



# 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

T. Eickenscheidt<sup>1</sup>, A. Freibauer<sup>2</sup>, J. Heinichen<sup>1</sup>, J. Augustin<sup>3</sup>, and M. Drösler<sup>1</sup>

<sup>1</sup>University of Applied Sciences Weihenstephan-Triesdorf, Chair of Vegetation Ecology, Weihenstephaner Berg 4, 85354 Freising, Germany

<sup>2</sup>Thünen Institute of Climate-Smart Agriculture, Bundesallee 50, 38116 Braunschweig, Germany

<sup>3</sup>Leibniz Centre for Agricultural Landscape Research e.V., Institute of Landscape Matter Dynamics, Eberswalder Straße 84, 15374 Müncheberg, Germany

Correspondence to: T. Eickenscheidt (tim.eickenscheidt@hswt.de)

**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 (N<sub>2</sub>O) emissions and organic fertilization is additionally known to increase N<sub>2</sub>O emissions from managed grasslands. Our study addressed the questions (a) to what extent biogas digestate and cattle slurry application increase N<sub>2</sub>O and methane (CH<sub>4</sub>) fluxes as well as the mineral nitrogen use efficiency (NUE<sub>min</sub>) and grass yield, and (b) how different soil organic matter contents (SOMs) and nitrogen contents promote the production of N<sub>2</sub>O. In addition NH<sub>3</sub> 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<sub>org</sub>-medium and C<sub>org</sub>-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 N<sub>2</sub>O and CH<sub>4</sub> were measured on three replicates over 2 years using the closed chamber method. For NH<sub>3</sub> measurements we used the calibrated dynamic chamber method. On an annual basis, the application of biogas digestate significantly enhanced the N<sub>2</sub>O fluxes compared to the application of cattle slurry and additionally increased the plant

N-uptake and NUE<sub>min</sub>. Furthermore, N<sub>2</sub>O fluxes from the C<sub>org</sub>-high treatments significantly exceeded N<sub>2</sub>O fluxes from the C<sub>org</sub>-medium treatments. Annual cumulative emissions ranged from  $0.91 \pm 0.49$  to  $3.14 \pm 0.91$  kg N ha<sup>-1</sup> yr<sup>-1</sup>. Significantly different CH<sub>4</sub> fluxes between the investigated treatments or the different soil types were not observed. Cumulative annual CH<sub>4</sub> exchange rates varied between  $-0.21 \pm 0.19$  and  $-1.06 \pm 0.46$  kg C ha<sup>-1</sup> yr<sup>-1</sup>. Significantly higher NH<sub>3</sub> losses, NUE<sub>min</sub> and grass yields from treatments fertilized with biogas digestate compared to those fertilized with cattle slurry were observed. The total NH<sub>3</sub> losses following the splash plate application were 18.17 kg N ha<sup>-1</sup> for the digestate treatments and 3.48 kg N ha<sup>-1</sup> for the slurry treatments (36 and 15 % of applied NH<sub>4</sub><sup>+</sup>-N). The observed linear increase of 16 days' cumulative N<sub>2</sub>O-N exchange or annual N<sub>2</sub>O 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<sub>org</sub>-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 (N<sub>2</sub>O) 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 N<sub>2</sub>O losses through denitrification (Clayton et al., 1997). Enhanced N<sub>2</sub>O emissions are of major concern due to the fact that N<sub>2</sub>O acts as a radiative forcing GHG (IPCC, 2007) and contributes to the chemical destruction of stratospheric ozone (Crutzen, 1979). In Germany, about 78 % of N<sub>2</sub>O 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 N<sub>2</sub>O, 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), N<sub>2</sub>O 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 N<sub>2</sub>O emissions from drained organic grassland soils revealed very high N<sub>2</sub>O emissions of up to 41.0 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Velthof et al., 1996).

In Germany, 50 % of the drained peatlands are used as grasslands (Dröslér et al., 2011), particularly in the smallholder structure of south Germany. Grassland soils in Europe and Germany produce more N<sub>2</sub>O 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 N<sub>2</sub>O 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 N<sub>2</sub>O 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 (NH<sub>4</sub><sup>+</sup>) content as well the NH<sub>4</sub><sup>+</sup> : N<sub>org</sub> 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 N<sub>2</sub>O 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 N<sub>2</sub>O 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 NH<sub>4</sub><sup>+</sup>-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 N<sub>2</sub>O 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 N<sub>2</sub>O, slurry application leads to short-term methane (CH<sub>4</sub>) and ammonia (NH<sub>3</sub>) emissions. Methane acts as a strong GHG, whereas NH<sub>3</sub> is considered an indirect GHG through ammonia deposition which could promote the formation of N<sub>2</sub>O (Moiser, 2001). Moreover, NH<sub>3</sub> 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 NH<sub>3</sub> emissions (Haanel et al., 2010). Particularly high NH<sub>4</sub><sup>+</sup> contents and high pH values, which are typically for the biogas digestate, promote accelerated NH<sub>3</sub> volatilization (Quakernack et al., 2011). High NH<sub>3</sub> 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 N<sub>2</sub>O and CH<sub>4</sub> 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 <sup>3</sup> ha <sup>-1</sup> ]
20 Aug 2010	mowing
25 Aug 2010	manuring [20 m <sup>3</sup> ha <sup>-1</sup> ]
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 <sup>3</sup> ha <sup>-1</sup> ]
1 Aug 2011	mowing
13 Sep 2011	mowing
22 Sep 2011	manuring [20 m <sup>3</sup> ha <sup>-1</sup> ]
4 Nov 2011	manuring [25 m <sup>3</sup> ha <sup>-1</sup> ]

be tested. Furthermore, NH<sub>3</sub> 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 N<sub>2</sub>O is emitted after biogas digestate than after slurry application because of higher NH<sub>4</sub><sup>+</sup>-N concentrations in the substrate and, thus, higher NH<sub>4</sub><sup>+</sup>-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) N<sub>2</sub>O emissions increase with increasing soil C<sub>org</sub> 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<sup>-1</sup> yr<sup>-1</sup>, with NH<sub>4</sub><sup>+</sup>-N: NO<sub>3</sub><sup>-</sup>-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<sub>org</sub>-medium) and as sapric Histosol (named C<sub>org</sub>-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 m<sup>2</sup>) 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 NH<sub>3</sub> 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 m<sup>3</sup> ha<sup>-1</sup>). This method is typical for farming practices, but produces diverging N application rates per event between slurry and digestate based on NH<sub>4</sub><sup>+</sup> or N<sub>tot</sub> 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 <sub>Org</sub> -medium	C <sub>Org</sub> -high	<i>n</i>
Soil type (WRB, 2006) <sup>1</sup>		mollic Gleysol	sapric Histosol	
Soil type (German classification KA5)		GMq	KV-KM	
Peat depth [cm] <sup>1</sup>		80	70	1
pH value <sup>2</sup>		4.1	4.2	
Total nitrogen [%] <sup>2</sup>		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 <sup>-3</sup> ]	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. <sup>1</sup> World Reference Base for Soil Resources. <sup>2</sup> Relative to the upper horizon (C<sub>Org</sub>-medium 0–20 cm; C<sub>Org</sub>-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 m<sup>2</sup> 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 N<sub>2</sub>O and CH<sub>4</sub> flux measurements

As a background, we measured fluxes of N<sub>2</sub>O and CH<sub>4</sub> 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 N<sub>2</sub>O (ECD temperature 380 °C) and a flame ionization detector (FID) for CH<sub>4</sub> 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 <sup>3</sup> ha <sup>-1</sup> ]	20	20	25	20	20
Total carbon [kg ha <sup>-1</sup> ]	579	676	798	797	1073
Organic carbon [kg ha <sup>-1</sup> ]	410	573	655	706	960
Total nitrogen [kg ha <sup>-1</sup> ]	47	64	70	85	97
NO <sub>3</sub> <sup>-</sup> [kg N ha <sup>-1</sup> ]	0	0	0	0	0
NH <sub>4</sub> <sup>+</sup> [kg N ha <sup>-1</sup> ]	20	28	23	33	38
NH <sub>4</sub> <sup>+</sup> : N <sub>tot</sub> ratio	0.42	0.44	0.33	0.38	0.39
C : N ratio	12	11	11	9	11
pH (CaCl <sub>2</sub> )	–	–	6.8	7.0	7.0
Dry matter content [%]	5	7	7	9	10
Biogas digestate					
Fertilizer quantity [m <sup>3</sup> ha <sup>-1</sup> ]	20	20	25	20	20
Total carbon [kg ha <sup>-1</sup> ]	384	373	167	184	178
Organic carbon [kg ha <sup>-1</sup> ]	306	337	148	161	178
Total nitrogen [kg ha <sup>-1</sup> ]	49	52	78	35	61
NO <sub>3</sub> <sup>-</sup> [kg N ha <sup>-1</sup> ]	0	0	0	0	0
NH <sub>4</sub> <sup>+</sup> [kg N ha <sup>-1</sup> ]	22	28	51	17	40
NH <sub>4</sub> <sup>+</sup> : N <sub>tot</sub> ratio	0.45	0.53	0.65	0.49	0.66
C : N ratio	8	7	2	5	3
pH (CaCl <sub>2</sub> )	–	–	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 N<sub>2</sub>O or CH<sub>4</sub> fluxes, fluxes were also accepted if the coefficient of determination was  $\geq 0.90$  and the regression slope was between  $-1$  and  $1$  ppb min<sup>-1</sup>. The cumulative annual mean exchange rate was calculated by linear interpolation between the measurement dates.

## 2.4 NH<sub>3</sub> 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 NH<sub>3</sub> 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 cm<sup>2</sup>) 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<sup>-1</sup>) through four connected (via Teflon tubes) conical stainless

steel chambers to an ammonia indicator tube (Drägerwerk AG, Lübeck, Germany). The NH<sub>3</sub> volume concentration was corrected for air temperature and air pressure (Pacholski et al., 2006). To prevent overestimation of NH<sub>3</sub> volatilization through NH<sub>3</sub> enriched ambient air from surrounding area, ammonia concentration from the control treatments was subtracted from the fertilized treatments prior to NH<sub>3</sub> flux calculation. Different studies report a distinct underestimation of up to one order of magnitude of NH<sub>3</sub> 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 NH<sub>3</sub>-N losses determined by the DTM, Pacholski et al. (2006) developed the following calibration formula to correct the NH<sub>3</sub> 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 NH<sub>3</sub> flux<sub>IHF</sub> is NH<sub>3</sub> flux measured by the integrated horizontal flux method (kg N ha<sup>-1</sup> h<sup>-1</sup>); NH<sub>3</sub> flux<sub>DTM</sub> is NH<sub>3</sub> flux measured by the DTM (kg N ha<sup>-1</sup> h<sup>-1</sup>);  $v_{2\text{m}}$  is wind speed at 2 m height (m s<sup>-1</sup>). Quakernack et al. (2011) compared the DTM method with the frequently used micrometeorological method, concluding that the corrected DTM method also allows quantitative NH<sub>3</sub>-loss measurements. The total cumulative NH<sub>3</sub> 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  $\text{NH}_3$  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 m<sup>2</sup>). 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  $\text{N}_2\text{O}$  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 ( $C_{\text{tot}}$ ) and total nitrogen ( $N_{\text{tot}}$ ) 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  $N_{\text{tot}}$  or  $N_{\text{min}}$  use efficiency (NUE,  $\text{NUE}_{\text{min}}$ ) 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  $N_{\text{tot}}$  or  $N_{\text{min}}$  applied, corrected by  $\text{NH}_3$ -N losses. Emission factors for  $\text{NH}_3$  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<sup>-1</sup> related to applied  $\text{NH}_4^+$ -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  $N_{\text{min}}$  contents, a simple N balance was calculated:

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

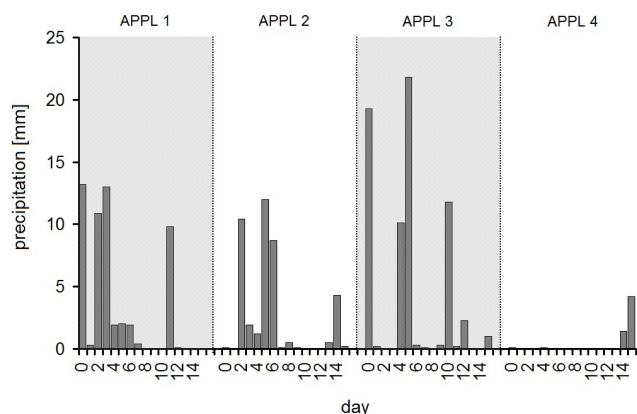
where “N applied” is the amount of  $N_{\text{tot}}$  applied,  $\text{N min}_{t_1}$  and  $\text{N min}_{t_2}$  are the amounts of  $N_{\text{min}}$  at time 1 (6 April 2011; early April represents the beginning of the vegetation period in 2011) and time 2 (18 October 2011; end of October represents the end of the vegetation period in 2011) for the soil depth 0–20 cm,  $N_{\text{dep}}$  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  $\text{N}_2\text{O}$ -N losses, and  $\text{NH}_3_{\text{cum}}$  is the amount of the annual cumulative  $\text{NH}_3$ -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  $\text{CaCl}_2$  (0.0125 M) for 1 hour. The extracts were filtered through a 4–7  $\mu\text{m}$  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  $C_{\text{tot}}$  and organic carbon ( $C_{\text{org}}$ ) 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 cm<sup>3</sup>) 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  $\text{N}_2\text{O}$  emissions and treatment  $\text{NO}_3^-$  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  $\text{NO}_3^-$  comparison in 2010) or the nonparametric Mann–Whitney *U* test (for soil type  $\text{NO}_3^-$  comparison in 2011). For time series data ( $\text{N}_2\text{O}$ ,  $\text{CH}_4$  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  $\text{N}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{NH}_3$  fluxes. We accepted significant differences if  $P \leq 0.05$ . Results in the text are given as means  $\pm 1$  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  $\text{C}_{\text{org}}$ -medium site and was slightly higher with  $10.5$  °C at the  $\text{C}_{\text{org}}$ -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  $\text{C}_{\text{org}}$ -high treatments were significantly higher (all  $P < 0.001$ ) compared to the  $\text{C}_{\text{org}}$ -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  $252$   $\text{kg N ha}^{-1}$  for slurry treatments and  $101$  and  $174$   $\text{kg N ha}^{-1}$  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  $\text{N}_{\text{min}}$  contents of the soils were dominated by  $\text{NO}_3^-$  whereas  $\text{NH}_4^+$  was only of minor importance, especially at the  $\text{C}_{\text{org}}$ -medium treatments (Fig. 2b and c). The  $\text{NO}_3^-$  content was significantly higher ( $P < 0.001$ ) at the  $\text{C}_{\text{org}}$ -high treatments than at the  $\text{C}_{\text{org}}$ -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  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{C}_{\text{org}}$ -medium site; Table 4).

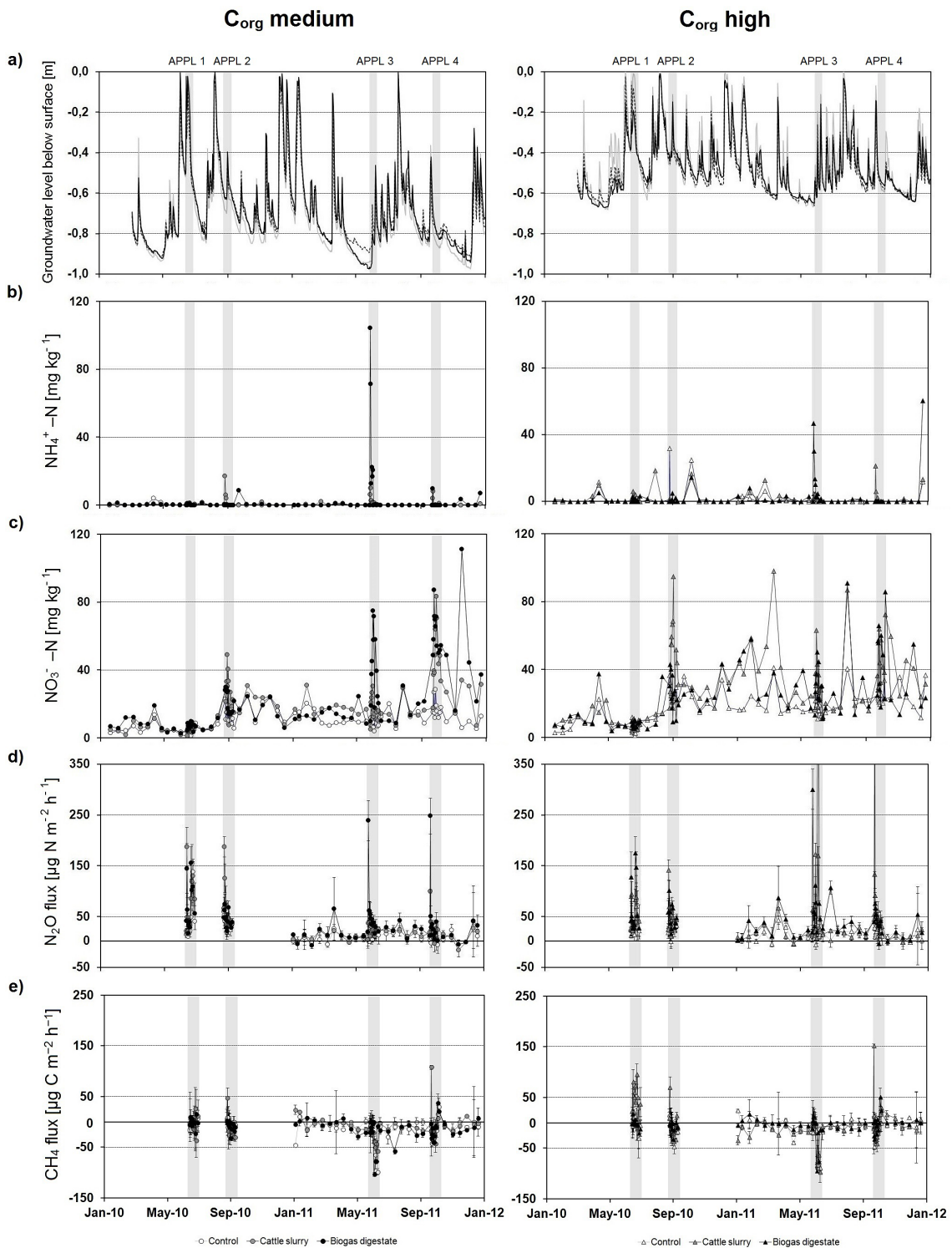
#### 3.3 $\text{N}_2\text{O}$ emissions

$\text{N}_2\text{O}$  fluxes were generally low for all treatments (Fig. 2d). Background emissions rarely exceeded  $50$   $\mu\text{g N m}^{-2} \text{h}^{-1}$ . Highest  $\text{N}_2\text{O}$  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  $\text{C}_{\text{org}}$ -medium treatments  $\text{N}_2\text{O}$  fluxes returned to background emission level within 3 to 7 days, whereas the  $\text{C}_{\text{org}}$ -high treatments had longer lasting increased  $\text{N}_2\text{O}$  emissions, particularly for the digestate treatment.

Short-term (16 days)  $\text{N}_2\text{O}$  fluxes of fertilized treatments significantly ( $P < 0.01$ ) exceeded  $\text{N}_2\text{O}$  fluxes of control treatments at all fertilization events. However, only in one out of four fertilization events were short-term  $\text{N}_2\text{O}$  fluxes significantly ( $P < 0.001$ ) higher for the digestate treatments compared to the slurry treatments. Additionally, significantly ( $P < 0.001$ ) higher short-term  $\text{N}_2\text{O}$  fluxes were observed at the  $\text{C}_{\text{org}}$ -high treatments compared to the  $\text{C}_{\text{org}}$ -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  $\text{NH}_4^+$  (b) and  $\text{NO}_3^-$  (c) contents for the soil depth 0–10 cm,  $\text{N}_2\text{O}$  (d) and  $\text{CH}_4$  fluxes (e) (mean  $\pm$  SD,  $n = 3$ ) of the  $\text{C}_{\text{org}}$ -medium and  $\text{C}_{\text{org}}$ -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), NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> content in the soil following organic fertilizer application and for the investigated years 2010 and 2011.

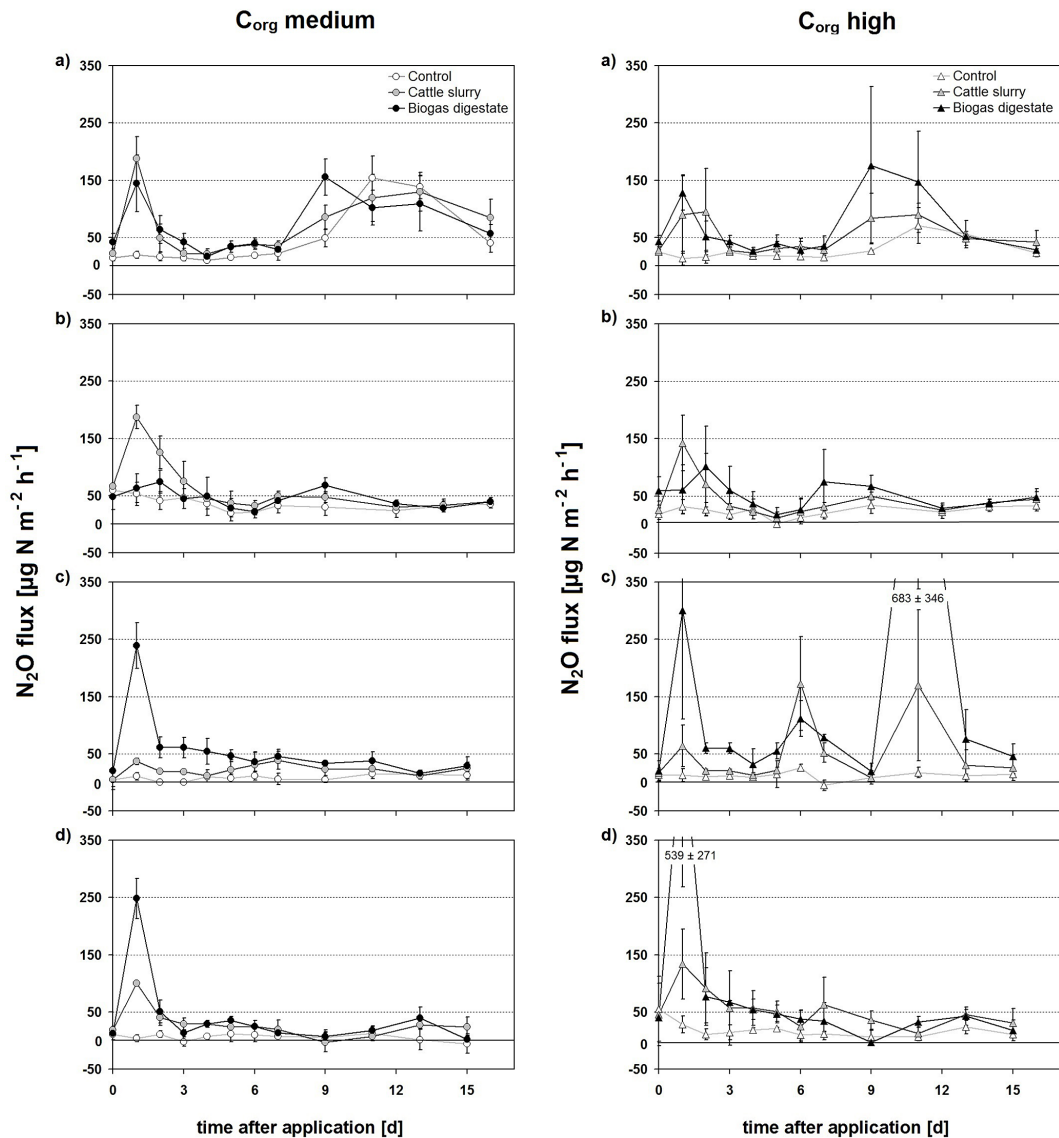
Sampling depth [cm]	C <sub>org</sub> -medium			C <sub>org</sub> -high			n
	Control	Cattle slurry	Biogas digestate	Control	Cattle slurry	Biogas digestate	
1 Application (14 Jun–30 Jun 2010)							
GW level [cm]	-32 (-62/-2)	-39 (-60/-5)	-31 (-58/-2)	-21 (-46/-1)	-26 (-45/-7)	-33 (-45/-19)	
NO <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	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 <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	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 <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	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 <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	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 <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	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 <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	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 <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	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 <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	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 <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	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 <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	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 <sub>3</sub> <sup>-</sup> [mg N kg <sup>-1</sup> ]	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 <sub>4</sub> <sup>+</sup> [mg N kg <sup>-1</sup> ]	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 N<sub>2</sub>O emissions were not significantly different from the control treatments in 2010 (Fig. 4), but for 2011 short-term cumulative N<sub>2</sub>O 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 N<sub>2</sub>O fluxes compared to unfertilized treatments. Additionally, the application of biogas digestate significantly ( $P < 0.01$ ) enhanced the N<sub>2</sub>O fluxes compared to the application of cattle slurry. Furthermore, N<sub>2</sub>O fluxes from the C<sub>org</sub>-high treatments significantly ( $P < 0.001$ ) exceeded N<sub>2</sub>O fluxes from the C<sub>org</sub>-medium treat-

ments. Annual cumulative emissions ranged from  $0.91 \pm 0.49 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (control treatment, C<sub>org</sub>-medium site) to  $3.14 \pm 0.91 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  (digestate treatment, C<sub>org</sub>-high site; Table 5). Calculated EFs based on the amount of N<sub>tot</sub> 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 N<sub>2</sub>O 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 N<sub>2</sub>O–N exchange rates, 53 % was explained by the amounts of applied NH<sub>4</sub><sup>+</sup>-N and the mean groundwater levels below surface during the same time



**Figure 3.** Mean ( $\pm$  SD,  $n = 3$ )  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  emissions, but regression analysis was not possible due to the small sample size ( $n = 6$ ).

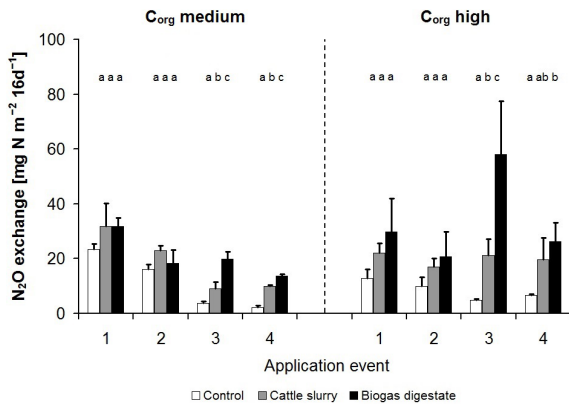
### 3.4 $\text{CH}_4$ emissions

Most of the time,  $\text{CH}_4$  emissions could not be detected (Fig. 2e). Occasionally  $\text{CH}_4$  peaks were only found immediately after cattle slurry application. However, with the exception of the slurry treatment of the  $\text{C}_{\text{org}}$ -high site at the first application event, the organic fertilization did not result in significantly different short-term (15 or 16 days)  $\text{CH}_4$  fluxes between the treatments or the investigated soil types. The observed weak  $\text{CH}_4$  emissions or uptakes amounted to cumulative annual  $\text{CH}_4$  exchange rates of  $-0.21 \pm 0.19$

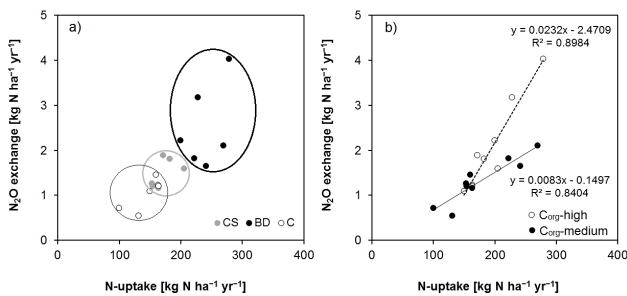
to  $-1.06 \pm 0.46 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ . Significantly different  $\text{CH}_4$  fluxes between the investigated treatments or the different soil types could not be observed regarding the annual fluxes in 2011.

### 3.5 $\text{NH}_3$ volatilization

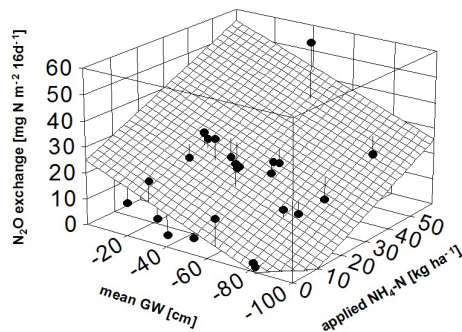
Highest  $\text{NH}_3$  losses were observed immediately after fertilization (Fig. 7). During the first 24 h, 64 and 100 % of total  $\text{NH}_3$  losses occurred at the digestate and slurry treatments, respectively. Since differences in the response of  $\text{NH}_3$  volatilization were not significant, treatment data were pooled by soil type prior to regression analysis. The total  $\text{NH}_3$  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 N<sub>2</sub>O 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<sub>Org</sub>-medium and C<sub>Org</sub>-high respectively (ANOVA, Tukey HSD test at *P* < 0.05).



**Figure 5.** Relationship between cumulative annual N<sub>2</sub>O 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 N<sub>2</sub>O-N emissions of the four application events (*y*) to mean groundwater level (*x*<sub>1</sub>) and the amount of applied NH<sub>4</sub>-N (*x*<sub>2</sub>). 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<sub>tot</sub>) without consideration of NH<sub>3</sub>-N losses.

	Control	Cattle slurry	Biogas digestate
<b>C<sub>Org</sub>-medium</b>			
N <sub>2</sub> O exchange [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	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
<b>C<sub>Org</sub>-high</b>			
N <sub>2</sub> O exchange [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	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

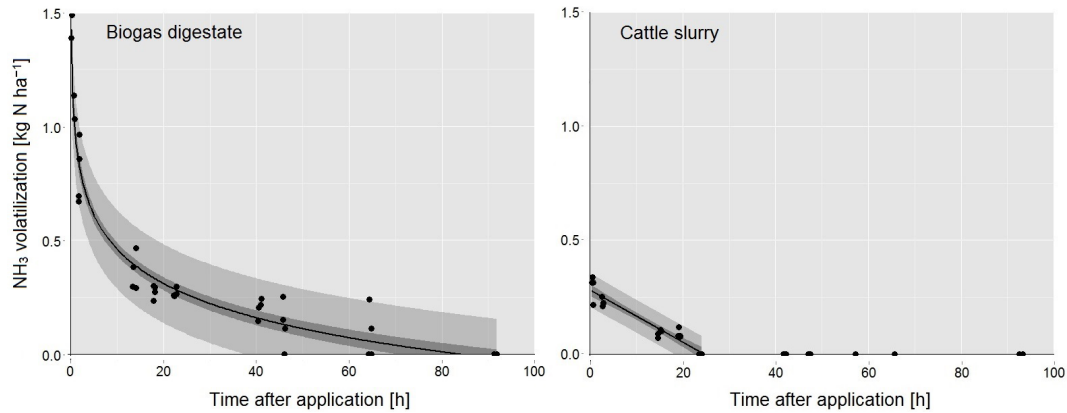
treatments. The relative N loss was 36 and 15 % of applied NH<sub>4</sub><sup>+</sup>-N, or 23 and 5 % of total applied N for the digestate and slurry treatments, respectively.

**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<sub>Org</sub>-medium) to 13.1 t DM ha<sup>-1</sup> yr<sup>-1</sup> (digestate C<sub>Org</sub>-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<sub>Org</sub>-high treatments exceeded yields from the C<sub>Org</sub>-medium treatments of both years, but differences were not significant.

The application of biogas digestate markedly increased apparent NUE and NUE<sub>min</sub> 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<sub>min</sub> values were always > 100 % for biogas digestate treatments, whereas for cattle slurry NUE<sub>min</sub> values averaged 74 ± 68 % in 2011 but were > 100 % in 2010. Besides fertilizer type effects, higher NUE and NUE<sub>min</sub> were observed at the C<sub>Org</sub>-medium treatments compared to the C<sub>Org</sub>-high treatments.

The estimated N balances revealed N surpluses of up to 70 kg N ha<sup>-1</sup> yr<sup>-1</sup> for cattle slurry treatments but deficits of



**Figure 7.** Ammonia ( $\text{NH}_3$ ) volatilization following organic fertilizer application at event 3 (27 May 2011). Dots present single  $\text{NH}_3$  measurements for a time period of 94 h. Black lines show the estimated  $\text{NH}_3$  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 [ $\text{kg N ha}^{-1}$ ]	N applied [ $\text{kg N ha}^{-1}$ ] <sup>b</sup>	$N_{\text{min}}$ applied [ $\text{kg N ha}^{-1}$ ] <sup>b</sup>	N use efficiency [%]	$N_{\text{min}}$ use efficiency [%]
Control $C_{\text{org}}$ -medium	24 May 2010	–	2.04 <sup>a</sup>	2.52	51	–	–	–	–
Control $C_{\text{org}}$ -high	24 May 2010	–	2.14	2.93	63	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	24 May 2010	N.A.	2.37	3.19	76	–	–	–	–
Cattle slurry $C_{\text{org}}$ -high	24 May 2010	N.A.	2.14	3.58	77	–	–	–	–
Biogas digestate $C_{\text{org}}$ -medium	24 May 2010	N.A.	2.04	4.17	85	–	–	–	–
Biogas digestate $C_{\text{org}}$ -high	24 May 2010	N.A.	2.27	4.39	100	–	–	–	–
Control $C_{\text{org}}$ -medium	20 Aug 2010	–	2.03	2.02	41	–	–	–	–
Control $C_{\text{org}}$ -high	20 Aug 2010	–	2.00	2.63	53	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	20 Aug 2010	14 Jun 2010	2.19	3.06	67	45	17	58	153
Cattle slurry $C_{\text{org}}$ -high	20 Aug 2010	14 Jun 2010	1.93	3.23	62	45	17	22	57
Biogas digestate $C_{\text{org}}$ -medium	20 Aug 2010	14 Jun 2010	2.03	2.99	61	38	14	52	140
Biogas digestate $C_{\text{org}}$ -high	20 Aug 2010	14 Jun 2010	2.00	3.51	70	38	14	47	125
Control $C_{\text{org}}$ -medium	23 May 2011	–	1.96	2.66	52	–	–	–	–
Control $C_{\text{org}}$ -high	23 May 2011	–	1.70	3.82	65	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	23 May 2011	25 Aug 2010	2.01	2.58	52	61	24	0	0
Cattle slurry $C_{\text{org}}$ -high	23 May 2011	25 Aug 2010	1.70	4.20	71	61	24	11	27
Biogas digestate $C_{\text{org}}$ -medium	23 May 2011	25 Aug 2010	1.96	3.97	78	40	18	64	144
Biogas digestate $C_{\text{org}}$ -high	23 May 2011	25 Aug 2010	1.83	4.54	83	40	18	45	101
Control $C_{\text{org}}$ -medium	1 Aug 2011	–	1.71	2.06	35	–	–	–	–
Control $C_{\text{org}}$ -high	1 Aug 2011	–	1.48	2.88	43	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	1 Aug 2011	27 May 2011	1.71	2.73	47	67	20	17	58
Cattle slurry $C_{\text{org}}$ -high	1 Aug 2011	27 May 2011	1.51	3.19	48	67	20	8	28
Biogas digestate $C_{\text{org}}$ -medium	1 Aug 2011	27 May 2011	1.78	4.88	87	60	33	86	158
Biogas digestate $C_{\text{org}}$ -high	1 Aug 2011	27 May 2011	1.48	5.34	79	60	33	61	112
Control $C_{\text{org}}$ -medium	13 Sep 2011	–	2.53	1.71	43	–	–	–	–
Control $C_{\text{org}}$ -high	13 Sep 2011	–	2.26	2.27	51	–	–	–	–
Cattle slurry $C_{\text{org}}$ -medium	13 Sep 2011	27 May 2011	2.57	2.28	59	(55) <sup>c</sup>	(8) <sup>c</sup>	28	189
Cattle slurry $C_{\text{org}}$ -high	13 Sep 2011	27 May 2011	2.53	2.64	67	(61) <sup>c</sup>	(14) <sup>c</sup>	25	110
Biogas digestate $C_{\text{org}}$ -medium	13 Sep 2011	27 May 2011	2.53	3.15	80	(8) <sup>c</sup>	(0) <sup>c</sup>	436	–
Biogas digestate $C_{\text{org}}$ -high	13 Sep 2011	27 May 2011	2.26	3.25	74	(24) <sup>c</sup>	(0) <sup>c</sup>	94	–

<sup>a</sup> N contents from control treatments were estimated from fertilized treatments. <sup>b</sup> Applied  $N_{\text{tot}}$  and  $N_{\text{min}}$  were corrected by  $\text{NH}_3$ -N losses (23 and 5 % from  $N_{\text{tot}}$ , or 36 and 15 % from  $N_{\text{min}}$  for biogas digestate and cattle slurry, respectively). <sup>c</sup> Hypothetically remaining  $N_{\text{tot}}$  and  $N_{\text{min}}$  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 <sup>-1</sup> yr <sup>-1</sup> ]	N <sub>min</sub> t <sub>1</sub> <sup>a</sup> [kg N ha <sup>-1</sup> ]	N <sub>min</sub> t <sub>2</sub> <sup>a</sup> [kg N ha <sup>-1</sup> ]	N deposition [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	N uptake [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	N <sub>2</sub> O [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	NH <sub>3</sub> <sup>b</sup> [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]	N balance [kg N ha <sup>-1</sup> yr <sup>-1</sup> ]
Control C <sub>org</sub> -medium	0	27.5	29.4	7.2	130	0.9	0.0	-122.4
Control C <sub>org</sub> -high	0	22.8	27.7	7.2	159	1.2	0.0	-148.0
Cattle slurry C <sub>org</sub> -medium	252	35.7	51.2	7.2	157	1.2	46.1	70.4
Cattle slurry C <sub>org</sub> -high	252	27.3	68.1	7.2	186	1.8	46.1	66.1
Biogas digestate C <sub>org</sub> -medium	174	29.8	83.3	7.2	244	1.9	52.4	-64.1
Biogas digestate C <sub>org</sub> -high	174	26.2	28.4	7.2	236	3.1	52.4	-108.1

<sup>a</sup> Reference date for t<sub>1</sub> is 6 April 2011 and for t<sub>2</sub> 18 October 2011. <sup>b</sup> NH<sub>3</sub>-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 NH<sub>4</sub><sup>+</sup>; Haenel et al., 2014).

up to 108 kg N ha<sup>-1</sup> yr<sup>-1</sup> 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<sub>org</sub>-high treatments than at the C<sub>org</sub>-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<sup>-1</sup> yr<sup>-1</sup> (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 NH<sub>4</sub><sup>+</sup> : N<sub>tot</sub> ratios and thus relatively higher NH<sub>4</sub><sup>+</sup> contents than the cattle slurries (see also Möller and Stinner 2009). The amounts of NH<sub>4</sub><sup>+</sup>-N were not distinctly different between the applied organic fertilizers but in 2011 biogas treatments received 15 % more NH<sub>4</sub><sup>+</sup>-N compared to cattle slurry treatments.

We observed an unexpected small change in the NH<sub>4</sub><sup>+</sup> 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 NH<sub>4</sub><sup>+</sup> from the organic fertilizer was lost in a few hours after splash plate application via NH<sub>3</sub> volatilization. Thirdly,

and probably most importantly, in well aerated soils applied NH<sub>4</sub><sup>+</sup> underwent rapid nitrification, as was indicated by the increasing soil NO<sub>3</sub><sup>-</sup> contents in the upper soil layer after fertilizer application. In general, the continuously observed absent or low NH<sub>4</sub><sup>+</sup> contents with simultaneously high extractable NO<sub>3</sub><sup>-</sup> in the soil indicate that net nitrification entirely controlled net nitrogen mineralization at all treatments of the investigated study sites. Nitrification requires sufficient oxygen (O<sub>2</sub>) 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<sub>min</sub>. This becomes evident in the observed significantly higher NO<sub>3</sub><sup>-</sup> 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<sub>min</sub> 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<sub>tot</sub> and NH<sub>4</sub><sup>+</sup> 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., N<sub>2</sub>O losses, NO<sub>3</sub><sup>-</sup> 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<sup>-1</sup> yr<sup>-1</sup>. However, the strong negative N balances of the control treatments reveal that large amounts of up to 148 kg N ha<sup>-1</sup> yr<sup>-1</sup> 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 NO<sub>3</sub><sup>-</sup> in the soil, as observed especially at the fertilized treatments of the C<sub>org</sub>-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  $NH_4^+/N_{\text{tot}}$  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  $C_{\text{org}}$ -high treatments compared to  $C_{\text{org}}$ -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  $C_{\text{org}}$ -high site significantly exceeded those from the  $C_{\text{org}}$ -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  $C_{\text{org}}$ -high treatments compared to the  $C_{\text{org}}$ -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  $C_{\text{org}}$  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  $\text{NH}_3$  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,  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  produced from applied N compared to cattle slurry, yet at a low level.

One reason of generally low  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  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  $\text{NO}_3^-$  content close to the groundwater level (van Beek et al., 2004). Given the high  $\text{NO}_3^-$  contents, in particular in the  $C_{\text{org}}$ -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  $\text{N}_2\text{O}$  emissions. Moreover, through the splash plate application technique high amounts of  $\text{NH}_4^+$  were rapidly lost as  $\text{NH}_3$ , and therefore reduced the proportion of immediately available N for nitrification and denitrification.

As expected from the literature, highest  $\text{N}_2\text{O}$  fluxes were found immediately after fertilizer application. The initial  $\text{N}_2\text{O}$  peak could mainly be attributed to the denitrification of available soil  $\text{NO}_3^-$ , 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  $\text{N}_2\text{O}$  could be ascribed to the rapid nitrification (Chadwick et al., 2000) or to nitrifier denitrification of slurry  $\text{NH}_4^+$ . In contrast, the partially observed second  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  emissions from the digestate treatments compared to the slurry treatments. Higher  $\text{N}_2\text{O}$  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  $C_{\text{org}}$  content compared to  $C_{\text{org}}$  rich soils. However, contrary to our hypothesis, the significantly higher  $\text{N}_2\text{O}$  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  $\text{NH}_4^+$ -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  $\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  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  $\text{O}_2$  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  $\text{N}_2\text{O}$  emissions and which N pathways and processes are involved.

The observed linear increase in the cumulative  $\text{N}_2\text{O}$ -N emissions during the first 16 days or annual  $\text{N}_2\text{O}$  emissions,



due to a higher mean groundwater level and a higher application rate of  $\text{NH}_4^+-\text{N}$ , reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of  $\text{C}_{\text{org}}$ -rich grasslands. The same was postulated for mineral soils by Ruser (2010).

#### 4.4 Fertilizer- and site-induced $\text{CH}_4$ emissions

The observed consumption rates of  $\text{CH}_4$  were in the range of  $\text{CH}_4$  uptakes reported by Flessa et al. (1998) for two different meadows in a southern German fen peatland. Slightly higher  $\text{CH}_4$  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  $\text{CH}_4$  (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  $\text{CH}_4$  increased with lowering of the groundwater level. Nevertheless, significant differences in the amount of the annual  $\text{CH}_4$  uptake capacity between the two study sites  $\text{C}_{\text{org}}$ -medium and  $\text{C}_{\text{org}}$ -high could not be seen, although distinct differences in the groundwater table were observed.

The occasionally observed  $\text{CH}_4$  peak emissions were only found immediately after cattle slurry application. This was in line with several other studies that reported short-term  $\text{CH}_4$  emissions immediately after organic fertilizer application, due probably to volatilization of dissolved  $\text{CH}_4$  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  $\text{CH}_4$  emissions observed after the first application event at the slurry treatment of the  $\text{C}_{\text{org}}$ -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  $\text{CH}_4$  during this time period. However, we could not find any significant differences in the short term or annual  $\text{CH}_4$  emissions between the two investigated fertilizers. According to Chadwick et al. (2000) more than 90 % of total  $\text{CH}_4$  emissions occur during the first 24 h following fertilizer application. Therefore, we must assume that we have missed most of the fertilizer-induced  $\text{CH}_4$  emissions. However, all studies from literature confirm the minor importance of  $\text{CH}_4$  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 $\text{NH}_3$ volatilization

The  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_4^+-\text{N}$  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  $\text{NH}_3$  loss rates were rather low (Haenel et al., 2014). It can be assumed that the higher concentration of  $\text{NH}_4^+$  ( $\text{NH}_4^+/\text{N}_{\text{tot}}$  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  $\text{NH}_3$  losses (Sommer et al., 1996; Ni et al., 2011). There over a limited range (slurry DM of 2–5 %),  $\text{NH}_3$  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  $\text{NH}_3$ -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  $\text{NH}_3$  exchange with the atmosphere and has been proposed as an  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_4^+$ -N demonstrates that  $\text{NH}_3$  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  $\text{NH}_3$  volatilization decreases N fertilizer use efficiency. One of the most effective measures to reduce  $\text{NH}_3$  emissions from grassland is the incorporation of slurry (Rodhe et al., 2006). However, several studies reported a considerable increase of GHGs, mainly  $\text{N}_2\text{O}$ , 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  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{NH}_3$  fluxes after splash plate application of biogas digestate and cattle slurry in a region known for its risk of high  $\text{N}_2\text{O}$  and  $\text{NH}_3$  emissions and we were the first to study digestate application on high organic carbon soils with 10 to 17%  $\text{C}_{\text{org}}$  content in the topsoil. To our surprise,  $\text{N}_2\text{O}$  emissions and EFs were lower than generally observed on mineral soils in the vicinity of the sites. We attributed the low  $\text{N}_2\text{O}$  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  $\text{NUE}_{\text{min}}$ .  $\text{N}_2\text{O}$  emissions increased with  $\text{C}_{\text{org}}$  content and fertilization. As hypothesized,  $\text{N}_2\text{O}$  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,  $\text{CH}_4$  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  $\text{N}_2\text{O}$

emissions with increasing  $\text{NH}_4^+$  fertilization and increasing groundwater table reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of  $\text{C}_{\text{org}}$ -rich grasslands.

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