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

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## Abstract

The change in the German energy policy has resulted in a strong increase in the number of biogas plants in Germany. As a consequence, huge amounts of nutrient rich residues, the by-products of the fermentative process, are used as organic fertilizers. Drained peatlands are increasingly used to satisfy the huge demand for fermentative substrates (e.g. energy-crops, grass silage) and the digestate is returned to the peatlands. However, drained organic soils are considered as hot spots for nitrous oxide ($N_2O$) 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 $N_2O$ and methane ($CH_4$) fluxes as well as the mineral nitrogen use efficiency ($NUE_{min}$) and grass yield, and b) how different soil organic matter contents (SOM) and nitrogen (N) contents promote the production of $N_2O$. In addition $NH_3$ volatilization was determined at one application event to obtain first clues with respect to the effects of

soil and fertilizer types. The study was conducted at two sites within a grassland parcel, which differed in their soil organic carbon (SOC) and N contents. At each site (named $C_{org}$-medium and $C_{org}$-high) three plots were established, one was fertilized five times with biogas digestate, one with cattle slurry and the third served as control plot. On each plot, fluxes of $N_2O$ and $CH_4$ were measured on three replicates 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 plant N-uptake and $NUE_{min}$. 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 the splash plate application were 18.17 kg N $ha^{-1}$ for the digestate treatments and 3.48 kg N $ha^{-1}$ for the slurry treatments (36% and 15% of applied $NH_4^+$-N). The observed linear increase of 16 days cumulative $N_2O$-N exchange or rather annual $N_2O$ emissions, with mean groundwater level and ammonium application rate, 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 have been operated in Germany (Fachverband Biogas, 2014). Heat and power from biogas substitute fossil fuels and therefore can 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 represented the second most important fermentation substrate after maize silage.

During the fermentative process high amounts of nutrient rich residues are produced as a by-product. Today, this new form of organic fertilizer is used instead of mineral fertilizers or animal slurries to maintain soil fertility and productivity. Several studies reported a significant increase in nitrous oxide ($N_2O$) emissions due to the application of nitrogen fertilizers (e.g. Bouwman, 1996; Chadwick et al., 2000; Rodhe et al., 2006; Ruser, 2010). Liquid organic fertilizers such as animal slurry add easily degradable organic carbon (Christensen 1983) and moisture, both further favoring $N_2O$ losses through denitrification (Clayton et al., 1997). Enhanced $N_2O$ emissions are of major concern 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 78% of $N_2O$ emissions originate from the agricultural sector (Umweltbundesamt, 2014). 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, 50% of the drained peatlands are used as grasslands (Drösler et al., 2011), particularly in the smallholder structure of south Germany. Grassland soils in Europe and Germany produce more $N_2O$ 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.

99 Biogas digestate is depleted in easily degradable C compounds and in organic dry
100 matter content compared to fresh slurry due to anaerobic digestion (Möller and
101 Stinner, 2009). In return, the pH value and the ammonium ($NH_4^+$) content as well the
102 $NH_4^+/N_{org}$ ratio are higher than in fresh slurry (Wulf et al., 2002a; Möller and Stinner,
103 2009). Since digested products are more recalcitrant than fresh slurry it could be
104 assumed that microbial degradation is slow, resulting in less anoxic microsites and
105 reduced $N_2O$ emissions than after fresh slurry application (Clemens and Huschka,
106 2001; Oenema et al., 2005; Möller and Stinner, 2009). However, the few available
107 field and laboratory experiments are contradictory regarding the effect of biogas
108 digestate application on $N_2O$ emissions (e.g. Clemens and Huschka, 2001; Wulf et al.,
109 2002a; Clemens et al., 2006; Senbayram et al.,2009; Sänger et al., 2010), and very
110 few studies exist for grasslands (e.g. Wulf et al., 2002a, Clemens et al., 2006).
111 The different properties of biogas digestate and cattle slurry (e.g. higher $NH_4^+$-N
112 concentrations, narrower C/N ratio, higher pH values) directly affect N transformation
113 processes, plant N availability and thus grass yield. Furthermore it can be assumed
114 that the plant N-uptake and the $N_2O$ emissions are closely interconnected since N-
115 uptake can be considered as a proxy for N availability, affecting N gaseous losses as
116 well. Currently, the effect of anaerobic digestates on crop growth after surface
117 application under field conditions is contradictory, since some authors reported
118 higher crop yields compared to undigested slurries (e.g. Odlare, 2005 cited in Möller
119 an Müller, 2012) whereas others found no effects (e.g. Möller et al., 2008). However,
120 only a few studies exist for grassland but it seems that fertilization with biogas
121 digestates positively affects grass yields, but only in single years (Elsässer et al.,
122 1995; Rubæk et al., 1996; Möller et al., 2008; Möller and Müller, 2012).
123 Beside $N_2O$, slurry application also releases short-term methane ($CH_4$) and ammonia
124 ($NH_3$) emissions. Methane acts as strong greenhouse gas, whereas $NH_3$ is
125 considered as indirect greenhouse gas through ammonia deposition which could
126 promote the formation of $N_2O$ (Moiser, 2001). Moreover, $NH_3$ deposition causes soil
127 acidification and eutrophication of ecosystems (e.g. Fangmeier et al., 1994; Galloway,
128 1995; Smith et al., 1999; Galloway, 2001). In Germany, agriculture is responsible for
129 95.3% of the anthropogenic $NH_3$ emissions (Haenel et al., 2010). Particularly high
130 $NH_4^+$ contents and high pH values, which are typically for the biogas digestate,
131 promote accelerated $NH_3$ volatilisation (Quakernack et al., 2011). High $NH_3$
132 emissions particularly occur after splash plate application on grassland (Rubæk et al.,

1996; Wulf et al., 2002b), which is still common practice in the smallholder farms of South Germany.

The objective of this study was to quantify short-term $N_2O$ and $CH_4$ emissions after application of biogas digestate and cattle slurry on grassland on two types of organic soils in South Germany, which differed in their soil organic carbon (SOC) and N contents. Additionally it should be tested to what extent biogas digestate and cattle slurry application affect N availability and grass yield. Furthermore $NH_3$ volatilization was determined at one application event to obtain first clues with respect to the effects of soil and fertilizer types. 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 and thus, higher $NH_4^+$-N amounts when using equal volumetric application rates. The more recalcitrant nature of the carbon in the biogas digestate does not matter for GHG formation in high organic carbon soils. b) $N_2O$ emissions increase with increasing soil $C_{org}$ and N content due to more favorable conditions for denitrification after organic fertilizer application. c) Biogas digestate leads to a significantly higher grass yield and N-use efficiency compared to cattle slurry due to the higher N availability of the digestate.

# 2. Materials and methods

## 2.1. Study site

The study was conducted on a permanent grassland at a drained fen peatland 30 km 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 practice in this region. A summary of the complete grassland management over both vegetation periods can be found in Table 1. The grass was used as silage or hay for cattle or as substrate for biogas plants. According to the climate station in Weihenstephan, located 10 km northeast of the site, the 30-years mean annual temperature was 7.5 ℃ 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 sites within the grassland parcel, which differed in their soil organic carbon (SOC) contents in the top soil (Table 2). According to the WRB (2006) soil types were classified as mollic Gleysol (named $C_{org}$-medium) and as sapric Histosol (named $C_{org}$-high) (Roßkopf personal communication).

## 2.2. Experimental design

At each site of the grassland parcel, three adjacent plots (plot dimension 12 x 12 m) were selected. At one plot biogas digestate and at another plot cattle slurry was applied, whereas the third plot served as control (whitout fertilization). Centrally at each plot, three PVC-collars for GHG measurements (inside dimension 75 x 75 cm; 0.5625 $m^2$) were permanently inserted 10 cm into the soil with a distance of 1.5 m to each other. To prevent oscillations of the peat through movements during the measurements, boardwalks were installed. At each site a climate station was set up in March 2010 for the 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) and soil temperatures at the depth of −2, −5 and –10 cm (109-L, Campbell Scientific). 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 to obtain individual groundwater tables for all repetitions during each gas flux measurement. In April 2010, we equipped one tube per plot with a water level logger (Type MiniDiver, Schlumberger water services), which logged the water tables every 15 minutes. Additionally to the recorded data, plot-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 14$^{th}$ June 2010, 25$^{th}$ August 2010, 27$^{th}$ Mai 2011, 22$^{th}$ September 2011 and 04$^{th}$ November 2011 by the landowners (see Table 1). The surface application technique via splash plate is the most common application technique in the smallholder structure of the region. The organic fertiliser was applied on the basis of equal volumetric rates per application event (20 or 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 precision in their application evenness compared to conventional splash plates (approximately 15% and 18–27% application variability for swivelling slurry spreader and gooseneck scatterer and up to 47% for conventional splash plate; Frick, 1999). In the present study, the application of an equal volumetric slurry rate was controlled via the barrel content and the tractor speed. At all plots, the tractor lane were 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 precision of the application evenness.

The physical and chemical composition of the slurries and digestates varied between the four different application events (Table 3). 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 ℃ 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 ground of the collars 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 14$^{th}$ June 2010, 25$^{th}$ August 2010, 27$^{th}$ Mai 2011, and 22$^{th}$ 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℃) and a flame ionization de tector (FID) for $CH_4$ analyses (FID temperature 310℃). Gas samples from the first fertilization event (14$^{th}$ June to 30$^{th}$ June of 2010) were immediately analysed at the Max Planck Institute for Biogeochemistry in Jena, whereas samples from the second fertilization event (25$^{th}$ August to 10$^{th}$ 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 27$^{th}$ 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 plot, 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; sample area = 0.5625 m²). There was no visible disturbance from trace gas measurements in the collars. The grassland parcel showed a strong spatial heterogeneity in grass yield so that only sampling inside the collars allowed to relate grass yield and N uptake with $N_2O$ emissions. Mowing events took place on 24$^{th}$ Mai 2010, 20$^{th}$ August 2010, 23$^{th}$ Mai 2011, 01$^{st}$ August 2011 and 13$^{th}$ September 2011 (see Table 1). To determine the dry mass (DM), grass samples were oven dried at 60℃ for 48 hours. 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 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. Emission factors for $NH_3$ were taken from the German national greenhouse gas inventory (Haenel et al., 2014; Table 4.6 – broadcast, grassland, EF of 0.60 kg $kg^{-1}$ related to applied $NH_4^+$-N), whereas for the third application event own estimated values based on our measurements were used.

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 plot during every gas flux measurement. Samples were immediately cooled and stored in an ice box before analyses. Mineral N was extracted after shaking 40 g of fresh soil with 160 ml $CaCl_2$ (0.0125 M) for 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 plot.

## 2.7. Statistical analysis

Statistical analyses were conducted using R 2.12.1 (R Development Core Team, 2010). We used analysis of variance (ANOVA) (for grass yield, 16 days cumulative $N_2O$ emissions and treatment $NO_3^-$ comparison) or the nonparametric Kruskal-Wallis Rank Sum test (for GW level) to compare means of samples. In case of significant differences among the means, we used Tukey's honest significant differences (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 collar) nested in time as random effect. Non-significant terms were removed from the fixed structure. We extended the basic model by a variance function when heteroscedasticity was observed. In case of significant serial correlation in data, a moving average or a first-order temporal autoregressive function was included in the model. Autocorrelation was tested using the Durbin-Watson test and by plotting the empirical autocorrelation structure. The model extension was proved by the Akaike Information Criterion (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 4). Mean groundwater levels following the fertilizer applications are shown in Table 4.

## 3.2. N input and N availability

The amount of N applied was 111 and 252 kg N $ha^{-1}$ for slurry treatments 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 (2010) or slightly higher (15% more $NH_4^+$-N; 2011) than for the slurry treatments (Table 3). Additional physical and chemical properties of the slurry and digestate are shown in Table 3.

The extractable $N_{min}$ contents of the soils were dominated by $NO_3^-$ whereas $NH_4^+$ was only of minor importance especially at the $C_{org}$-medium 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 4). 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 4). 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 for 0–10 cm soil depth at the $C_{org}$-medium site) (Table 4).

### 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 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, $C_{org}$-

433 medium site) to 3.14 ± 0.91 kg N $ha^{-1}$ $yr^{-1}$ (digestate treatment, $C_{org}$-high site) (Table
434 5). Calculated emission factors (EF) based on the amount of $N_{tot}$ ranged from 0.12 to
435 0.23 for the slurry treatments and from 0.55 to 1.13 for the digestate treatments
436 (Table 5).
437 Observed collar specific cumulative annual $N_2O$ fluxes were strongly related to collar
438 specific annual plant N-uptake (Fig. 5a and 5b). 53% of the temporal and spatial
439 variation in the 16 days cumulative $N_2O$-N exchange rates was explained by the
440 amounts of applied $NH_4^+$-N and the mean groundwater levels below surface during
441 the same time (Fig. 6). A similar trend was additionally observed for the annual
442 cumulative $N_2O$ emissions but regression analysis was not possible due to the small
443 sample size ($n$ = 6).

444 ## 3.4. $CH_4$ emissions

445 Most of the time, $CH_4$ emissions could not be detected (Fig. 2e). Occasionally $CH_4$
446 peaks were only found immediately after cattle slurry application. However, with
447 exception of the slurry treatment of the $C_{org}$-high site at the first application event, the
448 organic fertilization did not result in significantly different short term (15 or 16 days)
449 $CH_4$ fluxes between the treatments or the investigated soil types. The observed weak
450 $CH_4$ emissions or uptakes amounted to cumulative annual $CH_4$ exchange rates of
451 −0.21 ± 0.19 kg C $ha^{-1}$ $yr^{-1}$ to −1.06 ± 0.46 kg C $ha^{-1}$ $yr^{-1}$. Significantly different $CH_4$
452 fluxes between the investigated treatments or the different soil types could not be
453 observed regarding the annual fluxes in 2011.

454 ## 3.5. $NH_3$ volatilisation

455 Highest $NH_3$ losses were observed immediately after fertilization (Fig. 7). During the
456 first 24 hours, 64% and 100% of total $NH_3$ losses occurred at the digestate and slurry
457 treatments, respectively. Since differences in the response of $NH_3$ volatilization were
458 not significant, treatment data were pooled by soil type prior to regression analysis.
459 The total $NH_3$ loss following application was 18.17 kg N $ha^{-1}$ for the digestate
460 treatments and 3.48 kg N $ha^{-1}$ for the slurry treatments. The relative N loss was 36%
461 and 15% of applied $NH_4^+$-N, or 23% and 5% of total applied N for the digestate and
462 slurry treatments, respectively.

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

In 2010 and 2011, the mean annual grass yield ranged from 4.5 (control $C_{org}$-medium) to 13.1 t DM $ha^{-1}$ $yr^{-1}$ (digestate $C_{org}$-high) (Table 6). In both years the mean annual grass yield from the digestate treatments were significantly ($P < 0.05$) higher compared to the slurry treatments. This pattern was also found in the annual plant N-uptake which showed a clear partitioning between the treatments investigated (Fig. 5a). Additionally, the mean annual grass yield from the $C_{org}$-high 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 6). NUE values were on average 115 ± 136% for biogas digestate treatments and 24 ± 23% for cattle slurry. $NUE_{min}$ values were always >100% for biogas digestate treatments, whereas for cattle slurry $NUE_{min}$ values averaged 74 ± 68% in 2011 but were >100% in 2010. 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 70 kg N $ha^{-1}$ $yr^{-1}$ for cattle slurry treatments but deficits of up to 108 kg N $ha^{-1}$ $yr^{-1}$ for biogas digestate treatments, for the year 2011 (Table 7).

## 4. Discussion

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

Mineral nitrogen contents were consistently higher at the $C_{org}$-high treatments than at the $C_{org}$-medium treatments, in line with the considerably higher amount of SOC and N at this site. It is well known that drainage enhances the degradation of 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. In the present study, the biogas digestates had narrower C/N ratios (see also e.g. Tambone et al., 2009), higher pH values (see also Wulf et al., 2002a and Quakernack et al., 2011), wider $NH_4^+/N_{tot}$ ratios and thus relatively higher $NH_4^+$ contents than the cattle slurries (see also Möller and Stinner 2009). The amounts of $NH_4^+$-N were not distinctly different between the applied organic fertilizers but in 2011 biogas treatments received 15% more $NH_4^+$-N compared to cattle slurry treatments.

We observed an unexpected small change in the $NH_4^+$ content of the soil immediately after fertilizer application which can be attributed to different reasons. Firstly, the fertilizers partly remained on the plant canopy after splash plate application and therefore soil contact and infiltration 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. Thirdly and probably most important, in well aerated soils applied $NH_4^+$ underwent rapid nitrification, as was indicated by the increasing soil $NO_3^-$ contents in the upper soil layer after fertilizer application. 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 controlled 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.

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 by plants at the digestate treatments was on average 27% higher and that distinct differences in the amount of $N_{tot}$ and $NH_4^+$ of the applied organic fertilizers were only observed in the second study year.

To maintain soil fertility and yield and to reduce harmful side effects (e.g $N_2O$ 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 period (Merino et al., 2002; Sänger et al., 2010).

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

In line with investigations from Schils et al. (2008) most of the applied and produced $N_{min}$ was probably rapidly absorbed by the grassland as the soil $N_{min}$ content usually decreased within a few days after fertilizer application (Figure 2b, 2c). This becomes 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 was 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 microbial immobilization of applied N (Velthof et al., 2003, de Boer, 2008). We hypothesized that the application of biogas digestate leads to a significantly higher grass yield and N-use efficiency compared to the application of cattle slurry due to the higher N availability of the digestate. This could partly be confirmed, but the much higher grass yields from biogas digestate treatments cannot solely be explained by differences in applied $NH_4^+$, since differences were only small. However, the much higher N-uptake at the digestate treatments (Fig. 5a) indicated that much more N must have been

available at these treatments. Many studies have shown that the utilization of N derived from organic fertilizer is relatively small in the year of application, due to the slow release of organically bound N (Jensen et al., 2000; 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 or fertilizer had a larger share in the uptake by the plants due to lower competition of microbial immobilization as was reported by Gutser et al. (2010). Probably the assumed higher SOM mineralization at the digestate treatments could partly be related to a priming effect since the higher biomass production probably caused a higher release of root exudates, containing easily available C and N which enhanced microbial activity (Mounier et al. 2004; Henry et al. 2008) promoting SOM mineralisation. However, further investigations are needed to prove this explanation. 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.

### 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 $ha^{-1}$ $yr^{-1}$ (; Flessa et al., 1997; Augustin et al., 1998; Flessa et al., 1998; Beetz et al., 2013). Also investigations from other European countries showed that much higher $N_2O$ emissions can be released from grasslands on drained peatlands. For example, Velthof et al. (1996) and van Beek et al. (2010; 2011) reported $N_2O$ emissions, ranging from 4.2 to 41.0 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. Additionally, the observed distinctly stronger increase of cumulative annual $N_2O$ emissions with increasing N-uptake by plants (Fig. 5b) reveals that with increasing N availability a higher proportion is lost as $N_2O$ at the $C_{org}$-high sites compared to the $C_{org}$-medium sites. 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 also reported 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 so far not for organic soils. Indeed, $N_2O$ studies on organic soils rarely differentiate between fertilizer and soil derived N sources by unfertilized control plots as we do in this study. In line with Möller and Stinner (2009) the application of biogas digestate resulted in a distinctly higher percentage of $N_2O$ produced from applied N, compared to cattle slurry, yet at a low level.

One reason of generally low $N_2O$ emissions observed in the present study could be the small number of frost–thaw cycles in 2011. In general frost–thaw cycles are

631 considered to favor high $N_2O$ emissions (Flessa et al., 1998, Jungkunst et al., 2006)
632 but these observations seem to be more pronounced for croplands than for
633 grasslands in Germany (Dechow and Freibauer, 2011). Denitrification activity is
634 strongly related to the $NO_3^-$ content close to the groundwater level (van Beek et al.,
635 2004). Given the high $NO_3^-$ contents, in particular in the $C_{org}$-high soil, the evidence
636 for fast nitrification and high net nitrogen mineralization, we argue that frequent but
637 low dosage application of fertilizer and quick N uptake by plants avoid conditions
638 favorable for high $N_2O$ emissions. Moreover through the splash plate application
639 technique high amounts of $NH_4^+$ where rapidly lost as $NH_3$, and therefore reduced the
640 proportion of immediately available N for nitrification and denitrification.
641 As expected from the literature, highest $N_2O$ fluxes were found immediatly after
642 fertilizer application. The initial $N_2O$ peak could mainly be attributed to the
643 denitrification of available soil $NO_3^-$, presumably due to the more favorable conditions
644 for denitrification through the addition of easily degradable organic C and water
645 (Comfort et al., 1990; Chadwick et al., 2000; Velthof et al., 2003). Additionally, a
646 probably smaller part of initial $N_2O$ could be ascribed to the rapid nitrification
647 (Chadwick et al., 2000) or to nitrifier denitrification of slurry $NH_4^+$. In contrast, the
648 partially observed second $N_2O$ peak, mostly found a week after fertilizer application,
649 can be attributed to the denitrification of mineralized and nitrified organic components
650 of fertilizer N (Velthof et al., 2003).
651 Several authors proposed that the more recalcitrant digestate might reduce the rate
652 of microbial degradation and oxygen consumption in the soil, thus resulting in
653 reduced $N_2O$ emissions through less anaerobic soil conditions (Clemens and
654 Huschka, 2001; Oenema et al., 2005; Möller and Stinner, 2009). In contrast, our
655 study on organic soils found significantly higher $N_2O$ emissions from the digestate
656 treatments compared to the slurry treatments. Higher $N_2O$ emissions derived from
657 biogas digestates were also reported from a few other authors (e.g. Senbayram et al.,
658 2009; Sänger et al., 2010), whereas Clemens et al. (2006) found no differences
659 between untreated and digested slurry.
660 It can be assumed that at drained organic soils, like in the present study, sufficient
661 metabolizable C is generally widely available in the upper soil profile (e.g. van Beek
662 al., 2004). Thus, as hypothesized, labile carbon is not limiting on organic soils. This
663 was in line with Velthof et al. (2003) who supposed that the application of available C
664 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. Nevertheless, as mentioned before, the much higher N-uptake at the biogas treatments (Fig. 5a) indicates that the application of this fertilizer resulted in a distinctively higher N availability, promoting $N_2O$ production. It could be assumed that the high pH and the lower C/N ratio of the biogas digestate, obviously slightly enhanced SOM mineralization probably due to increased microbial activity compared to cattle slurry fertilizer, leading to extra N for nitrification and denitrification. Moreover, as proposed before it is also conceivable that the higher biomass production at these treatments itself is related to the increased $N_2O$ emissions, due to the stimulating effect of plant roots on denitrification activity (Klemedtsson et al. 1987; Bakken, 1988). Considering that increasing biomass production means increasing root growth and activity it could be assumed that exudation of easily available organic C and N (Hailer and Stolp, 1985), as well as the $O_2$ demand due to root respiration is higher at the digestate treatments, promoting more anaerobic microsites and thus denitrification compared to cattle slurry (Erich et al. 1984; Klemedtsson et al. 1987). Furthermore several authors have suggested that root exudates may increase bacterial metabolism (Klemedtsson, 1987; Mounier et al. 2004; Henry et al. 2008), further lowering the oxygen concentration and thus increasing denitrification (Klemedtsson et al., 1987). However, the enhanced biomass production simultaneously should have depleted mineral N in the soil and thus reduced available N for nitrification and denitrification processes. Obviously, despite the negative apparent N balance of the biogas digestate treatment, there was no real nitrogen competition between plants and microbes. However, further investigations are required to prove whether digestates enhanced SOM mineralization or to what extent increased biomass production favors $N_2O$ emissions and which N pathways and processes are involved.

The observed linear increase in the cumulative $N_2O$-N emissions during the first 16 days or annual $N_2O$ emissions, due to a higher mean groundwater level and a higher application rate of $NH_4^+$-N 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 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., 2002a; 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., 2002a). 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 24h 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 of $CH_4$ emissions from applied organic fertilizers in the GHG balance of agricultural grasslands (Wulf et al., 2002a; Amon et al., 2006; Dietrich et al., 2012).

## 4.5. N-losses by $NH_3$ volatilization

The $NH_3$ losses measured after splash plate application at the third application event followed the typical pattern of lost ammonia (Clemens et al., 2006), particularly at the digestate treatments. Significantly higher $NH_3$ losses from treatments fertilized with biogas digestate were observed compared to those fertilized with cattle slurry. This is in line with several other studies (Messner, 1988, Döhler and Haring, 1989 (cited in Döhler and Horlacher, 2010); Amon et al., 2006; Möller and Stinner, 2009; Pacholski et al., 2010; Ni et al., 2011), whereas Pain et al. (1990), Rubæk et al. (1996), Wulf et al. (2002b) and Clemens et al. (2006) found no differences between anaerobic digested slurries compared to other animal slurries. However, it has to be taken into account that the present results are based only on measurements from a single application event. The observed relative N losses of 36% of applied $NH_4^+$-N at the biogas digestate treatments were in the range reported for liquid slurries and digestates applied via surface application, whereas the significantly lower relative N losses (15%) at the cattle slurry treatments stands in strong contrast to those reported in literature (e.g. Döhler and Haring, 1989 (cited in Döhler and Horlacher, 2010); Smith et al., 2000; Wulf et al., 2002b; Chantigny et al., 2004). However, compared to the EF of 60% used in the German national greenhouse gas inventory both estimated $NH_3$ loss rates were rather low (Haenel et al., 2014). It can be assumed that the higher concentration of $NH_4^+$ ($NH_4^+/N_{tot}$ ratio 0.65 vs. 0.33) and the distinctly higher pH value (7.7 vs. 6.8) of the applied digestate compared to the cattle slurry caused the observed differences in the current study, since temperature and wind speed were equal. According to Sommer and Hutchings (2001) a change in the pH value from 7.7 to 8.0 will double the emission. However, the factors controlling the rise in pH are complex (Sommer and Husted, 1995b cited in Sommer and Hutchings, 2001) and the pH value was not determined after fertilization in the present study. Several authors propose that a lower dry matter content of slurries favors the infiltration into the soil with a subsequent faster decrease of $NH_3$ losses (Sommer et al. 1996; Ni et al. 2011). There over a limited range (slurry DM of 2–5%), $NH_3$ losses increase by approximately 6% for every 1% DM content (Smith et al., 2000). Although the observed dry matter content of the biogas digestates was very low and at the lower end of values reported in literature (e.g. Gutser et al., 2005; Möller et al., 2008; Quarkernack et al., 2011) no corresponding effect was found in the present study as was also reported by Möller and Stinner (2009). According to Döhler and

764 Horlacher (2010) and Smith et al. (2000), water saturated grassland soils as well as
765 very dry grassland soils high in organic matter lead to higher $NH_3$-losses due to the
766 reduced infiltration of slurries. Thus it could be assumed that the infiltration of the
767 slurries was possibly hampered in the current study, removing the effect of the
768 different DM contents, due to the strong rain event which took place before the
769 fertilizer application. The cattle slurry in our experiment had very favorable
770 characteristics for crust formation (high DM content, grass silage diet; Smith et al.
771 2007). Warm weather also supported crust formation after application of cattle slurry,
772 which can effectively inhibit $NH_3$ exchange with the atmosphere and has been
773 proposed as $NH_3$ mitigation measure for slurry storage (Smith et al. 2007). The
774 emission pattern observed in our study on soil with limited infiltration capacity
775 supports the effectiveness of crusts for low $NH_3$ losses. Additionally, at low dosage
776 applications a large part of the organic fertilizer remained on the plant canopy and
777 thus soil contact and infiltration was limited after spreading. We conclude that this
778 was also the main reason why no significant differences in the pattern of $NH_3$
779 volatilization between the soil types were found in the present study. Nevertheless,
780 the distinct lower relative N losses from cattle slurry compared to literature values
781 could not be explained in this way, but $NH_3$ volatilization reported in literature showed
782 a high variability in respect to climatic and soil conditions, slurry composition, and
783 application technique.
784 The observed relative N losses of 15–36% of applied $NH_4^+$-N demonstrates that $NH_3$
785 volatilization is quantitatively the most important N-loss from slurry application, as
786 was also proposed by Flessa and Beese (2000). Beside the negative effects of
787 eutrophication and acidification of ecosystems (e.g. Fangmeier et al., 1994; Galloway,
788 1995; Smith et al., 1999; Galloway, 2001), distinct $NH_3$ volatilization decreases the N
789 fertilizer use efficiency. One of the most effective measures to reduce $NH_3$ emissions
790 from grassland is the incorporation of slurry (Rodhe et al., 2006). However, several
791 studies reported a considerable increase of greenhouse gases (GHG), mainly $N_2O$,
792 after injection of slurries and biogas digestates (Dosch and Gutser, 1996; Flessa and
793 Beese, 2000; Wulf et al., 2002a). Up to date no study has examined the effect of the
794 injection technique on organic soils.

## 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 and EF were lower than generally observed on mineral soils in the vicinity of the sites. We attributed the low $N_2O$ emissions to a mild winter without clear freeze-thaw cycles, but maybe also to frequent application with low dosage of N, which was quickly taken up by the grass vegetation, as was indicated by the apparent $NUE_{min}$. $N_2O$ emissions increased with $C_{org}$ content and fertilization. As hypothesized, $N_2O$ were distinctly higher after digestate than after slurry fertilization, which probably could be attributed to a priming effect caused by increased SOM mineralization or other sources of labile carbon triggered by digestate application. Due to the deep drainage, $CH_4$ emissions were of only minor importance and were independent of fertilizer type. Estimated N balances were negative for the control and the digestate treatments, but strongly positive in all cases when the net N supply from SOM mineralization was considered. The observed linear increase in cumulative $N_2O$ emissions with increasing $NH_4^+$ fertilization and increasing groundwater table reveals the importance of site adapted N fertilization and the avoidance of N surpluses during agricultural use of $C_{org}$ rich grasslands.

## 6. Acknowledgements

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1285 **Table 1** Summary of the grassland management for both vegetation periods.

| Date | Management event |
|---|---|
| 2010-03-26 | levelling |
| 2010-04-07 | rolling |
| 2010-05-24 | mowing |
| 2010-06-14 | manuring [20 $m^3$ $ha^{-1}$] |
| 2010-08-20 | mowing |
| 2010-08-25 | manuring [20 $m^3$ $ha^{-1}$] |
| 2010-09-23 | herbicide against common sorrel (*Rumex acetosa*) |
| 2011-03-16 | levelling |
| 2011-05-23 | mowing |
| 2011-05-27 | manuring [25 $m^3$ $ha^{-1}$] |
| 2011-08-01 | mowing |
| 2011-09-13 | mowing |
| 2011-09-22 | manuring [20 $m^3$ $ha^{-1}$] |
| 2011-11-04 | manuring [25 $m^3$ $ha^{-1}$] |

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1288 **Table 2** Soil properties of the study sites.

| | Sampling depth | $C_{org}$-medium | $C_{org}$-high | *n* |
|---|---|---|---|---|
| Soil type (WRB 2006)[1] | | mollic Gleysol | sapric Histosol | |
| Soil type (German classification KA5) | | GMq | KV-KM | |
| Peat depth [cm] [1] | | 80 | 70 | 1 |
| pH value* | | 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 |

1289 Values present means ± standard error

1290 [1] World Reference Base for Soil Resources

1291 * Relative to the upper horizon ($C_{org}$-medium 0–20 cm; $C_{org}$-high 0–15 cm); Roßkopf personal communication

**Table 3** Physical and chemical properties from the applied digestates and slurries.

| | 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 |
| $NH_4^+/N_{tot}$ ratio | 0.42 | 0.44 | 0.33 | 0.38 | 0.39 | 0.45 | 0.53 | 0.65 | 0.49 | 0.66 |
| 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 4** Mean (minimum/maximum) groundwater levels (GW), $NO_3^-$ and $NH_4^+$ contents of the soils following organic fertilizer application and for the years 2010 and 2011.

| | | $C_{org}$-medium | | | $C_{org}$-high | | | |
|---|---|---|---|---|---|---|---|---|
| | Sampling depth [cm] | 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 5** Calculated emission factors (EF) for the year 2011 and for single application events (16 days) (Apl. 1 – Apl. 4). The EF is 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 6** Grass yields, 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 (27$^{th}$ May 2011).

N.A. = not available.

**Table 7** Estimated nitrogen balance for the year 2011.

| Treatment | N applied [kg N ha$^{-1}$ yr$^{-1}$] | $N_{min}$ 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 | 46.1 | 70.4 |
| Cattle slurry $C_{org}$-high | 252 | 27.3 | 68.1 | 7.2 | 186 | 1.8 | 46.1 | 66.1 |
| Biogas digestate $C_{org}$-medium | 174 | 29.8 | 83.3 | 7.2 | 244 | 1.9 | 52.4 | −64.1 |
| Biogas digestate $C_{org}$-high | 174 | 26.2 | 28.4 | 7.2 | 236 | 3.1 | 52.4 | −108.1 |

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

† $NH_3$–N losses at the fourth and fifth application event were estimated based on EF taken from the German national greenhouse gas inventory (EF =0.6 related to applied $NH_4^+$; Haenel et al., 2014).

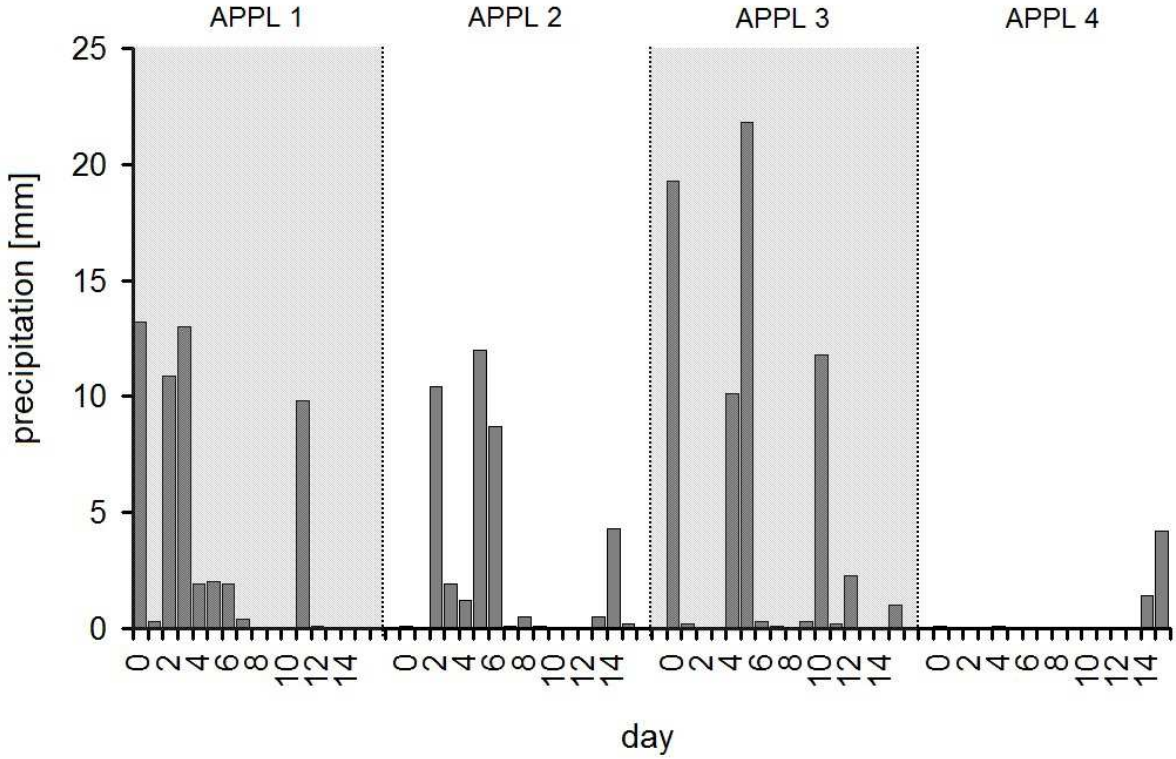


**Fig. 1** Daily sums of precipitation following the organic fertilizer application events (APPL).

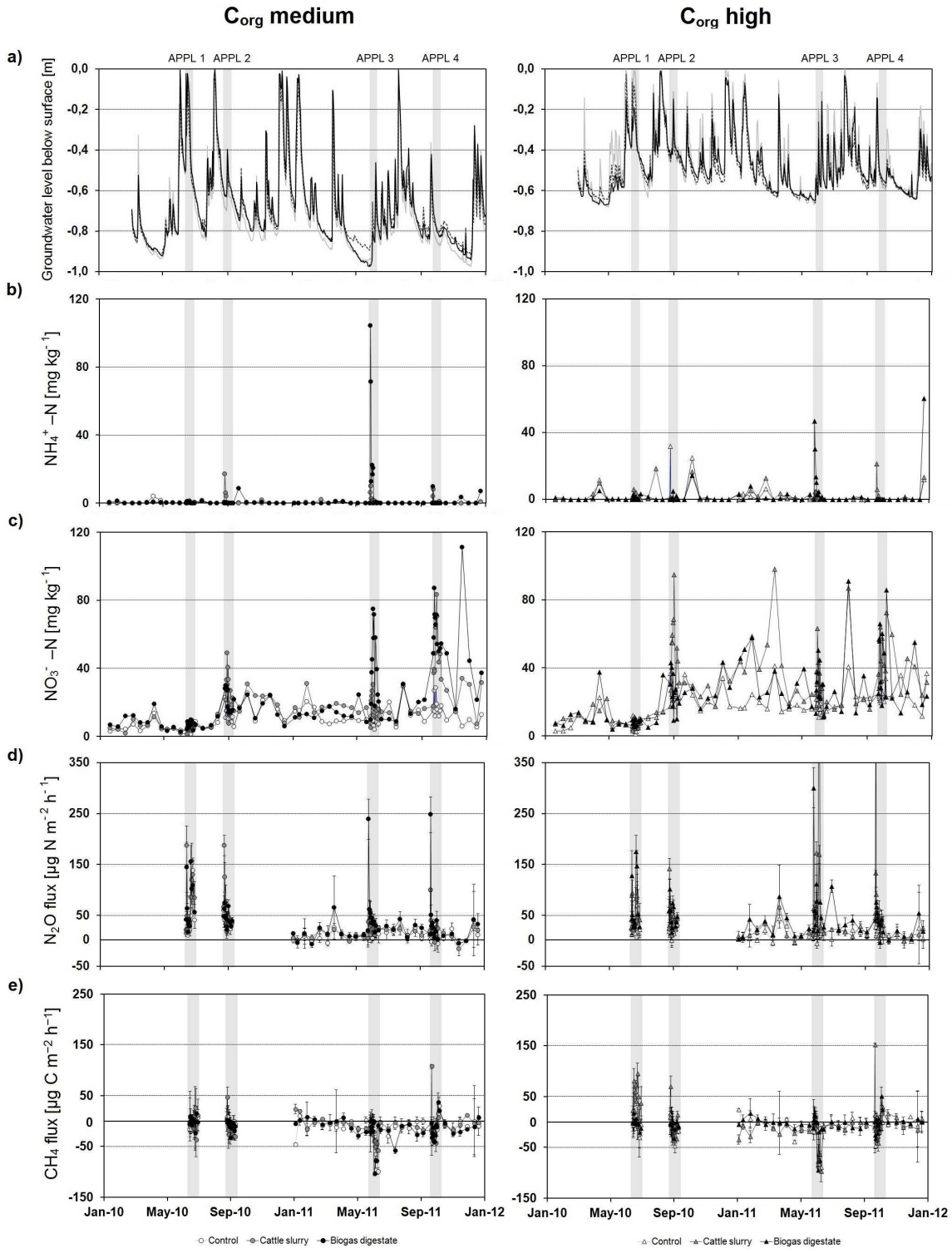


**Fig. 2** Variation in groundwater level (a), extractable $NH_4^+$ (b) and $NO_3^-$ (c) contents for the soil depth 0–10 cm, $N_2O$ (d) and $CH_4$ fluxes (e) (Mean ± SD, *n* = 3) of the $C_{org}$-medium and $C_{org}$-high sites from January 2010 to January 2012. Gray bars mark the 15 or 16 days period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

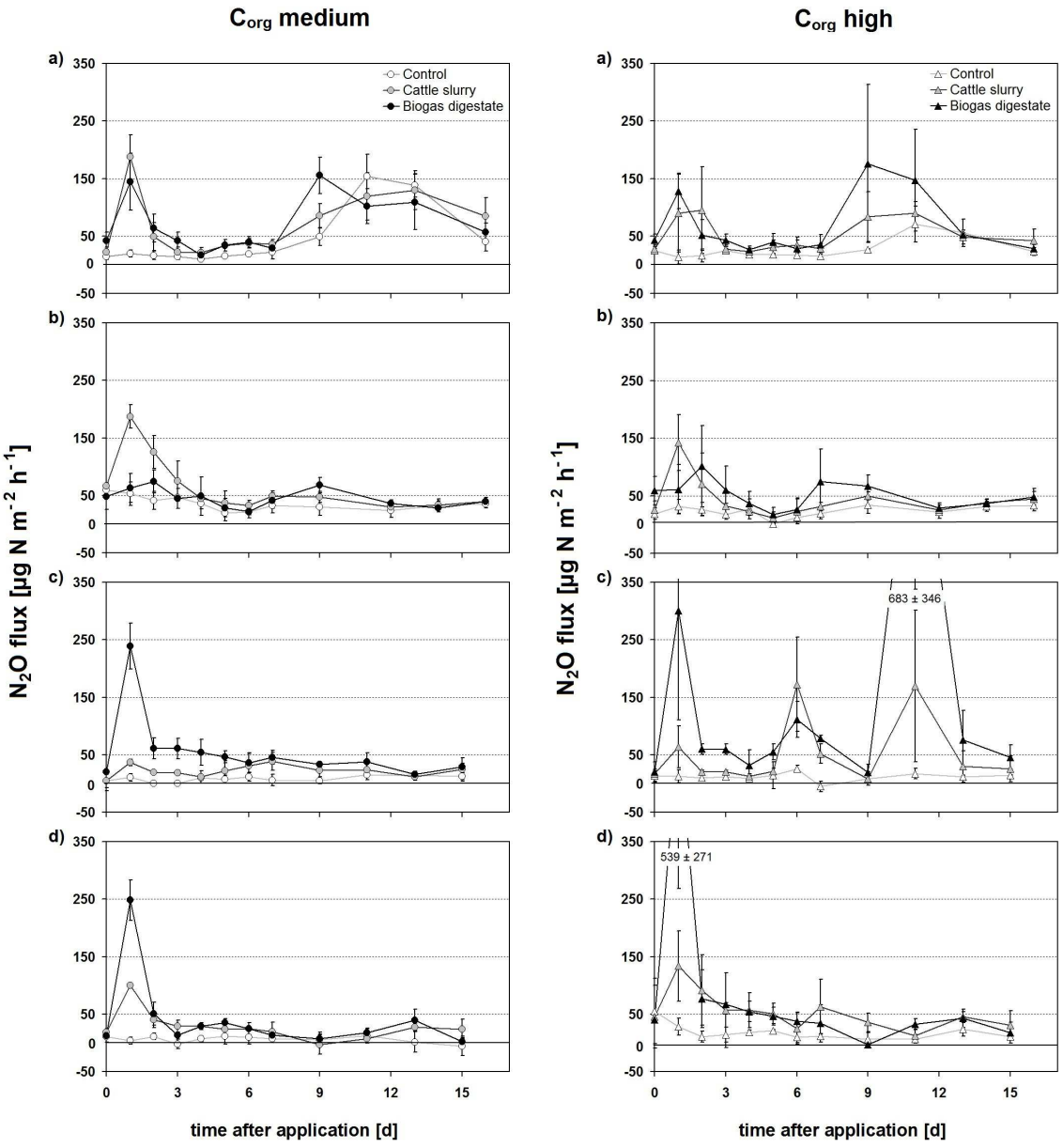


**Fig. 3** Mean (± SD, *n* = 3) $N_2O$ fluxes following organic fertilizer application events (a) 14.06–30.06.2010; (b) 25.08.–10.09.2010; (c) 27.05.–11.06.2011 and (d) 22.09.–07.10.2011.

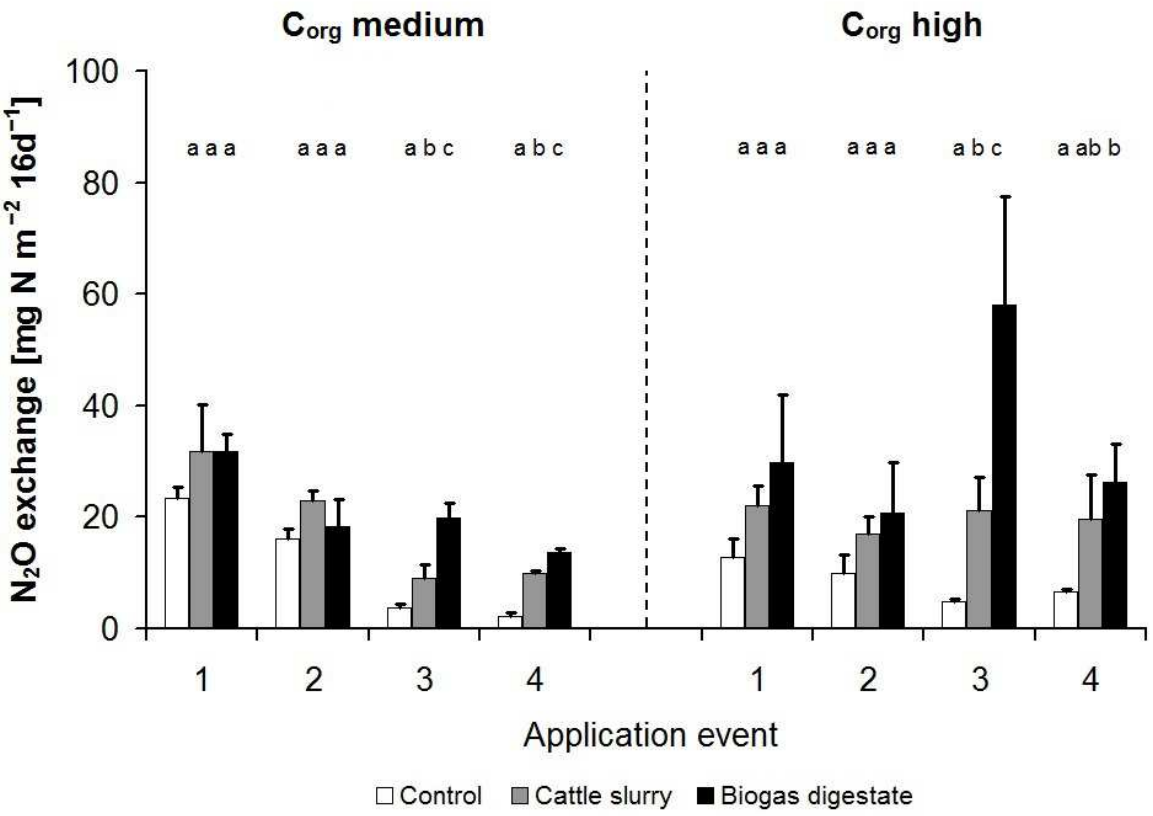


**Fig. 4** Cumulative $N_2O$ exchange during 16 days following organic fertilizer application. Bars indicate mean values + SD (*n* = 3). Means followed by the same letter indicated no significant differences between treatments at a single application event for sites $C_{org}$-medium and $C_{org}$-high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

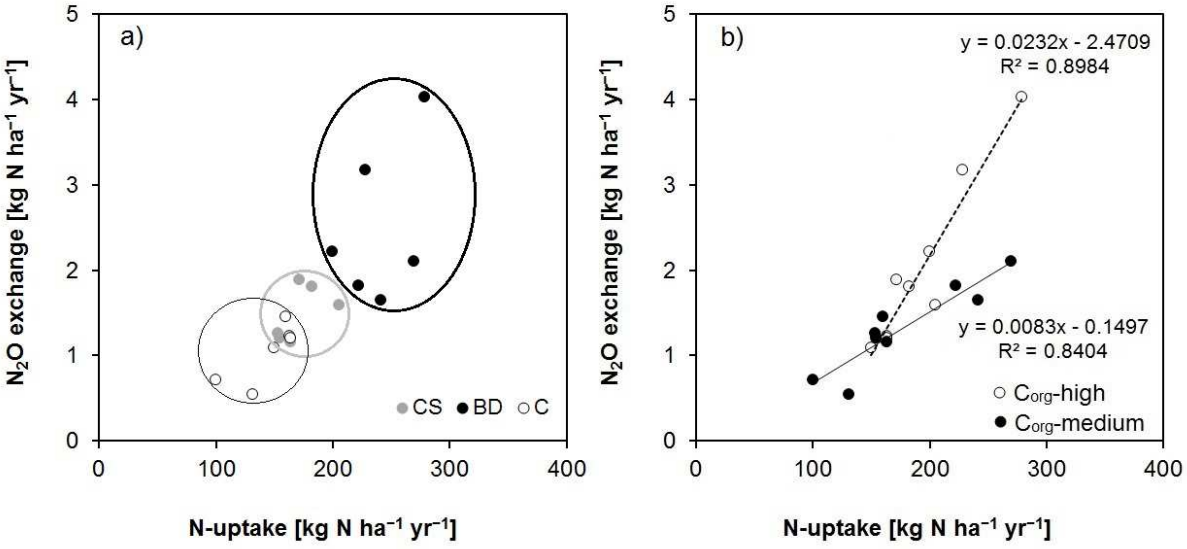


**Fig. 5** Relationship between cumulative annual $N_2O$ emissions and annual plant N uptake regarded for the treatments a) and for the investigated soil types b). Dots represent mean annual values of each PVC-collars. CS = Cattle slurry, BD = Biogas digestate, C = Control.

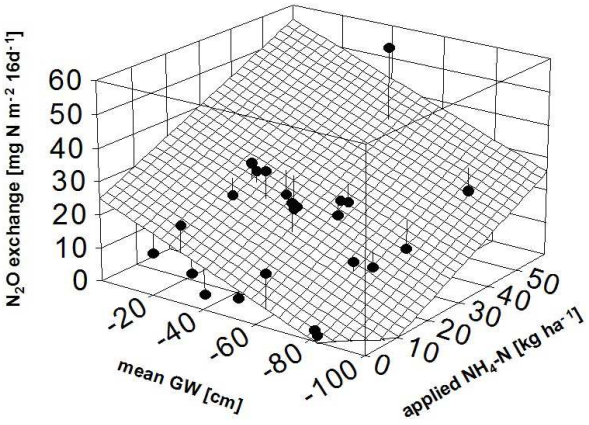


**Fig. 6** Relationship of plot-wise mean 16 days cumulative $N_2O$–N emissions of the four application events (y) to mean groundwater level (x1) and the amount of applied $NH_4$–N (x2). The regression equation is y = 24.98 (± 4.98) + x1 · 0.30 (± 0.09) + x2 · 0.51 (± 0.11); $R^2$ *adj.* = 0.53, *P* < 0.001, *df* = 21. Solid lines indicate the deviation of measured data from the model surface.

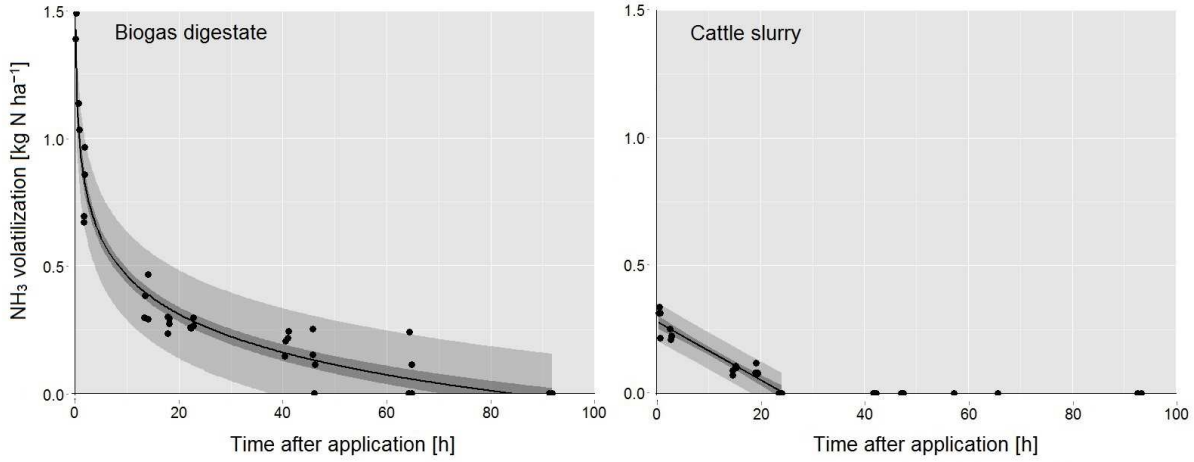


**Fig. 7** Ammonia ($NH_3$) volatilization following organic fertilizer application at event 3 (27.05.2011). Dots present single $NH_3$ measurements for a time period of 94 hours. Black lines show the estimated $NH_3$ volatilization with 95% confidence band (dark grey) and 95% prediction band (light grey). The model function for biogas digestate is: y = −0.2619 (± 0.025) · ln(x) + 0.9605 (± 0.008); $r^2$ = 0.96; *P* < 0.0001; the model function for cattle slurry is: y = 0.2818 (± 0.012) − 0.0114(x) (± 0.001); $r^2$ = 0.92; *P* < 0.0001.