Short-term effects of biogas digestate and cattle slurry application on greenhouse gas emissions and N availability from high organic carbon grasslands

T. Eickenscheidt[1], A. Freibauer[2], J. Heinichen[1], J. Augustin[3] and M. Drösler[1]

[1] {University of Applied Sciences Weihenstephan-Triesdorf, Chair of Vegetation Ecology, Weihenstephaner Berg 4, 85354 Freising, Germany}

[2] {Thünen Institute of Climate-Smart Agriculture, Bundesallee 50, 38116 Braunschweig, Germany}

[3] {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**)

Keywords: Nitrous oxide, methane, ammonia volatilization, fen peatland, mineral nitrogen, emission factor, fertilization, N-use efficiency, N-balance.

Abstract

The change in the German energy policy resulted in a strong increase in the number of biogas plants in Germany. As a consequence, huge amounts of nutrient rich residues remain from the fermentative process, which 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_2O) emissions and organic fertilization is additionally known to increase N_2O emissions from managed grasslands. Our study addressed the questions a) to what extent biogas digestate and cattle slurry application increase N_2O, methane (CH_4) and ammonia (NH_3) fluxes as well as the mineral nitrogen use efficiency (NUE_{min}) and grass yield, and b) how different soil organic matter contents (SOM) promote the production of N_2O. The study was conducted at two areas within a grassland parcel, which differed in their soil organic carbon (SOC) contents. At each area (named C_{org}-medium and C_{org}-high) three sites were established, one was fertilized five times with biogas digestate, one with cattle slurry and the third served as control site. For each

site, fluxes of N_2O and CH_4 were measured over two years using the closed chamber method. For NH_3 measurements we used the calibrated dynamic chamber method. On an annual basis, the application of biogas digestate significantly enhanced the N_2O fluxes compared to the application of cattle slurry and additionally increased the NUE_{min}. Furthermore, N_2O fluxes from the C_{org}-high site significantly exceeded N_2O fluxes from the C_{org}-medium sites. Annual cumulative emissions ranged from 0.91 ± 0.49 kg N ha^{-1} yr^{-1} to 3.14 ± 0.91 kg N ha^{-1} yr^{-1}. Significantly different CH_4 fluxes between the investigated treatments or the different soil types were not observed. Cumulative annual CH_4 exchange rates varied between −0.21 ± 0.19 kg C ha^{-1} yr^{-1} and −1.06 ± 0.46 kg C ha^{-1} yr^{-1}. Significantly higher NH_3 losses, NUE_{min} and grass yields from treatments fertilized with biogas digestate compared to those fertilized with cattle slurry were observed. The total NH_3 losses following 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 NH_4^+-N). The observed linear increase of 16 days cumulative N_2O-N exchange or rather annual N_2O emissions, due to a higher mean groundwater level and a higher application rate of NH_4^+-N, reveal 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 the change in the German energy policy and the enactment of the German Renewable Energy Act (Weiland, 2010). At the end of 2012, more than 7,500 agricultural biogas plants operated in Germany (Fachverband Biogas, 2014). Heat and power from biogas substitute fossil fuels and therefore reduce greenhouse gas (GHG) emissions (Weiland, 2010; Don et al., 2011). The strong increase in the number of biogas plants caused a land-use change towards agro-biomass production and additionally raised the land-use intensity to satisfy the huge demand for fermentative substrates (Don et al., 2011). In 2011, the proportion of grass silage accounted for 9% of the total renewable resources for biogas production (DBFZ, 2012) and thus, grass silage represented the second most important fermentation substrate after maize silage.

During the fermentative process high amounts of nutrient rich residues are left over. 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_2O) emissions due to the application of nitrogen fertilizers (e.g. Bouwman, 1996; Chadwick et al., 2000; Rodhe et al., 2006; Ruser, 2010). Additionally liquid organic fertilizers such as animal slurry add easily degradable organic carbon (Christensen 1983) and moisture, both favoring N_2O losses through denitrification (Clayton et al., 1997). Enhanced N_2O emissions are of great interest due to the fact that N_2O acts as a radiative forcing greenhouse gas (IPCC, 2007) and contributes to the chemical destruction of stratospheric ozone (Crutzen, 1979). In Germany, about 67.4% of N_2O emissions originate from the agricultural sector (Möller and Stinner, 2009). Particularly organic soils (e.g. drained peat soils and soils developed in wet conditions) are considered as hotspots of GHG emissions including N_2O, which is due to the very high mineralization rates of degrading peat (Kasimir-Klemedtsson et al., 1997; Freibauer et al., 2004; Klemedtsson et al., 2005; Goldberg et al., 2010) and to soil moisture conditions which favor anaerobic micro-sites. According to Maljanen et al. (2010), N_2O emissions from drained organic soils under agricultural use were on average four times higher than those from mineral soils. The few field studies of organic fertilization effects on annual N_2O emissions from drained organic grassland soils revealed very high N_2O emissions of up to 41.0 kg N ha^{-1} yr^{-1} (Velthof et al., 1996).

In Germany, 40% of the drained peatlands are used as grasslands (Drösler et al., 2008), particularly in the smallholder structure of south Germany. Grassland soils in Europe and Germany produce more N_2O per unit of fertilizer-N than croplands and emission factors further increase with soil organic carbon and nitrogen content (Freibauer and Kaltschmitt 2003; Dechow and Freibauer 2011). Moreover agricultural soils in the southern part of Germany emit, about three times more of the applied N as N_2O than 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 wide-spread high-risk situation for high N_2O emissions after cattle slurry or biogas digestate application, which has to our knowledge not yet 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). In return, the pH value and the ammonium (NH_4^+) content as well the NH_4^+/N_{org} ratio are higher than in fresh slurry (Wulf et al., 2002; Möller and Stinner, 2009). Since digested products are more recalcitrant than fresh slurry it could be

assumed that microbial degradation is slow, resulting in less anoxic microsites and reduced N_2O emissions than after 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_2O emissions (e.g. Clemens and Huschka, 2001; Wulf et al., 2002; Clemens et al., 2006; Senbayram et al.,2009; Sänger et al., 2010), and very few studies exist for grasslands.

Slurry application also releases short-term methane (CH_4) and ammonia (NH_3) emissions. Methane acts as strong greenhouse gas, whereas NH_3 is considered as indirect greenhouse gas through ammonia deposition which could promote the formation of N_2O (Moiser, 2001). Moreover, NH_3 deposition causes soil acidification and eutrophication of ecosystems (Dragosits et al., 2002; Sanderson et al., 2006; Ni et al., 2011). In Germany, agriculture is responsible for 95.3% of the anthropogenic NH_3 emissions (Haenel et al., 2010). Particularly high NH_4^+ contents and high pH values, which are typically for the biogas digestate, promote accelerated NH_3 volatilisation (Quakernack et al., 2011). High NH_3 emissions particularly occur after splash plate application on grassland (Rubæk et al., 1996; Quakernack et al., 2011), which is still common practice in the smallholder farms of South Germany.

The anaerobic fermentation leads to distinct differences in the composition of the remaining residues compared to untreated slurries, as mentioned before. The different properties of these fertilizers (e.g. higher NH_4^+ concentrations, narrower C/N ratio, higher pH values) directly effect N transformation processes, plant N availability and thus crop yield. 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 an Müller, 2012) whereas others found no effects (e.g. Möller et al., 2008). However, 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). In general the application technique seems to have the greatest influence as this directly affects ammonia losses and thus immediately available N for plant growth (Möller and Müller, 2012).

The objective of this study was to quantify short-term N_2O, CH_4 and NH_3 emissions after application of biogas digestate and cattle slurry on grassland on two types of

high organic carbon soils in South Germany. Additionally it should be tested to what extent biogas digestate and cattle slurry application affect N availability and grass yield. We hypothesize: a) More N_2O is emitted after biogas digestate than after slurry application because of higher NH_4^+-N concentrations in the substrate. The more recalcitrant nature of the carbon in the biogas digestate does not matter for GHG formation in high organic carbon soils. b) N_2O emissions increase with increasing soil C_{org} 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 area

The study was conducted on a permanent grassland at a drained fen peatland 30 km north-east 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 practise in this region. The grass was used as silage or hay for cattle or as substrate for biogas plants. According to the climate station in Weihenstephan, located 10 km northeast of the site, the 30-years 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 a NH_4^+-N:NO_3^--N ratio of 46:54 and 49:51 in 2010 and 2011. Data of N deposition was collected by the Bavarian State Institute of Forestry at a German Level II monitoring area (Forest Intensive Monitoring Programme of the UNECE), located in 7 km distance to the investigated grassland. In October 2009, we selected two areas within the grassland parcel, which differed in their soil organic carbon (SOC) contents in the top soil (Table 1). According to the WRB (2006) soil types were classified as mollic Gleysol (named C_{org}-medium) and as sapric Histosol (named C_{org}-high) (Roßkopf personal communication).

2.2. Experimental design

At each area of the grassland parcel, three adjacent sites (site dimension 12 x 12 m) were selected. At one site biogas digestate and at another site cattle slurry was applied, whereas the third site served as control (whitout fertilization). Centrally at

each site, three PVC-collars for GHG measurements (inside dimension 75 x 75 cm) 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 area a climate station was set up in March 2010 for the continous recording (every 0.5 hour; CR200X Datalogger, Campbell Scientific) of air temperature and humidity at 20 cm above soil surface (CS215-L, Campbell Scientific), soil temperatures at the depth of −2, −5 and –10 cm (109-L, Campbell Scientific) and soil moisture content at −5 cm depth (SM200, Delta-T Devices). For NH_3 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 seconds (GP1, Delta-T Devices). For measuring the ground water table, plastic perforated tubes (JK-casings DN 50, 60 mm diameter, 1 m length) were inserted close to each collar for plot-specific measurements of groundwater tables during gas flux measurements. In April 2010, we equipped one tube per site with a water level logger (Type MiniDiver, Schlumberger water services), which logged the water tables every 15 minutes. Additionally to the recorded data, site-specific soil temperatures in 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 (swivelling slurry spreader for biogas digestate; gooseneck scatterer for cattle slurry) on 14th June 2010, 25th August 2010, 27th Mai 2011, 22th September 2011 and 04th November 2011 by the landowners. The surface application technique via splash plate is the most common application technique in the smallholder structure of the region. The organic fertiliser was applied on the basis of equal volumetric rates per application event (between 20–25 m^3 ha^{-1}). This method is typical for farming practices, but produces diverging N application rates per event between slurry and digestate based on NH_4^+ or N_{tot} applications. It is known that the splash plate application technique can result in very uneven spreading regarding the application rate and/or the evenness. Both chosen spreading devices are known for the higher accuracy in their application evenness compared to conventional splash plates (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 sites, 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 can not give any estimation about the actually achieved accuracy of the application evenness.

The physical and chemical composition of the slurries and digestates varied between the four different application events (Table 2). Composition of organic fertilizers was analysed from 1 L samples which were taken from the slurry tank in the field. Slurries were immediately frozen at −20 °C until analysis which 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 plots and on a 120 m^2 adjacent area. To ensure an equal volumetric amount of organic fertilizer a 1x1 m grid, built by cords, was previously installed. The same method was used at the fourth application event for the digestate.

2.3. N_2O and CH_4 flux measurements

As a background, we measured fluxes of N_2O and CH_4 every second week from January 2010 to January 2012 using the static manual chamber method (volume 309 L) (Livingston & 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 fertilisation events on 14th June 2010, 25th August 2010, 27th Mai 2011, and 22th September 2011. Immediately after fertilization flux measurements were carried out daily for a week and on every second day for another eight to nine days. To minimize diurnal variation in the flux pattern, sampling was always carried out between 9.00 a.m. and 11.30 a.m. A detailed description of chamber dimensions and configuration is given in Drösler (2005). Four gas samples were taken at four 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 seconds 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 & 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_2O (ECD temperature 380°C) and a flame ionization detector

(FID) for CH_4 analyses (FID temperature 310℃). Gas samples from the first fertilization event (14th June to 30th June of 2010) were immediately analysed at the Max Planck Institute for Biogeochemistry in Jena, whereas samples from the second fertilization event (25th August to 10th September of 2010) were analysed at the Thünen Institute in Braunschweig with a Varian CP-3800 GC-FID/-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_2O or CH_4 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. NH_3 flux measurements

Ammonia volatilization was measured at the third organic fertilizer application event on 27th of May 2011. Measurements were performed immediately after fertilizer application and thereafter in irregular time intervals of few hours (in total 96 measurements). For NH_3 measurements we used the calibrated dynamic chamber method (‘Dräger-Tube Method’; DTM) which was described in detail bei Pacholski et al. (2006). One day before application, eight stainless steel rings (104 cm^2) were inserted into the upper soil (3 cm) at each treatment, from which four were grouped close together. Ambient air was sucked with a defined flow rate (1 L min^{-1}) through four (via teflon tubes) connected conical stainless steel chambers to an ammonia indicator tube (Drägerwerk AG, Lübeck, Germany). The NH_3 volume concentration was corrected for air temperature and air pressure (Pacholski et al., 2006). To prevent overestimation of NH_3 volatilization through NH_3 enriched ambient air from surrounding area, ammonia concentration from the control treatments were subtracted from the fertilized treatments prior to NH_3 flux calculation. Different studies report a distinct underestimation of up to one order of magnitude of NH_3 fluxes determined by the DTM, mainly due to the low air exchange rate in the chambers (Roelcke, 2002; Pacholski et al., 2006). To avoid underestimation of cumulative NH_3-N losses determined by the DTM, Pacholski et al. (2006) developed the following calibration formula to correct the NH_3 fluxes:

$$\ln(NH_3\,flux_{IHF}) = 0.444 * \ln(NH_3\,flux_{DTM}) + 0.590 * \ln(v_{2m}) \quad (1)$$

where NH_3flux_{IHF} is NH_3 flux measured by the integrated horizontal flux method (kg N ha^{-1} h^{-1}); NH_3flux_{DTM} is NH_3 flux measured by the DTM (kg N ha^{-1} h^{-1}); v_{2m} 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 NH_3-loss measurements. The total cumulative NH_3 volatilization was estimated by curve fitting and integration of the area obtained by the fitted 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 scissor at each mowing event (same cutting height as the farmer, at about 5 cm). Mowing events took place on 24th Mai 2010, 20th August 2010, 23th Mai 2011, 01st August 2011 and 13th September 2011. To determine the dry mass (DM), grass samples were oven dried at 60℃ for 48 hours. To de termine the total carbon (C_{tot}) and total nitrogen (N_{tot}) concentrations of plant biomass, dried grass samples were milled (0.5 mm) and mixed sub samples were analysed according to DIN ISO 10694 and DIN ISO 13878 by the AGROLAB Labor GmbH (Bruckberg, Germany). The apparent N_{tot} or rather N_{min} use efficiency (NUE, NUE_{min}) was calculated as:

$$NUE\ or\ NUE_{\min} = \left(\frac{N\,uptake_{treatment} - N\,uptake_{control}}{total\ N\ applied} \right) * 100\% \quad 2)$$

where $N\ uptake_{treatment}$ is the amount of N taken up by the plants in the fertilized treatments, $N\ uptake_{control}$ 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 (23% and 5% of N_{tot}, or 36% and 15% of N_{min} for biogas digestate and cattle slurry, respectively).

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

$$N\,balance = \left(N\,applied + \left(N\min_{t2} - N\min_{t1}\right) + N_{dep}\right) - \left(N\,uptake + N_2O_{cum} + NH_{3cum}\right) \quad (3)$$

where $N\ applied$ is the amount of N_{tot} applied, $N\min_{t1}$ and $N\min_{t2}$ are the amounts of N_{min} at time 1 (06th April 2011; early April represents the beginning of the vegetation period in 2011) and time 2 (18th 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), N_2O_{cum} is the amount of the annual cumulative N_2O-N losses, and NH_{3cum} 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_{min} = NH_4^+–N + NO_3^-–N) contents, one mixed soil sample consisting of nine individual samples was collected at two soil depths (0–10, 10–20 cm) at each treatment 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 one hour. The extracts were filtered through a 4–7 µm filter paper (Whatman 595 ½) and the first 20 ml of the extract were discarded. The solution was frozen at −20 ℃ 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 hours at 40 ℃, 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 (Humbold Universität zu Berlin, Germany). For the determination of bulk density and porosity, three undisturbed core cutter samples (100 cm^3) were randomly taken at four depths (0–5, 5–10, 10–15, 15–20 cm) for each treatment.

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 (TukeyHSD) 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 non parametric 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 plot) 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 (Eickenscheidt et al. 2011). The model extension was proved by the Akaike Information Criterion (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 by plotting 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 regressions 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 standard deviation.

3. Results

3.1. Environmental drivers

Temperatures between the two investigated soil types did not differ. In 2010 and 2011, air temperature in 20 cm height ranged from −17.5 to 39.5℃ with an annual mean of 8.6℃ in 2011 at both investigated areas. Soil temperature in −2 cm soil depth averaged 10.3℃ at the C_{org}-medium sites and was slightly higher with 10.5℃ at the C_{org}-high sites in 2011. Air temperature in 20 cm height following 15 or 16 days after fertilization averaged 16.0, 13.1, 15.4 and 11.5℃ for application events one to four at both investigated soil types. Soil temperature in −2 cm soil depth was approximately 2℃ 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-years 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 only weak and amounted to 3 mm in the time span between 16:00 and 00:00 hours.

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 3). Mean groundwater levels following the fertilizer applications are shown in Table 3.

3.2. N input and N availability

The amount of N applied was 111 and 252 kg N ha^{-1} for slurry treatments or rather 101 and 174 kg N ha^{-1} for digestate treatments in 2010 and 2011, respectively. However, due to the distinctly higher NH_4^+-N/N_{tot} ratio of the biogas digestate, total NH_4^+-N input was comparable or slightly higher in 2010 and 2011 than at the slurry treatments (Table 2). Additional physical and chemical properties of the slurry and digestate are shown in Table 2.

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 sites (Fig. 2b and 2c). The NO_3^- content was significantly higher ($P < 0.001$) at the C_{org}-high sites than at the C_{org}-medium sites in 0–10 cm soil depth in both years and in 10–20 cm soil depth in 2010 ($P < 0.01$) (Table 3). With exception of the first application event, all fertilization events increased the NO_3^- contents of the soil for a short period (Fig. 2c, Table 3). However, only in 2011 the fertilized sites showed significantly ($P < 0.01$) higher NO_3^- contents compared to the control treatments, but differences between digestate and slurry were generally not significant (except of 0–10 cm soil depth at the C_{org}-medium site) (Table 3).

3.3. N_2O emissions

Nitrous oxide fluxes were generally low at all treatments (Fig. 2d). Background emissions rarely exceeded 50 µg N m^{-2} h^{-1}. Highest N_2O fluxes were found immediately after fertilizer application (Fig. 2d and 3), sometimes followed by a second phase of higher emissions after 6 to 12 days. In case of the C_{org}-medium sites N_2O fluxes returned to background emission level within 3 to 7 days, whereas

398 the C_{org}-high sites had longer lasting increased N_2O emissions, particularly at the
399 digestate treatment.
400 Short term (16 days) N_2O fluxes of fertilized treatments significantly ($P < 0.01$)
401 exceeded N_2O fluxes of control treatments at all fertilization events. However, only in
402 one out of four fertilization events short term N_2O fluxes were significantly ($P < 0.001$)
403 higher at the digestate treatments compared to the slurry treatments. Additionally
404 significantly ($P < 0.001$) higher short term N_2O fluxes were observed at the C_{org}-high
405 sites compared to the C_{org}-medium sites in 2011, but the opposite was observed at
406 the second fertilization event in 2010.
407 However, due to the high variability and the partially fast return to the background
408 emission level, short term (16 days) cumulative N_2O emissions were not significantly
409 different from the control treatments in 2010 (Fig 4), but for 2011 short term
410 cumulative N_2O emissions had a clear trend in the order digestate > slurry > control
411 (although not significant in one case).
412 On an annual basis organic fertilization led to significantly ($P < 0.001$) higher N_2O
413 fluxes compared to unfertilized treatments. Additionally, the application of biogas
414 digestate significantly ($P < 0.01$) enhanced the N_2O fluxes compared to the
415 application of cattle slurry. Furthermore, N_2O fluxes from the C_{org}-high site
416 significantly ($P < 0.001$) exceeded N_2O fluxes from the C_{org}-medium sites. Annual
417 cumulative emissions ranged from 0.91 ± 0.49 kg N ha^{-1} yr^{-1} (control treatment, C_{org}-
418 medium site) to 3.14 ± 0.91 kg N ha^{-1} yr^{-1} (digestate treatment, C_{org}-high site) (Table
419 4). Calculated emission factors (EF) based on the amount of N_{tot} ranged from 0.12 to
420 0.23 for the slurry treatments and from 0.55 to 1.13 for the digestate treatments
421 (Table 4).
422 Observed N_2O fluxes could not be explained by any of the measured environmental
423 drivers. However, 53% of the temporal and spatial variation in the 16 days cumulative
424 N_2O-N exchange rates was explained by the amounts of applied NH_4^+-N and the
425 mean groundwater levels below surface during the same time (Fig. 5). A similar trend
426 was observed for the annual cumulative N_2O emissions but regression analysis was
427 not possible due to the small sample size ($n = 6$).

428 ### 3.4. CH_4 emissions

429 Most of the time, CH_4 emissions could not be detected (Fig. 2e). Occasionally CH_4
430 peaks were only found immediately after cattle slurry application. However, with
431 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 kg C ha^{-1} yr^{-1} to −1.06 ± 0.46 kg C ha^{-1} 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 volatilisation

Highest NH_3 losses were observed immediately after fertilization (Fig. 6). During the first 24 hours, 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 kg N ha^{-1} for the digestate treatments and 3.48 kg N ha^{-1} for the slurry treatments. The relative N loss was 36% and 15% of applied NH_4^+-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 5). In both years the mean annual grass yield from the digestate treatments were significantly ($P < 0.05$) higher compared to the slurry treatments. Additionally, the mean annual grass yield from the C_{org}-high sites exceeded those from the C_{org}-medium sites of both years, but differences were not significant.

The application of biogas digestate distinctively increased apparent NUE and NUE_{min} compared to cattle slurry treatments (Table 5). NUE values were on average 111 ± 133% for biogas digestate treatments and 21± 18% for cattle slurry. NUE_{min} values were always >100% for biogas digestate treatments, whereas for cattle slurry NUE_{min} values averaged 54 ± 53%. Beside fertilizer type effects, higher NUE and NUE_{min} were observed at the C_{org}-medium site compared to the C_{org}-high site.

The estimated N balances revealed N surpluses of up to 79 kg N ha^{-1} yr^{-1} for cattle slurry treatments but deficits of up to 95 kg N ha^{-1} yr^{-1} for biogas digestate treatments, for the year 2011 (Table 6).

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 soil organic matter (SOM) at this site. It is well known that drainage enhances the degradation of SOM and thus stimulates net nitrogen mineralization and N transformation processes (Kasimir Klemedtsson et al., 1997; Freibauer et al., 2004; Klemedtsson 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 which were recently drained (Hacin et al., 2001; Renger et al., 2002; Sonneveld and Lantinga, 2011) or contain higher amounts of SOM.

As expected from literature the biogas digestates differed in their physical and chemical properties from the cattle slurries. The biogas digestates had narrower C/N ratios (e.g. Tambone et al., 2009), higher pH values (Wulf et al., 2002; Quakernack et al., 2011), wider NH_4^+/N_{tot} ratios and thus relatively higher NH_4^+ contents than the cattle slurries (Möller and Stinner 2009). However, the amounts of NH_4^+ were not distinctly different between the applied organic fertilizers (with one exception).

We observed an unexpected small change in the NH_4^+ content of the soil immediately after fertilizer application which could be attributed to different reasons. Firstly, the fertilizers partly remained on the plant canopy after splash plate application and therefore soil contact and infiltration was limited (Quakernack et al., 2011). Secondly, a significant fraction of NH_4^+ from the organic fertilizer was lost in a few hours after splash plate application via NH_3 volatilization. But most importantly, in well aerated soils applied NH_4^+ undergoes rapid nitrification, as indicated by the increasing soil NO_3^- contents after fertilizer application in the upper soil layer. In general, the continuously observed absent or low NH_4^+ contents with simultaneously high extractable NO_3^- in the soil indicate that net nitrification entirely controls net nitrogen mineralization at all treatments of the investigated study sites. Nitrification requires sufficient oxygen (O_2) availability in the soil (Davidson et al., 1986) hence we

495 can assume well aerated soil conditions, at least in the upper soil layer, for most of
496 the time at the study sites.
497 Several studies (e.g. Gutser et al., 2005; Jones et al., 2007) reported that the
498 infiltration of organic fertilizer may enhance the soil N pool and further stimulates the
499 SOM mineralization, leading to additional N_{min}. This becomes also evident in the
500 observed significantly higher NO_3^- contents of the fertilized treatments compared to
501 the unfertilized control treatments, especially in the 0–10 cm soil layer. However,
502 significant differences in the N_{min} contents between the two investigated organic
503 fertilizers were not found in 2010 and 2011. This may be due to the fact that the N
504 uptake by plants at the digestate treatments was on average 27% higher and that
505 distinct differences in the amount of N_{tot} and NH_4^+ of the applied organic fertilizers
506 were only observed in the second study year.
507 To maintain soil fertility and yield and to reduce harmful side effects (e.g N_2O losses,
508 NO_3^- leaching) site adapted fertilization is necessary. The estimated negative N
509 balances for biogas treatments are in line with Andres et al. (2013) who reported that
510 positive N balances could only be achieved when the amount of applied digestate
511 contains more than 200 kg N ha^{-1} yr^{-1}. However, the strong negative N balances of
512 the control treatments reveal that large amounts of up to 148 kg N ha^{-1} yr^{-1} originate
513 from peat mineralization, demonstrating the unsustainable agricultural use of drained
514 peatlands. Assuming that the fertilized treatments received equal amounts of N from
515 peat mineralization, all N balances of these treatments were strongly positive. N
516 surpluses as estimated for the cattle slurry treatments enhance the soil N pool, but
517 the gradual release of N at a non predictable stage from the soil N pool carries the
518 risk of leaching or gaseous losses (Amon et al., 2006). Particularly in wintertime, high
519 amounts of available NO_3^- in the soil, as observed especially at the fertilized
520 treatments of the C_{org}-high sites, carry the risk of N leaching due to the reduced N
521 demand by plant uptake and by the microbial community during this time (Merino et
522 al., 2002; Sänger et al., 2010).

523 ## 4.2. Fertilizer effect on N-use efficiency and grass yield

524 In line with investigations from Schils et al. (2008) most of the applied and produced
525 N_{min} was probably rapidly absorbed by the grassland as the soil N_{min} content usually
526 decreased within a few days after fertilizer application (Figure 2b, 2c). This becomes
527 also evident in the apparent NUE_{min}, especially from biogas digestate treatments. A
528 significant effect of biogas digestate on crop yields and apparent NUE_{min} as observed

in the present study were also reported from pot experiments (e.g. de Boer, 2008; Möller and Müller, 2012), but not for field applications without incorporation of the digestate into the soil (Möller and Müller, 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; Sänger et al., 2010), whereas the lower C/N ratio reduced the potential for 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 only small, in particular when accounting for NH_3 losses. 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; Sørensen 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; Möller and Stinner, 2009), it can be assumed that the digestate enhanced SOM mineralization more than cattle slurry, or that N mineralized from SOM had a larger share in the uptake by the plants due to lower competition of microbial immobilization. The lower NUE at the C_{org}-high sites compared to C_{org}-medium sites 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 before. However, in the present study the observed yield differences between the treatments fertilized with biogas digestate and cattle slurry cannot fully be explained on the basis of available N in the applied fertilizers and further investigations are necessary.

4.3. Fertilizer and site induced N_2O emissions

The observed annual N_2O emissions were distinctly lower than the actual default emission factor from the Tier 1 approach for temperate, deep drained, nutrient rich grassland of 8.2 kg N_2O-N ha^{-1} 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 kg N ha^{-1} yr^{-1} (Augustin et al., 1998; Flessa et al., 1997; 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 kg N ha^{-1} yr^{-1} for the Netherlands, whereas at boreal regions N_2O emissions of up to 9 kg N ha^{-1} yr^{-1} were measured (Nykänen 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 sites significantly exceeded those from the C_{org}-medium sites in all treatments, which was in line with higher N_{min} contents and higher groundwater levels. 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 before, 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 micro sites can occur within close proximity and thus nitrification and denitrification as well 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 percentage of applied N without consideration of the NH_3 losses were lower for all treatments than the IPCC default value. Several other studies reported also emission factors < 1% of applied N (Chadwick et al., 2000; Velthof et al., 2003; Clemens et al., 2006; Jones at al., 2007; Möller and Stinner, 2009), but never 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 distinctly higher percentage of produced N_2O 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^+ where 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 immediatly 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, thus 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 significantly higher N_2O emissions from the digestate treatments compared to the slurry treatments. Higher N_2O emissions derived from biogas digestates were also reported from a few other authors (e.g. Senbayram et al.,

2009; Sänger et al., 2010), whereas Clemens et al. (2006) found no differences between untreated and digested slurry.

It can be assumed that at drained organic soils, like in the present study, sufficient metabolizable C is generally widely available in the upper soil profile (e.g. van Beek 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 can not 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 distinctively different in particular when accounting for NH_3 losses. As mentioned before, the high pH and the lower C/N ratio of the biogas digestate, obviously slightly enhanced SOM mineralization compared to cattle slurry fertilizer, leading to extra N for nitrification and denitrification. Thus the significantly higher N_2O emissions from the digestate treatments compared to the cattle slurry treatments could probably be attributed to a priming effect caused by increased SOM mineralization. However, further investigations are required to prove whether digestates enhanced SOM mineralization or if the additional released N_{min} is derived from the organically bounded N in the fertilizer.

Nevertheless, 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 reveal the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of C_{org} rich grasslands. The same was also 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 kg CH_4–C ha^{-1} yr^{-1} were reported from Beetz et al. (2013) for a drained intensive grassland in northern German 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 as 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

664 lowering of the groundwater level. Nevertheless, significant differences in the amount
665 of the annual CH_4 uptake capacity between the two study sites C_{org}-medium and C_{org}-
666 high could not be seen, although distinct differences in the groundwater table were
667 observed.
668 The occasionally observed CH_4 peak emissions were only found immediately after
669 cattle slurry application. This was in line with several other studies which reported
670 short-term CH_4 emissions immediately after organic fertilizer application due probably
671 to volatilization of dissolved CH_4 from the applied substrate (Sommer et al., 1996;
672 Chadwick et al., 2000; Wulf et al., 2002; Jones et al., 2005; Amon et al., 2006). The
673 longer lasting CH_4 emissions observed after the first application event at the slurry
674 treatment of the C_{org}-high site might result from the degradation of volatile fatty acids
675 by methanogenic bacteria (Chadwick et al., 2000; Wulf et al., 2002). Furthermore, the
676 high groundwater level promotes the formation of CH_4 during this time period.
677 However, we could not find any significantly differences in the short term or annual
678 CH_4 emissions between the two investigated fertilizers. According to Chadwick et al.
679 (2000) more than 90% of total CH_4 emissions occur during the first 24h following
680 fertilizer application. Therefore, we must assume that we have missed most of
681 fertilizer induced CH_4 emissions. However, all studies from literature confirm the only
682 minor importance of CH_4 emissions from applied organic fertilizers in the GHG
683 balance of agricultural grasslands (Wulf et al., 2002; Amon et al., 2006; Dietrich et al.,
684 2012).

685 ## 4.5. N-losses by NH_3 volatilization

686 The NH_3 losses measured after splash plate application at the third application event
687 followed the typical pattern of lost ammonia (Clemens et al., 2006), particularly at the
688 digestate treatments. Significantly higher NH_3 losses from treatments fertilized with
689 biogas digestate were observed compared to those fertilized with cattle slurry. This is
690 in line with several other studies (Amon et al., 2006; Möller and Stinner, 2009; Ni et
691 al., 2011). However, it has to be taken into account that the present results are based
692 only on measurements from a single application event, on which the largest
693 differences in the fertilizer compositions occurred (see Table 2).
694 The higher NH_3 losses from treatments fertilized with biogas digestate could be
695 attributed to the higher amount of NH_4^+ and the distinctly higher pH value of the
696 applied digestate compared to the cattle slurry at the third fertilization event. Several
697 authors propose that a lower dry matter content of slurries favors the infiltration into

698 the soil with a subsequent faster decrease of NH_3 losses (Sommer et al. 1996; Ni et
699 al. 2011). However, although the observed dry matter content of the biogas
700 digestates was very low and at the lower end of values reported in literature (e.g.
701 Gutser et al., 2005; Möller et al., 2008; Quarkernack et al., 2011) no corresponding
702 effect was found in the present study. According to Döhler and Horlacher (2010),
703 water saturated and dry soils lead to higher NH_3-losses due to the reduced infiltration
704 of slurries. Thus it could be assumed that the infiltration of the slurries was possibly
705 hampered due to the strong rain event which took place before the fertilizer
706 application. Additionally, at low dosage applications a large part of the organic
707 fertilizer remained on the plant canopy and thus soil contact and infiltration was
708 limited after spreading. We conclude that this was also the main reason why no
709 significant differences in the pattern of NH_3 volatilization between the soil types were
710 found in the present study.
711 The observed relative N losses of 15–36% of applied NH_4^+-N, were in the range
712 reported in the literature (Sommer et al., 1996; Clemens et al., 2006; Quakernack et
713 al., 2011). This demonstrates that NH_3 volatilization is quantitatively the most
714 important N-loss from slurry application, as was also proposed by Flessa and Beese
715 (2000). Beside the negative effects of eutrophication and acidification of ecosystems
716 (Dragosits et al., 2002; Sanderson et al., 2006; Ni et al., 2011), distinct NH_3
717 volatilization decreases the N fertilizer use efficiency. One of the most effective
718 measures to reduce NH_3 emissions from grassland is the incorporation of slurry
719 (Rodhe et al., 2006). However, several studies reported a considerable increase of
720 greenhouse gases (GHG), mainly N_2O, after injection of slurries and biogas
721 digestates (Dosch and Gutser, 1996; Flessa and Beese, 2000; Wulf et al., 2002).
722 However, up to date no study has examined the effect of the injection technique on
723 organic soils.

724 ## 5. Conclusion

725 We studied N_2O, CH_4 and NH_3 fluxes after splash plate application of biogas
726 digestate and cattle slurry in a region known for its risk of high N_2O and NH_3
727 emissions and we were the first to study digestate application on high organic carbon
728 soils with 10 to 17% C_{org} content in the topsoil. To our surprise, N_2O emissions
729 remained lower than typical rates and EFs observed on mineral soils in the vicinity of
730 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 could be seen in the apparent NUE_{min}. N_2O emissions increased with C_{org} content and fertilization. As hypothesized, N_2O and NH_3 emissions were distinctly higher after digestate than after slurry fertilization, which probably could be attributed to a priming effect caused by increased SOM mineralization for N_2O. Due to the deep drainage, CH_4 emissions were of only minor importance 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 soil organic matter 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.

6. Acknowledgements

We thank the landowners Ludwig Büchler and Josef Pellmeyer for the opportunity to conduct the measurements during the regular management as well for their excellent cooperation and help. Furthermore we would thank Caroline Müller, Michael Schlapp, Susanne Köstner, Melissa Mayer, Phillip Metzner and Lukas Aberl for their help during field and laboratory work. Further the authors thank Nadine Eickenscheidt (Thünen Institute) for helpful discussion and critical review, Niko Roßkopf (Humboldt-Universität zu Berlin) for soil description and providing N_{tot} and pH values as well as Stephan Raspe from the Bavarian State Institute of Forestry for providing the N deposition data. This study was part of the joint research project ‘Organic soils’; Acquisition and development of methods, activity data and emission factors for the climate reporting under LULUCF/AFOLU, founded by the Thünen Institute (TI).

7. 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, 07.-12.09.2013, Rostock, 2013.

Augustin, J., Merbach, W., Steffens, L., and Snelinski, B.: Nitrous Oxide Fluxes of Disturbed Minerotrophic Peatlands, Agribiol. Res., 51 (1), 47–57, 1998.

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, 2013.

Bouwman, A.F.: Direct emissions of nitrous oxide from agricultural soils, Nutrient Cycling in Agroecosystems, 45, 53–70, 1996.

Butterbach-Bahl, K., Baggs, E.M., Dannenmann, M., Kiese, R., Zechmeister-Boltenstern, S.: Nitrous oxide emissions from soils: how well do we understand the processes and their controls?, Phil trans R Soc B, 368:20130122, 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. Enivron. Qual., 29, 277–287, 2000.

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 (5), 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 Fertil 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 anerobic digestion of cattle slurry, Agriculture, Ecosystems and Environment, 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 (54), 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 (10), 1331–1339, 1994.

Crutzen, P.J.: the role of NO and NO_2 in the chemistry of the troposphere and stratosphere, Annu. Rev. Earth Planet. Sci., 7 (1), 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, Applied and Environmental Microbiology, 52 (6), 1280–1286, 1986.

DBFZ (Deutsches BiomasseForschungsZentrum gemeinnützige GmbH): Monitoring zur Wirkung des Erneuerbare-Energien-Gesetz (EEG) auf die Entwicklung der

817 Stromerzeugung aus Biomasse - Endbericht zur EEG-Periode 2009 bis 2011, p. 120.,
818 2012.
819
820 De Boer, H.C.: Co-digestion of animal slurry can increase short-term nitrogen
821 recovery by crops, J. Environ. Qual., 37, 1968–1973, 2008.
822
823 Dechow, R., and Freibauer, A.: Assesment of German nitrous oxide emissions using
824 empirical modelling approaches, J. Nutr. Cycl. Agroecosyst., 91, 235–254, 2011.
825
826 Dietrich, B., Finnan, J., Frost, P., Gilkinson, S., and Müller, C.: The extent of methane
827 (CH_4) emissions after fertilisation of grassland with digestate, Biol. Fertil. Soils, 48,
828 981–985, 2012.
829
830 Don, A., Osborne, B., Hastings, A., Skiba, U., Carter, M.S., Drewer, J., Flessa, H.,
831 Freibauer, A., Hyvönen, N., Jones, M.B., Lanigan, G.J., Mander, Ü., Monti, A., Djomo,
832 S.N., Valentine, J., Walter, K., Zegada-Lizarazu, W., and Zenone, T.: Land-use
833 change to bioenergy production in Europe: implications for the greenhouse gas
834 balance and soil carbon, GCB Bioenergy, doi: 10.1111/j.1757-1707.2011.01116.x,
835 2011.
836
837 Dosch, P., and Gutser, R.: Reducing N losses (NH_3, N_2O, N_2) and immobilization
838 from slurry through optimized application techniques, Fertilizer Research, 43, 165–
839 171, 1996.
840
841 Döhler, H., and Horlacher, D.: Ammoniakemissionen organischer Düngemittel, in
842 Emissionen landwirtschaftlich genutzter Böden, KTBL-Schrift, 483, p. 384, 2010.
843
844 Dragosits, U., Theobald, M. R., Place, C. J., Lord, E., Webb, J., Hill, J., ApSimon, H.
845 M., and Sutton, M. A.: Ammonia emission, deposition and impact assessment at the
846 field scale: a case study of sub-grid spatial variability, Environ. Pollut., 117, 147–158,
847 2002.
848
849 Drösler, M.: Trace gas exchange and climatic relevance of bog ecosystems,
850 Southern Germany, PhD thesis, Chair of Vegetation Ecology, Department of Ecology,
851 Technical University Munich, p. 179, 2005.
852
853 Drösler, M**.**, Freibauer, A., Christensen, T. and Friborg, T.: Observation and status of
854 peatland greenhouse gas emission in Europe, In: Dolman, H., Valentini, R. &
855 Freibauer, A. (eds) *The Continental-Scale Greenhouse Gas Balance of Europe*.
856 *Ecological Studies*, 203, 237–255, 2008.
857
858 Drösler, M., Freibauer, A., Adelmann, W., Augustin, J., Bergman, L., Beyer, C.,
859 Chojnicki, B., Förster, C., Giebels, M., Görlitz, S., Höper, H., Kantelhardt, J.,
860 Liebersbach, H., Hahn-Schöfl, M., Minke, M., Petschow, U., Pfadenhauer, J.,
861 Schaller, L., Schägner, P., Sommer, M., Thuille, A., and Wehrhan, M.: Klimaschutz
862 durch Moorschutz in der Praxis – Ergebnisse aus dem BMBF-Verbundprojekt
863 „Klimaschutz - Moornutzungsstrategien“ 2006-2010, 2011.
864
865 Eickenscheidt, N., Brumme, R., and Veldkamp, E.: Direct contribution of nitrogen
866 deposition to nitrous oxide emissions in a temperate beech and spruce forest – a ^{15}N
867 tracer study, Biogeosciences, 8, 621–635, 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.

Fachverband Biogas e.V.: Branchenzahlen – Prognosen 2013 / 2014, Entwicklung des jährlichen Zubaus von neuen Biogasanlagen in Deutschland, http://www.biogas.org/edcom/webfvb.nsf/id/DE_Branchenzahlen, (Stand: 11/2013), 2014.

Firestone, M. K., and Davidson, E. A.: Microbiological basis for NO and N_2O production and consumption in soils, in Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere, edited by M. Andreae and O. D. S. Schimel, pp. 7–21, John Wiley, New York, 1989.

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.

Flessa, H., Wild, U., Klemisch, M., and Pfadenhauer, J.: Nitrous oxide and methane fluxes from organic soils under agriculture, European Journal of Soil Science, 49, 327–335. 1998.

Freibauer, A., and Kaltschmitt, M.: Nitrous oxide emissions from agricultural mineral soils in Europe – controls and models, Biogeochemistry, 63(1), 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.

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 N_2O 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 biodigested 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.

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., Gensior, A., Menden, B.M., and Döhler, H.: Emissionen landwirtschaftlich genutzter Böden im Rahmen der deutschen Klimaberichterstattung, in Emissionen landwirtschaftklich genutzter Böden, KTBL-Schrift, 483, p. 384, 2010.

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 CH_4 and CO_2, Biogesciences, 8, 1539–1550, 2011.

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 ^{15}N-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 and Planetary 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 N_2O fluxes from temperate grassland, Agriculture, Ecosystems and Environment, 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 and Management, 13. 1–6, 1997.

Klemedtsson, L., von Arnold, K., Weslien, P., and Gundersen, P.: Soil CN ratio as a scalar parameter to predict nitrous oxide emissions, Global Change Biology, 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 and Soil, 184, 1–10, 1996.

969 Livingston, G.P., and Hutchinson, G.L.: Enclosure-based measurement of trace gas
970 exchange: application and sources of error, In: Matson, PA, Harriss, RC, (eds.),
971 Biogenic Trace Gases: Measuring Emissions from Soil and Water. Blackwell Science,
972 Cambridge, 14–50, 1995.
973
974 Maljanen, M., Komulainen, V.M., Hytönen, J., Martikainen, P.J., and Laine, J.:
975 Carbon dioxide, nitrous oxide and methane dynamics in boreal organic agricultural
976 soils with different soil characteristics, Soil Biology & Biochemistry, 36, 1801–1808,
977 2004.
978
979 Maljanen, M., Sigurdsson, B.D., Guðmundsson, J., Óskarsson, H., Huttunen, J.T.,
980 and Martikainen, P.J.: Greenhouse gas balances of managed peatlands in the Nordic
981 countries – present knowledge and gaps, Biogeosciences, 7, 2711–2738,
982 doi:10.5194/bg-7-2711-2010, 2010.
983
984 Merino, P., Estavillo, J.M., Graciolli, L.A., Pinto, M., Lacuesta, M., Muñoz-Rueda, A.,
985 and Gonzalez-Murua, C.: Mitigation of N_2O emissions from grassland by nitrification
986 inhibitor and Actilith F2 applied with fertilizer and cattle slurry, Soil Use and
987 Management, 18, 135–141, 2002.
988
989 Möller, K., Stinner, W., Deuker, A., and Leithold, G: Effects ofdifferent manuring
990 systems with and without biogas digestion on nitrogen cycle and crop yield in mixed
991 organic dairy farming systems, Nutr. Cycl. Agroecosyst, 82, 209–232, DOI:
992 10.1007/s107505-008-9196-9, 2008.
993
994 Möller, K., and Stinner, W.: Effects of different manuring systems with and without
995 biogas digestion on soil mineral nitrogen content and gaseous nitrogen losses
996 (ammonia, nitroux oxide), Europ. J. Agronomy, 30, 1–16, 2009.
997
998 Möller, K., and Müller, T.: Effects of anaerobic digestion on digestate nutrient
999 availability and crop growth: A review, Eng. Life Sci., 12(3), 242–257, 2012.
1000
1001 Moiser, A.R., 2001. Exchange of gaseous nitrogen compounds between agricultural
1002 systems and the atmosphere. Plant Soil 228, 17–27.
1003
1004 Ni, K., Pacholski, A., Gericke, d., and Kage, H.: Analysis of ammonia losses after
1005 field application of biogas slurries by an empirical model, J. Plant Nutr. Soil sci., 000,
1006 1–12, DOI: 10.1002/jpln.201000358, 2011.
1007
1008 Nykänen H., Alm, J., Lång, K., Silvola, J., and Martikainen, P.J.: Emissions of CH_4,
1009 N_2O and CO_2 from a virgin fen and a fen drained for grassland in Finland, Journal of
1010 Biogeography, 22, 351-357, 1995.
1011
1012 Oenema, O., Wrage, N., Velthof, G.L., van Groenigen, J.W., Dolfing, J., and Kuikman,
1013 P.J.: Trends in global nitrous oxide emissions from animal production systems,
1014 Nutrient Cycling in Agroecosystems, 72, 51–65, 2005.
1015
1016 Pacholski, A., Cai, G., Nieder, R., Richter, J., Fan, X., Zhu, Z., and Roelcke, M.:
1017 Calibration of a simple method for determining ammonia volatilization in the field –
1018 comparative measurements in Henan Province, China, Nutr. Cycl. Agroecosyst., 74,
1019 259–273, 2006.

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., doi:10.1016/j.agee.2011.05.030, 2011.

Regina, K., Syväsalo, E., Hannukkala, A., and Esala, M: Fluxes of N_2O from farmed peat soils in Finland, European Journal of Soil Science, 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, 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, Journal of Soil Use and Management, 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.

Sanderson, M.G., Collins, W.J., Johnson, C.E., and Derwent, R.G.: Present and future acid deposition to ecosystems: The effect of climate change, Atmos. Environ. 40, 1275–1283, 2006.

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 Groeningen, 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.

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., Sherlock, R.R., and Khan, R.Z.: Nitrous oxide and methane emissions from pig slurry amended soils, Soil Biol. Biochem., 28 (10/11), 1541–1544, 1996.

Sommer, S.G., Zhang, G.Q., Bannink, A., Chadwick, D., Misselbrook, T., Harrison, R., Hutchings, N. J., Menzi, H., Monteny, G. J., Ni, J. Q., Oenema, O., and Webb, J.: Algorithms determining ammonia emission from buildings housing cattle and pigs and from manure stores, Adv. Agron., 89, 261–335, 2006.

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, Bioresource Technology, 100, 3140–3142, 2009.

van Beek, C.L., Hummelink, E.W.J., Velthof, G.L., and Oenema, O.: Denitrification rates in relation to roundwater 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 N_2O 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 and 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.

Wichtmann, W., Couwenberg, J., and Kowatsch, A.: Klimaschutz durch Schilfanbau, Ökologisches Wirtschaften Online, 24 (1), 2009.

Whalen, S.C.: Biogeochemistry of methane exchange between natural wetlands and the atmosphere, Environmental Engineering Science, 22 (1), 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: II Greenhouse Gas Emissions, J. Environ. Qual., 31, 1795–1801, 2002.

1129 **Table 1** Soil properties of the study site

	Sampling depth	C_{org}-medium	C_{org}-high	*n*
Soil type (WRB 2006)[1]		mollic Gleysol	sapric Histosol	
Soil type (German calssification KA5)		GMq	KV-KM	
Peat depth [cm] [1]		80	70	1
pH value*		4.1	4.2	
Total nitrogen [%]*		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

1130 Values present means ± standard error

1131 [1] World Reference Base for Soil Resources

1132 * Relative to the upper horizon (C_{org}-medium 0–20 cm; C_{org}-high 0–15 cm); Roßkopf personal communication

Table 2 Physical and chemical properties from the applied digestates and slurrys.

	Cattle slurry					Biogas digestate				
	1. Application (14.06.2010)	2. Application (25.08.2010)	3. Application (27.05.2011)	4. Application (22.09.2011)	5. Application (04.11.2011)	1. Application (14.06.2010)	2. Application (25.08.2010)	3. Application (27.05.2011)	4. Application (22.09.2011)	5. Application (04.11.2011)
Fertilizer quantity [m^3 ha^{-1}]	20	20	25	20	20	20	20	25	20	20
Total carbon [kg ha^{-1}]	579	676	798	797	1073	384	373	167	184	178
Organic carbon [kg ha^{-1}]	410	573	655	706	960	306	337	148	161	178
Total nitrogen [kg ha^{-1}]	47	64	70	85	97	49	52	78	35	61
NO_3^- [kg N ha^{-1}]	0	0	0	0	0	0	0	0	0	0
NH_4^+ [kg N ha^{-1}]	20	28	23	33	38	22	28	51	17	40
C/N ratio	12	11	11	9	11	8	7	2	5	3
pH ($CaCl_2$)	–	–	6.8	7.0	7.0	–	–	7.7	7.4	7.7
Dry matter content [%]	5	7	7	9	10	4	4	2	2	3

Table 3 Mean (minimum/maximum) groundwater level (GW), NO_3^- and NH_4^+ 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			
		Control	Cattle slurry	Biogas digestate	Control	Cattle slurry	Biogas digestate	*n*
1 Application (14.06. – 30.06.2010)								
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 (25.08. – 10.09.2010)

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 (27.05. – 11.06.2011)

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 (22.09. – 07.10.2011)

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

Table 4 Calculated emission factors (EF) for the year 2011 and for single application events (16 days) (Apl. 1 – Apl. 4). EF based on the amount of total nitrogen (N_{tot}) without consideration of NH_3-N losses.

	C_{org}-medium			C_{org}-high		
	Control	Cattle slurry	Biogas digestate	Control	Cattle slurry	Biogas digestate
N_2O exchange [kg N ha^{-1} yr^{-1}]	0.91 ± 0.49	1.21 ± 0.05	1.86 ± 0.23	1.18 ± 0.07	1. 77 ± 0.15	3.14 ± 0.91
Annual EF		0.12	0.55		0.23	1.13
EF Apl. 1		0.18	0.17		0.20	0.35
EF Apl. 2		0.11	0.05		0.11	0.21
EF Apl. 3		0.08	0.21		0.23	0.68
EF Apl. 4		0.09	0.33		0.15	0.56

Table 5 N uptake and N use efficiency for the years 2010 and 2011.

Treatment	Cutting date	Fertilization date	N content plant [%]	DM [t ha^{-1} yr^{-1}]	N uptake [kg N ha^{-1}]	N applied [kg N ha^{-1}]†	N_{min} applied [kg N ha^{-1}]†	N use efficiency [%]	N_{min} use efficiency [%]
Control C_{org}-medium	24-May-10	–	2.04*	2.52	51	–	–	–	–

Control C_{org}-high	24-May-10	–	2.14	2.93	63	–	–	–	–
Cattle slurry C_{org}-medium	24-May-10	N.A.	2.37	3.19	76	–	–	–	–
Cattle slurry C_{org}-high	24-May-10	N.A.	2.14	3.58	77	–	–	–	–
Biogas digestate C_{org}-medium	24-May-10	N.A.	2.04	4.17	85	–	–	–	–
Biogas digestate C_{org}-high	24-May-10	N.A.	2.27	4.39	100	–	–	–	–
Control C_{org}-medium	20-Aug-10	–	2.03	2.02	41	–	–	–	–
Control C_{org}-high	20-Aug-10	–	2.00	2.63	53	–	–	–	–
Cattle slurry C_{org}-medium	20-Aug-10	14-Jun-10	2.19	3.06	67	45	17	58	153
Cattle slurry C_{org}-high	20-Aug-10	14-Jun-10	1.93	3.23	62	45	17	22	57
Biogas digestate C_{org}-medium	20-Aug-10	14-Jun-10	2.03	2.99	61	38	14	52	140
Biogas digestate C_{org}-high	20-Aug-10	14-Jun-10	2.00	3.51	70	38	14	47	125
Control C_{org}-medium	23-May-11	–	1.96	2.66	52	–	–	–	–
Control C_{org}-high	23-May-11	–	1.70	3.82	65	–	–	–	–
Cattle slurry C_{org}-medium	23-May-11	25-Aug-10	2.01	2.58	52	61	24	0	0
Cattle slurry C_{org}-high	23-May-11	25-Aug-10	1.70	4.20	71	61	24	11	27
Biogas digestate C_{org}-medium	23-May-11	25-Aug-10	1.96	3.97	78	40	18	64	144
Biogas digestate C_{org}-high	23-May-11	25-Aug-10	1.83	4.54	83	40	18	45	101
Control C_{org}-medium	1-Aug-11	–	1.71	2.06	35	–	–	–	–
Control C_{org}-high	1-Aug-11	–	1.48	2.88	43	–	–	–	–
Cattle slurry C_{org}-medium	1-Aug-11	27-May-11	1.71	2.73	47	67	20	17	58
Cattle slurry C_{org}-high	1-Aug-11	27-May-11	1.51	3.19	48	67	20	8	28
Biogas digestate C_{org}-medium	1-Aug-11	27-May-11	1.78	4.88	87	60	33	86	158
Biogas digestate C_{org}-high	1-Aug-11	27-May-11	1.48	5.34	79	60	33	61	112
Control C_{org}-medium	13-Sep-11	–	2.53	1.71	43	–	–	–	–
Control C_{org}-high	13-Sep-11	–	2.26	2.27	51	–	–	–	–
Cattle slurry C_{org}-medium	13-Sep-11	27-May-11	2.57	2.28	59	(55)‡	(8)‡	28	189
Cattle slurry C_{org}-high	13-Sep-11	27-May-11	2.53	2.64	67	(61)‡	(14)‡	25	110
Biogas digestate C_{org}-medium	13-Sep-11	27-May-11	2.53	3.15	80	(8)‡	(0)‡	436	–

Biogas digestate C_{org}-high	13-Sep-11	27-May-11	2.26	3.25	74	(24)‡	(0)‡	94	–

* N contents from control treatments were estimated from fertilized treatments.

† Applied N_{tot} and N_{min} were corrected by NH_3–N losses (23% and 5% from N_{tot}, or rather 36% and 15% from N_{min} for biogas digestate and cattle slurry, respectively).

‡ Hypothetically remaining N_{tot} and N_{min} from the application event 3 (27th May 2011).

N.A. = not available.

Table 6 Estimated nitrogen balance for the year 2011.

Treatment	N applied [kg N ha^{-1} yr^{-1}]	N_{min} t1* [kg N ha^{-1}]	N_{min} t2* [kg N ha^{-1}]	N deposition [kg N ha^{-1} yr^{-1}]	N uptake [kg N ha^{-1} yr^{-1}]	N_2O [kg N ha^{-1} yr^{-1}]	NH_3† [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	37.8	78.6
Cattle slurry C_{org}-high	252	27.3	68.1	7.2	186	1.8	37.8	74.0
Biogas digestate C_{org}-medium	174	29.8	83.3	7.2	244	1.9	40.0	-51.6
Biogas digestate C_{org}-high	174	26.2	28.4	7.2	236	3.1	40.0	-95.3

* Reference date for t1 is the 06th April 2011 and for t2 the 18th October 2011.

† NH_3–N losses at the fourth and fifth application event were estimated based on NH_3 measurements at the third application event (23% and 5% from N_{tot} for biogas digestate and cattle slurry, respectively).

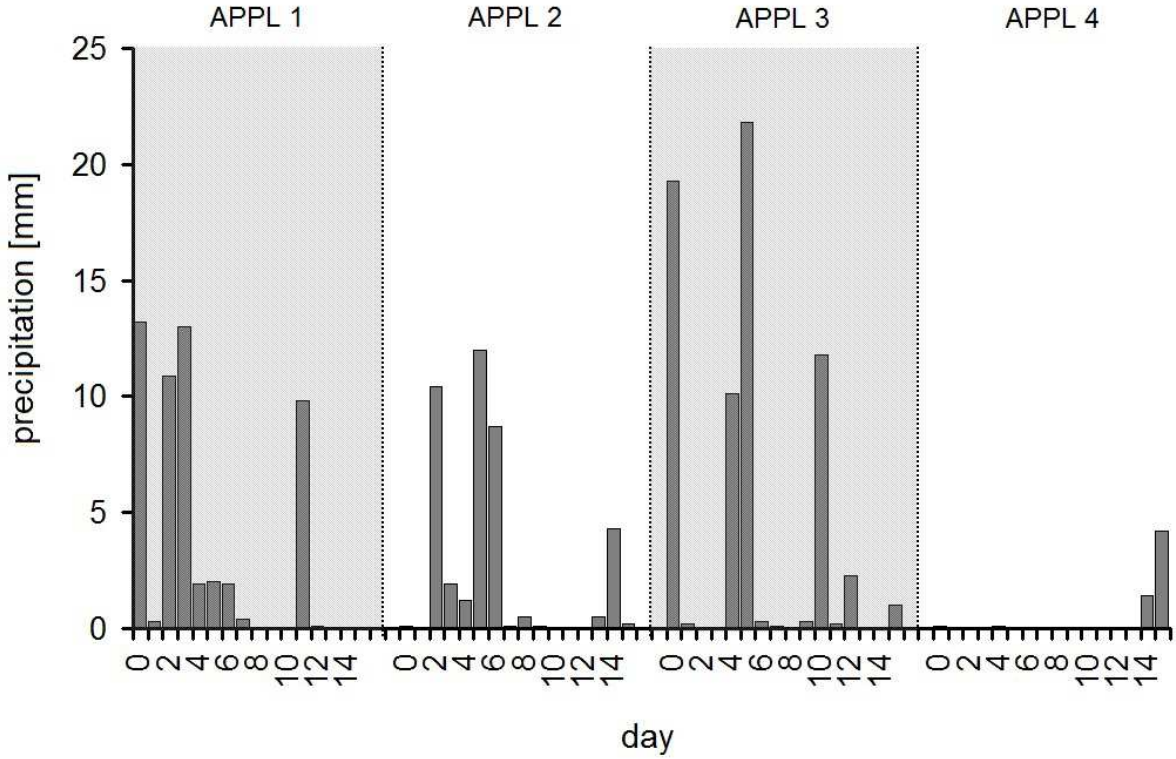

Fig. 1 Daily sums of precipitation following the organic fertilizer application events (APPL).

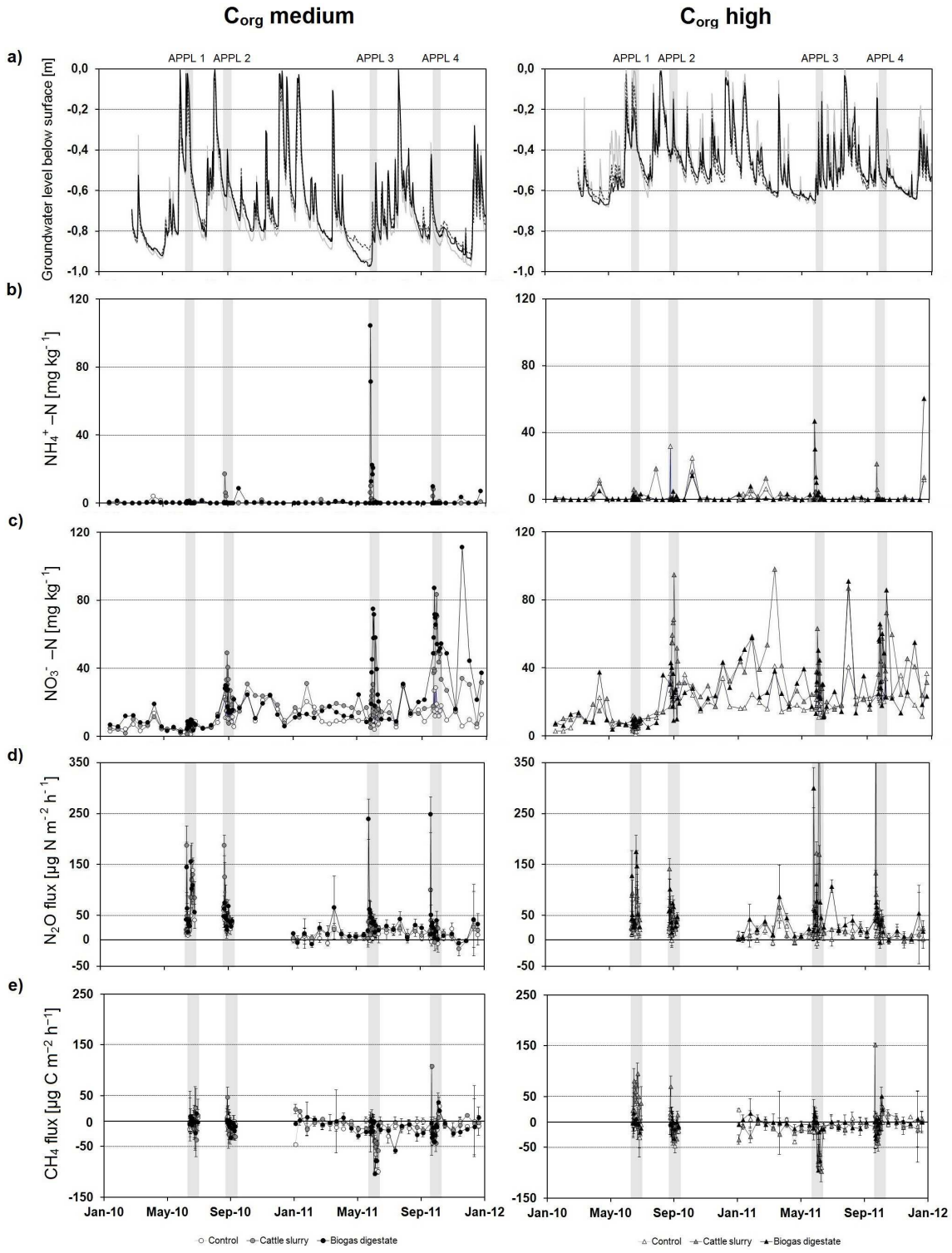

Fig. 2 Variation in groundwater level (a), extractable NH_4^+ (b) and NO_3^- (c) contents for the soil depth 0–10 cm, N_2O (d) and CH_4 fluxes (e) (Mean ± SD, *n* = 3) of the C_{org}-medium and C_{org}-high sites from January 2010 to January 2012. Gray bars mark the 15 or 16 days period of intensiv gas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

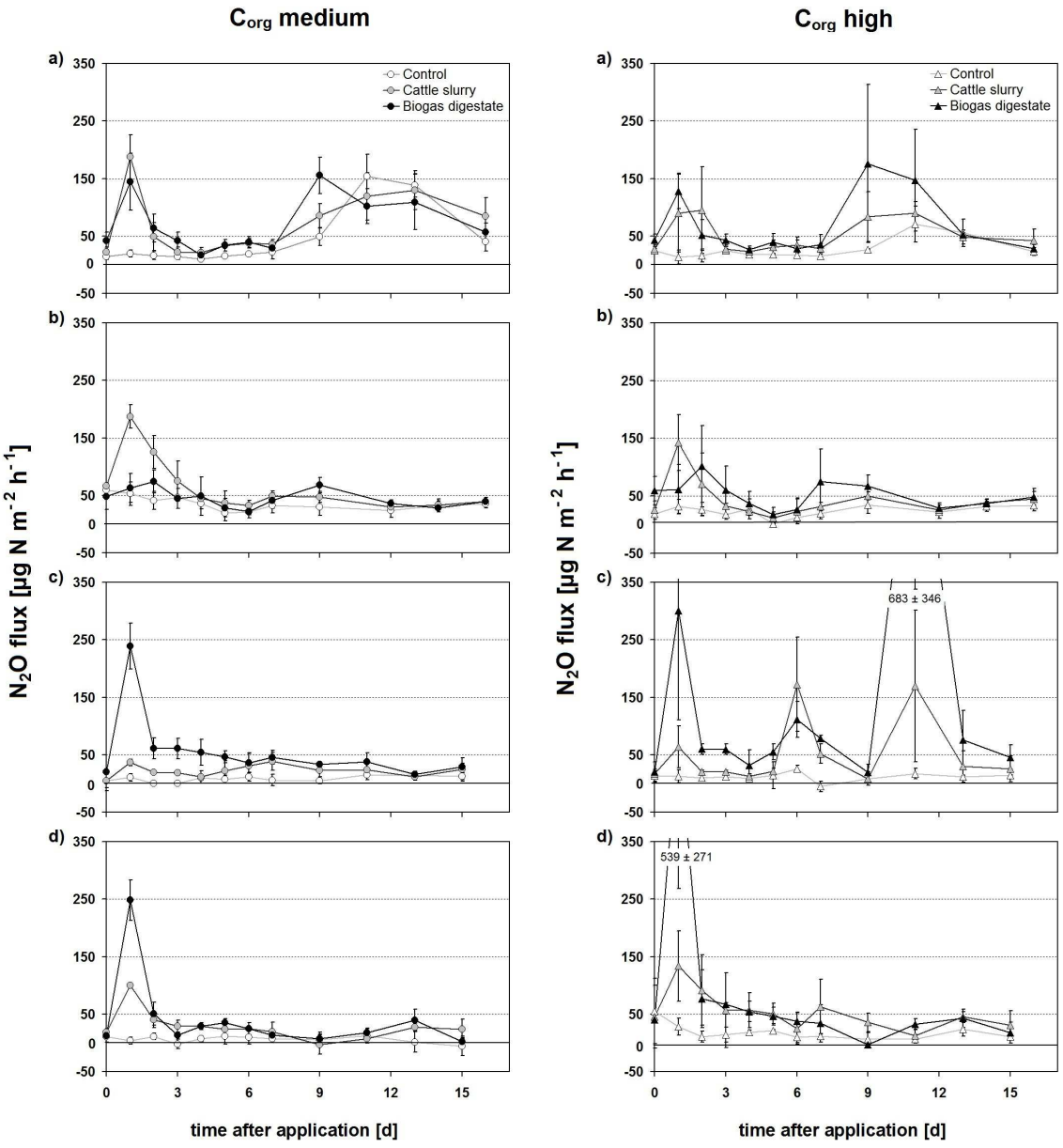

Fig. 3 Mean (± SD, *n* = 3) N_2O fluxes following organic fertilizer application events (a) 14.06–30.06.2010; (b) 25.08.–10.09.2010; (c) 27.05.–11.06.2011 and (d) 22.09.–07.10.2011.

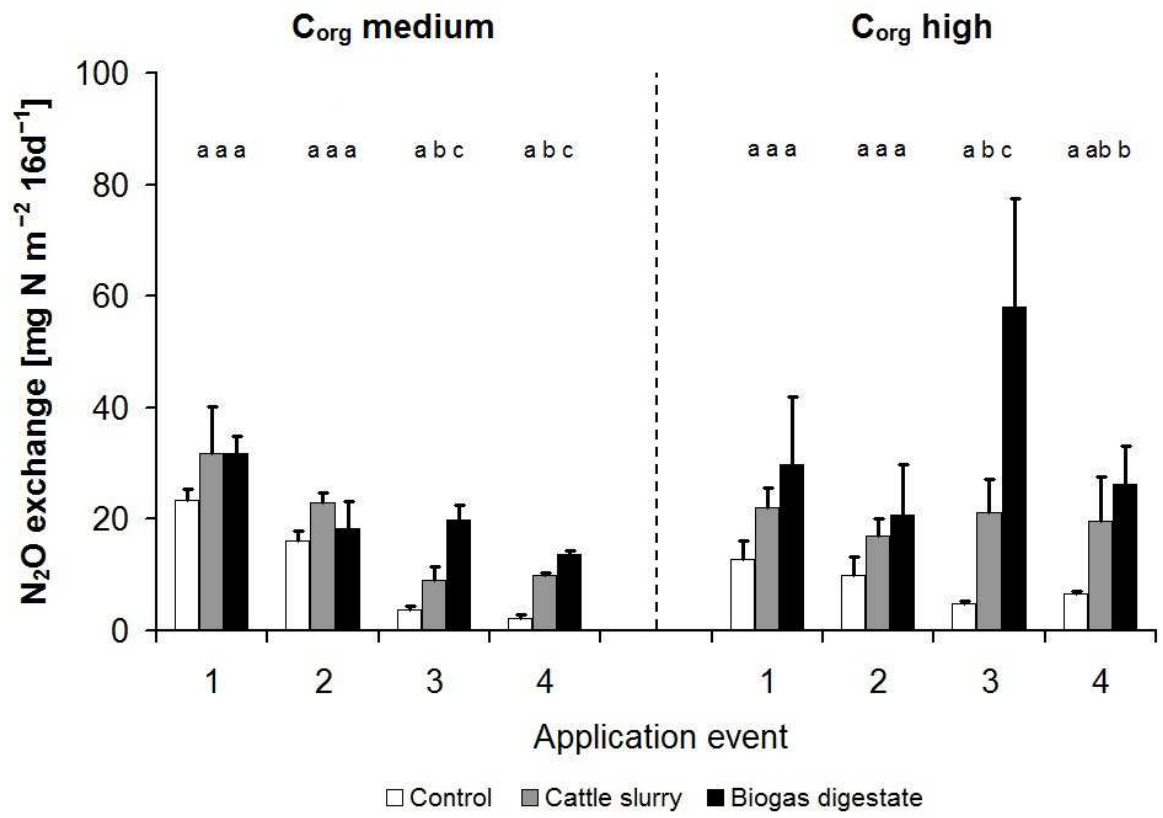

Fig. 4 Cumulative N_2O exchange during 16 days following organic fertilizer application. Bars indicate mean values + SD (n = 3). Means followed by the same letter indicated no significant differences between treatments at a single application event for sites C_{org}-medium and C_{org}-high respectively (ANOVA, Tukey HSD-test at $P \leq 0.05$).

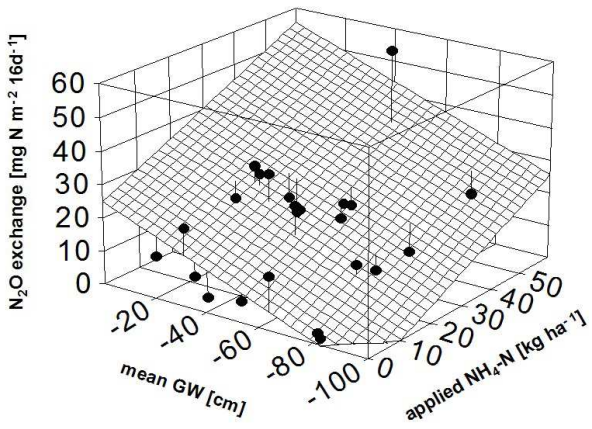

Fig. 5 Relationship of 16 days cumulative N_2O–N emissions (y) to mean groundwater level (x1) and the amount of applied NH_4–N (x2). The regression equation is $y = 24.98 (\pm 4.98) + x1 \cdot 0.30 (\pm 0.09) + x2 \cdot 0.51 (\pm 0.11)$; R^2 *adj.* = 0.53, $P < 0.001$, $df = 21$. Solid lines indicate the deviation of measured data from the model surface.

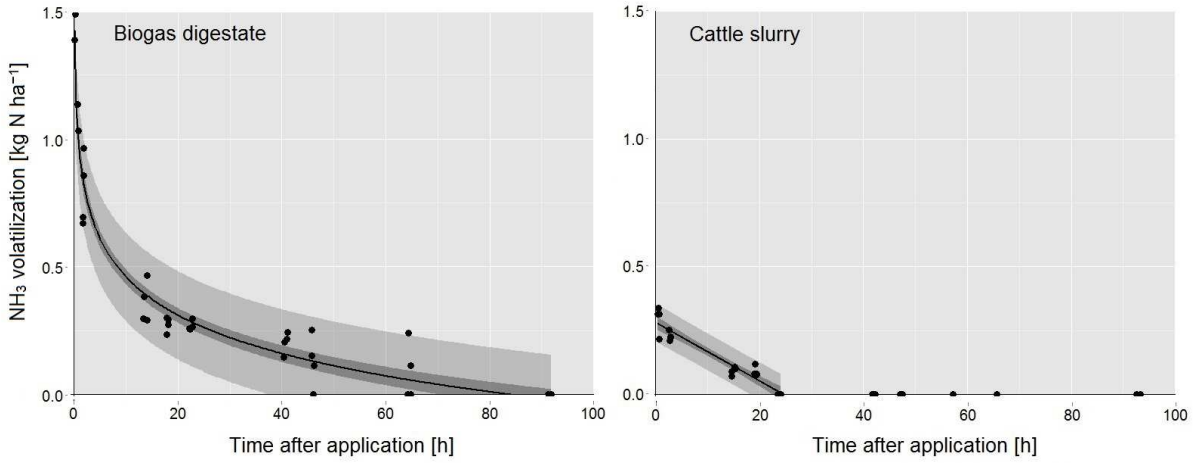

Fig. 6 Ammonia (NH_3) volatilization following organic fertilizer application at event 3 (27.05.2011). Dots present single NH_3 measurements for a time period of 94 hours. Black lines show the estimated NH_3 volatilization with 95% confidence band (dark grey) and 95% prediction band (light grey). Model function for biogas digestate is: y = −0.2619 (± 0.025**)** · ln(x) + 0.9605 (± 0.008); r^2 = 0.96; *P* < 0.0001; Model function for cattle slurry is: y = 0.2818 (± 0.012) − 0.0114(x) (± 0.001); r^2 = 0.92; *P* < 0.0001.