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Ammonia volatilization and yield response of energy crops after fertilization with biogas residues in a coastal marsh of Northern Germany

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ABSTRACT

Anaerobic co-fermentation of animal slurries and crop silages leads to new types of biogas residues with an uncertain fertilizer value. Ammonia volatilization losses and crop productivity after supplying co-fermented biogas residues were investigated at a marshland site in Northern Germany. Due to the ecological risks of monocultures, maize (*Zea mays*) in monoculture as the dominant biogas crop in the marsh was tested against a crop rotation (maize, wheat (*Triticum aestivum*), Italian ryegrass (*Lolium multiflorum*)) and perennial ryegrass (*Lolium perenne*). Biogas residues, applied by trail hoses, and CAN (mineral fertilizer) were used as nitrogen fertilizers. Ammonia losses at all application dates were investigated by an approach including passive flux samplers and a calibrated dynamic chamber method. Simultaneously a micrometeorological technique was used as a reference. A comparison of methods showed a close correlation ($r^2 = 0.92$) between micromet and passive flux sampler techniques. Ammonia volatilization losses (on average 15% NH_4^+-N applied) occurred mainly within the first 10 h. Concomitant with high ammonia losses, a significant yield depression of 5 t DM ha^{-1} for ryegrass fertilized by biogas residues compared to CAN was observed. Little or no affect of biogas was observed for maize and wheat. The crop rotation had yields (34 t DM ha^{-1} 2 year^{-1}) that were comparable with the maize monoculture (31 t DM ha^{-1} 2 year^{-1}).

1. Introduction

Biogas production plays an important role in the European bioenergy supply and has increased particularly rapidly in Germany within recent years (FNR, 2010). Because of higher methane yields and subsidization, the majority of biogas plants operate by co-fermentation of crop silage and slurry from animal husbandry (Weiland, 2003). New types of biogas residues (BR) with a high proportion of crop biomass are produced in large quantities.

As the subsidization of biogas production is mainly motivated by the aim of producing a clean, renewable energy source, negative effects on the environment are particularly undesirable. Due to high NH_4^+ contents and high pH in the biogas residues, ammonia (NH_3) emissions play an important role in the environmental assessment of biogas production.

NH_3 emissions are among the main sources of acidifying and eutrophying atmospheric compounds because the deposition of ammonia-derived compounds causes acidification of soil (Asman et al., 1998) and natural water resources through nitrification to nitric acid (HNO_3) (Sutton and Fowler, 2002). Ammonia is also considered as indirect greenhouse gas because ammonia deposition could induce the formation of nitrous oxide (N_2O) (Moiser, 2001).

Characteristics of organic fertilizers like the proportion of ammoniacal nitrogen, pH-value and dry matter content are of major importance in determining the intensity of ammonia losses after application (Sommer and Huchtings, 2001). Weather conditions, especially high air temperature and high wind speed, affect atmospheric transfer processes of ammonia and result in high relative ammonia losses (Sommer et al., 2003). The interactions of slurries with soil, mainly due to soil-pH and texture, are relevant for adsorption, fixation, immobilisation of ammonium and microbial N-turnover processes. High inherent fertilizer and site specific ammonia loss potentials can be mitigated by the choice of appropriate application techniques (injection and incorporation) while surface application (splash plate and trail hoses) entail comparatively high ammonia losses (Huijsmans et al., 2001, 2003; Wulf et al., 2002).

The application of digested residues as N-fertilizer is an essential component of cropping systems for biogas production and is considered to have a high fertilization value (Möller and Stinner, 2009). However, the fermentation process increases the pH of the

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fermented substrates, resulting in a higher proportion of ammonia in total ammoniacal nitrogen (TAN), which is at risk of loss by ammonia volatilization (Loria et al., 2007; Chantigny et al., 2004b). On the other hand, fermentation decreases the dry matter content, which can result in low viscosity biogas residues, causing higher infiltration rates after field application and a potentially lowered risk of ammonia volatilization (Sommer and Huchtings, 2001; Wulf et al., 2002; Birkmose, 2007). But in the case of crops used as co-substrates, in particular grass silage which is characterized by a coarse and inhomogeneous structure (Plöchl et al., 2009), this dry matter effect cannot be strong enough to result in digested residues with low viscosities. Increased ammonia emissions after application of biogas residues by comparison with conventional slurries were observed in a first comparative study (Möller and Stinner, 2009). Therefore, the N-fertilizer value and ammonia loss potential of these residues still requires further investigation.

The marsh region of Northern Germany is characterized by high contents of clay in soil and shallow groundwater levels which both lead to a high water saturation level. Due to these conditions and to local climate, soil temperature in the spring rises very slowly. This has a strong effect on the crop cultivation system, with respect to slow crop development in spring (Hayhoe et al., 1996). In addition, the high water saturation level of soil causes limited infiltration rates and decreased NH_4^+ sorption to clay particles, especially after application of organic fertilizers, which could result in increased ammonia emissions (Sommer and Huchtings, 2001; Sommer et al., 2006; Liu et al., 2007). Strong winds are typical across the marsh and can lead to high ammonia emissions after application of organic fertilizers (Sommer and Olesen, 2000). By contrast, high NH_4^+ sorption capacities of the clay soil and low temperatures in the vegetative period could reduce potential ammonia losses. However, the N-fertilizer value of co-fermented residues with high contents of grass and wheat silages as well as the unwanted emissions of ammonia after field application of organic fertilizers under conditions of clayey marshland soils has not yet been studied in detail. This should be done by an appropriate approach for in situ investigations as in multi-plot field experiments, but available methods for this approach (Gericke et al., 2011; Pacholski et al., 2006) have not yet been tested under the conditions represented by the German marsh region. Multi-plot ammonia loss measurements should therefore include an evaluation of the applied method by a standard measurement technique.

Due to highest average dry matter yield per hectare (which is a crucial factor for methane production on a unit area basis (Amon et al., 2007a; Mähnert and Linke, 2009)), silage maize is the main feedstock for biogas production in Central Europe (Amon et al., 2007b). The proportion of silage maize of the total acreage for crop production in Germany has therefore increased considerably. But due to expected losses of soil carbon attributed to maize cultivation (John et al., 2005), in connection with negative influences on landscape scenery, alternative cropping systems to maize monoculture are being investigated. Maize, grown in monoculture, also increases pressures of pests and diseases (Bauer et al., 2009). For these reasons, crop rotation systems with similar or higher methane yields compared to maize monocultures are envisaged as being most appropriate for sustainable biogas production (Amon et al., 2007a). Because maize cultivation is only marginally profitable under the cool climate and soil conditions of the marshes in Northern Germany, winter cereals and field grasses could potentially be competitive as biogas substrates.

The aims of this study included the determination of N-losses by ammonia volatilization after application of biogas residues by trailing hoses under the particular site conditions of a marshland soil and their effect on the performance of different energy-crop rotations. A new measurement set-up for determination of ammonia losses in small field plots was used for the first time under conditions of a coastal marsh. The validity of this approach was extensively tested by comparison with simultaneous micrometeorological measurements. For comparison of dry matter yields of different energy-cropping systems and the N-fertilization effects of biogas residues two fertilizer-types were used: CAN as mineral fertilizer and anaerobic digestates from co-fermentation of energy crops with pig slurry.

The following hypotheses were tested for the conditions of a marshland site: (1) N-loss by ammonia volatilization can decrease the efficiency of co-fermented residues as N-fertilizer after application by trail hoses. (2) A crop rotation system consisting of maize, winter wheat and Italian ryegrass as intercrop is competitive to maize grown in monoculture and perennial ryegrass as substrate for biogas production. (3) The tested measurement approach is appropriate for determining ammonia emissions in small plot-experiments.

2. Material and methods

2.1. Experimental site

The experimental site was located in the coastal marsh region of the federal state of Schleswig–Holstein in Northern Germany (55°69′N; 8°82′E). The marsh region is characterized by very particular growing conditions because of shallow groundwater levels (about 1 m depth) and heavy, silt-clayey soils with about 40% clay and 55% silt (Fluvimollic Gleysol). The annual average precipitation is 845 mm and the average temperature is 9.3 °C (Fig. 1).

Furthermore, high wind speeds prevail in the marsh region due to its proximity to the North Sea and its planar morphology. Average wind speeds during all ammonia measurement campaigns at 2 m height were about 4.0 m s^{-1} in 2009 and 3.9 m s^{-1} in 2010.

2.2. Experimental design

The investigations were carried out in a randomized block design with four blocks. Treatment factors were crop type, fertilizer type and fertilizer level. Each plot was 12 m × 12 m and included a strip of 3 m width for final harvest (by combine), which was not affected by measurement activities during the vegetation period (Fig. 2).

The field trial was set-up in 2008. Perennial ryegrass was already sown in 2007. The cropping systems comprised of (a) bi-annual energy crop rotation consisting of maize (*Zea mays L.*; cv. Amatus, 9–10 plants per m^2), winter wheat (*Triticum aestivum L.*; cv. Magnus) and Italian ryegrass (*Lolium multiflorum L.*; mixture: 60% cv. Gisel, 40% cv. Lema) as intercrop and the monocultures of (b) maize and (c) perennial ryegrass (*Lolium perenne L*; cv. Trend), cut 4 times. The experimental time span covered two cropping years (from the beginning of 2009 to October 2010). In the year 2010, winter wheat was cultivated as planned but in autumn 2008 high water contents in the clayey soils did not allow sowing of winter wheat, so spring wheat (cv. Thasos) was sown instead in April 2009.

Crop fertilization treatments included three different N-levels (control; moderate; and high) for every crop type by organic (BR) and mineral (CAN) fertilization (Table 1). Co-fermented digested residues were taken from a nearby biogas plant, which was operated with 30% pig slurry and 70% crop silage of grass and wheat as substrates for fermentation. Anaerobic digestates were applied by trail hoses without subsequent incorporation, based on total N-concentrations. Fertilizers for wheat were applied in two equal doses. For maize, an additional mineral basal dressing (50 kg N ha^{-1}) was applied for both fertilizer type treatments, at sowing. All fertilizers were applied in the morning hours (8–10 a.m.).

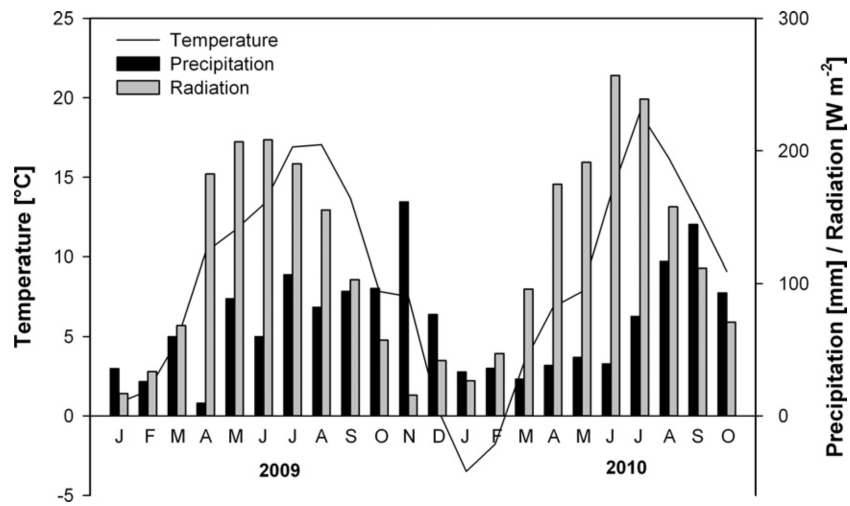

Fig. 1. Monthly averages of temperature [°C], precipitation [mm] and radiation [W m^{-2}] at the experimental site in the coastal marsh region of Schleswig–Holstein, Northern Germany, in the year 2009 and 2010.

2.3. NH_3 measurements after application of biogas residues

Ammonia volatilization after application of biogas residues by trail hoses was determined by two approaches: (1) by a combination of passive flux samplers and dynamic chamber method in the plots of the field trial and (2) simultaneous reference measurements with a micrometeorological technique on an adjacent field (Fig. 2). The micrometeorological method applied on large plots served as control measure for the validity of approach 1. Ammonia losses from mineral fertilization (CAN) were considered as negligible (Van der Werden and Jarvis, 1997; Sommer et al., 2004).

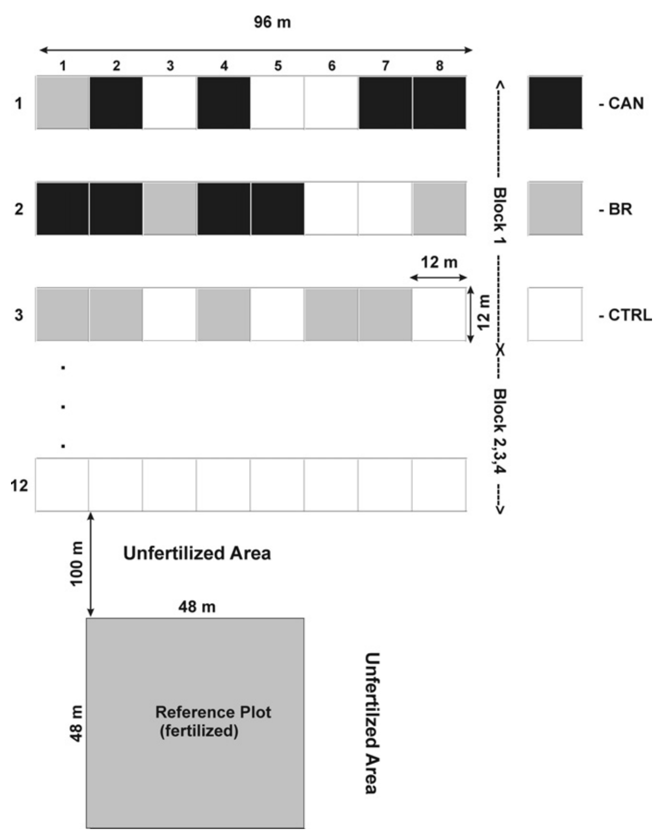

Fig. 2. Layout of the experimental design, including a reference plot for micrometeorological NH_3 measurements and a multi-plot field trial. Biogas residues (BR) and calcium ammonium nitrate (CAN) were used as fertilizer types in the plot experiment. Among the fertilized treatments hide various crops that have been fertilized at different times.

2.3.1. NH_3 loss measurements in plots: combined plot method (cpm)

A new approach (Gericke et al., 2011), consisting of passive flux samplers, similar to those employed by Vandré and Kaupenjohann (1998) for the standard comparison method (SCM), combined with a calibrated dynamic chamber method (Draeger Tube Method DTM, Pacholski et al., 2006) was used for the determination of ammonia losses in the plots. For this combined plot method (cpm) passive flux samplers, containing 20 ml of 0.05 M sulphuric acid, were installed in the centre of each treatment-plot inside the field trial, directly after residue application. The solution in the samplers was exchanged every 3–4 h and analyzed by an ammonia-electrode (Thermo Scientific, Beverly, MA, USA). The resulting semi-quantitative ammonia emissions were finally converted to absolute losses by a transfer factor obtained from DTM-measurement. Stainless steel rings were installed into the upper soil of one plot for each treatment directly after fertilization; 2 on the slurry strip, and 2 between the slurry strips to record representative residue coverage. Four chambers were inserted, and connected to an ammonia indicator tube and an automatic pump to ensure a defined flow rate (Pacholski et al., 2006). Two measurements were undertaken for each treatment at 3–4 h intervals. The resulting ammonia fluxes of the calibration plots allowed the calculation of the terminal cumulative N-loss by ammonia volatilization for each plot of each treatment. Details of this approach are presented in Gericke et al. (2011) where the comparison of this measurement approach with ammonia losses obtained from micrometeorological measurements showed very good agreement. However, as wind speeds in the coastal marsh were much higher than during the calibration of the dynamic chamber method (Pacholski et al., 2006), results of the new approach were again extensively tested against comparative measurements with a micrometeorological approach.

2.3.2. NH_3 loss measurements by micrometeorological reference method (bLS)

The micrometeorological backwards Lagrangian stochastic dispersion technique (bLS, Wilson et al., 1983; Flesch et al., 1995; Sommer et al., 2005) was used on larger field sites close to the plot experiment. The bLS determines ammonia emission rates by calculating gas concentrations and wind characteristics above a fertilized

Table 1
Experimental factors including cropping systems, N application levels and fertilizer types of a field trial at a marshland site in Northern Germany.

Cropping systems	N-levels (control/moderate/high)	Fertilizer types
• Monoculture Maize • Monoculture Perennial ryegrass (4 cuts) • Crop rotation Maize, wheat, Italian ryegrass (1 cut in autumn)	• Maize 0/100/150 kg N ha^{-1} + 50 kg N ha^{-1} mineral basal dressing • Perennial ryegrass 0/360 (120, 120, 70, 50) kg N ha^{-1}/480 (165, 145,100, 70) kg N ha^{-1} • Spring wheat (2009) 0/180/240 kg total N ha^{-1} • Winter wheat (2010) 0/220/300 kg total N $^{-1}$ • Italian ryegrass 0/80 kg total N ha^{-1} (moderate + high)	• Calcium ammonium nitrate (CAN) Spreader • Co-fermented residues (BR) Trail hoses pH: ~7.8 Ntot: ~5 kg/m^3 NH_4-N: ~68% Dry matter:~6.5%

source area. For measuring NH_3 concentrations a passive flux sampler (Leuning et al., 1985), which was evaluated by Sherlock et al. (1989), was installed on a centred pole at a specific height (ZINST, Wilson et al., 1982), which was dependant on the stand height. Air flux through the sampler is linearly proportional to the wind speed and so ammonia is absorbed quantitatively. The bLS-model simulates the dynamic of ammonia trajectories and records the particles backwards from the sensor inside and outside the plot, so that ammonia fluxes from a source area can be calculated. This was done using WindTrax software (Thunderbeach Scientific, Canada). Three bLS-measurements were carried out in 2009 and six in 2010 on the same date and with the same N-supply of the moderate N-treatment of the plot experiment. The bLS-plot size varied between the different dates of fertilization at a range from 30 m × 30 m to 54 m × 54 m, depending on the working width of the trail hoses.

2.4. Meteorological measurements

A weather station was installed at the experimental site, that included 2 cup anemometers at heights of 0.2 m and 2 m (Thies economy, Thies GmbH, Göttingen, Germany), a Thermo Hygro Sensor STANDARD (Wilmers Messtechnik, Hamburg, Germany) at 1.5 m height for measurement of air temperature and air pressure and a CM3 (Kipp and Zonen, Delft, Netherlands) to determine global radiation (Fig. 1).

An additional wind station (Campbell 03002-5 wind sentry, Campbell Germany, Bremen) was used in the experimental area during the bLS measurement campaigns. Wind speeds and wind direction were determined in the same mounting height as the ammonia samplers (ZINST sampling height, Wilson et al., 1983; Sommer et al., 2005).

2.5. Harvest

Crop yield was determined by machine harvest of a subplot, which was excluded from any measurement during the vegetative period. The subplot size varied between 17.7 m^2 for grass and 13.5 m^2 for wheat and maize. Dry matter was determined by taking a mixed sample of about 1 kg and drying at 57 °C to constant weight. The main criterion assessed at harvest of maize was a dry matter proportion of at least 30%. Wheat was harvested between late milk and early dough (BBCH-scale; Lancashire et al., 1991). Ryegrass was cut at early stages of inflorescence emergence (1st cut) or depending on dry matter development (2nd–4th cut).

2.6. Statistical analysis

Dry matter yields of crops were analyzed by a mixed effects model with crop type, fertilizer type and fertilizer level as main factors and all interactions, for each experimental year separately. Multiple comparisons were conducted by *t*-test and the Bonferroni–Holm adjustment. The years 2009 and 2010 had to be tested separately due to changes in the crop the rotation. Cumulative NH_3 losses in the studied cropping systems were tested by analysis of variance (ANOVA) with the cropping system as single main factor. Here, both years were combined in the analysis, due to similar canopy conditions and similar fertilization dates in winter wheat as opposed to spring wheat. Cumulative yields were tested in a similar way, except for separation of winter wheat and spring wheat. The ANOVA was conducted using the statistic software R (version 2.8.1; R Development Core Team, 2004). Linear regression analysis was calculated in SigmaPlot (Version 11.0; Systat Software Inc., San Jose, USA).

3. Results

Absolute and relative cumulative ammonia losses after application of biogas residues differed between dates of fertilizer application. Fig. 3 shows sample time courses of cumulative absolute and relative ammonia losses after BR application on grassland and wheat, determined in 3 experimental campaigns, 2009 and 2010, with both, bLS and cpm technique. The duration of

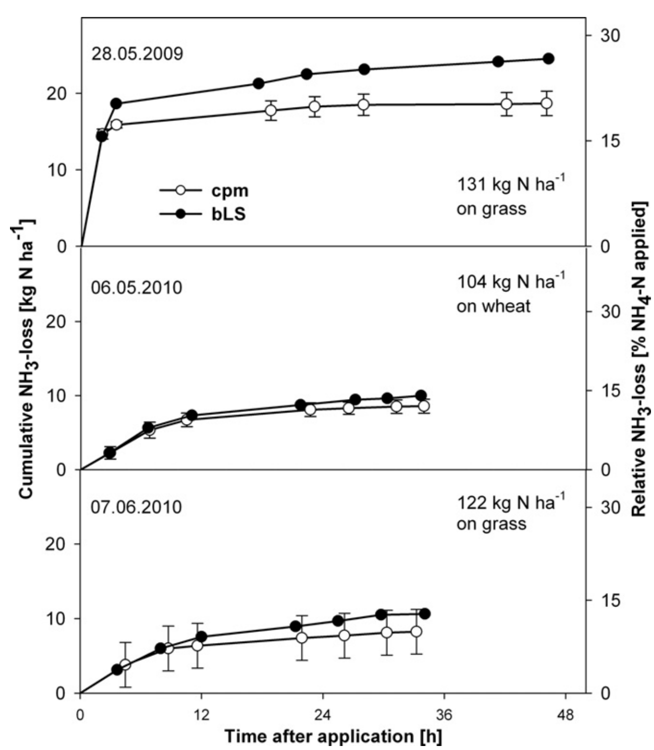

Fig. 3. Cumulative and relative N-loss by NH_3 volatilization after application of biogas residues by trail hoses in moderate N level, perennial ryegrass and wheat, marsh region of Schleswig–Holstein, micrometeorological bLS-technique and combined passive flux samplers/calibrated dynamic chamber method (cpm), 3 dates in 2009 and 2010. Error bars indicate standard error (SD), *n* = 4.

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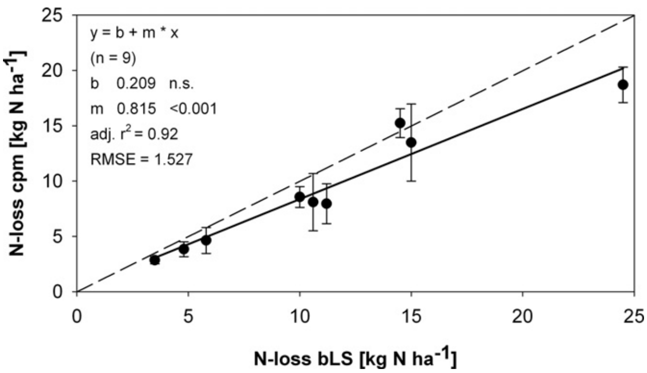

Fig. 4. Correlation between bLS and cpm technique for determining N-losses by NH_3 volatilization after application of co-fermented biogas residues by trail hoses for 9 measurement campaigns 2009 and 2010 in the marsh region of Northern Germany. Dotted line = one-to-one line. Error bars indicate standard deviation (SD, $n = 4$).

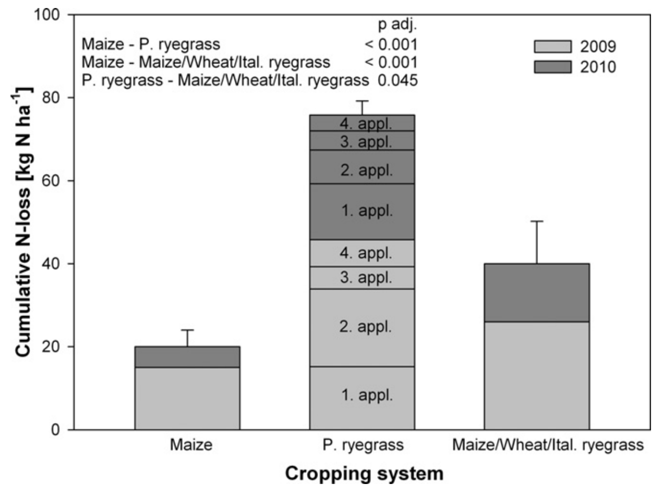

Fig. 5. Crop system specific, cumulative N-loss by NH_3 volatilization after application of biogas residues (moderate N-treatment) by trail hoses in the marsh region of Northern Germany, 2009 and 2010, measured by cpm. Calculation of average N-loss of Maize and wheat (2009: spring wheat; 2010: winter wheat) + Ital. ryegrass for each year. Standard errors indicate standard deviation (SD, $n = 4$). Significance levels were determined by ANOVA.

measurements did not usually exceed two days after BR application due to a strong decrease in emission rates and up-coming rainfall. Depending on wind speed, temperature and humidity, crust formation was observed during most of the measurement campaigns.

Relative N-losses of about 25% (bLS) and 20% (cpm) of NH_4-N applied were observed on the application date 28 May 2009, whereas on the 6 May and 7 June 2010 the relative ammonia losses were within a range of 15% of supplied NH_4-N determined by both methods. Values of cumulative losses varied between 24 kg N ha^{-1} (bLS) and 19 kg N ha^{-1} (cpm) for the measurement campaign on the 28 May 2009. On the 6 May and 7 June 2010 the cumulative N-losses were about 8–10 kg N ha^{-1} for bLS and cpm. Except for the second sampling point during the measurement campaign on the 28 May 2009, the dynamic of N-loss by ammonia volatilization were in close agreement for all sampling dates (Fig. 3).

Fig. 4 shows a linear regression of cumulative ammonia losses by cpm on accumulated losses determined by bLS for all 9 experimental campaigns with simultaneous application of both methods. A strong correlation ($r^2 = 0.92$) existed between the N losses determined by micrometeorological bLS-technique and the cpm method. Most values were scattered close to the 1:1 line. Only the data point with the highest cumulative losses showed an underestimation by the cpm approach. As a result, a low underestimation of cpm was observed with an RMSE of 1.5 kg N ha^{-1}.

The highest amount of total ammonia loss by volatilization was observed in grassland, followed by wheat and maize cropping systems, in 2009 and 2010 (Table 2). In 2009 the total N-loss as well as the relative ammonia loss by volatilization was higher when compared with the N-losses in 2010, for each crop type. The highest relative N-loss in 2009 was observed for the moderate treatment of wheat (19–28% NH_4-N applied) and in 2010 for the moderate treatment of grass (9–16% NH_4-N applied). Maize showed lowest relative N-losses in each year. Generally, the relative ammonia losses were higher for the moderate N-treatments as compared to the high N-treatments, except for the maize fertilization in 2010 with identical losses (Table 2).

Cumulative ammonia emissions (cpm) of the 3 cropping systems (monoculture of maize, perennial ryegrass and crop rotation: maize, wheat + Italian ryegrass) over the two years 2009 and 2010 are shown in Fig. 5. Lowest N-loss with about 20 kg N ha^{-1} was observed for the maize monoculture. The crop rotation showed N-losses, which were two fold higher (about 40 kg N ha^{-1}) and cultivation of perennial ryegrass resulted in losses, which were four times higher (about 80 kg N ha^{-1}), than those of the maize monoculture (Fig. 5). For each cropping system N-losses in 2009 were higher than in 2010, as also shown in Table 2.

Dry matter yields of the main crops (perennial ryegrass, maize in monoculture, maize in crop rotation and wheat) are presented in Fig. 6. Treatment factors were crop type, fertilizer type and

Table 2
Total N/NH_4-N supply and total/relative N-losses by NH_3 volatilization after application of biogas residues by trail hoses on a multi-plot field trial including grass (4 applications), wheat (2 applications) and maize (1 application) in the marshland of Schleswig–Holstein, Northern Germany, 2009 and 2010, measured by a combination of passive flux samplers and a calibrated dynamic chamber method (cpm) and bLS technique. For each treatment: $n = 4$.

	N-treatment	Total-N applied [kg N ha^{-1}]	NH_4-N applied [kg N ha^{-1}]	NH_3 loss [kg N ha^{-1}]	Rel. NH_3 loss [% NH_4-N applied]
2009					
Grass	Moderate	374	254	47 ± 5	17–21
	High	497	338	59 ± 7	15–19
Wheat	Moderate	196	133	31 ± 6	19–28
	High	261	177	40 ± 7	19–27
Maize	Moderate	108	74	15 ± 5	14–27
	High	162	110	15 ± 4	10–17
2010					
Grass	Moderate	345	235	30 ± 8	9–16
	High	459	313	35 ± 7	9–13
Wheat	Moderate	217	149	17 ± 4	9–14
	High	296	204	21 ± 3	8–12
Maize	Moderate	104	71	5 ± 1	6–8
	High	156	106	7 ± 1	6–8

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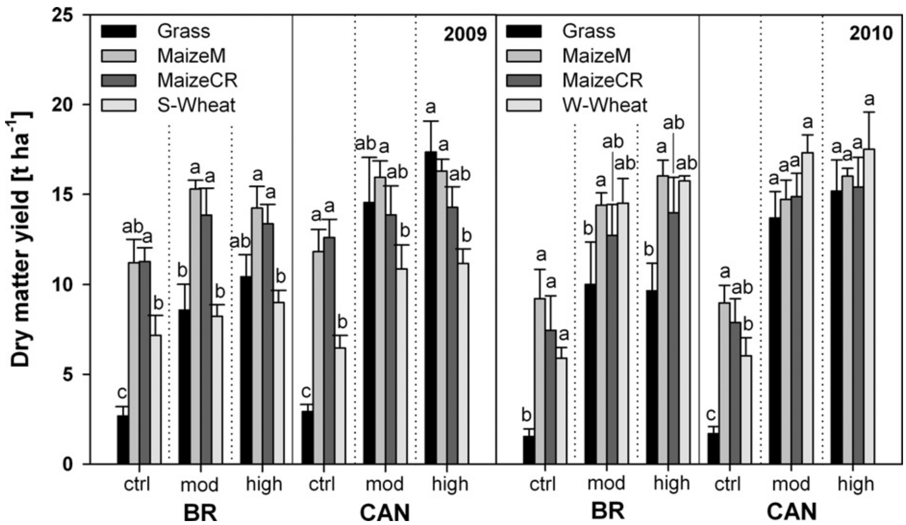

Fig. 6. Dry matter yield [t ha^{-1}] of wheat (2009: spring wheat; 2010: winter wheat), maize in crop rotation system (MaizeCR), maize in monoculture (MaizeM) and perennial ryegrass, cut 4 times a year, at control, moderate and a high level of N fertilization with biogas residues (BR) and mineral N-fertilizer (CAN) in the marsh region of Schleswig–Holstein. Error bars indicate standard deviation (SD, $n = 4$). Values with different letters are statistically different for each N-treatment in each year at $P < 0.05$ (T-test, $n = 4$).

Table 3
Significance levels of treatment factors crop type (Crop), fertilizer type (N-type), fertilizer level (N-level) and interactions for analysis of crop dry matter yields of a multi-plot field trial in a coastal marsh region of Northern Germany, 2009 and 2010.

	2009				2010			
	NumDF	DenDF	*F*-Value	*p*-Value	NumDF	DenDF	*F*-Value	*p*-Value
Intercept	1	69	12241.3	<0.0001	1	67	3633.7	<0.0001
Crop	3	69	167.8	<0.0001	3	67	72.7	<0.0001
N-type	1	69	84.8	<0.0001	1	67	46.3	<0.0001
N-level	2	69	234.4	<0.0001	2	67	538.1	<0.0001
Crop:N-type	3	69	16.4	<0.0001	3	67	7	0.0004
Crop:N-level	6	69	36.6	<0.0001	6	67	10.7	<0.0001
N-type:N-level	2	69	14.7	<0.0001	2	67	8.2	0.0007
Crop:N-type:N-level	6	69	6.5	<0.0001	6	67	2	0.0725

fertilizer level. Comparing the two treatment factors, a large number of highly significant interactions were detected and even significant triple interactions in 2009 (Table 3). Due to this complex model structure it was not possible to test for statistical differences between all factor combinations against each other. For this reason, independent statistical models were calculated for 2009 and 2010, which allowed separate testing of statistical differences between crop dry matter yields for each factor combination (N type:N level) (Fig. 6).

The yields of every crop type were mostly lower in the BR treatment compared to mineral fertilization in 2009 and 2010. Highest differences between BR and CAN fertilization were determined for grass. Wheat showed only low significant differences between the fertilizer types, whereas maize showed no effects in response to fertilizer type (Fig. 6). By comparison to the fertilized treatments, the dry matter yields of the control treatments for maize and wheat were considerably higher in 2009. The fertilization effect increased clearly for each crop type in 2010 (Fig. 6). The most productive crops in 2009 were perennial ryegrass under mineral fertilization and maize for both fertilizer type treatments. Spring wheat was not competitive with latter crops. Maize cultivated by monoculture showed low increased dry matter yields compared to maize in the crop rotation, in 2009 and 2010. The highest dry matter yields in 2010 were observed under winter wheat with about 17.4 t ha^{-1} for the mineral treatment. Perennial ryegrass produced the significantly lowest yields using organic fertilization, with an average of 5 t ha^{-1} less dry matter yield, compared to maize and winter wheat, equally to 2009 (Fig. 6).

The productivity of different cropping systems over the whole duration of the rotation (2 years) as a substrate for biogas co-fermentation in the coastal marsh region of Northern Germany is depicted in Fig. 7 for the moderate N-fertilization level of both

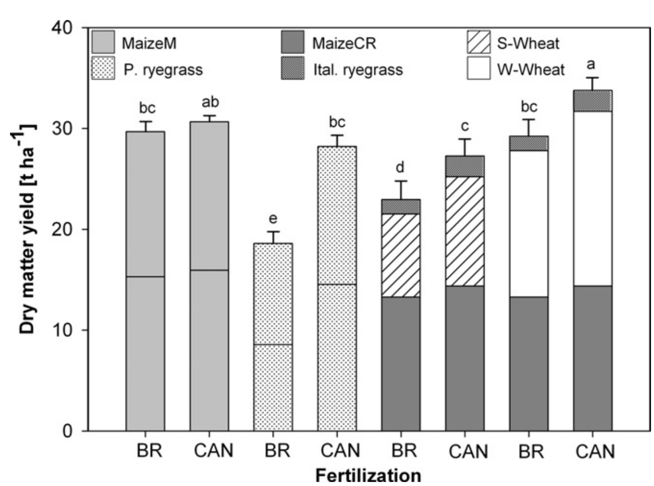

Fig. 7. Yields of cropping systems for biogas production in the marsh region of Northern Germany under moderate N-application level, aggregated for 2009–2010. For the crop rotation, yields of maize and Ital. ryegrass are averaged over 2 years. Yields of each wheat variety consist only of data from one year (2009: spring wheat; 2010: winter wheat). Error bars indicate standard deviation (SD, $n = 4$). Different letters shows statistically difference for each rotation at $P < 0.05$ (Tukey-test, $n = 4$).

fertilizer types. Highest cumulative yields (33.7 t DM ha^{-1}) were determined for the crop rotation, consisting of maize, winter wheat and Italian ryegrass of the mineral treatment, followed by the corresponding organic treatment and both maize monoculture varieties. The yield of grass receiving mineral N was close to the maize varieties as well as to the mineral crop rotation treatment with summer wheat. The lowest yields were observed for the BR fertilized perennial ryegrass with about 18.6 t DM ha^{-1} (Fig. 7).

4. Discussion

4.1. Comparison of methods

The general dynamics of N-loss by ammonia volatilization after application of BR by trail hoses in the coastal marsh region of Northern Germany showed a close correlation between the bLS technique and cpm. That was detected for diverse conditions like different amounts of total N-application or fertilization of different crop types within 2 vegetation periods. There was an exception at the second sampling point of the measurement campaign starting on the 28 May 2009, where the increase of N-loss was much lower for cpm than for bLS (Fig. 3). On this date the average wind speed of 7.4 m s^{-1} at a height of 2 m for the first few hours after application was much higher than on the other two example dates with about 4 m s^{-1}. Such a strong wind can cause problems for dynamic chamber measurements with respect to calibration of the combined method (Gericke et al., 2011).

However, even including the campaign on the 28 May 2009, the regression of final cumulative losses obtained by both methods for all 9 experimental campaigns showed a high coefficient of determination (Fig. 4) that supports our third hypothesis. In the marsh, the combined dynamic chamber and passive flux sampler method (cpm) can be considered as an appropriate method for sampling and quantifying ammonia emissions after organic fertilizer application in plot experiments. A low underestimation of cpm compared to bLS could be overcome by introducing a correction factor for very high wind speeds, but this requires further investigation.

4.2. Dynamics of NH_3 emissions

The strong winds, which were characteristic of this site were important in promoting high N-losses by ammonia volatilization in the year 2009. The effect of strong winds can further be increased in connection with high global radiation (Sommer and Huchtings, 2001). In 2010, slightly lower average wind speeds and precipitation events during most of the application period caused lower cumulative ammonia emissions as compared to 2009 (cf. Sommer and Olesen, 2000).

In addition to climatic factors, the status of plant coverage during application by trail hoses influences ammonia losses by volatilization (Sommer and Huchtings, 2001). After application on wheat and grass the residues partly remained on the canopy, so that the residue surface area which could potentially be affected by wind increased, resulting in higher potential ammonia emissions. Additionally the contact with the soil and consequently infiltration was limited by comparison with the application on nearly bare soil (maize). Coarse and non-homogeneous structure of residues applied, due to the high content of grass silage, probably increased these effects. Apart from that, high water saturation of clayey soils can stimulate ammonia volatilization after application of organic fertilizers, due to limited infiltration and decreased NH_4^+ adsorption (Sommer and Huchtings, 2001; Sommer et al., 2006; Liu et al., 2007), although in other studies no significant relationship between soil properties and ammonia volatilization has been observed (Huijsmans et al., 2001).

Ammonia losses of 6–28% of applied NH_4-N (Table 2) were in a similar range of those (4–26%) reported by Sommer et al. (1997) after slurry application, under similar climate conditions. Average ammonia volatilization losses (15% NH_4-N applied) in the marsh region were higher than those observed in other landscapes of Schleswig–Holstein with average losses of 10% of applied NH_4-N (Ni et al., submitted for publication).

Due to the prevailing strong wind, highest ammonia fluxes occurred at the beginning of each measurement campaign which also favours crust formation, so that the major part of the total N-loss volatilized within the first 5–10 h after residue application and decreased rapidly, afterwards (Fig. 3). The process of ammonia volatilization was faster than usual under marshland conditions. Sommer and Huchtings (2001) supposed that cumulative ammonia loss would reach about 50% of its maximum within the first 12 h after slurry application.

Due to unwanted ammonia emissions after application of BR and its consequences, several techniques were developed to decrease N-loss by volatilization. One concept is, to acidify the BR until the pH-value is in the range of 5–6 or lower, which is necessary to reduce emissions significantly (Stevens et al., 1989, 1992; Kai et al., 2008). This might be not as effective as would be expected in the marsh region, with respect to high soil pH and buffer capacity. Other possibilities are to incorporate the residues, directly after application (Misselbrook et al., 2000; Webb et al., 2010) or by injection, but this is connected with higher costs for application technique and fuels and risks for damage of crop roots, which can result in yield reductions (Rees et al., 1993). However, slurry injection can be connected with higher N_2O emissions (Webb et al., 2010).

4.3. Crop specific NH_3 emissions

The differences of N-loss by ammonia volatilization among crop types were, on the one hand, related to the crop specific N-demand. On the other hand, climatic conditions stand density and soil properties at each application date can have a pronounced effect. Relative N-losses were lowest for maize because of the early application date on nearly bare soil whereas for wheat and especially for grass, residues also were applied in the warmer summer months. Besides that high, crop coverage during application by trail hoses probably increased relative ammonia losses for wheat and grass. Therefore, particularly with respect to climatic conditions, plant and soil properties in combination with crop specific amounts of applied nitrogen, maize can be considered as crop type with lowest ammonia loss potential (Table 2). By slurry incorporation the N-loss by ammonia volatilization can even be further decreased for maize (Sommer and Huchtings, 2001). Consequently, cumulative biennial N-losses for each cropping system as illustrated in Fig. 5, shows that cultivation of perennial ryegrass resulted in significantly highest environmental impact by ammonia volatilization (acidification, eutrophication, and indirect GHG emissions) of the tested cropping systems in the marsh region, whereas maize, cultivated in monoculture showed significantly lowest cumulated ammonia emissions.

4.4. Effect of fertilizer types on crop yields

The data indicate that N-losses by ammonia volatilization were coincident with differences in yield levels between the two N-fertilizer types for grassland and wheat. The minor yield differences for maize treatments were probably due to low N demand by this crop and to high nutrient availability, with respect to long-time pig slurry applications before implementation of the field trial. In addition, low N-loss by ammonia volatilization and the comparatively higher proportion of mineral nitrogen (mineral basal dressing) prevents N-limitation during early growing stages in the BR-treatment

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of maize. However, differences in dry matter yield of up to 5 t ha^{-1} for perennial ryegrass between CAN and BR treatment (Figs. 6 and 7) cannot solely be explained by ammonia emissions. Lower yield levels can also be attributed to the high proportion of organic N in the residues and slow mineralization of these compounds, which were probably not sufficient to meet the high N demand of this crop.

Other negative yield effects could also be due to ammonium adsorption and fixation in the soil, characterized by high contents of clay minerals. The ammonium fixation capacity of those minerals can lead to NH_4-N contents [kg N ha^{-1} 30 cm^{-1}] of up to 675 kg N ha^{-1} in the ploughing layer of marshland soils (Nieder et al., 2011). As an additional factor, the broad distribution of BR by trail hoses on the soil, including infiltration processes, maybe resulted in a potentially higher proportion of fixed NH_4^+. This was probably related to higher soil surface contact, as compared to CAN, which was spread on the soil surface as grains. On the first day after organic fertilization 34% of applied NH_4-N can be fixed by clayey soils (Chantigny et al., 2004a). Further paths of N-loss result from denitrification in the form of nitrous oxide (N_2O) and molecular N (N_2) or N-leaching. But these processes cannot explain the high yield differences between BR and CAN fertilization, due to low amounts of N-loss by denitrification on similar soils, determined by Dobbie and Smith (2003) and no fertilization in autumn, regarding N-leaching. To sum up, N-losses by NH_3 volatilization may be an important factor of strongly decreased N-fertilization values of co-fermented BR, which can result in limitation of yield, especially for perennial ryegrass and partially for wheat. However, our first hypothesis was not supported strongly enough by our data to accept it. Further analyses are necessary (e.g. on crop growth dynamics and N-uptake by crops) to clearly answer the question of the effect of NH_3-emissions on crop yields in our study.

4.5. Cropping systems

The crop rotation including maize, winter wheat and Italian ryegrass under mineral fertilization was, except for the maize monoculture with a yield level of about 31 t DM ha^{-1}, the significantly most productive cultivation system (~34 t DM ha^{-1}) in this experiment (Fig. 7). The yield depressions of the organic compared to the mineral treatments were most pronounced for winter wheat with BR fertilization as part of the crop rotation, but both fertilizer treatments were comparable with the reference cropping system for biogas production, maize monoculture. In 2009, when winter wheat had to be replaced by spring wheat, as a consequence of unfavourable conditions for sowing in autumn, the crop rotation produced significantly lower yields for each fertilizer type (Fig. 7). Further, an average yield of about 15 t DM ha^{-1} for perennial ryegrass under mineral fertilization was also as productive as maize, at this site, whereas fertilization of perennial rye grass with BR showed significantly lower productivity than other production systems. Slightly decreased yields of maize in the crop rotation compared to maize in monoculture might have been due to delayed germination with respect to slower warming of soil in spring caused by reflection of incident light by the overlaying Italian ryegrass. In general, slow soil-warming is a critical factor for maize cultivation under conditions of the marshland, due to the heavy soils and high water saturation. Additionally, long dry periods during April and May, such as those in 2008 (data not shown) can strongly inhibit the development of maize, so cultivation of maize is connected with high risks at the experimental site. With respect to dry matter yield, which is a crucial factor for methane production (Amon et al., 2007a; Weiland, 2003) cultivation of perennial ryegrass is probably inappropriate for a biogas production system in the marshland, due to inefficiency of BR as N-fertilizer, applied by trail hoses. Increased doses of applied N are no alternative to growing grass, as impacts on the environment would strongly increase as well. As a result, the data strongly support our second hypothesis, and the crop rotation system can be considered as an adequate alternative to maize in monoculture, due to competitive dry matter yields of wheat. An exclusion of Italian ryegrass (1 cut) which only contributed to a very low share of total DM yield might be a reasonable improvement of the rotation, as management effort and thereby costs for the farmers could be reduced. However, the cultivation of ryegrass such as catch crops probably reduced NO_3 leaching over winter, which would support the inclusion of this crop in a production system.

5. Conclusions

Fertilization of biogas residues by trail hoses without immediate soil incorporation can lead to high ammonia emissions by volatilization, resulting in significant environmental impacts which could include acidification, eutrophication and denitrification after N-deposition. N-losses reached levels of more than 30% of NH_4-N applied in presence of strong winds and contributed to strongly decreased yields. Biannual total ammonia losses were highest for perennial ryegrass (77 kg N ha^{-1}) followed by wheat (48 kg N ha^{-1}) and maize (20 kg N ha^{-1}) at the moderate fertilization level. Application of biogas residues had a reduced fertilizer N-value for ryegrass and wheat as compared to CAN while no effect was observed for maize because of the lower N-fertilization demand of this crop.

Due to similar dry matter yields, the crop rotation system consisting of maize, wheat and Italian ryegrass (two-year average of 34 t DM ha^{-1}) was comparable with maize in monoculture (two-year average of 31 t DM ha^{-1}) as substrate for biogas production. An option to optimize the crop rotation could be decreased management effort and costs by excluding the one-time cut Italian ryegrass (<2 t DM ha^{-1}) which would in turn increase the risk of N-leaching in winter. Perennial ryegrass was characterized by a very low uptake efficiency of biogas residue N applied by trail hoses. Unless a more efficient biogas slurry application (e.g. injection) can be established under marshland conditions, perennial ryegrass as part of a biogas production system is inadvisable.

The combined plot method (cpm) showed a close correlation to the reference method (micrometeorological bLS technique) and can therefore be considered as appropriate for investigation of N-losses by ammonia volatilization after application of organic fertilizers by trail hoses. This study confirms that this applies also to locations characterized by high average wind speeds.

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