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# Slurry acidification outperformed injection as an ammonia emission-reducing technique in boreal grass cultivation

**Riikka Keskinen** [ID] · **Maarit Termonen** [ID] · **Tapio Salo** [ID] · **Sari Luostarinen** [ID] · **Mari Räty** [ID]

**Abstract** Ammonia ($NH_3$) constitutes the single largest loss of manure nitrogen (N), making measures targeted at reducing its emissions meaningful for the environment and the overall efficiency of manure N use. In this study, the performance of two emission-reducing techniques, acidification and injection, were studied in a field experiment with grass ley over two growing seasons. Emissions of $NH_3$, crop growth, and N use efficiency were determined from plots fertilized with cattle slurry either band spread, injected or band spread after acidification. The approximate cumulative $NH_3$ losses from the plots with band-spread untreated slurry amounted to about 22 kg $NH_3$-N ha$^{-1}$ over the observation periods in 2017 and 10 kg $NH_3$-N ha$^{-1}$ in 2018. The injection and acidification reduced the estimated cumulative $NH_3$ emissions by 43 and 95% respectively in 2018, and both by 97% in 2017. In 2017, the emission-reducing techniques had no impacts on crop growth, but in 2018, acidification increased dry matter yield by 29% and apparent N recovery by 65% compared with band-spread untreated slurry. According to the current results, acidification consistently produced the lowest $NH_3$ emissions and a discernible positive yield effect. It can therefore be recommended instead of injection for reducing $NH_3$ emissions in boreal grass cultivation.

**Keywords** Band spreading · Cattle slurry · Grass yield · Nitrogen · Sulfur · Sulfuric acid

## Introduction

Despite decades of efforts to improve nitrogen (N) use efficiency in agriculture, a major reservoir of N excreted in livestock manures remains underutilized (Bouwman et al. 2009; Leip et al. 2011; Liu et al. 2017). At best, roughly half of the manure N supply is used by crops, while the rest is lost to the environment in different forms (Oenema et al. 2007; McCrakin et al. 2018). Leached nitrate ($NO_3^-$) causes eutrophication of surface waters and pollution of groundwaters, volatilized ammonia ($NH_3$) induces the acidification and eutrophication of wider ecosystems, whereas nitrous oxide ($N_2O$) acts as a greenhouse gas (Webb et al. 2013). In addition to the environmental hazards, leakages of reactive N are not economically sensible. Reducing the losses of manure N requires systemic action comprised of ways to ensure sufficient field area for manure

R. Keskinen (✉) · T. Salo · S. Luostarinen
Natural Resources Institute Finland (Luke), Tietotie 4, 31600 Jokioinen, Finland
e-mail: riikka.keskinen@luke.fi

M. Termonen · M. Räty
Natural Resources Institute Finland (Luke), Halolantie 31 A, 71750 Maaninka, Finland

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application in relation to stock density, to identify alternative management strategies for direct land spreading, and to optimize animal diets, housing, manure storage, and application technologies (Rotz 2004; Sims et al. 2005; Liu et al. 2017).

Losses of manure N over storage and during and directly after soil application are dominated by $NH_3$ volatilization (Webb et al. 2013). According to the modeling of Oenema et al. (2007), an average of 19% of the N excreted in animal housing volatilized as $NH_3$ during storage, and another 19% following soil application. The relative proportions of $NH_3$ and its non-volatile conjugate acid ammonium ($NH_4^+$) depend on pH and temperature, so that the presence of $NH_3$ increases with an increase in these variables (Hartung and Phillips 1994; Martinelle and Häggström 1997). In fresh animal excreta, N occurs as mainly organically bound (Bristow et al. 1992; Kirchmann and Witter 1992). The organic N compounds are mineralized at various rates to an inorganic form as $NH_4^+$, the urea in urine being a major rapidly degradable source of N (Van Kessel et al. 2000). Marked $NH_3$ release can be expected at pH levels above 7, which are typically reached in manures (Sommer and Hutchings 2001). Due to the dominance of $NH_3$ in N losses, measures targeted at reducing its emissions are meaningful in increasing the overall efficiency of manure N use.

Lowering the slurry pH to 4.5–6.5 by the addition of acid can be used to increase the ratio of $NH_4^+$ to $NH_3$ and thus minimize $NH_3$ volatilization (Ndegwa et al. 2008). This acidification practice with strong sulfuric acid ($H_2SO_4$) has already become established in Denmark (e.g. Fangueiro et al. 2015). Its effectiveness varies, but in field applications, decreases of up to 80% in $NH_3$ emissions and several dozen kg of conserved N ha$^{-1}$ have been reported (e.g. Pain et al. 1994; Kai et al. 2008; Fangueiro et al. 2015). Although there are safety risks in handling $H_2SO_4$, its high efficacy in comparison to weaker acids and high accessory sulfur (S) content can be considered advantages, especially in conditions where there is a concern of sufficient S supply due to decreased atmospheric deposition and low S fertilization (Keskinen et al. 2016; Michalovicz et al. 2021).

An alternative to acidification with acids in preventing $NH_3$ volatilization is to quickly cover the manure with soil following application to minimize the surface area of slurry exposed to the atmosphere (Sommer and Hutchings 2001; Webb et al. 2013). In comparison to the conventional surface broadcasting method, emissions of $NH_3$ can be roughly halved by band spreading, and reduced by up to ca. 90% by slurry injection or incorporation below the soil surface (Webb et al. 2005). To make the most of the injection technique in $NH_3$ emission reduction, application rates need to be adjusted to the slot volume so that it can hold the amount of slurry applied (Webb et al. 2013). Increasing the volume of the slots decreases $NH_3$ losses but increases the demand for energy due to the soil's penetration resistance (Hansen et al. 2003).

In this study, the effects of applying cattle slurry with acidification and injection on $NH_3$ emissions, crop growth, and N use efficiency were studied in boreal grass cultivation during two growing seasons. It was hypothesized that the N conserved from volatilization increased the amount of N available for crop uptake and was thus reflected as increased yields. However, a successful reduction of emissions has not always resulted in significant increases in crop N uptake (Webb et al. 2010). This may be related to difficulties in measuring small changes against large background variations caused by the heterogeneity in manure composition, soil fertility, and/or weather conditions or that N has not been the growth limiting factor. On the other hand, the tested methods may have other than N-related influences on crop growth. The injection technique may mechanically damage the crops and thus impair growth (Rodhe et al. 2006). Acidification permits gentler surface application, but pH manipulation affects the composition and processes in the slurry, the impacts of which are not yet thoroughly understood (Fangueiro et al. 2015). This field scale comparison of the two slurry $NH_3$ reduction techniques aims to deepen the understanding of their overall performance in northern growing conditions and serves to encourage their adoption among farmers.

## Material and methods

### Study site and experimental design

The two-year field experiment was conducted in 2017–2018 in a grass ley field on fine sandy loam (Humic Dystric Regosol, WRB) on the premises of

the Natural Resources Institute Finland (Luke) in Maaninka, Kuopio, in east-central Finland (63°8'N, 27°18'E). In the plough layer, the soil pH ($H_2O$) was 6.2, and the content of total carbon (C) and N was 1.6 and 0.15% respectively (Supplementary Table 1). According to the Finnish agronomic soil test, the status of soil phosphorus (P), potassium (K), and S was classified as satisfactory, and calcium (Ca) and magnesium (Mg) as fair. In terms of acid-extractable nutrient reserves in a five-grade classification system ranging from poor to good, the reserves of P, K, and Mg were classified as good.

During the field experiment, meteorological data were obtained from Finnish Meteorological Institute's observation station located at Luke Maaninka, Kuopio (Finnish Meteorological Institute 2019), less than 200 m from the experimental site, and long-term averages for the climatological normal period 1981–2010 from Pirinen et al. (2012). The mean annual precipitations in 2017 and 2018 were 623 and 512 mm respectively, and the respective mean annual temperatures were 3.8 and 4.5 °C, exceeding the long-term average by 0.7 and 1.3 °C respectively (Supplementary Fig. 1). The Growing degree day (GDD) sum (the daily mean temperature $> +5$ °C) ranged from 1073 in 2017 to 1617 °C days in 2018. In 2017, the mean annual precipitation was nearly equal to the long-term average of 612 mm, whereas it was clearly lower in 2018. In the summer season, the monthly precipitation sum varied from 38 in June to 93 mm in July in 2017, the respective values being 99 and 21 mm in 2018. In comparison with the long-term averages of 66 mm in June and 77 mm in July, June and July 2017 were characterized by distinctly drier and wetter conditions respectively, the situation being the opposite in 2018.

On August 10 in 2016, an experimental field comprising grass ley plots of 15 m$^2$ (1.5 m × 10 m) was seeded with a mixture of timothy (*Phleum pratense* L., cv. Nuutti, seed rate 16 kg ha$^{-1}$) and meadow fescue (*Festuca pratensis* Huds., cv. Valtteri, seed rate 9 kg ha$^{-1}$), and fertilized with NPK compound fertilizer (31 kg N ha$^{-1}$, 11 kg P ha$^{-1}$, 10 kg K ha$^{-1}$). Slurry application treatments implemented after the first cuts in 2017 and 2018 were arranged on the field in a randomized complete block design with four replicates, including non-experimental plots between each experimental plot. The set-up included three cattle slurry treatments with an application rate of 42.5 t ha$^{-1}$: (1) surface application of untreated slurry (US); (2) (shallow) injection of untreated slurry (US inj.); and (3) surface application of Acidified slurry (AS) and four increasing mineral N fertilizer application levels of 0, 40, 70, and 90 kg ha$^{-1}$ (min-N). Surface-applied slurry was spread to the ley plots in bands at intervals of 0.25 m by a watering can, representing the band-spreading technique. In terms of injection technique, slurry was injected to a depth of 0.05–0.07 m by a plot-sized slurry spreader with 6 double disks, a capacity of 1 m$^3$, and a working width of 1.5 m. The mineral fertilizers were surface-applied using a Tume RL 1500 spreader.

Due to technical challenges in 2017, slurry injection was carried out on July 3 and surface applications the day after, whereas all slurry applications took place on June 20 in 2018. In 2018, one US inj. plot received less slurry than the other three plots due to a blockage in one of the injection hoses, and this plot was therefore removed from the statistical analysis. Otherwise, the injected amounts were assumed to be equal, despite the fact that the possibility of fluctuating amounts of injected slurry could not be completely excluded among the three other US inj. plots in 2018. The mean content of total N (2.9–3.2 kg t$^{-1}$), $NH_4^+$-N (1.6–2.1 kg t$^{-1}$), total P (0.56–0.65 kg t$^{-1}$), and total K (2.7–3.4 kg t$^{-1}$) were quite similar between the different slurries, with the notable exception of S, which averaged 0.4–0.5 kg t$^{-1}$ for the untreated slurries and 1.8–2.2 kg t$^{-1}$ for the acidified slurries. For the second cut, no additional mineral fertilizers were applied to the slurry plots. Mineral P and K fertilizer applications were provided to the treatments with increasing min-N application levels, equal to the amounts in slurries. Application rates of S were not adjusted equally between treatments. Application rates of nutrients (N, P, K, and S) for the second cut in 2017–2018 are given in Table 1. For the first cut in 2017–2018, all experimental plots were fertilized equally using mineral fertilizers (100 kg N ha$^{-1}$, 0 kg P ha$^{-1}$, 28 kg K ha$^{-1}$, and 16 kg S ha$^{-1}$). Similarly, all plots received an equal mineral fertilization (50 kg N ha$^{-1}$, 0 kg P ha$^{-1}$, 52 kg K ha$^{-1}$, and 7 kg S ha$^{-1}$) for the third cut in 2018, while the third cut in 2017 was unfertilized.

**Table 1** Application rates of total nitrogen (N), available nitrogen (N), and total phosphorus (P), potassium (K), and sulfur (S) in slurry (42.5 t ha$^{-1}$) and mineral fertilizers for the second cut in 2017–2018

| Treatment | Application rate (kg ha$^{-1}$)[a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Year 2017 | | | | | Year 2018 | | | | |
| | Total N[b] | Available N[c] | Total P[d] | Total K[d] | Total S[e] | Total N | Available N | Total P | Total K | Total S |
| US | 131 | 70 | 25 | 137 | 16 | 125 | 81 | 24 | 116 | 21 |
| US inj | 131 | 70 | 25 | 137 | 16 | 125 | 81 | 24 | 116 | 21 |
| AS | 131 | 69 | 26 | 144 | 91 | 134 | 87 | 28 | 130 | 78 |
| min-N 0 | 0 | 0 | 22 | 130 | 1 | 0 | 0 | 22 | 130 | 1 |
| min-N 40 | 40 | 40 | 22 | 131 | 7 | 40 | 40 | 22 | 131 | 7 |
| min-N 70 | 70 | 70 | 22 | 133 | 12 | 70 | 70 | 22 | 133 | 12 |
| min-N 90 | 90 | 90 | 22 | 133 | 15 | 90 | 90 | 22 | 133 | 15 |

US=untreated cattle slurry applied by band spreading, US inj.=untreated cattle slurry applied by injection, AS=cattle slurry acidified with sulfuric acid, applied by band spreading. Min-N=application levels of mineral nitrogen fertilizers of 0, 40, 70, and 90 kg ha$^{-1}$

[a] Slurry samples were taken during the field applications, with two replicated samples per treatment. The samples were composed of subsamples during applications. The average of US and US inj. results was used

[b] Kjeldahl method (EN 13,654–1 mod.; EN 13,342)

[c] In the slurries, available nitrogen ($NH_4^+$-N) was determined by the extraction of a fresh sample with 0.1 M $K_2SO_4$ (1:12.5 w:w) ratio, and filtrates were determined with the Kjeldahl method (EN 13,342; EN 13,654–1 mod). Slurry may also contain a very low amount of $NO_3^-$-N, included in the $NH_4^+$-N fraction in this context. Available N in mineral fertilizers comprises $NH_4^+$-N and $NO_3^-$-N

[d] Dry combustion at 550 °C and extraction with 4.0 M HCl (ISO 5516:1978)

[e] Aqua regia extraction (EN 13,650)

## Acidification procedure and slurry analysis

One week before slurry applications for the grass plots, cattle slurry was collected by a tractor-drawn tank from a covered storage pit (100 m$^3$) serving as a pre-tank for a farm-scale biogas plant on a dairy farm of the Natural Resources Institute Finland in Maaninka, Kuopio. After thorough mixing in the tank, slurry was poured gradually into four pre-weighed open plastic containers (each 1 m$^3$). In the containers, the slurry was weighed and then diluted by adding tap water with a 1:7.5–8.5 (v:w) ratio, targeting a Dry matter (DM) of about 7.7% to enable flow through the slurry spreader. Two containers were preserved untreated at the original pH, and the slurry in the other two containers was acidified, targeting a pH of 5.5 with commercially available concentrated $H_2SO_4$ (KemAcipro TECH™ 93%; density of 1.82 kg dm$^{-3}$). Prior to treatments and in situ pH measurements (Hanna Instruments HI98191, with pH sensor HI72911B, Pietiko Oy, Finland), all slurries were stirred with a container mixer (HLS 0.75/90, Mamec Oy, Finland) at 90 rpm

for about 3 min, with the exception of slower stirring to avoid foaming during the pouring of $H_2SO_4$. The containers were stored uncovered in an unheated storehouse until field applications. In situ pH measurement was conducted at the end of the short storage period. The acidification treatment represented short-term storage or spreading tank acidification techniques. The acidified slurry, in which the final pH was closer to the targeted value of 5.5, was selected for field applications. In the acidified slurries, the pH was 5.5 in 2017 and 5.6 in 2018, and the DM content was 7.5 and 8.1% respectively. For the untreated slurries, the pH averaged 7.3, with DM 7.4–8.1%. In total, 3.3 and 2.6 l $H_2SO_4$ were needed per tonne of slurry to achieve the target pH in 2017 and 2018 respectively.

## Soil analysis

After the last harvest of the year, soil samples were taken from each plot with an auger at the depths of 0–0.02, 0.02–0.10, and 0.10–0.25 m on October 23, 2017 and September 25, 2018. Easily available total

N and inorganic N ($NH_4^+$-N and $NO_3^-$-N) were extracted from fresh soil samples with 2 M KCl at a soil:solution ratio of 1:5 (w:v) for 2 h. The suspensions were filtered and frozen until analyzed for $NH_4^+$-N and $NO_3^-$-N with a Skalar San$^{++}$ auto-analyzer. Soluble organic N (SON) was taken as the difference between soluble total N acquired after oxidative digestion and inorganic N. Soil S was analyzed from acid ammonium acetate (AAAc, 0.5 M $CH_3COONH_4$, 0.5 M $CH_3COOH$, pH 4.65, at a soil:solution ratio of 1:10 (v/v) for 1 h) extracts obtained according to Vuorinen and Mäkitie (1955). Soil pH was measured in a soil–water suspension (1:2.5 v:v).

### Yields and plant analyses

The grass plots were harvested by a Haldrup 1500 plot harvester from a 12 m$^2$ area (1.5 m × 8 m) to a stubble height of 0.07 m three times per growing season. In 2017, the first cut was on June 28 and the second on August 11, and the third cut for the unfertilized grass ley was carried out on October 11. In 2018, the corresponding cuts were on June 15, July 27, and September 10.

The DM content was determined gravimetrically by drying fresh samples at 60 °C for 40–48 h, after which the DM yield was calculated. The content of crude protein and digestibility value (D value) of forage grass were analyzed from each cut using the Near-infrared spectroscopy (NIR) technique (Foss NIRSystems XDS analyzer, Valio Ltd). To calculate the total N content (g kg$^{-1}$ DM) and N yield (kg ha$^{-1}$), the content of crude protein was divided by a protein-to-N conversion factor of 6.25. The apparent recovery of total and available N was calculated using Eqs. 1 and 2 respectively, where N yield$_{min-N\,0}$ =N yield of min-N 0 treatment, where no N fertilizer was applied. Available N represents $NH_4^+$-N in terms of slurry, and $NH_4^+$-N and $NO_3^-$-N in terms of mineral fertilizers.

$$Apparent\ N\ recovery\ (\%)$$
$$= \frac{N\ yield\ (kgha^{-1}) - N\ yield_{min-N0}\ (kgha^{-1})}{total\ N\ content\ of\ applied\ fertilizer\ (kgha^{-1})} \times 100$$
$$(1)$$

$$Apparent\ available\ N\ recovery(\%)$$
$$= \frac{N\ yield\ (kgha^{-1}) - N\ yield_{min-N0}\ (kgha^{-1})}{available\ N\ content\ of\ applied\ fertilizer\ (kgha^{-1})} \times 100$$
$$(2)$$

Mineral N equivalences for the slurry treatments were calculated from the yield response curve of the ley to increasing min-N additions. Determination of total S was carried out according to Miller (1998), using a microwave wet digestion method in a closed vessel. Dry plant samples were digested in concentrated $HNO_3$-30% $H_2O_2$ mixtures in a microwave (CEM Mars 6). The concentration of S in extracts was analyzed by an iCAP 6500 DUO ICP emission spectrometer. The concentrations of P and K were determined using the X-ray fluorescence (XRF) method (Valio Ltd).

### Ammonia measurements

The $NH_3$ volatilization rates from slurry-treated plots were measured using the equilibrium concentration technique (JTI method) as in Hagner et al. (2021). The method combines the stirred dynamic chamber method with a passive diffusion sampler technique and enables simultaneous field measurements in small plots (Svensson 1994; Mattila 2006). Briefly, in the L-type passive diffusion samplers, adsorption filters (Whatman® Grade 40), which were impregnated with 2% oxalic acid ($C_2H_2O_4 \times 2\ H_2O$)–methanol ($CH_3OH$) solution and dried in a desiccator, were mounted at the top of the sampler and directly exposed to the ambient air. In turn, in the C-type samplers, the adsorption filters were placed at the bottom and membranes (Fluoropore® PTFE, hydrophobic) on top of the samplers. In each slurry plot, a steel frame was mounted in the ground, covering two slurry bands/slots and an area of 0.12 m$^2$, and the chamber was set then on top of the frame. A white plastic container (length 0.40 m × width 0.32 m × height 0.20 m) served as the ventilated chamber, which was equipped with a battery-operated air-mixing fan. A metal plate was placed in front of the opening of the chamber to exclude the influence of external wind. Both types of passive diffusion samplers were mounted with two replicates on the vertically adjustable holders and placed

between the bands/slots both inside the chamber and outside, at about 1.5 m from the chamber.

In 2017, the slurry injection treatment was carried out on July 3, during which three series of $NH_3$ measurements (1.6–2.0 h) were implemented on these plots. Band-applied slurries were spread a day after the injection, and in these plots, three series of measurement periods of 1.5–2.0 h were conducted on the first day (July 4), and one longer measurement period (5.0 h) on both the second (July 5) and third (July 6) day. In 2018, three series of measurement periods of 1.9–2.9 h were carried out during the day of slurry applications on June 20, and two series of 3.0 and 4.7 h on the following day (June 21). Surface applications of slurries were performed within about 1 h at 10–11 a.m., and slurry injection within about 0.5 h at around noon but before 1 p.m. The $NH_3$ measurements were started in each plot within 0.17 h after the slurry application. Furthermore, background concentrations of $NH_3$ were measured from a similar untreated grass ley and soil type within 50 m of the experimental site with two to three replicates, and their time and duration coincided with the $NH_3$ measurements in the experimental plots. After the measurements, the $NH_3$ filters were extracted with 8 ml of $H_2O$ for 0.5 h, and the $NH_4^+$-N concentrations of the extracts were then analyzed with a Skalar San$^{++}$ autoanalyzer. The ammonia volatilization rate was calculated using equations as fully described by Svensson (1994) and Mattila (2006). The data from the separate measurement series were extrapolated over the entire period until the end of the last measurement episode, covering an average period of 53 h in 2017 and 29 h in 2018. Exceptionally, the cumulative emissions from the plots that had received injected slurry in 2017 were estimated only over 9 h on the day of slurry application due to technical problems. For the approximate estimate of cumulative $NH_3$ emission, the averages of two consecutive measurements were applied for the intervals between the measurement periods, and the emission during the night (from 9 p.m. to 8 a.m.) was assumed to be insignificant. This was supported by Häni et al. (2016), who reported negligible nighttime emissions of $NH_3$ after application of livestock slurry to grassland.

Weather conditions during $NH_3$ measurements

In the experimental area, precipitation, temperature, and wind speed were recorded by a weather station (a-Weather, a-Lab Oy, Finland) at a sampling rate of 0.25 h. The wind speed was measured by a cup anemometer at a height of 1.7 m. During the growing season, soil moisture (matric suction) was followed by tensiometers (Irrometer®) at depths of 0.20 and 0.40 m with two replicates. To determine the dry bulk density at depths of 0−0.05, 0.05−0.10, 0.10−0.15, and 0.15−0.20 m, soil profile samples were taken by a window-type auger (Ø 0.048 m) with eight replicates and dried at 105 °C for 48 h. During the $NH_3$ measurements, soil samples were also taken by an auger (Ø 0.023 m) to determine the gravimetric soil water content. At depths of 0−0.05, 0.05−0.10, 0.10−0.15, and 0.15−0.20 m, the respective dry bulk density averaged 1.17, 1.27, 1.42, and 1.43 Mg m$^{-3}$, and was used to convert gravimetric soil water content into volumetric water content.

On July 3–4 in 2017, the injected and band-spread slurries were applied, and the first three $NH_3$ measurement series were conducted in calm and warm weather, with mean and maximum daily temperatures of 16.2–18.6 °C and 21.2–24.4 °C respectively (Supplementary Fig. 2). Thereafter, the weather cooled significantly, and during the last two measurement series, the mean and maximum daily temperatures had dropped to 8.4–11.3 °C and 9.6–13.1 °C respectively. Light rain, with total precipitations of 1.2 and 3.1 mm, fell between $NH_3$ measurements on July 3 and 4, and 4 and 5 respectively. Compared to 2017, the slurry applications and the following three $NH_3$ measurements series were conducted in cooler and windy weather conditions on June 20 in 2018. During the measurement periods on June 20–21, the air temperature varied from 7.3–9.9 °C in the night to 18.1–20.8 °C in the day, with a mean daily temperature of 14.0–15.3 °C. On the day of slurry applications in 2018, wind speed averaged 4.2 m s$^{-1}$ during spreading. After the last measurement period, rainfall appeared with a total precipitation of 35 mm on June 22. During slurry applications, the plough layer tended to be drier in 2017 than in 2018, as monitored by tensiometers (Supplementary Fig. 3). At depths of 0–0.05, 0.05–0.10, 0.10–0.15, and 0.15–0.20 m, the respective volumetric water contents averaged 25, 27,

31, and 32%, being significantly drier only at a depth of 0.05–0.10 m in 2017 than 2018.

Statistical analyses

Statistical analyses were performed using ANOVA (the MIXED procedure of the SAS software 9.4.; SAS Institute Inc. Cary, NC, USA). In the case of plant and $NH_3$ emission analyses, treatment was considered a fixed, and replicate a random, effect. Years and measurement periods were analyzed separately. Negative $NH_3$ emissions were assumed to be zero. A few outliers were removed from the analysis when required (a blockage in one of the injection hoses in 2018, or unconvincing $NH_3$ emission). Logarithmic or square root transformation was used if the assumption of the equality of variance was invalid. When transformation was used, the Standard error of the mean (SEM) is not presented. In the case of $NH_3$ emission, a 95% confidence interval is presented instead of SEM.

The model for soil analyses was constructed using treatment, soil profile, and treatment × soil profile interaction as fixed effects, while replicate and replicate × soil profile interaction were used as random effects. Years were analyzed separately. The soil profile was considered a repeated effect using a Compound Symmetry covariance structure. A few outliers were removed from the analysis when required. Logarithmic transformation was used if the assumption of the equality of variance was invalid. The analysis of pH was calculated by transforming pH to $H_3O$ because of the logarithmic scale of the pH. When transformations were used, SEM is not presented. In the case of volumetric water content, year was considered a fixed, and replicate a random effect.

The Residual maximum likelihood (REML) estimation method and the Kenward-Roger approximation for degrees of freedom were used in all models. Pairwise comparisons of means were determined using Tukey–Kramer's test with a significance level of 0.05.

## Results

### Ammonia emissions

In both study years, slurry injection and acidification treatments reduced $NH_3$ emissions in comparison to band-spread US (Table 2, Fig. 1). However, the reduction in $NH_3$-N volatilization rates was higher in AS compared to US inj., which did not differ significantly from US directly after the slurry application (the first measurement period). In contrast to US, higher $NH_3$ emissions were recorded from the injection treatment in 2018 than in 2017. The acidification treatment consistently produced the lowest $NH_3$ emissions but was not discerned from the US inj. in 2017. Variability between replicate measurements was partly large, generating the substantially wide confidence intervals.

The approximate cumulative $NH_3$ losses from the band-spread US plots over the whole 28–54-h periods amounted to about 22 kg $NH_3$-N $ha^{-1}$ in 2017 (54 h) and 10 kg $NH_3$-N $ha^{-1}$ in 2018 (28 h) (Fig. 1), composing 31 and 12% of the $NH_4^+$-N initially applied in the slurry respectively. For the US inj. (9 h) and AS (53 h), the estimated total $NH_3$-N losses averaged about 0.7 kg $ha^{-1}$ during the entire monitoring periods in 2017, reducing the cumulative $NH_3$ emissions by 97% in relation to the band-spread US. In 2018, the corresponding reductions were 43% for US inj. and 95% for AS, the estimated total emissions reaching about 5.7 kg $NH_3$-N $ha^{-1}$ (30 h) and 0.5 kg $NH_3$-N $ha^{-1}$ (29 h) respectively. Acidification led to a significant decrease in the estimated total $NH_3$-N emissions in both study years. During the day of slurry applications in 2017–2018, the average $NH_3$ volatilization rate from the band-spread US plots was about 3 and 18 times higher than during the measurement series on the second and third day respectively. Consequently, the majority of $NH_3$ losses occurred during the day of slurry application, accounting for an average of 66% of the estimated total losses in the band-spread US plots. Overall, acidification reduced the total $NH_3$-N losses to a very low level, and on the day of AS spreading, the $NH_3$-N losses amounted to 31–83% of the estimated cumulative losses.

**Table 2** Rate of ammonia volatilization (kg $NH_3$-N $ha^{-1}$ $h^{-1}$) during five consecutive measurement periods following slurry field applications in 2017 and 2018. Means ($n=4$) marked with a different letter differ significantly at $p \leq 0.05$ (Tukey's test) within columns and years

| Treatment | $NH_3$ measurement periods[d] | | | | |
|---|---|---|---|---|---|
| | 1 (kg $NH_3$-N $ha^{-1}$ $h^{-1}$) | 2 | 3 | 4 | 5 |
| **Year 2017** | | | | | |
| US | 0.91[b] | 1.79[b] | 1.27[b] | 0.46[b] | 0.07[a] |
| | (0.19, 4.27) | (0.38, 8.47) | (0.52, 3.06) | (0.09, 2.40) | (0.03, 0.19) |
| US inj | 0.16[ab] | 0.08[a] | 0.05[a] | - | - |
| | (0.03, 0.74) | (0.02, 0.37) | (0.02, 0.11) | | |
| AS | 0.02[a] | 0.01[a] | 0.02[a] | 0.00[a] | 0.04[a] |
| | (0.00, 0.08) | (0.00, 0.05) | (0.01, 0.05) | (0.00, 0.02) | (0.01, 0.09) |
| **Year 2018** | | | | | |
| US | 0.82[b] | 0.96[c] | 0.80[c] | 0.14[ab] | 0.44[b] |
| | (0.47, 1.17) | (0.66, 1.32) | (0.67, 0.94) | (0.06, 0.22) | (0.12, 1.67) |
| US inj | 0.54[ab] | 0.35[b] | 0.39[b] | 0.19[b] | 0.10[b] |
| | (0.12, 0.95) | (0.15, 0.62) | (0.25, 0.53) | (0.09, 0.29) | (0.02, 0.51) |
| AS | 0.09[a] | 0.01[a] | 0.04[a] | 0.02[a] | 0.00[a] |
| | (-0.26, 0.43) | (0.00, 0.08) | (-0.10, 0.17) | (-0.07, 0.10) | (0.00, 0.01) |

The lower and upper bound of 95% confidence intervals are given in parentheses. US=untreated cattle slurry applied by band spreading, US inj.=untreated cattle slurry applied by injection, AS=cattle slurry acidified with sulfuric acid, applied by band spreading

[d] The ammonia ($NH_3$) measurement periods of 1–3 (an average of 1.5–2.3 h) were conducted on the day of the slurry applications. The measurement periods of 4 and 5 were carried out on the second and third day after applications (5.0 h) in 2017 respectively, and the day after applications in 2018 (an average of 3.0–4.7 h)

Dry matter yield

The first forage cut in 2017, which preceded the slurry applications and was grown with equal mineral fertilization, showed a consistent yield response of an average of 5130 kg DM $ha^{-1}$ (SEM 168, $p=0.26$) and N yield of 93 kg $ha^{-1}$ (SEM 3.8, $p=0.21$) across the field. During the first harvest, the grass canopy was significantly lodged. Differences in the losses of $NH_3$ between the slurry treatments applied for the second cut in 2017 were not reflected in the DM yields (Fig. 2, Supplementary Table 2). The third cut grown without additional fertilizer application remained low, on average 500 kg DM $ha^{-1}$, and evidenced no residual N fertilizer effect for the slurry treatments in comparison to the min-N 70 treatment (Supplementary Table 2).

In 2018, sufficient mineral fertilization was again applied for the first cut, but somewhat higher DM yields were harvested from the US (5970 kg $ha^{-1}$) and US inj. (5950 kg $ha^{-1}$) than from the min-N 70 (5660 kg $ha^{-1}$) and AS (5550 kg $ha^{-1}$) treatments (SEM 129, $p<0.001$). Average N yield was 108 kg $ha^{-1}$ (SEM 4.6, $p=0.21$). In the second cut, having received the slurry applications, the min-N 70 treatment was discerned with the highest yield level when compared to the slurry treatments (Fig. 2, Supplementary Table 2). Among the slurry treatments, AS was more productive than the untreated slurries, whether surface spread or injected. In the third cut with a uniform mineral N fertilizer application, a small positive residual effect was attained for US inj. (2150 kg DM $ha^{-1}$) in comparison to the min-N 70 treatment (1740 kg DM $ha^{-1}$), whereas US and AS did not differ significantly from the min-N 70 (Supplementary Table 2).
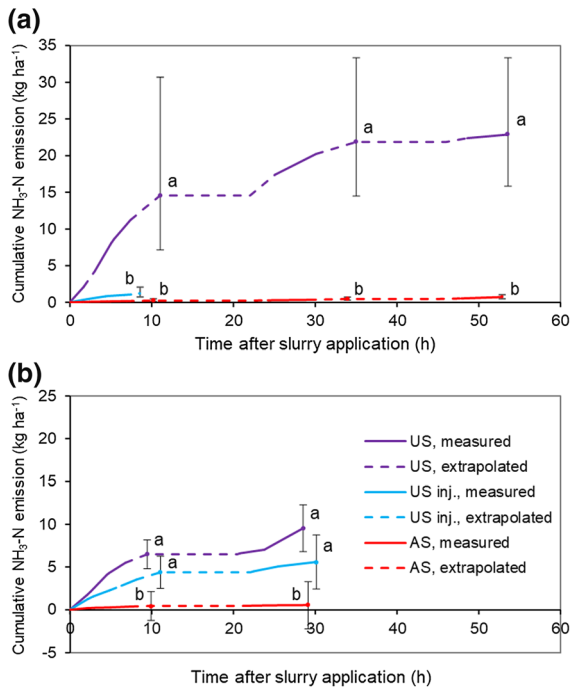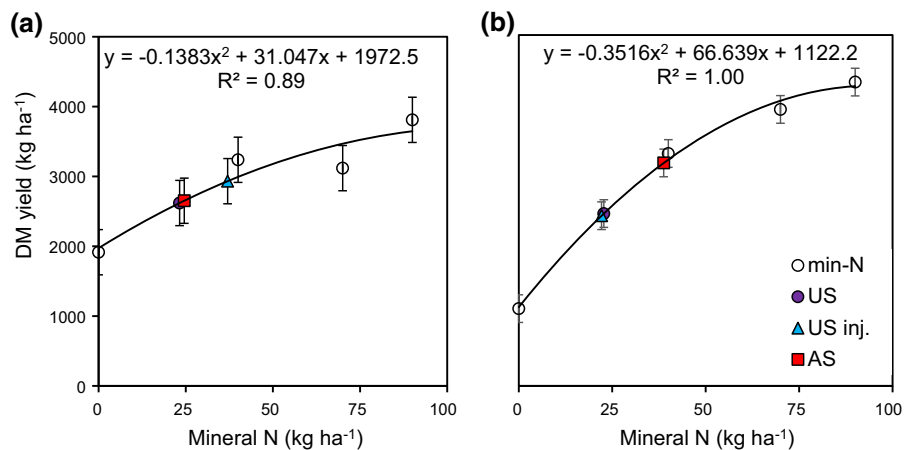
**(a)**



**(b)**



**Fig. 1** Approximate cumulative average ammonia emission (kg $NH_3$-N $ha^{-1}$) during **a** an average period of 53 h after slurry application in 2017, and **b** 29 h in 2018, except for 9 h for the slurry injection treatment in 2017. Bars represent the lower and upper bounds of 95% confidence intervals. Means ($n=4$) for estimated cumulative $NH_3$-N emissions marked with a different letter differ significantly at $p \leq 0.05$ (Tukey's test) within treatments after 1, 2, or 3 days. Note the difference in the scale of the Y-axis. US=untreated cattle slurry applied by band spreading, US inj.=untreated cattle slurry applied by injection, AS=cattle slurry acidified with sulfuric acid, applied by band spreading

Plant samples

Plant sample analyses are reported only for the second cut, for which the slurry treatments were applied. In 2017, no differences between treatments were recorded in plant N and S concentrations, or in total uptakes of these elements (Table 3). Apparent N recovery was clearly higher from mineral fertilizer than from slurries. When confined to the $NH_4^+$-N content of the slurries, higher N recoveries of 23–30% were achieved. According to the yield response curves (Fig. 2), ca. 18% of the total N in US and 18–30% in US inj. and AS were equivalent to min-N. The average D value, K concentration, and P concentration over all treatments were 682 g $kg^{-1}$ DM, 30 g $kg^{-1}$ DM, and 3.5 g $kg^{-1}$ DM respectively. The P concentration of AS (3.7 g $kg^{-1}$ DM) was significantly higher than the P concentration of US (3.4 g $kg^{-1}$ DM), but no other differences between treatments were observed.

In 2018, the N concentration of the grass fertilized with AS was higher than that derived from the US treatment (Table 3). The N yields followed DM yields. In apparent N recovery, AS was discerned as superior among the slurry treatments. The apparent N recoveries were higher overall in 2018 than in 2017. Of the $NH_4^+$-N content, 44% was recovered from AS, and nearly 30% from the other slurry treatments. The substantial S addition within AS was reflected as a slightly higher S concentration in the grass in 2018 (Table 3). The D value of min-N 70 was significantly

**Fig. 2** The yield response curves (DM yield, kg $ha^{-1}$) of increasing mineral nitrogen (N) additions (kg $ha^{-1}$) and the mineral-N equivalences of the slurry treatments in the second cut in **a** 2017 and **b** 2018. US= untreated cattle slurry applied by band spreading, US inj.=untreated cattle slurry applied by injection, AS=cattle slurry acidified with sulfuric acid, applied by band spreading

**(a)**



$$y = -0.1383x^2 + 31.047x + 1972.5$$
$$R^2 = 0.89$$

**(b)**



$$y = -0.3516x^2 + 66.639x + 1122.2$$
$$R^2 = 1.00$$

- ○ min-N
- ● US
- ▲ US inj.
- ■ AS

Table 3 Nitrogen (N) and sulfur (S) content, N and S yields, and apparent N recovery of the total N in the second cut in 2017 and 2018. Min-N 70=mineral N fertilizer application 70 kg ha$^{-1}$, US=untreated cattle slurry applied by band spreading, US inj.=untreated cattle slurry applied by injection, AS=cattle slurry acidified with sulfuric acid, applied by band spreading

| 2. cut | N | | S | | N yield | | S yield | | Apparent N recovery | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (g kg$^{-1}$ DM) | | (g kg$^{-1}$ DM) | | (kg ha$^{-1}$) | | (kg ha$^{-1}$) | | (%) | |
| Treatment | 2017 | 2018 | 2017 | 2018 | 2017 | 2018 | 2017 | 2018 | 2017 | 2018 |
| min-N 70 | 21.3[a] | 17.4[b] | 1.91[a] | 1.67[ab] | 66[a] | 69[c] | 6.0[a] | 6.6[b] | 41[b] | 72[c] |
| US | 20.0[a] | 16.3[a] | 1.74[a] | 1.64[ab] | 52[a] | 40[a] | 4.5[a] | 4.0[a] | 11[a] | 17[a] |
| US inj | 19.6[a] | 17.0[ab] | 1.87[a] | 1.57[a] | 56[a] | 41[a] | 5.2[a] | 3.9[a] | 15[a] | 19[ab] |
| AS | 20.7[a] | 17.6[b] | 1.70[a] | 1.82[b] | 55[a] | 56[b] | 4.5[a] | 5.7[b] | 13[a] | 28[b] |
| Average | 20.4 | 17.1 | 1.80 | 1.67 | 57 | 52 | 5.1 | 5.0 | 20 | 34 |
| SEM | 0.62 | 0.28 | 0.110 | 0.065 | 5.8 | 3.6 | 0.46 | 0.31 | .[1] | .[1] |
| p values | 0.27 | 0.016 | 0.43 | 0.036 | 0.22 | <0.001 | 0.079 | <0.001 | 0.013 | <0.001 |

SEM=standard error of the mean. Means ($n$=4) marked with a different letter differ significantly at $p \leq 0.05$ (Tukey's test) within columns

[1] Logarithmic transformation used; SEM not presented

lower than the D value of slurry treatments (638 g kg$^{-1}$ DM vs. 666 g kg$^{-1}$ DM). The average grass K concentration and P concentration over all treatments were 26 g kg$^{-1}$ DM and 2.8 g kg$^{-1}$ DM respectively. The K concentration of US (24 g kg$^{-1}$ DM) was significantly lower than the K concentration of min-N 70 and AS (27 g kg$^{-1}$ DM).

Soil

Soil analyses revealed that the non-acidified slurries (US and US inj.) tended to increase the soil pH in the uppermost 0.02-m layer in comparison to AS and min-N treatments (Table 4). A similar trend also occurred at a depth of 0.02–0.10 m, though the differences did not prove significant. High S-containing AS enriched S, especially in the deeper soil layers (0.02–0.10 and 0.10–0.25 m).

In soil easily available (KCl-extractable) N concentrations, no differences between treatments were observed at the end of the 2017 growing season (Table 5). In 2018, the concentration of $NO_3^-$-N was slightly higher in US than in the min-N 70 treatment in the 0–0.02 m surface layer and when averaged over all soil depths. In the top 0–0.02 m, the $NO_3^-$-N concentration in US was also identified from that in AS. The slurry treatments tended to exhibit somewhat higher SON and easily available total N concentrations in the 0.02–0.10 m layer than those found in the

min-N 70 treatment, but the difference proved significant only to US. In practice, the differences in soil easily available N among treatments were marginal. Nearly 90% of the acquired N occurred in organic form at all the studied depths in both years.

## Discussion

### Acidification was more dependable than injection in reducing ammonia emissions

Acidification proved efficient in minimizing $NH_3$ emissions to insignificant levels relative to band-spread US, because the AS treatment resulted in 90–99% reductions of $NH_3$ emission rates during three measurements periods on the day of slurry applications in the 2017 and 2018 study years. This finding agrees with the study by Hagner et al. (2021) conducted in the same experimental field area in 2019 with cattle slurry acidified by $H_2SO_4$ or pyrolysis liquid before band spreading to grass ley. During the consecutive years of 2017–2019 in these two studies, the average cumulative $NH_3$-N losses were estimated to represent roughly only 2% of the $NH_4^+$-N (58–87 kg ha$^{-1}$) applied in slurry within about two days following band spreading of acidified slurries. Indeed, these studies confirmed that a decrease of cattle slurry pH below 6 along with

**Table 4** Mean content of soil sulfur (S) and soil pH at depths of 0–0.02, 0.02–0.10, and 0.10–0.25 m at the end of growing seasons 2017 and 2018. Min-N 70=mineral N fertilizer application 70 kg ha$^{-1}$, US=untreated cattle slurry applied by band spreading, US inj.=untreated cattle slurry applied by injection, AS=cattle slurry acidified with sulfuric acid, applied by band spreading

| Year 2017 | S | | | pH | | |
|---|---|---|---|---|---|---|
| | (mg l$^{-1}$) | | | | | |
| | Depth (m) | | | Depth (m) | | |
| Treatment | 0–0.02 | 0.02–0.10 | 0.10–0.25 | 0–0.02 | 0.02–0.10 | 0.10–0.25 |
| min-N 70 | 7.0[a] | 7.3[a] | 8.8[a] | 6.1[a] | 6.3[a] | 6.3[a] |
| US | 7.8[a] | 7.0[a] | 7.9[a] | 6.5[b] | 6.4[a] | 6.3[a] |
| US inj | 6.4[a] | 8.3[a] | 7.7[a] | 6.4[b] | 6.5[a] | 6.4[a] |
| AS | 8.7[a] | 10.3[a] | 14.9[b] | 6.2[ab] | 6.2[a] | 6.2[a] |
| Average | 7.4 | 8.2 | 9.8 | 6.3 | 6.3 | 6.3 |
| SEM | | 0.98 | | | [1)] | |
| p values | | | | | | |
| Treatment | | 0.002 | | | 0.072 | |
| Soil profile | | <0.001 | | | 0.220 | |
| Interaction | | 0.006 | | | <0.001 | |

| Year 2018 | S | | | pH | | |
|---|---|---|---|---|---|---|
| | (mg l$^{-1}$) | | | | | |
| | Depth (m) | | | Depth (m) | | |
| Treatment | 0–0.02 | 0.02–0.10 | 0.10–0.25 | 0–0.02 | 0.02–0.10 | 0.10–0.25 |
| min-N 70 | 11.4[bc] | 12.3[a] | 11.5[a] | 5.6[a] | 6.0[a] | 6.1[a] |
| US | 9.7[ab] | 10.1[a] | 9.7[a] | 6.1[b] | 6.3[a] | 6.2[a] |
| US inj | 8.1[a] | 10.8[a] | 9.8[a] | 6.1[b] | 6.4[a] | 6.4[a] |
| AS | 12.4[c] | 22.3[b] | 32.0[b] | 5.7[a] | 6.0[a] | 6.1[a] |
| Average | 10.4 | 13.9 | 15.8 | 5.9 | 6.2 | 6.2 |
| SEM | | [2)] | | | [1)] | |
| p values | | | | | | |
| Treatment | | <0.001 | | | 0.012 | |
| Soil profile | | 0.024 | | | <0.001 | |
| Interaction | | <0.001 | | | <0.001 | |

M=standard error of the mean. Means ($n$=4) marked with a different letter differ significantly at $p \leq 0.05$ (Tukey's test) within columns

[1]MH$_3$O -transformation used; SEM not presented

[2]Logarithmic transformation used; SEM not presented

acidification may also enable remarkable reductions in NH$_3$ emissions associated with band-spread slurry in grassland farming in boreal conditions, and offer an alternative low-emission application technique for injection as proposed by Fangueiro et al. (2017, 2018). Although acidification treatment eradicated the liming effect of manure, it was not found to cause soil acidification beyond the level in soil that had received min-N.

Of the slurry application techniques, injection of slurry into the soil is generally regarded as a highly efficient mitigation practice to minimize NH$_3$ losses after field application (Misselbrook et al. 2002; Mattila and Joki-Tokola 2003; Webb et al. 2010;

**Table 5** Mean content of easily available nitrogen (N) fractions at depths of 0–0.02, 0.02–0.10, and 0.10–0.25 m at the end of growing seasons 2017 and 2018. SON (soluble organic N)= soluble total N (Tot.N)–soluble inorganic N ($NH_4^+$-N+$NO_3^-$-N). Min-N 70=mineral N fertilizer application 70 kg ha$^{-1}$, US =untreated cattle slurry applied by band spreading, US inj.= untreated cattle slurry applied by injection, AS=cattle slurry acidified with sulfuric acid, applied by band spreading

| Year 2017 | $NH_4^+$-N | | | $NO_3^-$-N | | | SON | | | Tot.N | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (mg kg$^{-1}$ dry soil) | | | (mg kg$^{-1}$ dry soil) | | | (mg kg$^{-1}$ dry soil) | | | (mg kg$^{-1}$ dry soil) | | |
| | Depth (m) | | | Depth (m) | | | Depth (m) | | | Depth (m) | | |
| Treatment | 0–0.02 | 0.02–0.10 | 0.10–0.25 | 0–0.02 | 0.02–0.10 | 0.10–0.25 | 0–0.02 | 0.02–0.10 | 0.10–0.25 | 0–0.02 | 0.02–0.10 | 0.10–0.25 |
| min-N 70 | 1.2[a] | 1.1[a] | 0.5[a] | 0.25[a] | 0.39[a] | 0.36[a] | 10.3[a] | 9.0[a] | 9.2[a] | 11.7[a] | 10.5[a] | 10.0[a] |
| US | 1.2[a] | 0.9[a] | 0.7[a] | 0.36[a] | 0.43[a] | 0.43[a] | 11.1[a] | 8.7[a] | 8.9[a] | 12.4[a] | 10.0[a] | 10.1[a] |
| US inj | 1.1[a] | 0.6[a] | 0.7[a] | 0.33[a] | 0.43[a] | 0.38[a] | 10.6[a] | 9.8[a] | 8.2[a] | 12.1[a] | 10.9[a] | 9.3[a] |
| AS | 1.0[a] | 1.1[a] | 0.9[a] | 0.31[a] | 0.49[a] | 0.39[a] | 11.6[a] | 9.3[a] | 9.0[a] | 12.9[a] | 10.8[a] | 10.4[a] |
| Average | 1.1 | 0.9 | 0.7 | 0.31 | 0.43 | 0.39 | 10.9 | 9.2 | 8.8 | 12.3 | 10.5 | 10.0 |
| SEM | 0.30 | | | 0.052 | | | 0.41 | | | 0.44 | | |
| p values | | | | | | | | | | | | |
| Treatment | 0.95 | | | 0.29 | | | 0.47 | | | 0.59 | | |
| Soil profile | 0.026 | | | 0.075 | | | <0.001 | | | <0.001 | | |
| Interaction | 0.49 | | | 0.41 | | | 0.002 | | | 0.19 | | |
| Year 2018 | $NH_4^+$-N | | | $NO_3^-$-N | | | SON | | | Tot.N | | |
| | (mg kg$^{-1}$ dry soil) | | | (mg kg$^{-1}$ dry soil) | | | (mg kg$^{-1}$ dry soil) | | | (mg kg$^{-1}$ dry soil) | | |
| | Depth (m) | | | Depth (m) | | | Depth (m) | | | Depth (m) | | |
| Treatment | 0–0.02 | 0.02–0.10 | 0.10–0.25 | 0–0.02 | 0.02–0.10 | 0.10–0.25 | 0–0.02 | 0.02–0.10 | 0.10–0.25 | 0–0.02 | 0.02–0.10 | 0.10–0.25 |
| min-N 70 | 0.9[a] | 1.0[a] | 1.1[a] | 0.26[a] | 0.44[a] | 0.48[a] | 12.2[a] | 9.9[a] | 10.5[a] | 13.4[a] | 11.2[a] | 12.1[a] |
| US | 1.4[a] | 1.9[a] | 0.8[a] | 0.68[c] | 0.60[a] | 0.49[a] | 12.8[a] | 12.8[b] | 11.4[a] | 14.9[a] | 15.3[b] | 12.8[a] |
| US inj | 1.3[a] | 1.5[a] | 0.8[a] | 0.55[bc] | 0.64[a] | 0.47[a] | 14.2[a] | 12.8[ab] | 10.3[a] | 16.1[a] | 14.8[ab] | 11.4[a] |
| AS | 1.3[a] | 0.7[a] | 0.6[a] | 0.41[ab] | 0.49[a] | 0.47[a] | 13.2[a] | 11.1[ab] | 10.7[a] | 14.9[a] | 12.3[ab] | 11.7[a] |
| Average | 1.2 | 1.3 | 0.8 | 0.48 | 0.55 | 0.48 | 13.1 | 11.6 | 10.7 | 14.8 | 13.4 | 12.0 |
| SEM | 0.36 | | | 0.054 | | | 0.59 | | | 0.80 | | |
| p values | | | | | | | | | | | | |
| Treatment | 0.26 | | | 0.012 | | | 0.038 | | | 0.055 | | |
| Soil profile | 0.35 | | | 0.010 | | | <0.001 | | | 0.002 | | |
| Interaction | 0.025 | | | <0.001 | | | 0.033 | | | 0.019 | | |

SEM=standard error of the mean. Means (n=4) marked with a different letter differ significantly at $p \leq 0.05$ (Tukey's test) within columns

Goedhart and Huijsmans 2017). A re-analysis of 199 Dutch emission experiments conducted on grasslands confirmed a clear ascending trend of total $NH_3$ emissions among manure application techniques as follows: shallow injection<narrow band<surface broadcast; although the results from individual experiments overlapped within these techniques (Goedhart and Huijsmans 2017). In the previous Finnish experiments on grass leys by Mattila and Joki-Tokola (2003), $NH_3$ volatilization was almost completely prevented with a shallow injection at an application rate of 33–62 t cattle slurry ha$^{-1}$ on mineral and peat soils. In the present study, slurry injection tended to strongly reduce $NH_3$ emission rates on the day of slurry applications in 2017 relative to US treatment, and the achieved reductions (83–96%) in the mean emission rates corresponded to those obtained from AS treatment. However, in 2018, the average emission rates from US inj. treatment were 3.4–8.5 times higher than in 2017, and the respective reductions relative to US remained substantially lower (35–64%). Hansen et al. (2003)

demonstrated that the NH$_3$ reduction potential of slurry injection techniques increased linearly when the volume of the slots increased, depending on the injection depth. The lower abatement efficiency achieved using shallow injection in the present study was therefore accounted for by an injection depth that was too shallow in relation to the amount of the applied slurry. This was the probable cause of the slurry surplus in the open slots and exposed slurry at the soil surface to the atmosphere.

As observed in the present study, especially in band-spread US, high emission rates are reported to appear during the first few hours after slurry applications, and consequently, a large proportion of the total NH$_3$ losses typically occur within 24 h (Sommer et al. 1991; Misselbrook et al. 2002; Pfluke et al. 2011; Häni et al. 2016). This general trend in the NH$_3$ emission pattern highlights the importance of abatement efforts to reduce NH$_3$ emissions immediately after slurry applications. The estimated total NH$_3$ losses of applied NH$_4^+$-N following band-spread US were in the same range, with an average 16–31% of ammoniacal N reported by Mattila and Joki-Tokola (2003) and Pfluke et al. (2011) for untreated cattle slurry applied in bands to grass ley at rates of 25–62 t ha$^{-1}$. In addition to application technique and slurry pH, the NH$_3$ emission potential from field-applied slurry is known to be related to e.g. air temperature, air humidity, wind speed, and the content of slurry DM and total ammoniacal N (e.g. Sommer et al. 1991; Sommer and Hutchings 2001; Häni et al. 2016). Compared with the NH$_3$ emission rates from band-spread US in 2018, the higher emissions recorded in 2017 in the present study and in 2019 in the study by Hagner et al. (2021) were probably attributed to the higher air temperature prevailing on the slurry spreading day. Relative dry topsoil conditions were assumed to allow infiltration of slurry into the soil, whereas organic matter-related soil water repellency may have a restrictive effect on water infiltration in grasslands (Rasa et al. 2007). Moreover, surface crusting of field-applied slurry along with drying have been associated with a decrease in NH$_3$ volatilization, with drying affected by the temperature, wind speed, and thickness of the slurry in bands (Sommer et al. 1991; Pfluke et al. 2011). On the slurry spreading day in 2018, the higher wind speed may have furthered the higher emission potential, but also crust formation. According to

visual observations, a gust of wind had an impact on the slurry bands, which were distributed to a wider area, resulting in thinner slurry layers. In consequence, the lower emission rates may be partly explained by hastened crust formation. Recently, Pedersen et al. (2021) recommended the measurement of the exposed surface area, i.e. the contact area between the applied manure on the soil surface and the atmosphere, which may help explain differences in abatement efficiency achieved in the prevailing circumstances.

## Only acidification generated a positive yield response

The manure N conserved by reduced NH$_3$ emissions is prone to subsequent losses by runoff, leaching, or denitrification (N$_2$O and/or N$_2$ emissions) unless utilized by the crop. In addition to avoiding transfer of environmental impacts from one form to another, agronomic benefits are desired to compensate the farmer for the costs of applying a reduced emission technique (Webb et al. 2010). Previous studies have reported yield increases of up to 25–35% due to N-conserving actions (Pain et al. 1994; Maguire et al. 2011). In the current study, the yield-increasing effect of AS in comparison to US in 2018 fell in this range (29%), and was also reflected in increased grass N concentration and N yield. However, smaller or insignificant effects of the reduced emission techniques on crop yields or N uptake, as evidenced in 2017 in the current study, are also commonly reported (e.g. Smith et al. 2000; Rodhe and Etana 2005; Sadeghpour et al. 2015). Webb et al. (2010) considered the inconsistent responses and lack of significance more likely to indicate the experiments' limited sensitivity than the lack of a true effect. The additional N uptake enabled by the conserved N may remain small in comparison to variation in manure composition, uniformity of spreading, inherent soil fertility and weather conditions. In the current study, relatively high variation between replicates in the second cut in 2017 (see SEM values in Supplementary Table 2) may have hidden possible treatment effects. Part of the variation probably resulted from unequal stubble height due to the lodged canopy in the preceding first cut, but the observed variability remained largely unexplained. In 2018, the D value of the grass was clearly lower in comparison to 2017,

indicating the higher development stage of the grass canopy, which explains the lower average N and S concentrations of the second cut in 2018. Grass K and P concentrations were sufficiently high to assume that K and P fertilization had been sufficient.

Although an approved and established technique for reducing $NH_3$ emissions, injection showed no positive yield effect in comparison to band spreading in either of the study years. Previous studies have shown that slurry injection may decrease crop yield due to mechanical damage caused to roots and the canopy (Rodhe et al. [2006]; Maguire et al. [2011]). Furthermore, negative effects related to the technique may arise from anaerobic conditions created around the injection band, which may lead to an increase in nitrous oxide ($N_2O$) emissions (Duncan et al. [2017]). However, Webb et al. ([2010]) stated that concern about $N_2O$ emissions should not discourage the adoption of $NH_3$ emission-reducing techniques. An advantage of the injection technique is that manure nutrients are introduced close to the root zone, where they may be more easily available to the crop than from surface spreading (Rasmussen [2002]). In this study, the difference between US inj. and AS in 2018 could have been smaller without uncertainty concerning the amount of injected slurry.

In the current study, apparent recoveries of manure total N remained generally low (11–15% in 2017 and 17–28% in 2018). Hagner et al. ([2021]) reported roughly similar values in a field experiment conducted in the same area in 2019. In their study, the apparent total N recovery was 10% from band-spread untreated cattle slurry and 18% from similarly applied acidified slurry. Min-N equivalents were likewise consistent between these studies. According to Powell et al. ([2010]), manure/fertilizer N use efficiencies (proportions of manure/fertilizer N recovered in the crop) range between 16 and 77%, with a high dependence on climate, crop species, and management factors. In this study, the apparent total N recovery was higher on average in 2018 than in 2017, which is mainly explained by the lower N yield of min-N 0 plots in 2018.

Due to their slowly mineralizable organic N component, manures are known to supply N over several years after application. This feature is emphasized in cattle/dairy manure in comparison to poultry or swine manures (Eghball et al. [2002]; Gutser et al. [2005]). In the current study, fall-centered growth

of the third crop due to delayed first harvests and N applications for all harvests in 2018 prevented a thorough observation of the residual N effect. However, the first and third DM yields in 2018 indicated that US and US inj. had supplied additional N for the grass. Furthermore, at the end of the experiment in 2018, soil easily available N concentrations tended to be somewhat higher in the 0.02–0.10 m soil layer in the soils that had received slurry as the N source than in min-N fertilized soil, though only the difference between min-N and US proved significant and corresponded to merely a few kg N per ha. Schröder et al. ([2007]) found the first-year residual effect for cattle manures ranged between 1 and 10% of the initial total N input. In the second and third residual years, the corresponding ranges were 2–5% and 1–4% respectively. Comparable residual availabilities have been reported by e.g. Cusick et al. ([2006]).

Overall, the most interesting observation regarding the soil KCl-extractable N concentrations was the dominance of organic N compounds in the available N pool among all treatments. On a hectare basis, only roughly 1–3 kg N was recovered in inorganic forms ($NH_4^+$-N and $NO_3^-$-N), while the amount of SON corresponded to ca. 30–40 kg. This finding may reflect the high N demand of continuously growing perennial grass. When N immobilization by plants and microorganisms limits the supply of $NH_4^+$ to nitrifiers, the rates of nitrification remain low, whereas at an abundant N availability, lesser competition for $NH_4^+$ accelerates the conversion of $NH_4^+$ to $NO_3^-$ (Schimel and Bennett [2004]).

## Acidification-induced extra sulfur drained in the soil profile but had minor effects on crop uptake

In this experiment, S application was unequal between treatments, but AS received markedly higher S application for the second cut (91 kg ha$^{-1}$ in 2017 and 78 kg ha$^{-1}$ in 2018) than the other treatments (1–21 kg ha$^{-1}$). However, the effect of the high S application on the plant S uptake was only minor. An excess of S in the diet of dairy cattle can be detrimental because of decreased absorption of selenium (Se) and copper (Cu) (National Research Council [2001]). If the diet consists only of grass forage, the safe S concentration of forage is below 4.0 g kg$^{-1}$ DM (National Research Council [2001]). In

this study, the S concentration of forage was always below 2.0 g kg$^{-1}$ DM, and the high S application in AS did not result in harmfully high S concentrations in the forage.

In the current study, the status of soil S was satisfactory, and it was assumed that S fertilizer application would not affect the DM yield as observed in the study of Hahtonen and Saarela (1995), and in a one-year study in the same experimental field area by Hyrkäs and Virkajärvi (2014). When comparing the N and S concentrations of this experiment with the critical S equations of Mathot et al. (2009), two observations from the AS treatment placed in the area were "probably sufficient," and the rest of the data points in the area were "certainly sufficient." In this study, the S yields of the second cut were 3.9–6.6 kg ha$^{-1}$, resulting in positive S balances. However, the balances of S in Finnish crop production have generally proved close to zero or negative, which has raised concern about the sufficiency of S (Yli-Halla et al. 2011; Keskinen et al. 2016). The plant availability of total S contained in cattle slurry is less than 40% (Eghball et al. 2002), while S in $H_2SO_4$ appears completely as plant available inorganic sulfate ($SO_4^{2-}$). In S deficiency conditions, slurry acidification may therefore be beneficial due to S fertilization.

Sulfate is known to be highly mobile in soil. In this study, the excess S had already drained more deeply into the soil profile during the fall soil sampling. Different S-containing additions or amendments may accelerate the leakage of $SO_4^{2-}$ from fields to waterbodies, contributing to aquatic biogeochemistry. As a side effect of gypsum amendments applied on clayey fields for reducing P losses to coastal water, Ekholm et al. (2011) measured an average of 1.6 to 3.2 times higher mean $SO_4^{2-}$ concentrations in runoff after amendments in a small catchment, in relation to the mean $SO_4^{2-}$ concentration of 19 mg l$^{-1}$ in the reference period. In a leaching test with repacked topsoil columns for ryegrass and cereal crops, Loide et al. (2020) also found an increase in leaching losses of $SO_4^{2-}$, with concomitant Ca and K mobilization, from soil columns treated with $H_2SO_4$-acidified slurries. Large-scale use of gypsum is not recommended in Finnish catchments with $SO_4^{2-}$-poor lakes due to sulfate-induced eutrophication, in which hydrogen sulfide, as the end product of $SO_4^{2-}$ reduction, reacts with iron oxides to form iron sulfide, accelerating the release of benthic P (e.g. Ekholm et al. 2011). According to rough estimates, approximately 18 times more S was applied in gypsum at a rate of 4.1 t ha$^{-1}$ in the study by Ekholm et al. (2011) than in the present study. However, to minimize the leaching losses of $SO_4^{2-}$, Loide et al. (2020) recommended that the timing of acidified slurry applications coincide with crops' high nutrient demand.

## Conclusions

The two-year field experiment on grass ley evidenced significantly lower NH$_3$ emission rates from acidified slurry and injected slurry than in the prevailing practice of band spreading untreated slurry. Both injection and acidification can therefore be considered credible techniques for reducing NH$_3$ emissions following field application of slurry in boreal conditions, though acidification appeared more reliable. Injection seemed somewhat susceptible to technical difficulties, leaving slurry exposed on the soil surface and potentially destructive to perennial crops. More detailed studies on recommended slot volumes in grass production that consider both the damaging and covering aspects are required. The effects of both acidification and injection on the availability of other nutrients, especially phosphorus, also deserve more attention in future studies. Regardless of the emission-reducing technique used, observable yield benefits resulting from the conserved N are uncertain and depend on the growing conditions.

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