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

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Abstract

The change in the German energy policy resulted in a strong development 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 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 (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) two sites were established, one was fertilized five times with biogas digestate and one with cattle slurry. For each treatment, 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 $0.91 \pm 0.49\,kg\,N\,ha^{-1}\,yr^{-1}$ to $3.14 \pm 0.91\,kg\,N\,ha^{-1}\,yr^{-1}$. 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 $-0.21 \pm 0.19\,kg\,C\,ha^{-1}\,yr^{-1}$ and $-1.06 \pm 0.46\,kg\,C\,ha^{-1}\,yr^{-1}$. Significantly higher NH_3 losses 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

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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 2011, more than 7300 agricultural biogas plants operated in Germany (Fachverband Biogas, 2013). Heat and power from biogas substitute fossil fuels and therefore reduce greenhouse gas (GHG) emissions (Weiland, 2010; Don et al., 2011). The strong development 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 fermantative process high amounts of nutrient rich digestate 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. It is well known that nitrogen fertilizers generally increase nitrous oxide (N_2O) emissions (e.g. Bouwman, 1996; Chadwick et al., 2000; Rhode 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.

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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 small peasant 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 distinctly 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 (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

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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, which is still common practice in the smallholder farms of South Germany.

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. We hypothesize: (a) more N_2O is emitted after biogas digestate than after slurry application because of higher amounts of NH_4^+-N 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) Distinctly more NH_3 volatilizes after surface application of biogas digestate than of cattle slurry.

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

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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) (N. Roßkopf, personal communication, 2013).

2.2 Experimental design

At each area of the grassland parcel, three adjacent sites (site dimension 12 m × 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 cm × 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 h) of air temperature and humidity at 20 cm above soil surface, soil temperatures at the depth of −2, −5 and −10 cm and soil moisture content at −5 cm depth. For NH_3 measurements, sensors for wind speed and wind direction in 2 m height were additionally integrated from May to July 2011, with a logging frequency of 5 s. 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

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equipped one tube per site with a water level logger (Type MiniDiver, Schlumberger water services), which logged the water tables every 15 min. 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 on 14 June 2010, 25 August 2010, 27 Mai 2011, 22 September 2011 and 4 November 2011 by the landowners. The surface application technique via splash plate is the most common application technique in the small peasant structure of the region. The organic fertiliser was applied on the basis of equal volumetric rates per application event (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. 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 1 m × 1 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 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 fertilisation events on 14 June 2010, 25 August 2010, 27 Mai 2011, and 22 Septem-

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ber 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 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 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 & 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 °C). Gas samples from the first fertilization event (14 June to 30 June of 2010) were immediately analysed at the Max Planck Institute for Biogeochemistry in Jena, whereas samples from the second fertilization event (25 August to 10 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 $1\,\mathrm{ppb\,min^{-1}}$. The cumulative annual mean exchange rate was calculated by linear interpolation between the measurement dates.

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2.4 NH_3 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 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:

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

where NH_3 $flux_{IHF}$ is NH_3 flux measured by the integrated horizontal flux method ($kg\,N\,ha^{-1}\,h^{-1}$); NH_3 $flux_{DTM}$ 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.

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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 24 Mai 2010, 20 August 2010, 23 Mai 2011, 1 August 2011 and 13 September 2011. To determine the dry mass (DM), grass samples were oven dried at 60 °C for 48 h. To determine the total carbon (C_{tot}) and total nitrogen (N_{tot}) concentrations of plant biomass, dried grass samples were milled (0.5 mm) and mixed sub samples were analysed by the AGROLAB Labor GmbH (Bruckberg, Germany). The apparent N_{tot} or rather N_{min} use efficiency (NUE, NUE_{min}) was calculated as:

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

where N $\text{uptake}_{treatment}$ is the amount of N taken up by the plants in the fertilized treatments, N $\text{uptake}_{control}$ 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:

$$\text{N balance} = (\text{N applied} + (\text{N min}_{t2} - \text{N min}_{t1}) + N_{dep}) - (\text{N uptake} + N_2O_{cum} + NH_{3cum}) \quad (3)$$

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 (6 April 2011; early April represents the beginning of the vegetation period in 2011) and time 2 (18 October 2011; end of October represents the end of the vegetation period in 2011) for the soil depth 0–20 cm, N_{dep} is the annual atmospheric N deposition, N uptake is the amount of N taken up by the plants (quantified in harvested biomass), 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.

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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 1/2) and the first 20 mL of the extract were discarded. The solution was frozen at −20 °C until analysis, which was conducted by the AGROLAB Labor GmbH (Bruckberg, Germany). A subsample of 20–30 g was used to determine the gravimetric water content, which was taken into account for the calculation of mineral N concentrations. For determination of C_{tot} and organic carbon (C_{org}) a mixed soil sample of nine individual samples was collected close to each collar at two soil depths (0–10, 10–20 cm) using a 3 cm diameter auger. After drying for 72 h at 40 °C, soil samples were sieved to 2 mm to remove stones and living roots. Analyses were conducted at the Division of Soil Science and Site Science (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–

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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 °C with an annual mean of 8.6 °C in 2011 at both investigated areas. Soil temperature in −2 cm soil depth averaged 10.3 °C at the C_{org}-medium sites and was slightly higher with 10.5 °C at the

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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 °C for application events one to four 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-years mean of the period 1961–1990. Figure 1 shows the precipitation following the fertilizer application.

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 c). 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

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

Short term (16 days) N_2O fluxes of fertilized treatments significantly ($P < 0.01$) exceeded N_2O fluxes of control treatments at all fertilization events. However, only in one out of four fertilization events short term N_2O fluxes were significantly ($P < 0.001$) higher at the digestate treatments compared to the slurry treatments. Additionally significantly ($P < 0.001$) higher short term N_2O fluxes were observed at the C_{org}-high sites compared to the C_{org}-medium sites 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) cumulative N_2O emissions were not significantly different from the control treatments in 2010 (Fig. 4), but for 2011 short term cumulative N_2O 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_2O fluxes compared to unfertilized treatments. Additionally, the application of biogas digestate significantly ($P < 0.01$) enhanced the N_2O fluxes compared to the application of cattle slurry. Furthermore, N_2O fluxes from the C_{org}-high site significantly ($P < 0.001$) exceeded N_2O fluxes from the C_{org}-medium sites. Annual cumulative emissions ranged from 0.91 ± 0.49 kg N $ha^{-1} yr^{-1}$ (control treatment, C_{org}-medium site) to

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$3.14 \pm 0.91\,kg\,N\,ha^{-1}\,yr^{-1}$ (digestate treatment, C_{org}-high site) (Table 4). Calculated emission factors (EF) based on the amount of N_{tot} ranged from 0.12 to 0.23 for the slurry treatments and from 0.55 to 1.13 for the digestate treatments (Table 4).

Observed N_2O fluxes could not be explained by any of the measured environmental drivers. However, 53 % of the temporal and spatial variation in the 16 days cumulative N_2O-N exchange rates was explained by the amounts of applied NH_4^+-N and the mean groundwater levels below surface during the same time (Fig. 5). A similar trend was observed for the annual cumulative N_2O emissions but regression analysis was not possible due to the small sample size (n = 6).

3.4 CH_4 emissions

Most of the time, CH_4 emissions could not be detected (Fig. 2e). Occasionally CH_4 peaks were only found immediately after cattle slurry application. However, with 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 $-0.21 \pm 0.19\,kg\,C\,ha^{-1}\,yr^{-1}$ to $-1.06 \pm 0.46\,kg\,C\,ha^{-1}\,yr^{-1}$. 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 h, 64 % and 100 % of total NH_3 losses occurred at the digestate and slurry treatments, respectively. Since differences in the response of NH_3 volatilization were not significant, treatment data were pooled by soil type prior to regression analysis. The total NH_3 loss following application was $18.17\,kg\,N\,ha^{-1}$ for the digestate treatments and $3.48\,kg\,N\,ha^{-1}$ for the slurry treatments. The relative N loss was 36 % and

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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 Fertilizer effect on N-availability, N-transformation and N use efficiency

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

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(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 stronger 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), narrower NH_4^+/N_{tot} ratios and thus relative higher NH_4^+ contents than the cattle slurries (Möller and Stinner, 2009). However, the absolute content of NH_4^+ was not distinct 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 can assume well aerated soil conditions, at least in the upper soil layer, for most of the time at the study sites.

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 be-

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comes also evident 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 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 narrower 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 (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). Nevertheless, 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). However, 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. 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 the SOM mineralization, leading to additional N_{min}. This becomes also evident in the observed significantly higher NO_3^- contents of the fertilized treatments compared to the unfertilized control treatments, especially in the 0–10 cm soil layer. However, significant differences in the N_{min} contents between the two investigated organic fertilizers were not found in 2010 and 2011. This may be due to the fact that the N uptake from digestate treatments was on average 27 % higher and that distinct differences in the amount of

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N_{tot} and NH_4^+ of the applied organic fertilizers were only observed in the second study year. 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.

To maintain soil fertility and yield and to reduce harmful side effects (e.g. N_2O losses, NO_3^- leaching) site adapted fertilization is necessary. The estimated negative N balances for biogas treatments are in line with Andres et al. (2013) who reported that positive N balances could only be achieved when the amount of applied digestate contains more than 200 kg N ha^{-1} yr^{-1}. However, the strong negative N balances of the control treatments reveal that large amounts of up to 148 kg N ha^{-1} yr^{-1} originate from peat mineralization, demonstrating the unsustainable agricultural use of drained peatlands. Assuming that the fertilized treatments received equal amounts of N from peat mineralization, all N balances of these treatments were strongly positive. N surpluses as estimated for the cattle slurry treatments enhance the soil N pool, but the gradual release of N at a non predictable stage from the soil N pool carries the risk of leaching or gaseous losses (Amon et al., 2006). Particularly in wintertime, high amounts of available NO_3^- in the soil, as observed especially at the fertilized treatments of the C_{org}-high sites, carry the risk of N leaching due to the reduced N demand by plant uptake and by the microbial community during this time (Merino et al., 2002; Sänger et al., 2010).

4.2 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, 1998; Beetz et al., 2013). Also investigations from other European countries showed

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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.

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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;

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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).

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4.3 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 lowering of the groundwater level. Nevertheless, significant differences in the amount of the annual CH_4 uptake capacity between the two study sites C_{org}-medium and C_{org}-high could not be seen, although distinct differences in the groundwater table were observed.

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

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of CH_4 emissions from applied organic fertilizers in the GHG balance of agricultural grasslands (Wulf et al., 2002; Amon et al., 2006; Dietrich et al., 2012).

4.4 N-losses by NH_3 volatilization

The NH_3 losses measured after splash plate application at the third application event followed the typical pattern of lost ammonia (Clemens et al., 2006), particularly at the digestate treatments. According to our hypothesis, significantly higher NH_3 losses from treatments fertilized with biogas digestate were observed compared to those fertilized with cattle slurry. This is in line with several other studies (Amon et al., 2006; Möller and Stinner, 2009; Ni et al., 2011). The higher NH_3 losses from treatments fertilized with biogas digestate could be attributed to the higher amount of NH_4^+ and the distinctly higher pH value of the applied digestate compared to the cattle slurry at the third fertilization event.

A large part of the organic fertilizer remained on the plant canopy and thus soil contact and infiltration was limited after spreading. We conclude that this was also the main reason why no significant differences in the pattern of NH_3 volatilization between the soil types were observed in the present study.

The observed relative N losses of 15–36 % of applied NH_4-N, were in the range reported in the literature (Sommer et al., 1996; Clemens et al., 2006; Quakernack et al., 2011). This demonstrates that NH_3 volatilization is quantitatively the most important N-loss from slurry application, as was also proposed by Flessa and Beese (2000). Beside the negative effects of eutrophication and acidification of ecosystems (Dragosits et al., 2002; Sanderson et al., 2006; Ni et al., 2011), distinct NH_3 volatilization decreases the N fertilizer use efficiency. One of the most effective measures to reduce NH_3 emissions from grassland is the incorporation of slurry (Rodhe et al., 2006). However, several studies reported a considerable increase of greenhouse gases (GHG), mainly N_2O, after injection of slurries and biogas digestates (Dosch and Gutser, 1996; Flessa and Beese, 2000; Wulf et al., 2002). However, up to date no study has examined the effect of the injection technique on organic soils.

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5 Conclusion

We studied N_2O, CH_4 and NH_3 fluxes after splash plate application of biogas digestate and cattle slurry in a region known for its risk of high N_2O and NH_3 emissions and we were the first to study digestate application on high organic carbon soils with 10 to 17 % C_{org} content in the topsoil. To our surprise, N_2O emissions remained lower than typical rates and EFs observed on mineral soils in the vicinity of the sites. We attributed the low N_2O emissions to a mild winter without clear freeze–thaw cycles, but maybe also to frequent application with low dosage of N, which was quickly taken up by the grass vegetation, as 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.

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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[2]		4.1	4.2	
Total nitrogen [%][2]		1.0	1.5	
Organic carbon [%]	0–10 cm	10.3 ± 0.2	17.0 ± 0.1	9
	10–20 cm	9.3 ± 0.2	16.3 ± 0.2	9
Bulk density [g cm^{-3}]	0–10 cm	0.79 ± 0.02	0.54 ± 0.02	18
	10–20 cm	0.90 ± 0.01	0.64 ± 0.01	18
Porosity [%]	0–10 cm	71 ± 1	78 ± 1	18
	10–20 cm	67 ± 1	72 ± 0	18

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

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

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

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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 Control	C_{org}-medium Cattle slurry	C_{org}-medium Biogas digestate	C_{org}-high Control	C_{org}-high Cattle slurry	C_{org}-high Biogas digestate	*n*
1 Application (14 Jun–30 Jun 2010)								
GW level [cm]		−32 (−62/−2)	−39 (−60/−5)	−31 (−58/−2)	−21 (−46/−1)	−26 (−45/−7)	−33 (−45/−19)	
NO_3^- [mgNkg^{-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^+ [mgNkg^{-1}]	0–10	0 (0/1)	0 (0/1)	0 (0/1)	1 (0/2)	1 (0/6)	1 (0/3)	12
	10–20	0 (0/1)	0 (0/1)	0 (0/1)	0 (0/2)	1 (0/11)	1 (0/2)	12
2 Application (25 Aug–10 Sep 2010)								
GW level [cm]		−64 (−70/−49)	−58 (−63/−42)	−57 (−63/−40)	−36 (−40/−37)	−40 (−46/−22)	−37 (−43/−15)	
NO_3^- [mgNkg^{-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^+ [mgNkg^{-1}]	0–10	0 (0/0)	2 (0/17)	0 (0/0)	3 (0/32)	0 (0/1)	1 (0/5)	12
	10–20	1 (0/10)	0 (0/0)	0 (0/1)		0 (0/1)	1 (0/3)	12
3 Application (27 May–11 Jun 2011)								
GW level [cm]		−82 (−94/−57)	−76 (−89/−52)	−80 (−97/−46)	−41 (−60/−11)	−47 (−62/−16)	−49 (−62/−16)	
NO_3^- [mgNkg^{-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^+ [mgNkg^{-1}]	0–10	0 (0/2)	2 (0/10)	21 (0/104)	0 (0/1)	1 (0/5)	10 (0/47)	12
	10–20	0 (0/1)	1 (0/2)	6 (0/26)	1 (0/2)	1 (0/3)	4 (0/12)	12
4 Application (22 Sep–7 Oct 2011)								
GW level [cm]		−83 (−87/−72)	−77 (−81/−70)	−76 (−83/−58)	−54 (−60/−33)	−55 (−58/−46)	−53 (−57/−41)	
NO_3^- [mgNkg^{-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^+ [mgNkg^{-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^- [mgNkg^{-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^+ [mgNkg^{-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^- [mgNkg^{-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^+ [mgNkg^{-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

* Period of record started in 2010 at 2 April.

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Table 4. Calculated emission factors (EF) for the year 2011 and for single application events (16 days) (Appl. 1–Appl. 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 Appl. 1		0.18	0.17		0.20	0.35
EF Appl. 2		0.11	0.05		0.11	0.21
EF Appl. 3		0.08	0.21		0.23	0.68
EF Appl. 4		0.09	0.33		0.15	0.56

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

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

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Table 6. Estimated nitrogen balance for the year 2011.

Treatment	N applied [kg N ha^{-1} yr^{-1}]	$N_{min}t1$[a] [kg N ha^{-1}]	$N_{min}t2$[a] [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[b] [kg N ha^{-1} yr^{-1}]	N balance [kg N ha^{-1} yr^{-1}]
Control C_{org}-medium	0	27.5	29.4	7.2	130	0.9	0.0	−122.4
Control C_{org}-high	0	22.8	27.7	7.2	159	1.2	0.0	−148.0
Cattle slurry C_{org}-medium	252	35.7	51.2	7.2	157	1.2	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

[a] Reference date for $t1$ is the 6 April 2011 and for $t2$ the 18 October 2011.
[b] 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).

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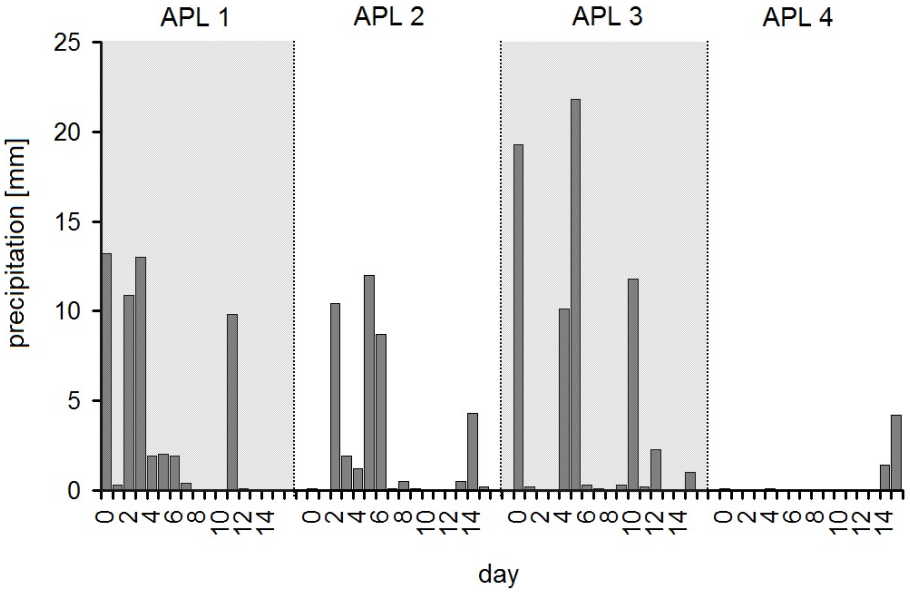

Fig. 1. Daily sums of precipitation following the organic fertilizer application events.

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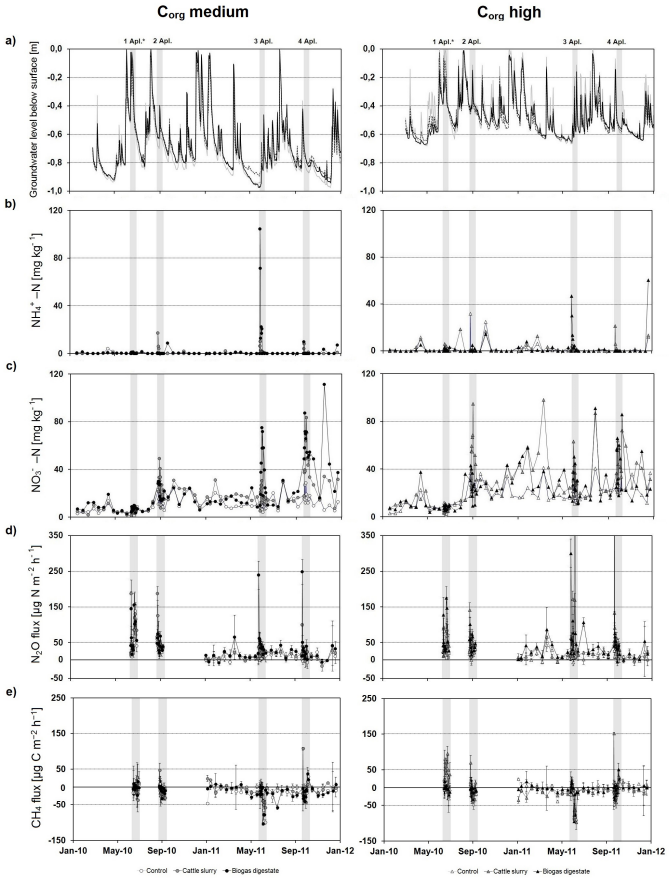

Fig. 2. Variation in groundwater level **(a)**, extractable NH_4^+ **(b)** and NO_3^- **(c)** contents for the soil depth 0–10 cm, N_2O **(d)** and CH_4 fluxes **(e)** (Mean ± SD, $n = 3$) of the C_{org}-medium and C_{org}-high sites from January 2010 to January 2012. Gray bars marke the 15 or 16 days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

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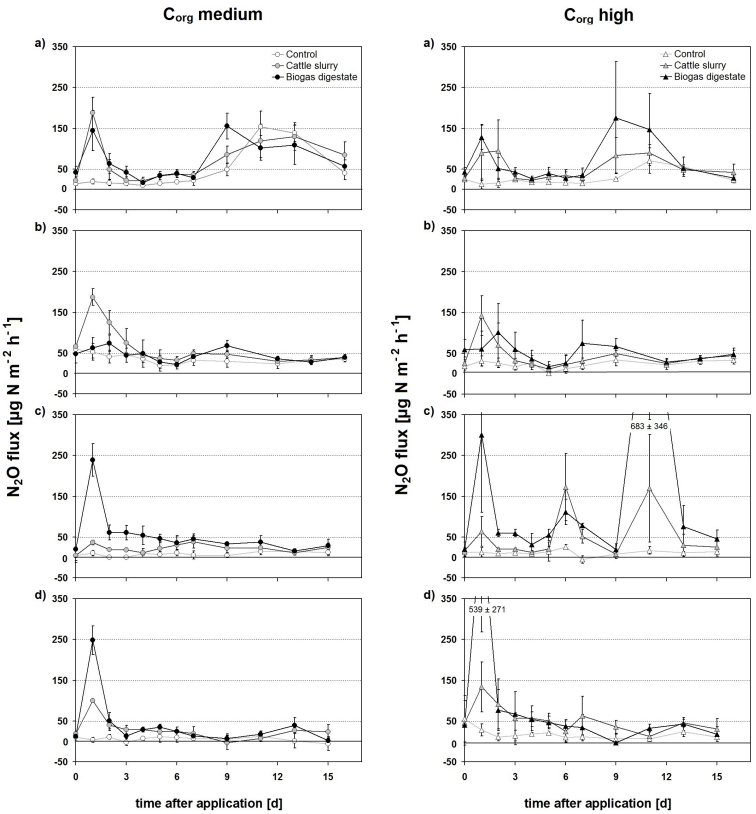

Fig. 3. Mean (±SD, $n = 3$) N_2O fluxes following organic fertilizer application events **(a)** 14 June–30 June 2010; **(b)** 25 August–10 September 2010; **(c)** 27 May–11 June 2011 and **(d)** 22 September–7 October 2011.

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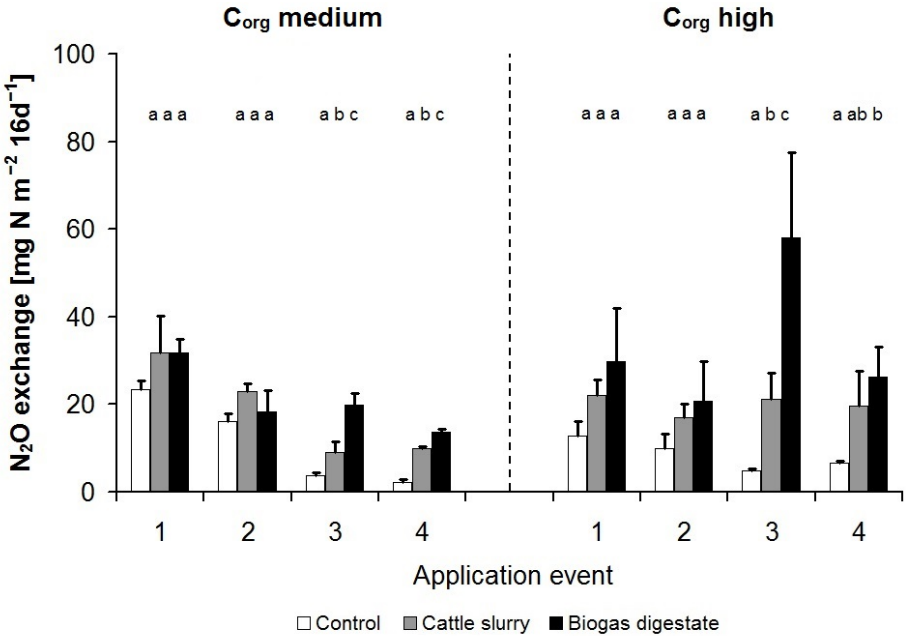

Fig. 4. Cumulative N_2O exchange during 16 days following organic fertilizer application. Bars indicate mean values + SD (n = 3). Means followed by the same letter indicated no significant differences between treatments at a single application event for sites C_{org}-medium and C_{org}-high respectively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

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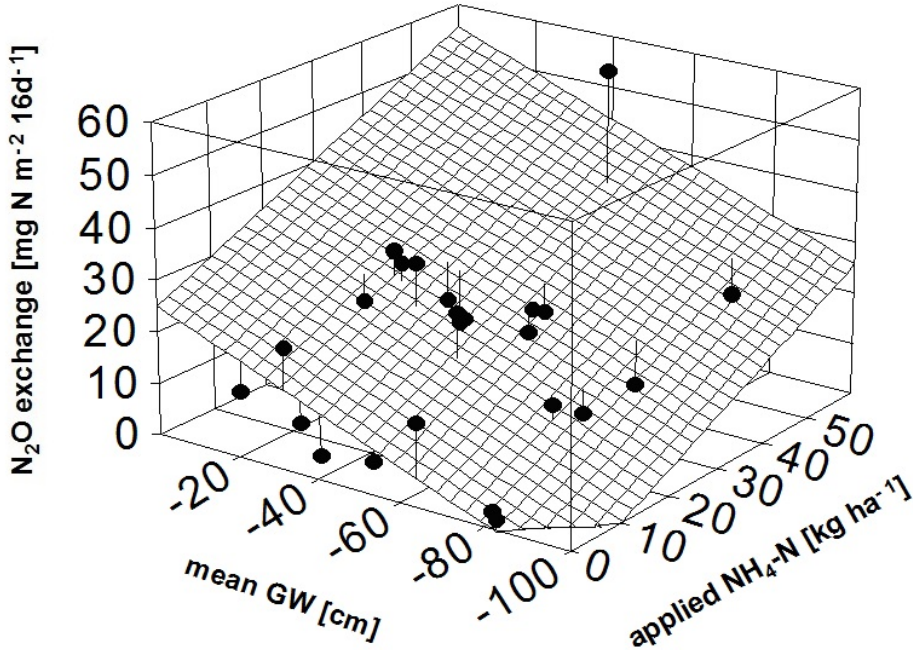

Fig. 5. Relationship of 16 days cumulative N_2O-N emissions (y) to mean groundwater level ($x1$) and the amount of applied NH_4-N ($x2$). The regression equation is $y = 24.98(\pm 4.98) + x1 \cdot 0.30(\pm 0.09) + x2 \cdot 0.51(\pm 0.11)$; R^2 adj. = 0.53, $P < 0.001$, df = 21. Solid lines indicate the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

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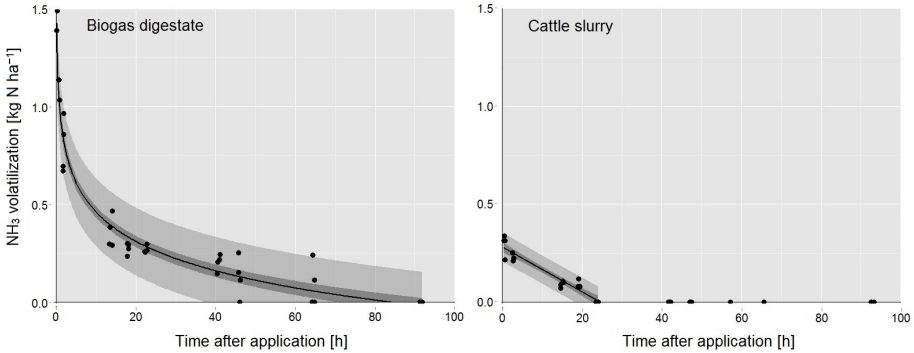

Fig. 6. Ammonia (NH_3) volatilization following organic fertilizer application at event 3 (27 May 2011). Dots present single NH_3 measurements for a time period of 94 h. Black lines show the estimated NH_3 volatilization with 95 % confidence band (dark grey) and 95 % prediction band (light grey). Model function for biogas digestate is: $y = -0.2619(\pm 0.025) \cdot \ln(x) + 0.9605(\pm 0.008)$; $r^2 = 0.96$; $P < 0.0001$; Model function for cattle slurry is: $y = 0.2818(\pm 0.012) - 0.0114(\pm 0.001)$; $r^2 = 0.92$; $P < 0.0001$.

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