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Slurry acidification is as effective as slurry injection at reducing ammonia emissions without increasing N_2O emissions: a short-term mesocosm study

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Abstract

Agriculture accounts for 90% of UK ammonia (NH_3) emissions, which must decrease to achieve legally-binding reductions of 16% by 2030. Slurry acidification abates NH_3 throughout the slurry management chain, yet is not currently used in the UK. Two mesocosm-scale experiments assess the potential for slurry acidification to reduce NH_3 emissions at application and measure impacts on NH_3 emissions and short-term changes to soil mineral dynamics and N_2O emissions. Experiment 1 determined the impacts of acidified cattle slurry (pH 6.5, 5.5, and 4.8) to conventional (non-acidified) slurry when simulating surface broadcasting. Experiment 2 assessed the impact of conventional and acidified slurry (pH 5.5) using simulated surface broadcasting and shallow injection of cattle slurry.

Acidification significantly abated NH_3 (% of NH_4-N applied) from 61.6% for conventional slurry to 26.6% at pH 5.5, and 2.5% at pH 4.8. Acidified surface broadcast was as effective at abating NH_3 emissions to injected conventional slurry, and also delayed nitrification, while not significantly altering N_2O emissions from conventional slurry. These results indicate slurry acidification could be used for the UK reach the NH_3 reduction target and exceed the current abatement potential through combining low emissions spreading techniques with acidification.

Keywords

Cambisol, Inceptisol, Ammonium, Nitrate, Agriculture

1 Introduction

Slurry acidification, the process of adding concentrated acid to slurry (Fangueiro et al., 2015a), is commercially used in Denmark as a Best Available Technique to abate NH_3 emissions (Thiermann and Latacz-Lohmann, 2022). The reduction of NH_3 emissions following acidification has been the subject of studies at all stages of the slurry management chain, validating the principle of shifting the dominance of total ammoniacal N in slurry to NH_4^+ with very clear outcomes, as well as additional benefits including the reduction of methane emissions (Bastami et al., 2016, Misselbrook et al., 2016). However, slurry type, target pH and soil type all contribute to the extent acidification reduces NH_3 emissions at land spreading. For example, a previous study reported that at pH 7.0, 23% of applied NH_4-N for cattle slurry was lost through volatilisation over the first three days following application, which was reduced by 95% when acidified to pH 5.5 (Stevens et al., 1989). While another study found that acidifying cattle slurry to pH 6.5 resulted in 20% of NH_4-N applied emitted volatilised as NH_3, which was reduced to 6.6% of applied NH_4-N at pH 6.0, over the first four days (Seidel et al., 2017).

Comparison of acidification to other land spreading NH_3 abatement technologies are not common. However, one Mediterranean based study (Fangueiro et al., 2018) reported that surface broadcasting of acidified slurry was found to have reduced NH_3 emissions by similar amounts to slurry injection of the conventional (non-acidified) treatment (Fangueiro et al., 2018). Similarly acidified band spread slurry has been found to abate a comparable quantity of NH_3 losses to a conventional slurry that was injected (Fangueiro et al., 2018). If NH_3 mitigation is the sole reason for using low trajectory slurry spreading methods, then the potential to surface broadcast acidified slurry to mitigate NH_3 emissions to the same extent, is potentially a lower cost technology for farmers, and could be explored as an alternative. However, there are other benefits of shallow injection and trailing hose slurry application methods, including more uniform nutrient distribution (Maguire et al., 2011), and reduced contamination of grass with slurry (Rodhe and Halling, 2015), that need to be considered.

There is also an increased risk of N pollution swapping from adopting NH_3 mitigation practices, and especially the release of nitrous oxide (N_2O), a greenhouse gas approximately 300 times more potent than CO_2 (IPCC, 2021). The latter has been reported to increase following the injection of slurry, when compared to surface broadcast, due to the formation of anaerobic nutrient “hot-spots” around injection slots (Wagner et al., 2021; Grosz et al., 2022). The main factors controlling N_2O emissions are the amount of NO_3-N (that arises following nitrification of the slurry NH_4-N) and soluble organic C for denitrification, both of which are impacted by acidification (Duncan et al., 2017), and soil moisture content. The timing of N_2O peaks from soil have been found to vary as a result of slurry acidification (Malique et al., 2021). An initial peak of N_2O following the application of acidified slurry has been found to be more intense than the second peak, with the latter often coinciding with a plateauing of soil NO_3^-

concentration and indicating the ceasing of nitrification (Park et al., 2017). A lag in N_2O emissions have been observed in a number of studies where acidification has delayed or reduced the initial release of N_2O indicating an inhibitory effect on nitrification and/or denitrification (Fangueiro et al., 2018; Gómez-Muñoz et al., 2016; Park et al., 2017).

Slurry application technique has been found to impact the N_2O emissions as a result of creating anaerobic hotspots within the soil profile, favouring denitrification (Chadwick et al., 2011; Fangueiro et al., 2017; Park et al., 2017). A study (Fangueiro et al., 2015b) reported that both injection, and slurry acidification combined with incorporation, increased N_2O emissions, while surface broadcast slurry emitted the lowest levels N_2O (Gómez-Muñoz et al., 2016). However, in terms of total N losses (NH_3+N_2O+NO_3 leaching), slurry injection has been found to be most effective means of application to retain slurry N within the soil, with acidified slurry found to be more effective than conventional slurry (Fangueiro et al., 2015b). This was confirmed in a later publication where acidified band spread slurry was found to have similar N losses (NH_3 and N_2O combined) to slurry injection, and was 92% lower than non-acidified band spread slurry (Fangueiro et al., 2018).

Given the majority of previous work has been carried out in Mediterranean soils and climate, this study aimed to assess the impact of both slurry pH and application technique on short-term NH_3 and N_2O emissions in a typical UK grassland soil. Soil mineral N dynamics were also measured to help understand the patterns of gaseous emissions observed. The results would provide an indication of the abatement potential for the use of acidification with surface broadcast slurry as an NH_3 emission mitigation approach, compared to other BAT methods (e.g. shallow injection), whilst exploring any potential co-benefits or trade-offs of NH_3 mitigation on N_2O losses. The study also aimed to provide information on any additional gains in combining low emissions application techniques with slurry acidification.

Two experiments were established to address the following hypotheses: i) the lowest slurry pH will retain the most slurry N in the soil and be most effective in reducing NH_3 emissions, ii) surface broadcasting of acidified slurry will be as effective as shallow injection of conventional slurry at reducing NH_3 emissions, iii) slurry injection will out-perform surface broadcast in terms of retaining greater levels of slurry-N, and iv) application of acidified slurry will result in lower short-term N_2O emissions compared to conventional slurry regardless of application method.

Hypotheses i) and iv) are addressed in experiment one, while hypotheses ii), iii) and iv) are addressed in experiment two. The two mesocosm-scale experiments used a bench-top NH_3 emissions measurement system to capture NH_3 emissions and measure N_2O emissions from the emitting surface of intact grassland soil cores over a minimum of 2 weeks.

2 Methods

2.1 Ammonia desktop system (DAVoS design)

A desktop ammonia volatilisation system (DAVoS) was constructed (Supplementary Information), consisting of 12 chambers (Misselbrook et al., 2005), and situated in a temperature controlled laboratory operating at 18°C. Briefly, acid traps containing 200 ml 0.0125 ml H_3PO_4 were located either side of an air tight chamber with a vacuum pump drawing NH_3-free ambient air through all chambers at a rate of 3 L min^{-1}, with any emitted NH_3 from each chamber being captured in the acid trap between the chamber and vacuum pump. Each chamber lid had a permanent silicone suba-seal inserted to allow N_2O sampling, via needle and syringe, when valves controlling the inlet and outlet air flows on either side of the chamber had been closed.

Prior to initiating the experiments, recovery tests (Misselbrook et al., 2005) were performed to measure system efficiency at capturing emitted NH_3. This involved placing a petri-dish containing 20 ml NH_4SO_4 (2g/L N) in each chamber. The pH of the solution was raised by adding, through injection via the suba-seal, 1ml of 1M sodium bicarbonate to stimulate volatilisation. Following 4 hours of operation at 3 L min^{-1}, 1 ml of 2M H_2SO_4 was added to cease volatilisation. The NH_3 in the acid traps and the contents of the petri dish was analysed colorimetrically for NH_4-N content. The average recovery following 1 trap change at 4 hours across all chambers was 94 % (± 1.8 %), which was deemed close enough to represent 100% of the losses without the need to use a correction factor.

2.2 Experimental design

Intact soil cores (0-15 cm) were collected from three discrete areas of a 26 month old Italian ryegrass grass ley which had received 50 kg N ha^{-1} of ammonium nitrate six months prior to sampling (Henfaes Research Station, North Wales 53°14′21.3 N, 4°0′50.3 W; 10 m above sea level). These were used as replicates for each slurry treatment (n=3). The soil is characterised as a free-draining Eutric Cambisol with a sandy clay loam texture. Prior to initiating each experiment, soil cores were acclimatised at 60% water filled pore space for a week before a single Rhizon™ sampler was inserted to a depth of 9 cm to enable sampling of soil solution.

Vegetation was cut to 5 cm from the top of the core prior to application of slurry to replicate a post-cut slurry application.

For each experiment slurry was collected from an aboveground slurry store located on a dairy farm (Abergwyngregyn, North Wales, 53°23’52.0 N, 4°02’18.5 W) and applied at an equivalent application rate of 40 m^3 ha^{-1}. Following application the slurry composition of each slurry treatment was analysed at a commercial laboratory (NRM laboratories, Cawood Scientific Ltd., Bracknell, UK) and slurry pH was measured in the Bangor University laboratory immediately after application.

At the conclusion of experiments, soil cores were divided into two soil layers (0-7.5cm and 7.5-15cm) and destructively sampled with the entire section of core combined. Each layer was analysed for soil pH and EC (1:2.5 DiH_2O w/v), and extractable NH_4-N and NO_3-N, using 1:5 (w/v) K_2SO_4 extractions for colorimetric analysis (Mulvaney, 1996; Miranda et al., 2001).

2.3 Experiment 1 – Effect of slurry pH on NH_3 and N_2O emissions

The impact of adjusting slurry pH, compared to a conventional unamended slurry, was measured on short-term NH_3 and N_2O emissions after application to soil. 20 L of slurry was homogenised by hand using a paddle, divided into 4 separate 5 L containers, and acidified to the target pH’s, 4.5, 5.5, and 6.5, using 96% H_2SO_4 (Sigma-Aldrich, UK), as well as a conventional slurry (pH 7.5) treatment (Table 2). Each slurry treatment was applied to the surface of each core (simulated surface broadcast) (n=3), and the cores were immediately inserted into the DAVoS. Sampling of N_2O and NH_3 emissions was carried out : 0 hour, 1 hour, 24 hour, 27 hour, and then daily on day 2, 3, 4, 5, 7, 8, 9, 11, 14. The N_2O sampling continued at regular intervals throughout the rest of the experiment (day 15, 18, 23, 27, 32, 34, 41, 77, 83, 94, and 109). The N_2O emission measurements continued for >3 months to ensure the majority of the emission ‘envelope’ was accounted for (Vangeli et al., 2022).

2.4 Experiment 2 – Effect of slurry application method and slurry pH on NH_3 and N_2O emissions

Experiment 2 was established to assess the effect of slurry application method and slurry pH on short-term NH_3 and N_2O emissions. 10 L of slurry was homogenised by hand using a paddle and divided into two 5 L containers. The slurry in one was acidified to pH 5.5, using 96% H_2SO_4 (Sigma-Aldrich, UK), with the other remaining as conventional slurry. The 4 experimental treatments were: acidified surface broadcast, acidified injection, conventional surface broadcast, conventional injection. Both acidified and conventional slurry injection simulated shallow injection with open slots created in the centre of the soil core 50 mm deep. NH_3 emissions, N_2O emissions and soil solution sampling were carried out over a 2 week period on this occasion (0 hour, 1 hour, 6 hour, 24 hour, 30 hour, and then days: 2, 3, 4, 5, 9, 10, 11, 14) to capture the initial 'envelope' of gaseous N loss (Grosz et al., 2022). This provided the opportunity to understand short-term changes to N forms, and support the findings from Experiment 1.

2.5 Analytical methods

2.5.1 Sample analysis

At each sample point, the exhaust acid trap was analysed using colorimetric determination of NH_4-N concentration (Mulvaney, 1996). The mass of NH_3-N emitted during a sampling period was then calculated by multiplying the NH_4-N concentration by the volume of H_3PO_4 in each acid trap (Misselbrook et al., 2005).

Soil solution samples were collected in 9 ml Vacutest® vials attached to the Rhizon samplers and analysed for NH_4-N and NO_3-N using colorimetric methods (Miranda et al., 2001; Mulvaney, 1996).

2.5.2 Nitrous oxide analysis

Gas samples were taken from the headspace (0.5 litres) using a needle and 20 ml syringe and injected into a pre-evacuated 20 ml glass vial. A headspace gas sample was taken at 0 minutes and 40 minutes, with three chambers randomly selected at each sample point for additional sampling to check the linearity of N_2O concentration accumulation in the headspace (with samples taken at T0, T10, T20, T30 and T40). Linearity samples were analysed, with emissions found to be linear on 56% of occasions when accepted at $R^2>0.95$, and 70% of occasions when accepting at $R^2>0.9$ in experiment 1, and 72% of occasions at $R^2>0.95$, and 81% of occasions at $R^2>0.9$ in experiment 2. The majority of occasions where linearity was not met was during periods of low flux, similar to the findings of others (Cardenas et al., 2016; Marsden et al., 2016).

N_2O analysis was carried out on a Perkin Elmer 580 Gas Chromatograph (GC) equipped with an ECD, with a Turbo Matrix 110 auto sampler (Perkin Elmer Inc., Beverly, CT, USA).

2.5.3 Data Processing

Replicate cores were taken from the same sites as experimental cores, dried at 105°C, with bulk density subsequently calculated from the volume of the core. The calculations to convert gravimetric soil moisture content into %WFPS used bulk density measurements and a particle density of 2.65 g cm^{-3} (Louro et al., 2013). Dionised water was added on a weekly basis to adjust for moisture loss over the period (this also accounted for the removal of water via the Rhizon samplers) to maintain the target 60% WFPS.

2.5.4 Method for calculating NH_3 fluxes and cumulative emissions

NH_3 fluxes were calculated based on the acid trap NH_4-N concentration data and trap volume, as outlined above. Cumulative NH_3-N emissions were then calculated by summing the mass trapped on consecutive sampling dates. This then allowed for percentages to be calculated for the quantity of N lost in terms of total N applied and total NH_4-N applied.

2.5.5 Method for calculating N_2O fluxes and cumulative emissions

N_2O cumulative emission fluxes were calculated based on the trapezoidal integration method (Cardenas et al., 2016). As a control receiving no treatment was absent from the study, it was not possible to calculate true emissions factors that are comparable to the IPCC standards. Instead, N_2O losses were calculated as a percentage of N applied lost as N_2O.

2.6 Statistical analysis

Throughout both experiments, statistical analysis was performed using R v. 4.1717 (R core team, 2016) where a significance level of $p < 0.05$ was accepted as significant. Where data were deemed normal, linear models were used and were then subjected to an ANOVA (R core team, 2016). If significant differences were found “lsmeans” (Lenth, 2017) was used to carry out Tukey post-hoc tests. Where data failed to meet normality assumptions data was log transformed, and if normality was still not met a non-parametric Kruskal-Wallis test (R core team, 2016) was performed. One-way ANOVAs (R core team, 2016) were carried out on single time point data including cumulative totals at the end of the experimental period. All results were graphical illustrated with “ggplot2” (Wickham, 2016).

3 Results

3.1 Soil properties

Analysis was carried out for soil used in both experiments (Table 1) with little variation found between replicate sites.

TABLE 1

3.2 Slurry properties

Original slurry properties (conventional, non-acidified slurry) for Experiment 1 were typical of those found in the UK, whilst those for Experiment 2 were found to have a low nutrient content, especially TN, when compared to typical values for the dry matter content. For both experiments, slurry acidification resulted in some loss of organic matter (Table 2). All other properties remained similar with the exception of sulphur, which increased with the addition of H_2SO_4.

TABLE 2

3.3 Experiment 1 – Effect of slurry pH on NH_3 and N_2O emissions

Slurry acidified to pH 4.5 clearly shows the lowest NH_3 emissions following surface broadcasting of cattle slurry (Figure 1). A Kruskal-Wallis test was performed and showed significant ($p<0.05$) differences between cumulative NH_3-N loss and slurry pH treatments, and sampling date.

Figure 1

Following log transformation and analysis, acidification (pH5.5) of cattle slurry was found to significantly lower NH_3-N emissions (26.6% ± 7.24 NH_4-N applied , 9.25% ± 1.22, TN applied) when compared to conventional slurry (61.6% ± 2.13 NH_4-N applied, 19.0% ± 0.33 TN applied). However acidification to pH 4.5 resulted in significantly lower cumulative NH_3-N emissions than all other treatments (2.5% ± 0.20 NH_4-N applied, 0.8% ± 0.03 TN applied).

Figure 2 indicates that the greatest reduction in slurry pH reduces cumulative N_2O emissions over the initial 24 days following application. However, once the delay in emissions has elapsed, slurry acidified to pH 4.5 became the greatest emitter of N_2O. A Kruskal-Wallis test was carried out, with a significant difference ($p<0.05$) found when analysing cumulative N_2O loss against time following application.

No significant differences were found between N_2O losses, as a percentage of total N applied for each treatment, but slurry acidified to pH 4.5 was found to have a greater percentage loss (0.13%) than other treatments (0.06-0.11%). This mirrors the findings shown in Figure 2, with pH 4.5 resulting in the greatest cumulative loss of N_2O.

Figure 2

3.4 Experiment 2 – Effect of slurry application method and slurry pH on NH_3 and N_2O emissions

After log transformation, acidification was found to significantly lower NH_3 emissions 1 hour after application (Figure 3) regardless of application technique (Acidified Broadcast 3.4 ± 0.23 % of NH_4-N applied and Acidified Injected 3.1 ± 0.37 % of NH_4-N applied) compared to Conventional Broadcast (11.4 ± 1.88 % of NH_4-N applied). Conventional Injected (4.6 ± 0.40 % of NH_4-N applied) also resulted in significantly lower NH_3-N losses than Conventional Broadcast after 1 hour. No significant differences were found between Acidified Broadcast and Conventional Broadcast, and Conventional Broadcast and Conventional Injected after day 11 ($p>0.05$). Additionally, NH_3-N loss following application by Acidified Injected was found to be significantly lower than Conventional Injection from hour 6 until the end of the experiment.

Cumulative NH_3-N loss, expressed as % total NH_4-N applied, highlighted that Acidified Injected (16.2% ± 1.40) was significantly lower than Acidified Broadcast (23.5% ± 1.35), Conventional Broadcast (38.0% ± 2.86) and Conventional Injected (27.2% ± 1.88), while Acidified Broadcast (23.5% ± 1.35) was significantly different from Conventional Broadcast (38.0% ± 2.86) when log transformed.

Figure 3

No significant differences were found when comparing N_2O flux data of acidified and conventional slurry applied via surface broadcast and shallow injection over the 14-day period experiment (Figure 4). Acidified Broadcast emitted the greatest cumulative quantity of N_2O (10.3 ± 5.02 $\mu g\ N\ kg^{-1}$) whilst Conventional Broadcast emitted the least (3.7 ± 2.23 $\mu g\ N\ kg^{-1}$). Both Acidified Injected (5.4 ± 2.06 $\mu g\ N\ kg^{-1}$) and Conventional Injected (5.8 ± 2.43 $\mu g\ N\ kg^{-1}$) emitted similar quantities.

Figure 4

Given the short-term nature of the experiment, only partial N_2O losses as a percentage of total N applied could be calculated given the potential for the longer-term nature of N_2O emissions. The greatest percentage loss was found following the application of acidified broadcast slurry (0.04%). However, all differences between treatments were found to be non-significant.

The greatest concentrations of soil solution NH_4-N were detected in the Acidified Injected treatment, peaking at a mean of 19.9 mg NH_4-N l^{-1} (± 12.4) (Figure 5 – panel a). Soil solution NH_4-N concentrations in the Acidified Injected treatment were found to be significantly greater

(p<0.05) than both conventional treatments (Conventional Broadcast and Conventional Injected) until day eight, after which no significant differences were found between treatments. Although greater concentrations of NH_4-N were found to be present in the Acidified Broadcast treatment (peaking at 3.1 mg NH_4-N l^{-1} ± 1.7) compared to conventional slurry (CB 2.6 mg NH_4-N l^{-1} ± 0.9, CI 1.7 mg NH_4-N l^{-1} ± 1.4), no significant differences were found.

Figure 5

Throughout the 14-day experimental period there were no differences between treatments for soil solution concentrations of NO_3-N (Figure 5 – panel b).

Acidified broadcast slurry had greater values of both K_2SO_4 extractable NH_4-N and NO_3-N at the conclusion of the experiment in the top 7.5 cm of the soil core (Figure 6), but no significant differences were found between treatments at 15 cm.

Figure 6

4 Discussion

The slurry used in both experiments were higher in dry matter than for typical UK cattle slurry (6-8%) presented in RB209, the UK nutrient management guide. However, the nutrient content was typical of slurries with a comparable dry matter content. In experiment 2, total Kjeldahl N was an order of magnitude lower, explaining the lower overall NH_3 loss found when compared to those found in experiment 1.

The results presented in experiment 1 support the findings of others (Fangueiro et al., 2015a; Seidel et al., 2017) who report that acidification reduced NH_3 emissions following slurry application in terms of percentage abated. However, based on NH_4-N applied, the overall quantity of NH_3 lost across all treatments was low when compared to other studies (Fangueiro et al., 2017; Seidel et al., 2017; Stevens et al., 1989). A previous study reported that when cattle slurry was acidified to pH 5.5, NH_3 loss was reduced by 95% compared to slurry at pH 7 within three days after application (Stevens et al., 1989). However, in this experiment a similar scale of reduction was only found between slurry at pH 7.4 and pH 4.5. This is likely a result of the greater than average UK slurry dry matter used in this study (8.3 – 10.2% DM), reducing infiltration and increasing the potential for volatilisation. In terms of NH_3 emissions, acidifying to pH 5.5 reduced total N loss by 46%, and total NH_4-N applied by 68% during the initial 14 days following application (Figure 1). Although not measured, the slurry used in this experiment was thought to have a rapid buffering capacity, with marked NH_3 emissions measured from pH 5.5 slurry from day 1 in both experiments (Figure 1 and Figure 3). Overall, these results highlight the important contribution acidification could offer in terms of UK agriculture delivering significant reductions in NH_3 emissions in order to reach a reduction in total NH_3 emissions set out in the NECR (Defra, 2018).

Slurry acidification resulted in NH_3 emission reduction and greater retention of slurry NH_4-N in the soil for longer (Figure 5). The findings presented in various studies (Fangueiro et al., 2015b, 2017, 2018) suggests that acidification inhibits and delays nitrification. The influence of acidification on delaying nitrification was seen to have the same effect regardless of the level of acidity, with all acidified slurry treatments resulting in a similar delay to peak soil solution NO_3-N concentration. By the end of the experiment soil extractable NH_4-N and NO_3-N concentrations were not significantly different between treatments (Figure 6), which further supports the short-term nature of any delays to nitrification. This initial increase in slurry NH_4-N retention in the soil, without increasing soil solution or extractable soil NO_3-N concentrations, indicates the increased fertiliser value of acidified slurry without evidence of pollution swapping, but highlights the importance of applying slurry at an appropriate time for maximum plant uptake.

Experiment 2 clearly shows the potential acidification has in reducing NH_3 emissions regardless of application technique (Figure 3). The combination of both abatement methods, acidification and injection, provided an insight to the potential maximum reduction in NH_3 abatement. Although the use of acidification would increase the economic burden on the agricultural sector to reduce NH_3 loss, this experiment has shown the use of acidification would be an effective means of reducing emissions. The reduction in NH_3-N loss was found to range between 55-70% when comparing both acidified (pH 5.5) treatments to conventional surface broadcasting of slurry, and acidified surface broadcasting of slurry was as effective at reducing NH_3 emissions as slurry injection in this experiment. Acidification in combination with surface broadcast and injection (Experiment 2) showed a reduction in total N loss of 29 and 50%, and total NH_4-N loss of 39 and 58% respectively. This research clearly demonstrates how slurry acidification is comparable to the current Best Available Techniques for NH_3 emission reductions. Although the use of acidification in combination with surface broadcast would make use of existing farm spreading equipment, it would not bring about other benefits from injection or using as trailing shoe. These include reducing sward contamination (Rodhe and Halling, 2015), and a more uniform distribution of nutrients (Maguire et al., 2011).

Current plans under UK policy is for all slurry to be spread using low emission techniques (HM Government, 2018), similar to the precedent set in Denmark where surface broadcasting of slurry has been banned since 2002 (Sommer and Knudsen, 2021). Experiment 2 outlines how the combination of slurry acidification and low emission spreading techniques can be combined to offer significantly lower NH_3 emissions, exceeding the abatement of slurry injection by itself. The use of slurry acidification in-house also increases the abatement potential, while eliminating the requirement to cover the slurry store (Defra, 2023). If UK government are to pursue an abatement strategy that combines slurry placement e.g. band spreading, with in-field acidification the change would cost approximately twice the amount, per m^{-2} applied, if currently bandspread compared to currently surface broadcast. However, the combination of low emission spreading techniques and acidification will maximise NH_3 abatement potential, while maintaining the additional benefits of placement accuracy and reduced sward contamination from low emission spreading techniques.

The results presented highlight the potential of acidification to increase the fertiliser value of slurry as shown by the greater concentrations of soil solution NH_4^+ (Figure 6). Similar findings are also presented in the literature (Bell et al., 2016; Fangueiro et al., 2016; Sánchez-Rodríguez et al., 2018) where greater concentrations of soil NH_4-N were also found following the application of acidified slurry. However, given the short-term nature of these increases (7-21 days) it is essential that acidified slurry is applied during periods of active plant growth to maximise benefits of greater concentrations of NH_4-N, and prevent N pollution swapping (Chadwick et al., 2011; Bell et al., 2016). In a practical sense, this underlines the potential value of slurry acidification for farmers in areas unsuitable for shallow injection, if similar results are found on different soil types.

Given the potential of increased N_2O emissions, as a result of greater NH_4-N concentrations available for nitrification and denitrification following the application of acidified slurry and injection of slurry, it was important to ensure that N pollution swapping does not occur. The results of both experiments (Figs 2 and 4) corroborate studies by others whereby acidification had no significant impact on N_2O emissions when compared to conventional slurry (Fangueiro et al., 2015b, 2017; Seidel et al., 2017). When slurry was acidified, nitrification and denitrification were potentially inhibited (as shown in Figs 2 and 4). Previously, injection has been reported to lead to localised hotspots of nutrients and anaerobic conditions in the soil profile resulting in greater N_2O emissions (Chadwick et al., 2011; Grosz and Kenmann, 2022; Petersen and Sommer, 2011). This was not found in experiment 2 (Figure 5) where no significant differences were found between both acidified and conventional slurry injection and the surface broadcast equivalents. The N_2O losses reported were low but comparable to slurry emission factors found by others (Bell et al., 2016), whereas the short-term nature of both experiments meant that only partial N losses from N_2O could be produced. However, the percentage losses of total N applied through N_2O emissions in both experiments show that acidified treatments are marginally greater than non-acidified, albeit non-significant which has been reported previously (Malique et al., 2021). This is of importance in terms of N pollution swapping and the sustainable use of slurry acidification across the UK as a NH_3 abatement strategy. However, further experimentation would be required on multiple soil types and at field scale to fully understand the potential of N emissions following acidification.

5 Conclusions

The results of these two short-term experiments show the potential of slurry acidification to reduce N loss through NH_3 emissions from a typical UK grassland soil, and provide a percentage reduction similar to those found in European studies. The reduction of NH_3 loss through combining slurry acidification and different slurry application techniques clearly shows that acidification of cattle slurry applied through surface broadcast was comparable to conventional slurry injection, and the extent in which combining techniques can exceed abatement from low emissions spreading techniques alone. This has strong policy implications by providing clear evidence of the performance of low emission slurry spreading practises compared with a potential new technology for UK agriculture, i.e. slurry acidification. Importantly combining slurry acidification with shallow injection demonstrates reduced NH_3 loss and increased NH_4-N availability without significantly increasing NO_3-N concentrations and N_2O emissions. This was the same for slurry acidified to pH 4.5, but also for all acidified treatments, showing the potential fertilizer benefits of acidification without increasing pollution. Ultimately, the use of slurry acidification has beneficial impacts on retaining N within a UK soil without leading to increased NO_3-N and N_2O.

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Competing interests

The authors declare no competing interests.

Table 1

	Site 1	Site 2	Site 3
Bulk Density (g cm^{-3})	1.0 ±0.03	1.0±0.06	1.0±0.01
Organic Matter (%)	5.3±0.1	5.8±0.03	5.6±0.14
pH	6.4±0.08	6.4±0.1	6.7±0.06
EC (µS cm^{-1})	41.3±12	32.1±7	29.7±10
Total N (mg N kg^{-1})	3.8±0.2	3.5±0.5	3.6±0.3
Total C (mg C kg^{-1})	32.2±6.5	28.9±4.2	30.6.±5.7
C:N ratio	8.5±0.4	8.3±0.3	8.5±0.5
Extractable NO_3^- (mg N kg^{-1})	0.9±0.2	1.2±0.4	2.4±0.7
Extractable NH_4^+ (mg N kg^{-1})	2.4±0.6	12.0±2.1	3.5±1.1

Table 1: Pre-application soil properties.

Multiple soil cores (N=3) were taken at each replicate sampling point and averaged with ± representing SEM. Data presented on a dry weight of soil basis.

Table 2

		Experiment 1				Experiment 2	
	Unit	**pH 4.5**	**pH 5.5**	**pH 6.5**	**pH 7.5**	**pH 5.5**	**pH 7.5**
Oven Dry Solids	**%**	10.30	9.25	9.07	8.92	7.68	9.01
Total Kjeldahl N	**% w/w**	0.40	0.37	0.41	0.41	0.15	0.17
NH_4^+-N	**mg kg^{-1}**	1616	1654	1638	1626	498	490
Total Phosphorus	**mg kg^{-1}**	625	621	609	629	384	381
Total Potassium	**mg kg^{-1}**	2164	2185	2160	2245	1516	1535
Total Magnesium	**mg kg^{-1}**	470	463	460	472	462	478
Total Copper	**mg kg^{-1}**	2.91	2.84	2.72	2.78	2.52	2.57
Total Zinc	**mg kg^{-1}**	15.6	13.6	14.1	16.1	12.5	13.2
Total Sulphur	**mg kg^{-1}**	3638	1343	824	453	1126	259
Total Calcium	**mg kg^{-1}**	1173	1127	1146	1204	1221	1291
Total Sodium	**mg kg^{-1}**	599	600	588	610	291	296
pH at application		4.47	5.43	6.60	7.69	5.39	7.62
Acid requirement (ml 1M H_2S0_4 100 ml^{-1})		8.0	5.5	2.0	-	7.7	-

Table 2: Slurry characteristics of each treatment applied to cores.

Analysis was performed by NRM laboratories (Bracknell, UK) with the exception of pH which was measured in the Bangor University laboratory just after slurry treatment applications. n=1. Data are expressed on a fresh weight basis.

Figure 1

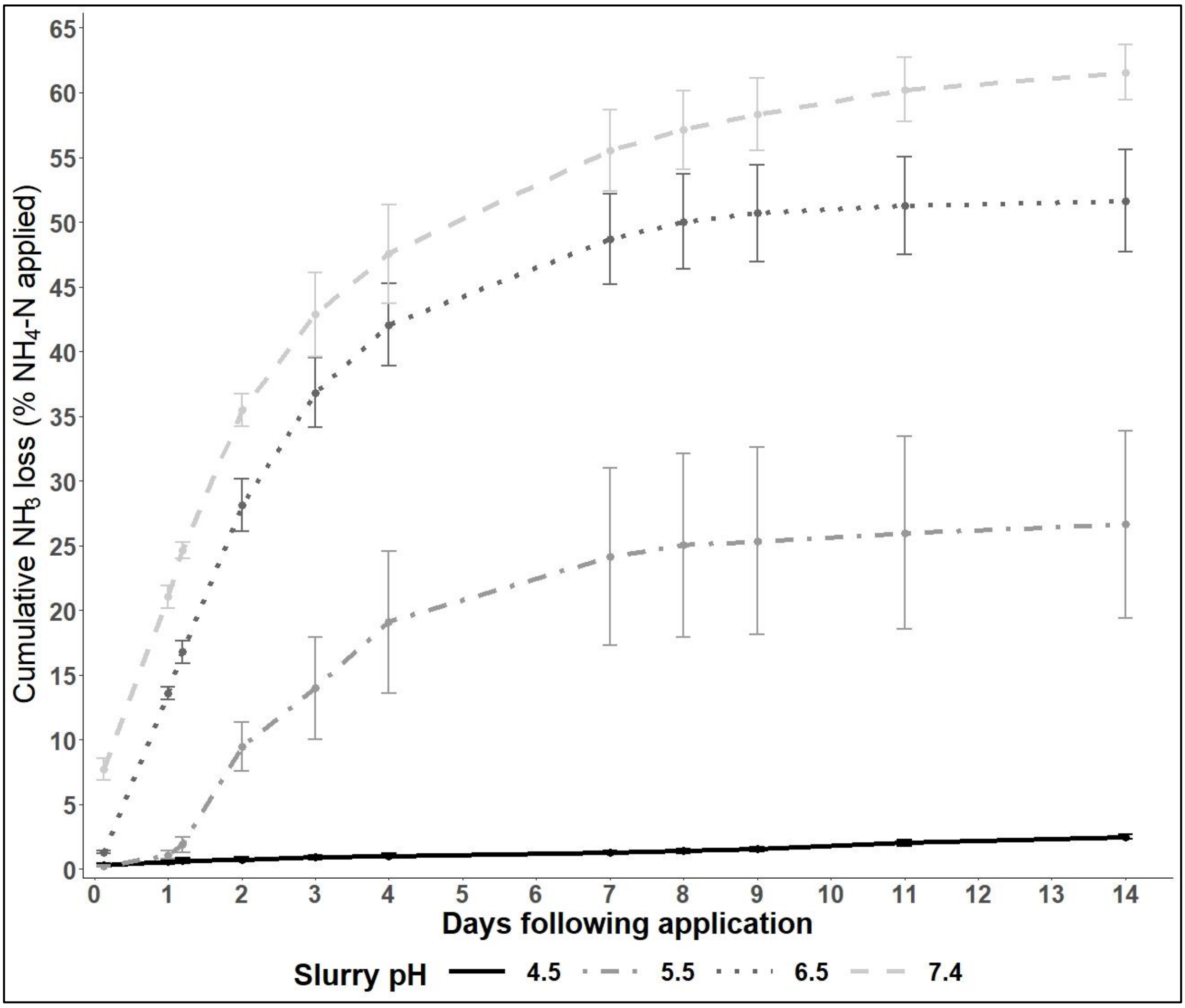


Figure 1: Cumulative NH_3 loss after acidification to varying pH values.

Points show mean values and error bars represent ± SEM (n=3)

Figure 2

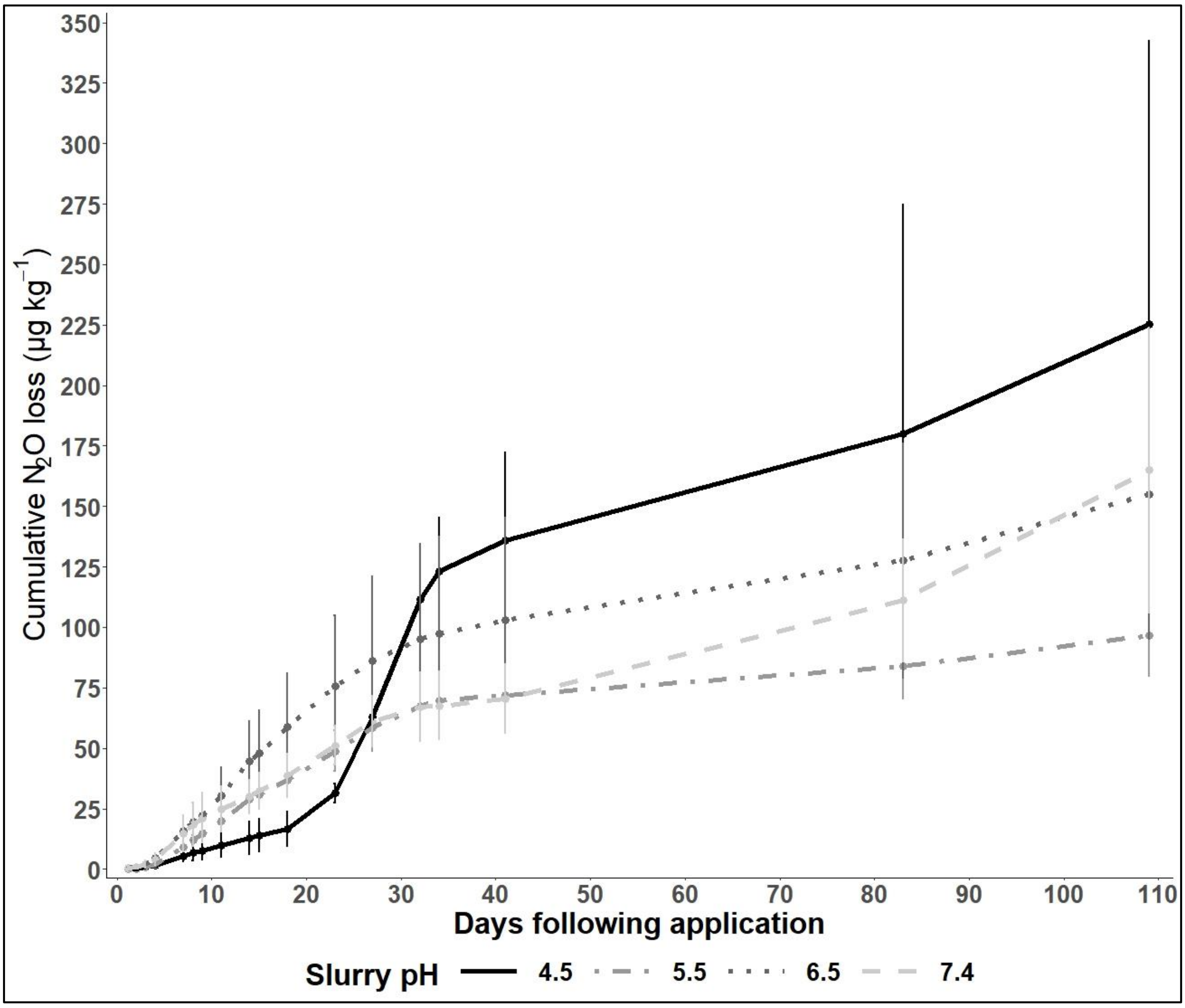


Figure 2: Cumulative N_2O loss after acidification slurry to varying pH.

Cumulative N_2O loss over the 109-day measurement period following application of slurry applied at four different pH with emissions displayed as mean for each treatment. Points show mean values and error bars represent SEM ± (n=3). Fluxes expressed on a soil dry weight basis.

Figure 3

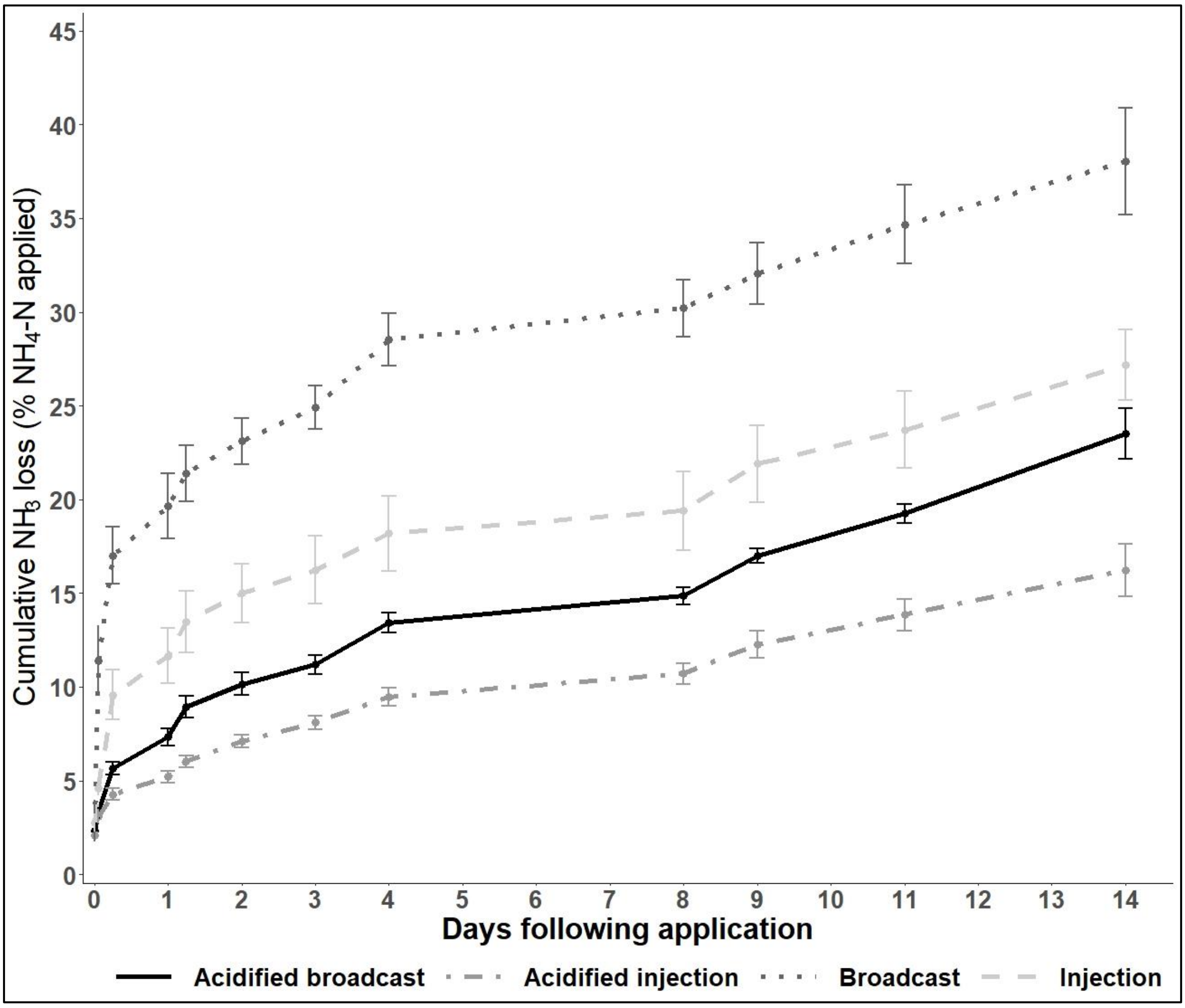


Figure 3: Cumulative ammonia loss after slurry acidification and different slurry application techniques.

Points show mean values and error bars represent ± SEM (N=3).

Figure 4

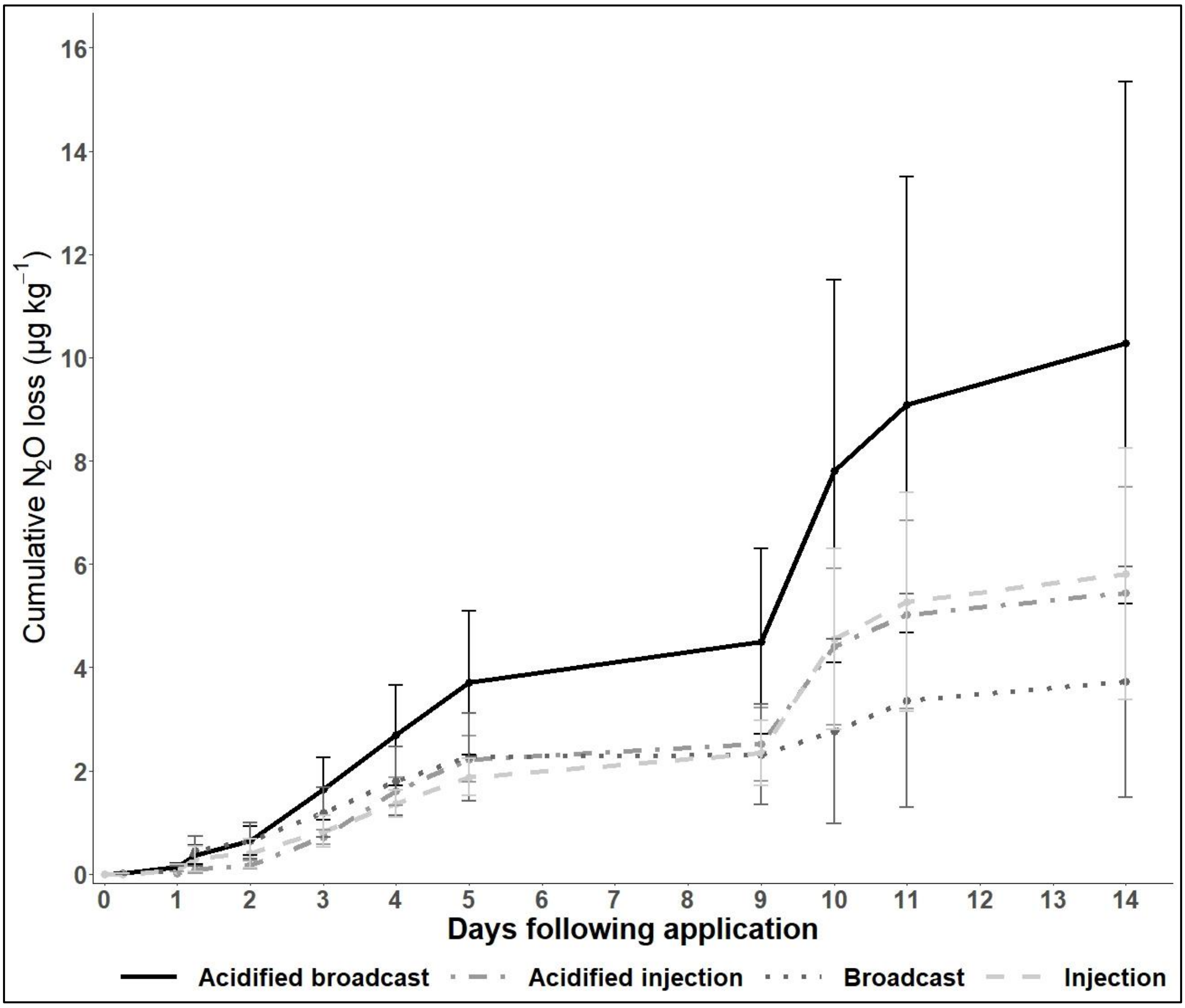


Figure 4: Cumulative N_2O loss after slurry acidification and different slurry application techniques.

Cumulative N_2O loss over the 14-day experiment following application of acidified (pH 5.5) and conventional slurry applied via surface broadcast and injection. Points show mean values and error bars represent ± SEM (n=3). Fluxes expressed on a soil dry weight basis.

595 **Figure 5**

596

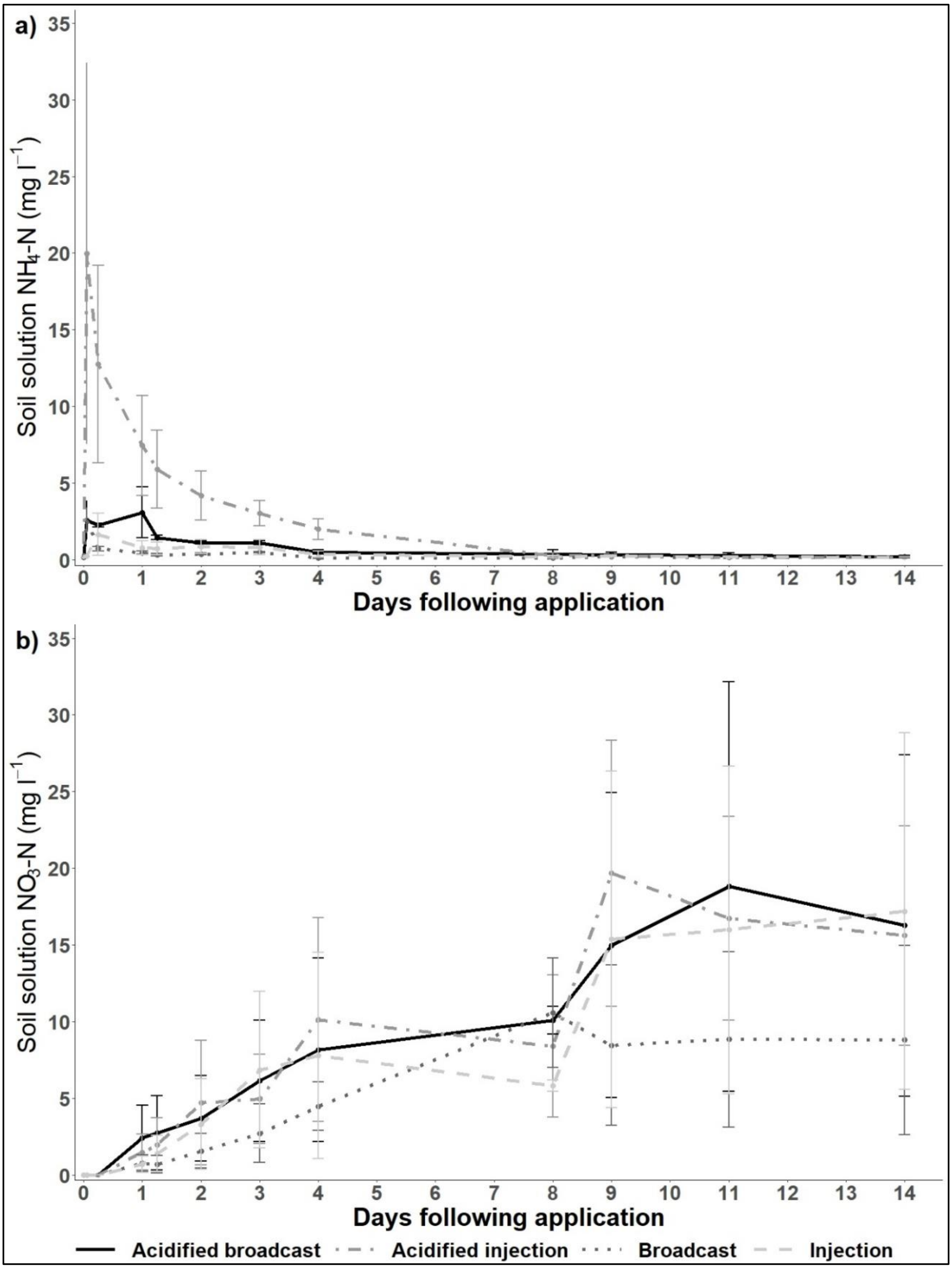


Figure 5: Soil solution NH_4-N and NO_3-N after slurry acidification and different slurry application techniques.

Concentrations of NH_4-N (panel a) and NO_3-N (Panel b) in soil solution following application of acidified slurry (pH 5.5) and conventional slurry via surface broadcast and shallow injection. Points show mean values and error bars represent ± SEM (n=3).

Figure 6

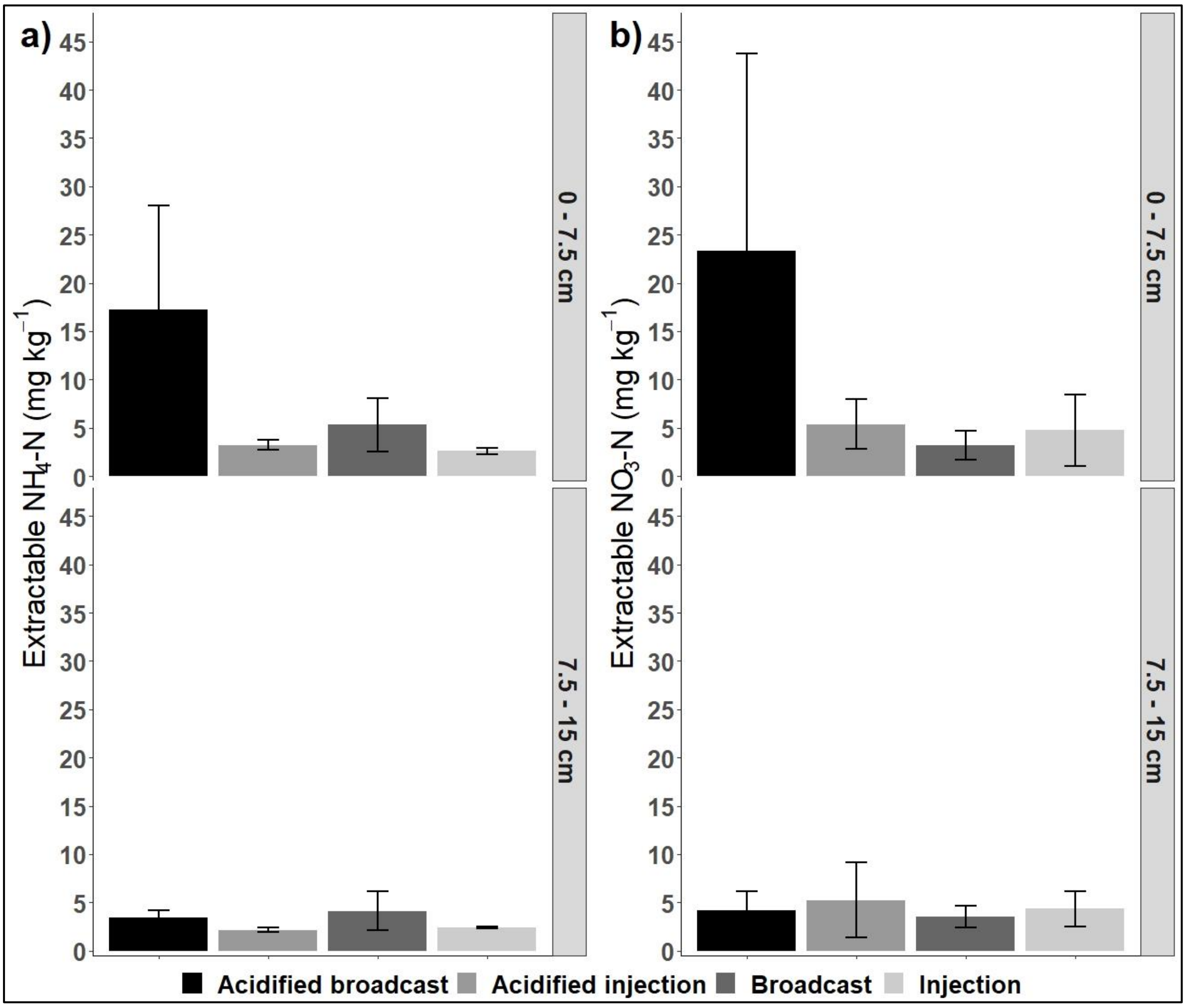
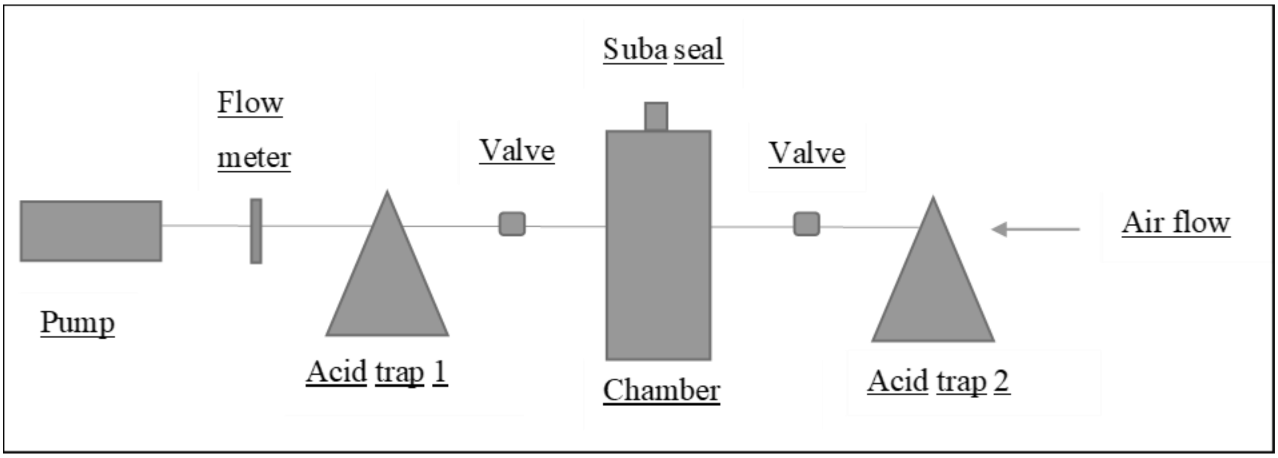


Figure 6: Extractable NH_4-N and NO_3-N at the end of the experiment after slurry application using acidified or conventional and surface broadcast or shallow injection.

Concentrations of extractable NH_4-N (panel a) and NO_3-N (Panel b) found at the conclusion of the experiment. Each core was separated into “Top” (0 - 7.5 cm) and “Base” (7.5 – 15 cm). Bars show mean values and error bars represent ± SEM (n=3). Data expressed on a soil dry weight basis.

Supplementary Information



Schematic of DAVoS

Each acid trap was filled with 200 ml 0.125 M H_3PO_4 with the pump drawing air through each chamber at 3 l min^{-1}. The contents of “acid trap 1” was retained for chemical analysis at each sampling point.