor high N_2O emissions (Flessa et al., 1998; Jungkunst et al., 2006) but these observations seem to be more pronounced for croplands than for grasslands in Germany (Dechow and Freibauer, 2011). Denitrification activity is strongly related to the NO_3^- content close to the groundwater level (van Beek et al., 2004). Given the high NO_3^- contents, in particular in the C_{org} -high soil, the evidence for fast nitrification and high net nitrogen mineralization, we argue that frequent but low dosage application of fertilizer and quick N uptake by plants avoid conditions favorable for high N_2O emissions. Moreover, through the splash plate application technique high amounts of NH_4^+ were rapidly lost as NH_3 , and therefore reduced the proportion of immediately available N for nitrification and denitrification.

As expected from the literature, highest N_2O fluxes were found immediately after fertilizer application. The initial N_2O peak could mainly be attributed to the denitrification of available soil NO_3^- , presumably due to the more favorable conditions for denitrification through the addition of easily degradable organic C and water (Comfort et al., 1990; Chadwick et al., 2000; Velthof et al., 2003). Additionally, a probably smaller part of initial N_2O could be ascribed to the rapid nitrification (Chadwick et al., 2000) or to nitrifier denitrification of slurry NH_4^+ . In contrast, the partially observed second N_2O peak, mostly found a week after fertilizer application, can be attributed to the denitrification of mineralized and nitrified organic components of fertilizer N (Velthof et al., 2003).

Several authors proposed that the more recalcitrant digestate might reduce the rate of microbial degradation and oxygen consumption in the soil, resulting in reduced N_2O emissions through less anaerobic soil conditions (Clemens and Huschka, 2001; Oenema et al., 2005; Möller and Stinner, 2009). In contrast, our study on organic soils found signif-

icantly higher N_2O emissions from the digestate treatments compared to the slurry treatments. Higher N_2O emissions derived from biogas digestates were also reported by a few other authors (e.g. Senbayram et al., 2009; Sanger et al., 2010), whereas Clemens et al. (2006) found no differences between untreated and digested slurry.

It can be assumed that in drained organic soils, as in the present study, sufficient metabolizable C is generally widely available in the upper soil profile (e.g. van Beek et al., 2004). Thus, as hypothesized, labile carbon is not limiting on organic soils. This was in line with Velthof et al. (2003), who supposed that the application of available C with the organic fertilizer has a larger effect on denitrification activity at soils with a lower C_{org} content compared to C_{org} rich soils. However, contrary to our hypothesis, the significantly higher N_2O emissions from the digestate treatments cannot solely be explained by the higher content of available N in the biogas digestate, since the amount of applied NH_4^+ -N in the substrate was not markedly different. Nevertheless, as mentioned above, the much higher N-uptake at the biogas treatments (Fig. 5a) indicates that the application of this fertilizer resulted in a markedly higher N availability, promoting N_2O production. It could be assumed that the high pH and the lower C:N ratio of the biogas digestate obviously slightly enhanced SOM mineralization, probably due to increased microbial activity compared to cattle slurry fertilizer, leading to extra N for nitrification and denitrification. Moreover, as proposed above, it is also conceivable that the higher biomass production at these treatments itself is related to the increased N_2O emissions, due to the stimulating effect of plant roots on denitrification activity (Klemedtsson et al., 1987; Bakken, 1988). Considering that increasing biomass production means increasing root growth and activity, it could be assumed that exudation of easily available organic C and N (Hailer and Stolp, 1985), as well as the O_2 demand due to root respiration, is higher for the digestate treatments, promoting more anaerobic microsites and thus denitrification compared to cattle slurry (Erich et al., 1984; Klemedtsson et al., 1987). Furthermore, several authors have suggested that root exudates may increase bacterial metabolism (Klemedtsson, 1987; Mounier et al., 2004; Henry et al., 2008), further lowering the oxygen concentration and thus increasing denitrification (Klemedtsson et al., 1987). However, the enhanced biomass production simultaneously should have depleted mineral N in the soil and thus reduced available N for nitrification and denitrification processes. Obviously, despite the negative apparent N balance of the biogas digestate treatment, there was no real nitrogen competition between plants and microbes. However, further investigations are required to prove whether digestates enhanced SOM mineralization or to what extent increased biomass production favors N_2O emissions and which N pathways and processes are involved.

The observed linear increase in the cumulative N_2O -N emissions during the first 16 days or annual N_2O emissions,

due to a higher mean groundwater level and a higher application rate of NH_4^+-N , reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of C_{org} -rich grasslands. The same was postulated for mineral soils by Ruser (2010).

4.4 Fertilizer- and site-induced CH_4 emissions

The observed consumption rates of CH_4 were in the range of CH_4 uptakes reported by Flessa et al. (1998) for two different meadows in a southern German fen peatland. Slightly higher CH_4 emissions of up to $1.46 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$ were reported from Beetz et al. (2013) for a drained intensive grassland in northern Germany and from Nykänen et al. (1995) for a drained grassland in Finland. It is known that drainage turns peatlands from a significant source back to a sink of CH_4 (Crill et al., 1994). In peatlands the position of the groundwater table is considered the key factor regulating methanogenic and methanotrophic processes (Whalen, 2005). In line with this, Flessa et al. (1998) showed that the consumption rate of CH_4 increased with lowering of the groundwater level. Nevertheless, significant differences in the amount of the annual CH_4 uptake capacity between the two study sites C_{org} -medium and C_{org} -high could not be seen, although distinct differences in the groundwater table were observed.

The occasionally observed CH_4 peak emissions were only found immediately after cattle slurry application. This was in line with several other studies that reported short-term CH_4 emissions immediately after organic fertilizer application, due probably to volatilization of dissolved CH_4 from the applied substrate (Sommer et al., 1996; Chadwick et al., 2000; Wulf et al., 2002b; Jones et al., 2005; Amon et al., 2006). The longer lasting CH_4 emissions observed after the first application event at the slurry treatment of the C_{org} -high site might result from the degradation of volatile fatty acids by methanogenic bacteria (Chadwick et al., 2000; Wulf et al., 2002b). Furthermore, the high groundwater level promotes the formation of CH_4 during this time period. However, we could not find any significant differences in the short term or annual CH_4 emissions between the two investigated fertilizers. According to Chadwick et al. (2000) more than 90 % of total CH_4 emissions occur during the first 24 h following fertilizer application. Therefore, we must assume that we have missed most of the fertilizer-induced CH_4 emissions. However, all studies from literature confirm the minor importance of CH_4 emissions from applied organic fertilizers in the GHG balance of agricultural grasslands (Wulf et al., 2002b; Amon et al., 2006; Dietrich et al., 2012).

4.5 N-losses by NH_3 volatilization

The NH_3 losses measured after splash plate application at the third application event followed the typical pattern of lost ammonia (Clemens et al., 2006), particularly at the digestate treatments. Significantly higher NH_3 losses from treatments

fertilized with biogas digestate were observed compared to those fertilized with cattle slurry. This is in line with several other studies (Messner, 1988, Döhler and Haring, 1989 (cited in Döhler and Horlacher, 2010); Amon et al., 2006; Möller and Stinner, 2009; Pacholski et al., 2010; Ni et al., 2011), whereas Pain et al. (1990), Rubæk et al. (1996), Wulf et al. (2002a) and Clemens et al. (2006) found no differences between anaerobic digested slurries and other animal slurries. However, it has to be taken into account that the present results are based only on measurements from a single application event. The observed relative N losses of 36 % of applied NH_4^+-N at the biogas digestate treatments were in the range reported for liquid slurries and digestates applied via surface application, whereas the significantly lower relative N losses (15 %) at the cattle slurry treatments stand in strong contrast to those reported in the literature (e.g., Döhler and Haring, 1989 (cited in Döhler and Horlacher, 2010); Smith et al., 2000; Wulf et al., 2002a; Chantigny et al., 2004). However, compared to the EF of 60 % used in the German national GHG inventory, both estimated NH_3 loss rates were rather low (Haenel et al., 2014). It can be assumed that the higher concentration of NH_4^+ ($\text{NH}_4^+/\text{N}_{\text{tot}}$ ratio 0.65 vs. 0.33) and the markedly higher pH value (7.7 vs. 6.8) of the applied digestate compared to the cattle slurry caused the observed differences in the current study, since temperature and wind speed were equal. According to Sommer and Hutchings (2001) a change in the pH value from 7.7 to 8.0 will double the emission. However, the factors controlling the rise in pH are complex (Sommer and Husted, 1995 cited in Sommer and Hutchings, 2001) and the pH value was not determined after fertilization in the present study. Several authors propose that a lower dry matter content of slurries favors the infiltration into the soil with a subsequent faster decrease of NH_3 losses (Sommer et al., 1996; Ni et al., 2011). There over a limited range (slurry DM of 2–5 %), NH_3 losses increase by approximately 6 % for every 1 % DM content (Smith et al., 2000). Although the observed dry matter content of the biogas digestates was very low and at the lower end of values reported in the literature (e.g., Gutser et al., 2005; Möller et al., 2008; Quarkernack et al., 2011), no corresponding effect was found in the present study, as was also reported by Möller and Stinner (2009). According to Döhler and Horlacher (2010) and Smith et al. (2000), water-saturated grassland soils as well as very dry grassland soils high in organic matter lead to higher NH_3 -losses due to the reduced infiltration of slurries. Thus it could be assumed that the infiltration of the slurries was possibly hampered in the current study, removing the effect of the different DM contents, due to the strong rain event that took place before the fertilizer application. The cattle slurry in our experiment had very favorable characteristics for crust formation (high DM content, grass silage diet; Smith et al., 2007). Warm weather also supported crust formation after application of cattle slurry, which can effectively inhibit NH_3 exchange with the atmosphere and has been proposed as an NH_3 mitigation measure for slurry

storage (Smith et al., 2007). The emission pattern observed in our study on soil with limited infiltration capacity supports the effectiveness of crusts for low NH_3 losses. Additionally, at low dosage applications a large part of the organic fertilizer remained on the plant canopy and thus soil contact and infiltration was limited after spreading. We conclude that this was also the main reason why no significant differences in the pattern of NH_3 volatilization between the soil types were found in the present study. Nevertheless, the markedly lower relative N losses from cattle slurry compared to literature values could not be explained in this way, but NH_3 volatilization reported in literature showed a high variability in respect to climatic and soil conditions, slurry composition, and application technique.

The observed relative N losses of 15–36% of applied NH_4^+ -N demonstrates that NH_3 volatilization is quantitatively the most important N loss from slurry application, as was also proposed by Flessa and Beese (2000). Besides the negative effects of eutrophication and acidification of ecosystems (e.g., Fangmeier et al., 1994; Galloway, 1995; Smith et al., 1999; Galloway, 2001), marked NH_3 volatilization decreases N fertilizer use efficiency. One of the most effective measures to reduce NH_3 emissions from grassland is the incorporation of slurry (Rodhe et al., 2006). However, several studies reported a considerable increase of GHGs, mainly N_2O , after injection of slurries and biogas digestates (Dosch and Gutser, 1996; Flessa and Beese, 2000; Wulf et al., 2002b). To date no study has examined the effect of the injection technique on organic soils.

5 Conclusions

We studied N_2O , CH_4 , and NH_3 fluxes after splash plate application of biogas digestate and cattle slurry in a region known for its risk of high N_2O and NH_3 emissions and we were the first to study digestate application on high organic carbon soils with 10 to 17% C_{org} content in the topsoil. To our surprise, N_2O emissions and EFs were lower than generally observed on mineral soils in the vicinity of the sites. We attributed the low N_2O emissions to a mild winter without clear freeze–thaw cycles, but maybe also to frequent application with low dosage of N, which was quickly taken up by the grass vegetation, as was indicated by the apparent NUE_{min} . N_2O emissions increased with C_{org} content and fertilization. As hypothesized, N_2O levels were markedly higher after digestate than after slurry fertilization, which probably could be attributed to a priming effect caused by increased SOM mineralization or other sources of labile carbon triggered by digestate application. Due to the deep drainage, CH_4 emissions were of minor importance and were independent of fertilizer type. Estimated N balances were negative for the control and the digestate treatments, but strongly positive in all cases when the net N supply from SOM mineralization was considered. The observed linear increase in cumulative N_2O

emissions with increasing NH_4^+ fertilization and increasing groundwater table reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of C_{org} -rich grasslands.

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References

- Amon, B., Kryvoruchko, G. M., and Amon, T.: Greenhouse gas and ammonia emission abatement by slurry treatment, *International Congress Series*, 1293, 295–298, 2006.
- Andres, M., Hagemann, U., Seidel, A., and Augustin, J.: Gasförmige N-Verluste (N_2O , NH_3) und N-Bilanzsalden beim Anbau von Energiemais mit Gärrestapplikation, in: Böden – Lebensgrundlage und Verantwortung, Jahrestagung der DBG, Symposium AG Bodengase, 7–12 September 2013, Rostock, 2013 (in German).
- Augustin, J., Merbach, W., Steffens, L., and Snelinski, B.: Nitrous Oxide Fluxes of Disturbed Minerotrophic Peatlands, *Agric. Res.*, 51, 47–57, 1998.
- Bakken, L. R.: Denitrification under different cultivated plants: effects of soil moisture tension, nitrate concentration, and photosynthetic activity, *Biol. Fertil. Soils*, 6, 271–278, 1988.
- Beetz, S., Liebersbach, H., Glatzel, S., Jurasinski, G., Buczko, U., and Höper, H.: Effects of land use intensity on the full greenhouse gas balance in an Atlantic peat bog, *Biogeosciences*, 10, 1067–1082, doi:10.5194/bg-10-1067-2013, 2013.
- Bouwman, A. F.: Direct emissions of nitrous oxide from agricultural soils, *Nutr. Cycl. Agroecosys.*, 45, 53–70, 1996.
- Butterbach-Bahl, K., Baggs, E. M., Dannenmann, M., Kiese, R., and Zechmeister-Boltenstern, S.: Nitrous oxide emissions from soils: how well do we understand the processes and their controls?, *Philos. T. R. Soc. B.*, 368, 1621, 2013.
- Chadwick, D. R., Pain, B. F., and Brookman, S. K. E.: Nitrous oxide and Methane Emissions following Application of Animal Manures to Grassland, *J. Environ. Qual.*, 29, 277–287, 2000.
- Chantigny, M. H., Rochette, P., Angers, D. A., Massé, D., and Côté, D.: Ammonia volatilization and selected soil characteristics fol-

- lowing application of anaerobically digested pig slurry, *Soil Sci. Soc. Am. J.*, 68, 306–312, 2004.
- Christensen, S.: Nitrous oxide emission from a soil under permanent grass: Seasonal and diurnal fluctuations as influenced by manuring and fertilisation, *Soil Biol. Biochem.*, 15, 531–536, 1983.
- Clayton, H., McTaggart, I. P., Parker, J., and Swan, L.: Nitrous oxide emissions from fertilised grassland: A 2-year study of the effects of N fertiliser form and environmental conditions, *Biol. Fert. Soils*, 25, 252–260, 1997.
- Clemens, J. and Huschka, A.: The effect of biological oxygen demand of cattle slurry and soil moisture on nitrous oxide emissions, *Nutr. Cycling Agroecosyst.*, 59, 193–198, 2001.
- Clemens, J., Trimborn, M., Weiland, P., and Amon, B.: Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry, *Agr. Ecosyst. Environ.*, 112, 171–177, 2006.
- Comfort, S. D., Kelling, K. A., Keeney, D. R., and Converse, J. C.: Nitrous oxide production from injected dairy manure, *Soil Sci. Soc. Am.*, 1, 421–427, 1990.
- Crawley, M. J.: *The R Book*, John Wiley and Sons Ltd, Chichester, p. 942, 2007.
- Crill, P. M., Martikainen, P. J., Nykänen, H., and Silvola, J.: Temperature and fertilization effects on methane oxidation in a drained peatland soil, *Soil Biol. Biochem.*, 26, 1331–1339, 1994.
- Crutzen, P. J.: The role of NO and NO₂ in the chemistry of the troposphere and stratosphere, *Annu. Rev. Earth Pl. Sc.*, 7, 443–472, 1979.
- Davidson, E. A., Swank, W. T., and Perry, T. O.: Distinguishing between nitrification and denitrification as sources of gaseous nitrogen production in soil, *Appl. Environ. Microb.*, 52, 1280–1286, 1986.
- DBFZ (Deutsches BiomasseForschungsZentrum gemeinnützige GmbH): Monitoring zur Wirkung des Erneuerbare-Energien-Gesetz (EEG) auf die Entwicklung der Stromerzeugung aus Biomasse – Endbericht zur EEG-Periode 2009 bis 2011, p. 120, 2012 (in German).
- De Boer, H. C.: Co-digestion of animal slurry can increase short-term nitrogen recovery by crops, *J. Environ. Qual.*, 37, 1968–1973, 2008.
- Dechow, R. and Freibauer, A.: Assessment of German nitrous oxide emissions using empirical modelling approaches, *J. Nutr. Cycl. Agroecosyst.*, 91, 235–254, 2011.
- Dietrich, B., Finnan, J., Frost, P., Gilkinson, S., and Müller, C.: The extent of methane (CH₄) emissions after fertilisation of grassland with digestate, *Biol. Fert. Soils*, 48, 981–985, 2012.
- Don, A., Osborne, B., Hastings, A., Skiba, U., Carter, M. S., Drewer, J., Flessa, H., Freibauer, A., Hyvönen, N., Jones, M. B., Lanigan, G. J., Mander, Ü., Monti, A., Djomo, S. N., Valentine, J., Walter, K., Zegada-Lizarazu, W., and Zenone, T.: Land-use change to bioenergy production in Europe: implications for the greenhouse gas balance and soil carbon, *GCB Bioenergy*, 4, 372–391, doi:10.1111/j.1757-1707.2011.01116.x, 2012.
- Dosch, P. and Gutser, R.: Reducing N losses (NH₃, N₂O, N₂) and immobilization from slurry through optimized application techniques, *Fer. Res.*, 43, 165–171, 1996.
- Döhler, H. and Horlacher, D.: Ammoniakemissionen organischer Düngemittel, in *Emissionen landwirtschaftlich genutzter Böden*, KTBL-Schrift, 483, p. 384, 2010 (in German).
- Drösler, M.: Trace gas exchange and climatic relevance of bog ecosystems, Southern Germany, PhD thesis, Chair of Vegetation Ecology, Department of Ecology, Technical University Munich, p. 179, 2005.
- Drösler, M., Freibauer, A., Adelman, W., Augustin, J., Bergman, L., Beyer, C., Chojnicki, B., Förster, C., Giebels, M., Görlitz, S., Höper, H., Kantelhardt, J., Liebersbach, H., Hahn-Schöfl, M., Minke, M., Petschow, U., Pfadenhauer, J., Schaller, L., Schägner, P., Sommer, M., Thuille, A., and Wehrhan, M.: Klimaschutz durch Moorschutz in der Praxis – Ergebnisse aus dem BMBF-Verbundprojekt “Klimaschutz – Moornutzungsstrategien” 2006–2010, 2011 (in German).
- Eickenscheidt, N., Brumme, R., and Veldkamp, E.: Direct contribution of nitrogen deposition to nitrous oxide emissions in a temperate beech and spruce forest – a ¹⁵N tracer study, *Biogeochemistry*, 8, 621–635, doi:10.5194/bg-8-621-2011, 2011.
- Elsässer, R. M., Kunz, H. G., and Briemle, G.: Unterschiedliche technische Behandlung von Gülle und deren Auswirkungen auf intensiv genutztes Grünland, *J. Agron. Crop. Sci.*, 174, 253–264, 1995 (in German).
- Erich, M. S., Bekerie, A., and Duxbury, J. M.: Activities of denitrifying enzymes in freshly sampled soils, *Soil Sci.*, 138, 25–32, 1984.
- Fachverband Biogas e.V.: Branchenzahlen – Prognosen 2013/2014, Entwicklung des jährlichen Zubaus von neuen Biogasanlagen in Deutschland, available at: http://www.biogas.org/edcom/webfvb.nsf/id/DE_Branchenzahlen, last access: November 2013.
- Fangmeier, A., Hadwiger-Fangmeier, A., van der Eerden, L., and Jäger, H. J.: Effects of atmospheric ammonia on vegetation – a review, *Environ. Pollu.*, 86, 43–82, 1994.
- Flessa, H. and Beese, F.: Laboratory Estimates of Trace Gas Emissions following Surface Application and Injection of Cattle Slurry, *J. Environ. Qual.*, 29, 262–268, 2000.
- Flessa, H., Wild, U., Klemisch, M., and Pfadenhauer, J.: C- und N-Stoffflüsse auf Torfstichsimulationsflächen im Donaumoos, *Z. f. Kulturtechnik und Landentwicklung*, 38, 11–17, 1997 (in German).
- Flessa, H., Wild, U., Klemisch, M., and Pfadenhauer, J.: Nitrous oxide and methane fluxes from organic soils under agriculture, *Eur. J. Soil Sci.*, 49, 327–335, 1998.
- Freibauer, A. and Kaltschmitt, M.: Nitrous oxide emissions from agricultural mineral soils in Europe – controls and models, *Biogeochemistry*, 63, 93–115, 2003.
- Freibauer, A., Rounsevell, M. D. A., Smith, P., and Verhagen, J.: Carbon sequestration in the agricultural soils of Europe, *Geoderma*, 122, 1–23, 2004.
- Frick, R.: Verteilgeräte an Güllefässern – Grosse Unterschiede bezüglich Arbeitsbreite und Verteilgenauigkeit, *FAT Berichte*, 531, 1–37, 1999 (in German).
- Galloway, J. N.: Acid deposition: Perspectives in time and space, *J. Water, Air Soil Poll.*, 85, 15–24, 1995.
- Galloway, J. N.: Acidification of the world: natural and anthropogenic, *J. Water, Air, Soil Poll.*, 130, 17–24, 2001.
- Goldberg, S. D., Knorr, K. H., Blodau, C., Lischeid, G., and Gebauer, G.: Impact of altering the water table height of an acidic fen on N₂O and NO fluxes and soil concentrations, *Global Change Biol.*, 16, 220–233, 2010.

- Gunnarsson, A., Bengtsson, F., and Caspersen, S.: Use efficiency of nitrogen from biodegraded plant material by ryegrass, *J. Plant Nutr. Soil Sci.*, 173, 113–119, 2010.
- Gutser, R., Ebertseder, Th., Weber, A., Schraml, M., and Schmidhalter, U.: Short-term and residual availability of nitrogen after long-term application of organic fertilizers on arable land, *J. Plant Nutr. Soil Sci.*, 168, 439–446, 2005.
- Gutser, R., Ebertseder, T., Schraml, M., Tucher von, S., and Schmidhalter, U.: Stickstoffeffiziente und umweltschonende organische Düngung, in *Emissionen landwirtschaftlich genutzter Böden*, KTBL-Schrift, 483, p. 384, 2010 (in German).
- Hacin, J., Cop, J., and Mahne, I.: Nitrogen mineralization in marsh meadows in relation to soil organic matter content and watertable level, *J. Plant Nutr. Soil Sci.*, 164, 503–509, 2001.
- Haenel, H. D., Freibauer, A., Rösemann, C., Poddey, E., Genzior, A., Menden, B. M., and Döhler, H.: Emissionen landwirtschaftlich genutzter Böden im Rahmen der deutschen Klimaberichterstattung, in *Emissionen landwirtschaftlich genutzter Böden*, KTBL-Schrift, 483, p. 384, 2010 (in German).
- Haenel, H. D., Rösemann, C., Dämmgen, U., Poddey, E., Freibauer, A., Wulf, S., Eurich-Menden, B., Döhler, H., Schreiner, C., Bauer, B., and Osterburg, B.: Calculations of gaseous and particulate emissions from German agriculture 1990–2012, *Johann Heinrich von Thünen-Institut, Braunschweig*, 348 pp., Thünen Rep 17, 2014.
- Hahn-Schöfl, M., Zak, D., Minke, M., Gelbrecht, J., Augustin, J., and Freibauer, A.: Organic sediment formed during inundation of a degraded fen grassland emits large fluxes of CH₄ and CO₂, *Biogeosciences*, 8, 1539–1550, doi:10.5194/bg-8-1539-2011, 2011.
- Hailer, T. and Stolp, H.: Quantitative estimation of root exudation of maize plants, *Plant Soil*, 86, 207–216, 1985.
- Henry, S., Texier, S., Hallet, S., Bru, D., Dambreville, C., Chèneby, D., Bizouard, F., Germon, J. C., and Philippot, L.: Disentangling the rhizosphere effect on nitrate reducers and denitrifiers: insight into the role of root exudates, *Environ. Microbiol.*, 10, 3082–3092, 2008.
- Hothorn, T., Bretz, F., Westfall, P., Heiberger, R. M., and Schuetzenmeister, A.: Simultaneous Inference in General Parametric Models: R package version 1.2-17, 2013.
- IPCC: Changes in atmospheric constituents and in radiative forcing, in: *Climate Change 2007: The physical science basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK and New York, USA, 2007.
- IPCC: 2013 Supplement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories: Wetlands, edited by: Hiraishi, T., Krug, T., Tanabe, K., Srivastava, N., Baasansuren, J., Fukuda, M. and Troxler, T. G., Published: IPCC, Switzerland, 2014.
- Jensen, L. S., Pedersen, I. S., Hansen, T. B., and Nielsen, N. E.: Turnover and fate of ¹⁵N-labelled cattle slurry ammonium-N applied in the autumn to winter wheat, *Eur. J. Agron.*, 12, 23–35, 2000.
- Jones, S. K., Rees, R. M., Skiba, U. M., and Ball, B. C.: Greenhouse gas emissions from managed grassland, *Global Planet. Change*, 47, 201–211, 2005.
- Jones, S. K., Rees, R. M., Skiba, U. M., and Ball, B. C.: Influence of organic and mineral N fertiliser on N₂O fluxes from temperate grassland, *Agriculture, Ecosystems Environ.*, 121, 74–83, 2007.
- Jungkunst, H. F., Freibauer, A., Neufeldt, H., and Bareth, G.: Nitrous oxide emissions from agricultural land use in Germany – a synthesis of available annual field data, *J. Plant Nutr. Soil Sci.*, 169, 341–351, 2006.
- Kasimir Klemedtsson, Å., Klemedtsson, L., Berglund, K., Martikainen, P., Silvola, J., and Oenema, O.: Greenhouse gas emissions from farmed organic soils: a review, *Soil Use Manage.*, 13, 1–6, 1997.
- Klemedtsson, L., Svensson, B. H., and Rosswall, T.: Dinitrogen and nitrous oxide produced by denitrification and nitrification in soil with and without barley plants, *Plant Soil*, 99, 303–319, 1987.
- Klemedtsson, L., von Arnold, K., Weslien, P., and Gundersen, P.: Soil CN ratio as a scalar parameter to predict nitrous oxide emissions, *Glob. Change Biol.*, 11, 1142–1147, 2005.
- Koops, J. G., Oenema, O., and van Beusichem, M. L.: Denitrification in the top soil of grassland on peat soil, *Plant Soil*, 184, 1–10, 1996.
- Livingston, G. P. and Hutchinson, G. L.: Enclosure-based measurement of trace gas exchange: application and sources of error, in: *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by: Matson, P. A. and Harriss, R. C., Blackwell Science, Cambridge, 14–50, 1995.
- Maljanen, M., Komulainen, V. M., Hytönen, J., Martikainen, P. J., and Laine, J.: Carbon dioxide, nitrous oxide and methane dynamics in boreal organic agricultural soils with different soil characteristics, *Soil Biol. Biochem.*, 36, 1801–1808, 2004.
- Maljanen, M., Sigurdsson, B. D., Gudmundsson, J., Óskarsson, H., Huttunen, J. T., and Martikainen, P. J.: Greenhouse gas balances of managed peatlands in the Nordic countries – present knowledge and gaps, *Biogeosciences*, 7, 2711–2738, doi:10.5194/bg-7-2711-2010, 2010.
- Merino, P., Estavillo, J. M., Gracioli, L. A., Pinto, M., Lacuesta, M., Muñoz-Rueda, A., and Gonzalez-Murua, C.: Mitigation of N₂O emissions from grassland by nitrification inhibitor and Actilith F2 applied with fertilizer and cattle slurry, *Soil Use Manage.*, 18, 135–141, 2002.
- Messner, H.: Düngewirkung anaerob fermentierter und unbehandelter Gülle, Dissertation, Fakultät für Landwirtschaft und Gartenbau, TU München, 1988 (in German).
- Möller, K. and Stinner, W.: Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and gaseous nitrogen losses (ammonia, nitrous oxide), *Eur. J. Agronomy*, 30, 1–16, 2009.
- Möller, K. and Müller, T.: Effects of anaerobic digestion on digestate nutrient availability and crop growth: A review, *Eng. Life Sci.*, 12, 242–257, 2012.
- Möller, K., Stinner, W., Deuker, A., and Leithold, G.: 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, doi:10.1007/s10705-008-9196-9, 2008.
- Moiser, A. R.: Exchange of gaseous nitrogen compounds between agricultural systems and the atmosphere, *Plant Soil*, 228, 17–27, 2001.
- Mounier, E., Hallet, S., Chèneby, D., Benizri, E., Gruet, Y., Nguyen, C., Piutti, S., Robin, C., Slezack-Deschaumes, S., Martin-

- Laurent, F., Germon, J. C., and Philippot, L.: Influence of maize mulch on the diversity and activity of the denitrifying community, *Environ. Microbiol.*, 6, 301–312, 2004.
- Ni, K., Pacholski, A., Gericke, D., and Kage, H.: Analysis of ammonia losses after field application of biogas slurries by an empirical model, *J. Plant Nutr. Soil Sci.*, 175, 1–12, doi:10.1002/jpln.201000358, 2011.
- Nykänen H., Alm, J., Lång, K., Silvola, J., and Martikainen, P. J.: Emissions of CH₄, N₂O and CO₂ from a virgin fen and a fen drained for grassland in Finland, *J. Biogeogr.*, 22, 351–357, 1995.
- Oenema, O., Wrage, N., Velthof, G. L., van Groenigen, J. W., Dolfing, J., and Kuikman, P. J.: Trends in global nitrous oxide emissions from animal production systems, *Nutr. Cycl. Agroecosyst.*, 72, 51–65, 2005.
- Pacholski, A., Cai, G., Nieder, R., Richter, J., Fan, X., Zhu, Z., and Roelcke, M.: Calibration of a simple method for determining ammonia volatilization in the field – comparative measurements in Henan Province, China, *Nutr. Cycl. Agroecosyst.*, 74, 259–273, 2006.
- Pacholski, A., Gericke, D., Ni, K., and Kage, H.: Ammoniakemissionen nach Ausbringung von Gärresten im Vergleich zu Gülle, *KTBL-Schrift*, 483, p. 384, 2010 (in German).
- Pain, B. F., Misselbrook, T. H., Clarkson, C. R., and Rees, Y. J.: Odour and ammonia emissions following the spreading of anaerobically-digested pig slurry on grassland, *Biol. Wastes*, 34, 259–267, 1990.
- Quarkernack, R., Pacholski, A., Techow, A., Herrmann, A., Taube, F., and Kage, H.: Ammonia volatilization and yield response of energy crops after fertilization with biogas residues in a coastal marsh of Northern Germany, *Agric. Ecosyst. Environ.*, 160, 66–74, doi:10.1016/j.agee.2011.05.030, 2011.
- Regina, K., Syväsalo, E., Hannukkala, A., and Esala, M.: Fluxes of N₂O from farmed peat soils in Finland, *Eur. J. Soil Sci.*, 55, 591–599, 2004.
- R Development Core Team: R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria, ISBN 3-900051-07-0, available at: <http://www.R-project.org> (last access: November 2013), 2010.
- Renger, M., Wessolek, G., Schwarzel, K., Sauerbrey, R., and Siewert, C.: Aspects of peat conservation and water management, *J. Plant Nutr. Soil Sci.*, 165, 487–493, 2002.
- Rodhe, L., Pell, M., and Yamulki, S.: Nitrous oxide, methane and ammonia emissions following slurry spreading on grassland, *J. Soil Use Manage.*, 22, 229–237, 2006.
- Roelcke, M., Li, S. X., Gao, Y. J., and Richter, J.: In situ comparisons of ammonia volatilization from N fertilizers in Chinese loess soils, *Nutr. Cycl. Agroecosyst.*, 62, 73–88, 2002.
- Rubæk, G. H., Henriksen, K., Petersen, J., Rasmussen, B., and Sommer, S. G.: Effects of application technique and anaerobic digestion on gaseous loss from animal slurry applied to ryegrass (*Lolium perenne*), *J. Agric. Sci. Camb.*, 126, 481–492, 1996.
- Ruser, R.: Möglichkeiten zur Minderung der Lachgasfreisetzung aus landwirtschaftlich genutzten Böden bei mineralischer Stickstoffdüngung, in: Emissionen landwirtschaftlich genutzter Böden, *KTBL-Schrift*, 483, p. 384, 2010 (in German).
- Sänger, A., Geisseler, D., and Ludwig, B.: Effects of rainfall pattern on carbon and nitrogen dynamics in soil amended with biogas slurry and composted cattle manure, *J. Plant Nutr. Soil Sci.*, 173, 692–698, 2010.
- Schils, R. L. M., van Groenigen, J. W., Velthof, G. L., and Kuikman, P. J.: Nitrous oxide emissions from multiple combined applications of fertiliser and cattle slurry to grassland, *Plant Soil*, 310, 89–101, 2008.
- Schothorst, C. J.: Subsidence of low moor peat soils in the Western Netherlands, *Geoderma*, 17, 265–291, 1977.
- Senbayram, M., Chen, R., Mühling, K. H., and Dittert, K.: Contribution of nitrification and denitrification to nitrous oxide emissions from soils after application of biogas waste and other fertilizers, *Rapid Commun. Mass Spectrom.*, 23, 2489–2498, 2009.
- Smith, V. H., Tilman, G. D., and Nekola, J. C.: Eutrophication: impacts of excess nutrient input on freshwater, marine, and terrestrial ecosystems, *Environ. Pollut.*, 100, 179–196, 1999.
- Smith, K. A., Jackson, D. R., Misselbrook, T. H., Pain, B. F., and Johnson, R. A.: Reduction of ammonia emission by slurry application techniques, *J. Agric. Engng. Res.*, 77, 277–287, 2000.
- Smith, K., Cumby, T., Lapworth, J., Misselbrook, T., and Williams, A.: Natural crusting of slurry storage as an abatement measure for ammonia emissions on dairy farms, *Biosyst. Eng.*, 97, 464–471, 2007.
- Sørensen, P. and Amato, M.: Remineralisation and residual effects of N after application of pig slurry to soil, *Eur. J. Agron.*, 16, 81–95, 2002.
- Sommer, S. G. and Husted, S.: A simple model of pH in slurry, *J. Agric. Sci. Camb.*, 124, 447–453, 1995.
- Sommer, S. G., Sherlock, R. R., and Khan, R. Z.: Nitrous oxide and methane emissions from pig slurry amended soils, *Soil Biol. Biochem.*, 28, 1541–1544, 1996.
- Sommer, S. G. and Hutchings, N. J.: Ammonia emission from field applied manure and its reduction – invited paper, *Eur. J. Agro.*, 15, 1–15, 2001.
- Sonneveld, M. P. W. and Lantinga, E. A.: The contribution of mineralization to grassland N uptake on peatland soils with anthropogenic A horizons, *Plant Soil*, 340, 357–368, 2011.
- Tambone, F., Genevini, P., D'Imporzano, G., and Adani, F.: Assessing amendment properties of digestate by studying the organic matter composition and the degree of biological stability during the anaerobic digestion of the organic fraction of MSW, *Biore-source Technol.*, 100, 3140–3142, 2009.
- Umweltbundesamt: Nationale Trendtabellen für die deutsche Berichterstattung atmosphärischer Emissionen seit 1990, available at: <http://www.umweltbundesamt.de/daten/klimawandel/treibhausgas-emissionen-in-deutschland/distickstoffoxid-emissionen>, 2014 (in German).
- van Beek, C. L., Hummelink, E. W. J., Velthof, G. L., and Oenema, O.: Denitrification rates in relation to groundwater level in a peat soil under grassland, *Biol. Fertil. Soils*, 39, 329–336, 2004.
- van Beek, C. L., Pleijter, M., Jacobs, C. M. J., Velthof, G. L., van Groenigen, J. W., and Kuikman, P. J.: Emissions of N₂O from fertilized and grazed grassland on organic soil in relation to groundwater level, *Nutr. Cycl. Agroecosyst.*, 86, 331–340, 2010.
- van Beek, C. L., Pleijter, M., and Kuikman, P. J.: Nitrous oxide emissions from fertilized and unfertilized grasslands on peat soil, *Nutr. Cycl. Agroecosyst.*, 89, 453–461, 2011.
- Velthof, G. L., Brader, A. B., and Oenema, O.: Seasonal variations in nitrous oxide losses from managed grasslands in the Netherlands, *Plant Soil*, 181, 263–274, 1996.

- Velthof, G. L., Kuikman, P. J., and Oenema, O.: Nitrous oxide emission from animal manures applied to soil under controlled conditions, *Biol. Fertil. Soils*, 37, 221–230, 2003.
- Weiland, P.: Biogas production: current state and perspectives, *Appl. Microbiol. Biotechnol.*, 85, 849–860, 2010.
- Whalen, S. C.: Biogeochemistry of methane exchange between natural wetlands and the atmosphere, *Environ. Eng. Sci.*, 22, 73–94, 2005.
- WRB, 2006 – IUSS Working Group: World Reference Base for Soil Resources 2006, 2nd edition, World Soil Resources Reports No. 103, Rome, 2006.
- Wulf, S., Maeting, M., and Clemens, J.: Application Technique and Slurry Co-Fermentation Effects on Ammonia, Nitrous Oxide, and Methane Emissions after Spreading: I Ammonia Volatilization, *J. Environ. Qual.*, 31, 1789–1794, 2002a.
- Wulf, S., Maeting, M., and Clemens, J.: 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, 2002b.