Reduction of ammonia emissions by acidification of cattle slurry applied to grassland

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Abstract
Agricultural ammonia (NH_3) losses originate mainly from handling and application of farmyard manure and slurries. In 2012 several abatement technologies to reduce ammonia emissions in the field were tested on grassland on sites in Northern Germany and Southern Denmark: 2 injection distances (17.5 and 35cm slot distance) and 2 acidification levels (pH 6.5 and 6.0) compared to trailhose application. Trailhose application showed highest losses from 8.2 - 40% NH_4^+-N applied, Injection 17.5 cm 1.7 - 28.5%, Injection 35cm 1.5 - 10.1%, Acidification pH 6.5 4.4 - 20% and Acidification pH 6.0 0.7 - 24% of applied NH_4^+-N. Acidification to a level of pH 6.0 and injection with 35cm slot distance can lower the ammonia emissions up to 90% as compared to trailhose application. In contrast to significant reduction of NH_3 losses, only at the Danish site significant yield differences occurred.

Introduction
Ammonia losses are the main cause of several environmental problems as soil acidification and air-borne eutrophication [1]. In 2005, 95% of German NH_3 emissions originated from agriculture and 84% of agricultural NH_3 emissions have been caused by livestock farming and the handling and application of manures[2]. Several techniques to reduce NH_3 losses from field applied liquid manure are available, like injection of slurry. But there exist several restrictions for the application of injection techniques like fertilization on dry compacted or stony soils as well as lower working capacity. Apart from covering and mixing of slurry with soil as reduction measure, a lowering of slurry pH is an alternative abatement measure as NH_3 evolves quantitatively only at slurry pH greater than 7. Against this background, a new technique of acidification of slurry while application was developed as new application technique. The SyreN® (Biocover A/S etc.) technology operates by decreasing slurry pH by mixing of slurry with concentrated sulphuric acid to suppress the dissociation of ammonium (NH_4^+) to NH_3 and H^+ in combination with a conventional trailhose application system. To compare the reduction potential of NH_3 emissions from cattle slurry applied to grassland between field based acidification, injection and trail hose spreading, a collaboration project between Aarhus University, Kiel University and the Danish Extension Service was established.

Material and Methods
The field trial was carried out at 2 perennial grassland sites, located close to each other: German Coastal Marsh (site A; 40% clay soil, 4 cut system) and Southern Denmark on sandy soil (site B). Cattle slurry was used site specific with a pH 7.2 – 7.4 and an ammonium N content ranging between 2.0 – 2.8 kg NH_4^+-N per ton. Following treatments were tested: 1. control, 2. trailhose application, 3. acidification A (pH 6.5), 4. acidification B (pH 6.0), 5. injection A (0.175 m slot distance), 6. injection B (0.35 m slot distance). To avoid fertilization effects by sulphuric acid used for acidification, a fertilization of 50 kg S ha^{-1} was done at the first application date. The application rate of slurry, calculated NH_4^+-N based, was 100% of the assumed site specific optimum N level (site A = 320 kg N ha^{-1} a^{-1} split into 4 doses; site B = 240 kg N ha^{-1} a^{-1} split into 3 doses). At site A slurry doses for applications 1, 2, 3 and 4 were 80, 80, 60 and 60 kg NH_4^+-N ha^{-1}, respectively, and for site B, 80 and 50 kg NH_4^+-N ha^{-1}, respectively. The N dose of the first application at site A was lower as planned (120 kg ha^{-1}) due to technical problems during application. At site B slurry treatments were also fertilized with Calcium Ammonium Nitrate (CAN) with doses of 40, 30 and 40 kg N ha^{-1} due to a regionally typical fertilization strategy. To estimate the mineral fertilizer equivalent, stepwise increased synthetic nitrogen fertilization (CAN) treatments were established. Yield was determined by plot harvest. Ammonia emissions were measured by a combined method of calibrated chamber

measurement and passive flux samplers [2]. In 2012 N_2O-emssions were measured on site A by a static chamber approach [3]. The field trial was set up as a fully randomized block design with plots of 9m x 9m and four replicates per treatment. Between the plots guard areas of the same dimension were established to reduce the influence of NH_3 drift between plots, resulting in a chess-board design. Ammonia losses and yields were statistically tested for each site by means of Oneway ANOVA and Tukey LSD posthoc test by using R (Version 2.15.1, The R Foundation for Statistical Computing). Linear regression analyses were calculated and depicted by using SigmaPlot (Version 11.0; Systat Software Inc., San Jose, USA).

Results and Discussion

Ammonia emissions

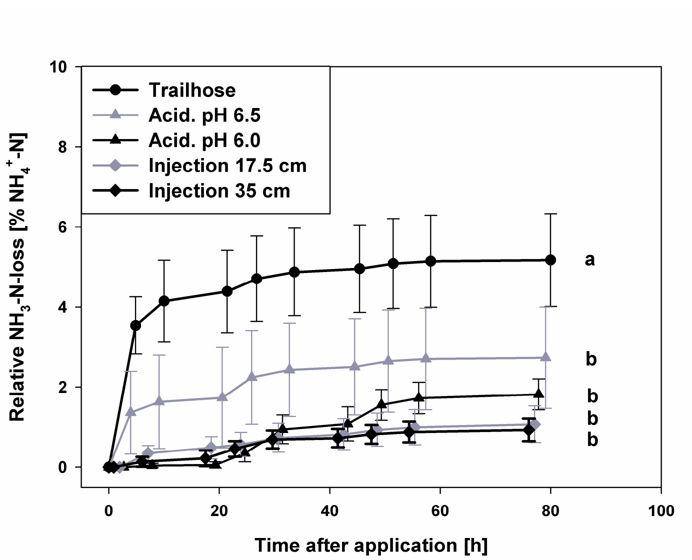

Figure 1: Ammonia loss dynamics of slurry treatments at second application 2012 on Site B. Letters behind curves indicate significant differences (p=0.05).

Compared to typical ammonia loss dynamics of surface applied slurries and digestates, the dynamics of acidification and injection treatments was not following a typical Michaelis-Menten type kinetics. As shown for example in figure 1, ammonia volatilization of slurry acidified to pH 6.0 was delayed for approximately one day. The rising emissions on day two after application may be caused by a pH increase in the slurry layer on the soil surface due to buffering processes in the slurry mixed with sulphuric acid. This effect was observed several times, especially for acidification to pH 6.0. Injection of slurry led to flattened volatilization dynamics.

As shown in figure 2, cumulated ammonia emissions differed significantly depending on application method. At site A trailhose application showed the significantly highest losses (53,4 kg NH_3-N ha^{-1}). Losses after injection A and acidification A were significantly lower compared to trailhose application (38,0 and 33.2 kg NH_3-N ha^{-1}, respectively). The significantly lowest ammonia losses were indicated by acidification B and injection B (19.9 and 16.6 kg NH_3-N ha^{-1}, respectively), whereas pH lowering for acidification B failed at the third application (pH 7.0).
On site B ammonia losses after acidification A, injection A and acidification B (8.6, 7.0 and 4.8 kg NH_3-N ha^{-1}, respectively) were significantly lower than after trailhose application (14.3 kg NH_3-N ha^{-1}). Following injection B (3.4 kg NH_3-N ha^{-1}) ammonia losses were significantly lower than after trailhose application and acidification A. The amounts of concentrated sulphuric acid (96%) to mix into the slurry were on a level of 1.5 litres per ton slurry for pH 6.5 and about 2.5 litres per ton slurry for pH 6.0.
Injection was done by double-disc injectors and soil conditions were appropriate to allow adequate penetration depth. Especially on heavy clay soils as on site A, injection may fail, when soil is too dry and may not reduce ammonia losses efficiently [4]. Site B with sandy soils always allowed appropriate injection conditions because of low penetration resistance. On both sites, damages of sward were no problem.
Higher N_2O-losses after injection of slurry into the soil as reported in many other studies was not observed on site A after analysis of the first five months' data (data not shown). CAN treatments were characterized by higher losses of N_2O as compared to slurry applied by trail hoses though not significantly. There was also a slight insignificant trend of higher N_2O emissions after application of acidified slurries.

Dry matter yields

Despite of differences in ammonia loss of the single application methods, no dry matter yield differences were found on site A (Fig. 2). In tendency, trailhose application showed lowest yields and Injection 0.35 m highest yields in comparison of all slurry treatments. Mineral fertilization on the same level (320 kg N ha^{-1}) showed significant higher yields.

Lowest yields at site B were determined for trailhose application, only. Acidification B resulted in significantly higher yields. Yields of slurry treatments were comparable to the same level of mineral fertilization with Calcium Ammonium Nitrate (240 kg N ha^{-1}).

Significant correlations between dry matter yield and ammonia loss (Fig. 3) were weak for site A (r^2 = 0.15) but stronger for site B (r^2 = 0.27). The small slope of these correlations can be explained by the high N-levels on both sites close to the optimum, and both sites have been fertilized with liquid manures for a long time. But other effects may also play a role. Yields in the slurry treatments on site A were low, compared to mineral fertilization with CAN. This is probably caused by fixation of ammonium to clay particles of the clay soil at this site. Therefore, mineral fertilizer equivalents at site A were obviously lower than at site B.

But the height of ammonia losses may not explain the higher yields of acidification B on site B compared to injection. A possible hypothesis is, that injection leads to a damage of the sward reducing the positive yield effect of NH_3 loss savings shown in an earlier study [4]. In addition acidification may lead to a higher uptake of other plant nutrients improving plant growth. Plant nutrient uptake will be analysed to test the second hypothesis.

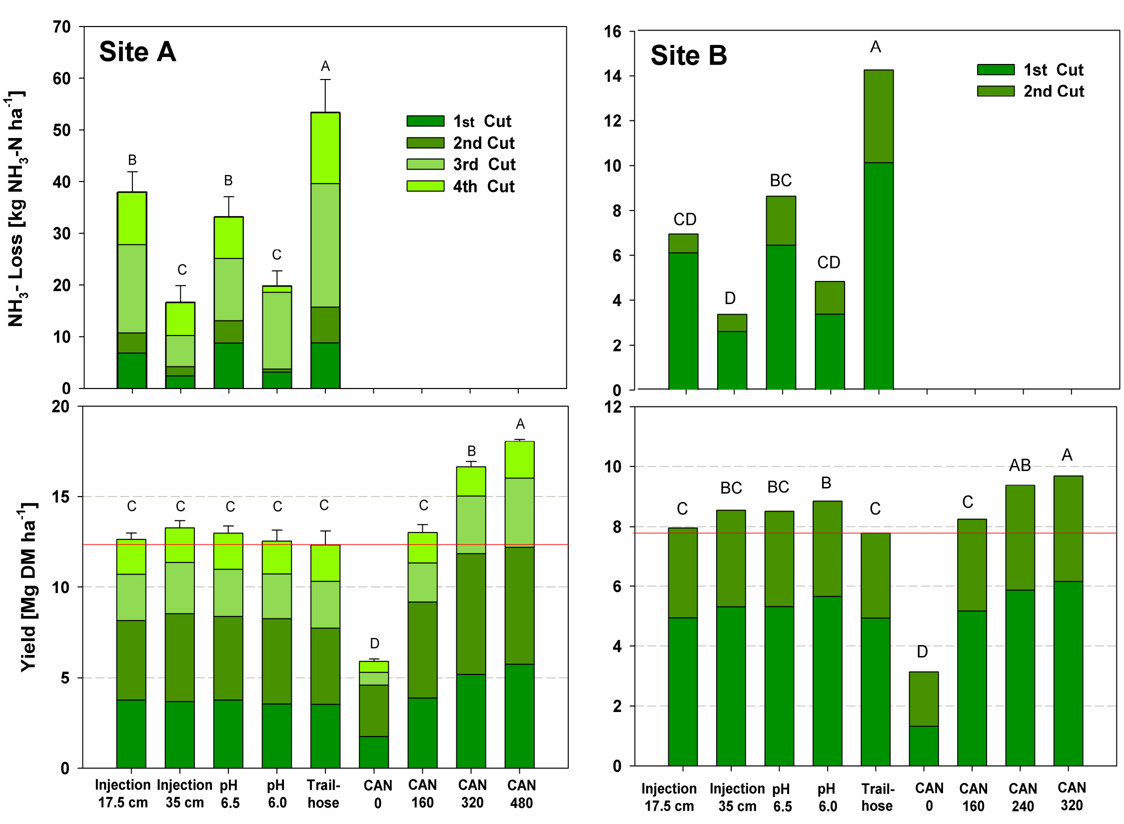

Figure 2: Ammonia losses and dry matter yields of different fertilization treatments on site A and B in 2012. Different letters indicate significant differences between treatments (p=0.05).

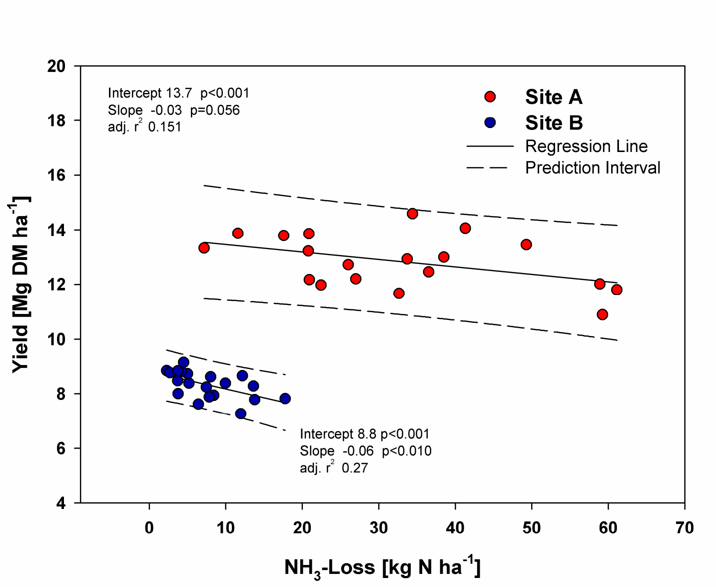

Figure 3: Correlation between drymatter yield and ammonia losses on single plots at site A and B

Conclusion and perspectives

Acidification proved to be very effective to reduce NH_3 losses when acidified to a level of pH 6.0 but also a pH of 6.5 resulted in about half the emissions compared to trail hose application. Injection with wide slot distance evenly reduced NH_3 losses in the same order of magnitude as acidification to pH 6.0. Reaching the aimed pH by adding sulphuric acid in the tank happened to be difficult at the field trial scale with non-commercial technology. Improvement of field trial technique as well as measurements in other crops and with other organic slurries are needed to confirm the applicability of slurry acidification as a general measure for the reduction of NH_3-emissions. First own results indicate, that the acid amount for anaerobic digestates to lower the pH to 6.0 needs about 3 times as much acid compared to the slurries used in this trial. To obtain data of several years, this trial at the German and the Danish sites will be continued in 2013.

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