EFFECTS OF ACIDIFICATION ON NITROGEN TRANSFORMATIONS IN STORED DAIRY EFFLUENT

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Executive Summary

A trial was carried out to determine the efficacy of using sulphuric acid (H_2SO_4) to acidify farm dairy effluent, with the aim of preserving the nitrogen (N) resource during storage. The acidified (pH 6.0, 5.5, 5.0 and 2.5) and control (without acid) effluents were placed into a series of plastic containers and buried with the effluent surface at ground level to simulate effluent storage conditions. The trial was outdoors under a covered clear plastic shelter. Samples of the effluent were regularly collected during an 81 day trial period and analysed for N fractions and pH.

The total N content of the effluent decreased in all treatments over the storage period. The largest N loss was observed from the control treatment, where 62% of the initial N content was lost after 81 days' storage. Ammonia (NH_3) volatilisation was likely to be the main reason for N loss from the effluent. When the effluent pH was lowered with addition of acid, N loss was reduced and ranged between 14 and 58% over 81 days.

The lowest pH of 2.5 was the most effective at N retention (86%) as urea hydrolysis was slowed, which delayed the availability of ammoniacal N (NH_4 plus NH_3) for volatilisation. The duration of the lowered pH was short-lived in the effluents adjusted to pH 6.0, 5.5 and 5.0. The data suggests that either the frequent application of acid to keep effluent at pH of 5-6, or an initial high dose rate that slows urea hydrolysis, would substantially reduce N losses from stored effluent.

We propose that acidification should be further tested for reducing N loss under more dynamic effluent storage conditions, replicating regular additions of both effluent and acid in order to better simulate a working pond system.

Introduction

The rapid intensification of dairying in New Zealand since 2000 has increasingly focused attention on issues relating to effluent management. Farmers are faced with managing greater quantities of effluents and manures while coming under increasing scrutiny from regional councils concerned about deteriorating water quality. One way of reducing water degradation is to store farm dairy effluent (FDE) in ponds when the environmental risk associated with leaching and runoff losses from land application of effluent are high. However, one of the compromises associated with effluent storage is the potential gaseous N emissions.

Factors affecting gaseous N emissions include the ammoniacal-N content and pH, while environmental factors such as air temperature, wind speed and solar radiation also influence losses (Luo and Longhurst, 2008).

The greatest potential N loss from an effluent system is NH_3 volatilisation following hydrolysis of the urea-N in the urine portion of fresh effluent (Houlbrooke et al., 2009). The ratio of ammonium (NH_4) to ammonia (NH_3) is affected by pH, the lower the pH the higher the ratio and consequently the lower the potential NH_3 volatilisation and N losses. Urea N in effluent is rapidly hydrolysed to NH_4 as a result of urease enzyme activity, a process which typically creates a rise in pH (Bolan et al., 2004). At a very low pH, microbial and enzyme (e.g. urease) activities can be affected which have a flow-on effect on the quantity of NH_3 available for volatilisation.

The magnitude of NH_3 losses during storage is dependent on the effluent type and duration of storage, as well as storage temperature. While liquid effluent may contain a low N content (approx. 0.05% N), the proportion lost as NH_3 when stored can be significant, ranging from 15% for holding ponds to 30% for anaerobic/aerobic ponds and advanced ponds (Luo and Longhurst, 2008). Current changes to the way FDE is being managed (increased use of pond storage during wet periods and deferred irrigation) means that there is an opportunity for greater gaseous emissions from pond systems during the spring period, as storage may be required for up to 3 months in some regions (Houlbrooke et al., 2004).

A trial was commissioned by Ballance Agri-Nutrients to test the effectiveness of different additives in preserving N within effluent during storage with the intention of retaining N for the subsequent land application. This paper outlines losses of N in effluent samples taken periodically from the stored effluent when treated with different rates of H_2SO_4.

Design and setup

The trial was conducted outdoors under a covered clear plastic shelter at the Ruakura Research Centre, Hamilton. Five rates of sulphuric acid (H_2SO_4) were used (Table 1) and replicated 3 times.

Table 1. Treatments used in the effluent additive trial.

pH	Acid added
7.8	Nil
6.0	0.38 ml H_2SO_4/L effluent
5.5	0.56 ml H_2SO_4/L effluent
5.0	0.66 ml H_2SO_4/L effluent
2.5	1.52 ml H_2SO_4/L effluent

Effluent used in the trial was made by mixing fresh dairy cow urine and dung and diluting with water to give an effluent of 2% dry matter (DM). The fresh urine was collected from dairy cows during milking, and dung was collected from a freshly grazed paddock. Selected baseline effluent properties were analysed and are shown in Table 2.

Table 2. Selected baseline properties in the effluent.

Dry Matter (%)	pH	TKN (mg/L)	Urea-N (mg/L)	Ammonium-N (mg/L)	Nitrate-N (mg/L)
2.0	7.8	1,006	517	32.1	0.6

Sulphuric acid was added to achieve an initial pH of 2.5, 5, 5.5 and 6 (Table 1). Concentrated sulphuric acid, diluted to 10% stock solution using distilled water was used as the acidification agent.

At trial establishment (February 2012) the dung and urine were weighed into individual 9.6 L buckets at the ratio of 1:1.3 (urine:dung), based on an average cow excreting 7000 L urine and 9000 kg dung wet weight/year (Haynes and Williams, 1993). The acid was measured and added and each treatment was diluted with tap water to give an effluent of 2% DM. After treatments were well mixed, the open buckets (each containing 7 L of amended effluent) were randomly positioned in a grid pattern under the covered shelter and buried with the effluent surface at ground level to simulate effluent storage conditions. The position of the buckets was re-randomised after every sampling to avoid potential edge effects.

Sampling and analysis

The effluent was sampled at 0, 6, 13, 20, 27, 40, 55, 69, and 81 days after the trial commenced. To compensate for evaporation, before each sampling, water was added to the effluent to maintain it at 2% DM. At each sampling time the effluent was mixed using a motorised stirrer which re-suspended the sludge allowing a representative sub-sample of the effluent to be taken. Sub-samples of the effluent were analysed for total Kjeldahl nitrogen (TKN), urea, NH_4, nitrate (NO_3) and pH. TKN was determined using a semi-micro Kjeldahl method. Urea, NO_3 and NH_4 were measured by weighing approximately 5 g of effluent sample into 150 mL flasks, and shaking with 50 mL of 2M potassium chloride for one hour using an end-over-end shaker (Mulvaney, 1996). The extractant was filtered (Whatman #42 filter paper) and stored frozen prior to analysis. Urea was determined using the diacetyl monoxime-thiosemicarbazide method (Wybenga et al., 1971) and NO_3-N and NH_4-N were determined using a Skalar segmented flow analyser. The pH was measured with a Model 920A Orion pH meter.

Results and discussion

In this trial, the total N content of the dairy effluent decreased in all treatments over the 81 day storage period (Figure 1).

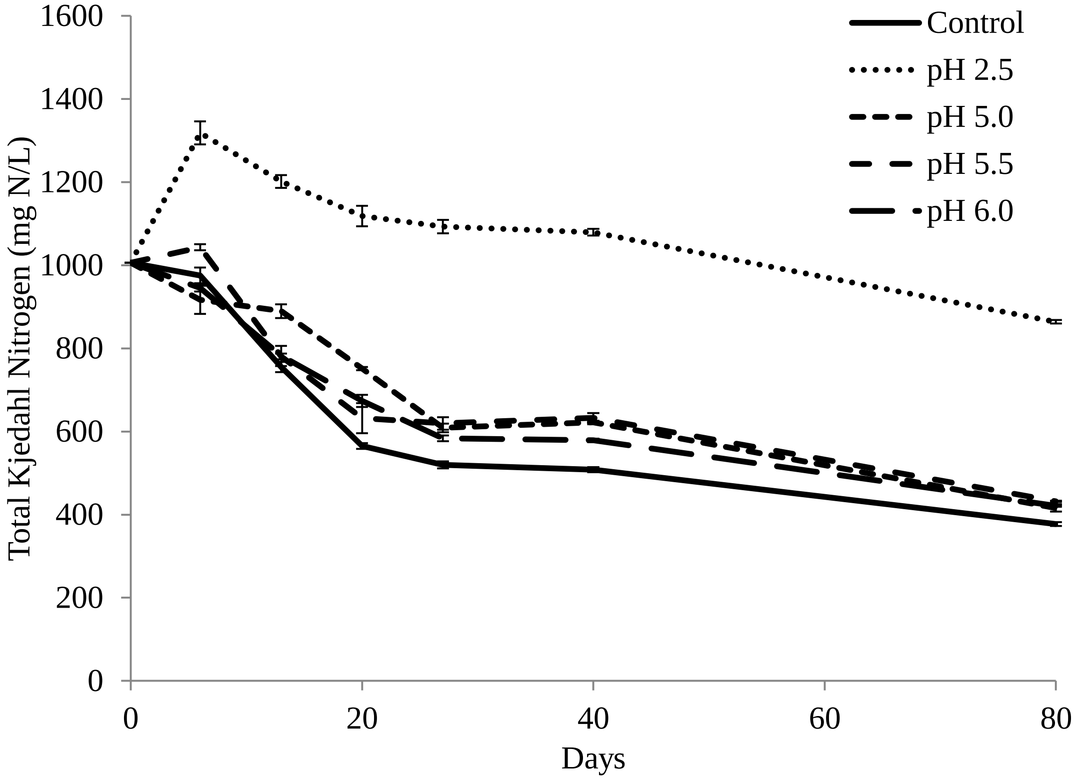

Figure 1. Changes in total effluent N content over the storage period (error bars represent one SEM), as affected by addition of sulphuric acid.

After 81 days' storage, 62% (629 mgN/L) of the initial effluent N was lost from the control (non-amended) treatment. The addition of H_2SO_4 to effluent increased the retention of N for all four acidification rates. The effluent lowered to pH 2.5 behaved differently to the other 3 rates and will be discussed separately. After 20 days' storage, losses of 25-37% of the initial effluent N were observed from the acid treatments where pH was reduced to between 5 and 6 (Figure 1). These losses were smaller than the 44% loss measured from the control treatment over the same 20 day period. At the end of the storage period (81 days) the losses were 57-59% compared to 62% from the control.

Figure 2 shows the increase in ammoniacal N levels with increasing acid addition in the treatments ranging between pH 5 and 6 when compared to the control suggesting decreased potential of volatilisation losses (more retained ammoniacal N).

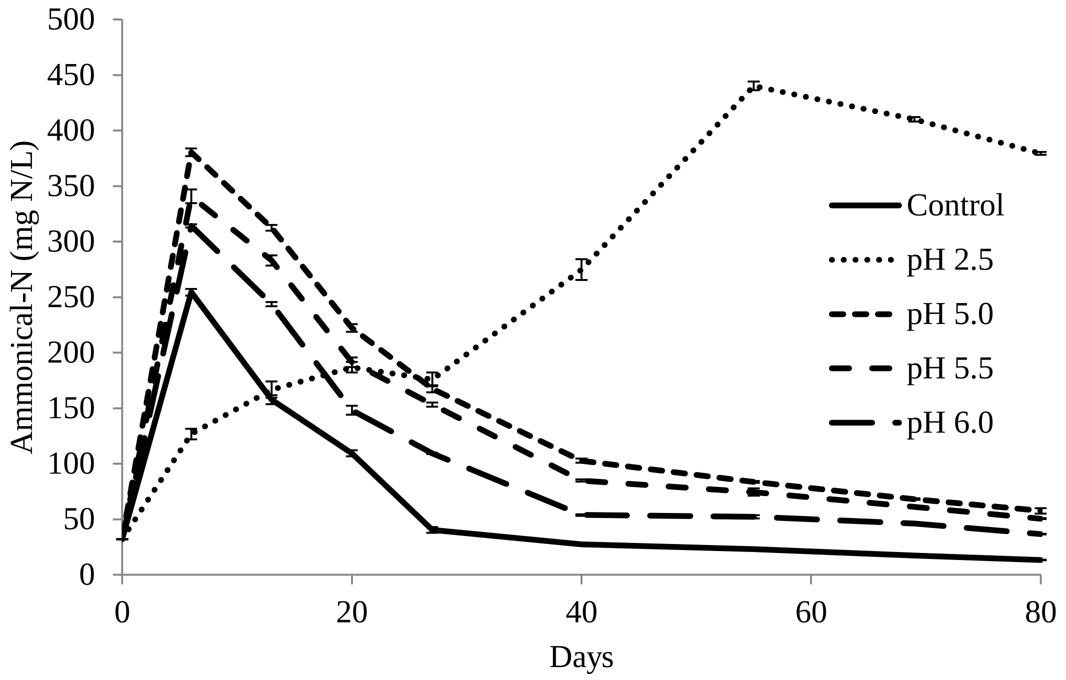

Figure 2: Changes in ammoniacal N content over the 81 day storage period, as affected by addition of sulphuric acid (error bars represent one SEM).

By day 6 (sampling occasion 1), the pH in treatments amended between pH 5 and 6 increased near to that of the control and remained at a similar pH for the duration of the experiment (Figure 3).

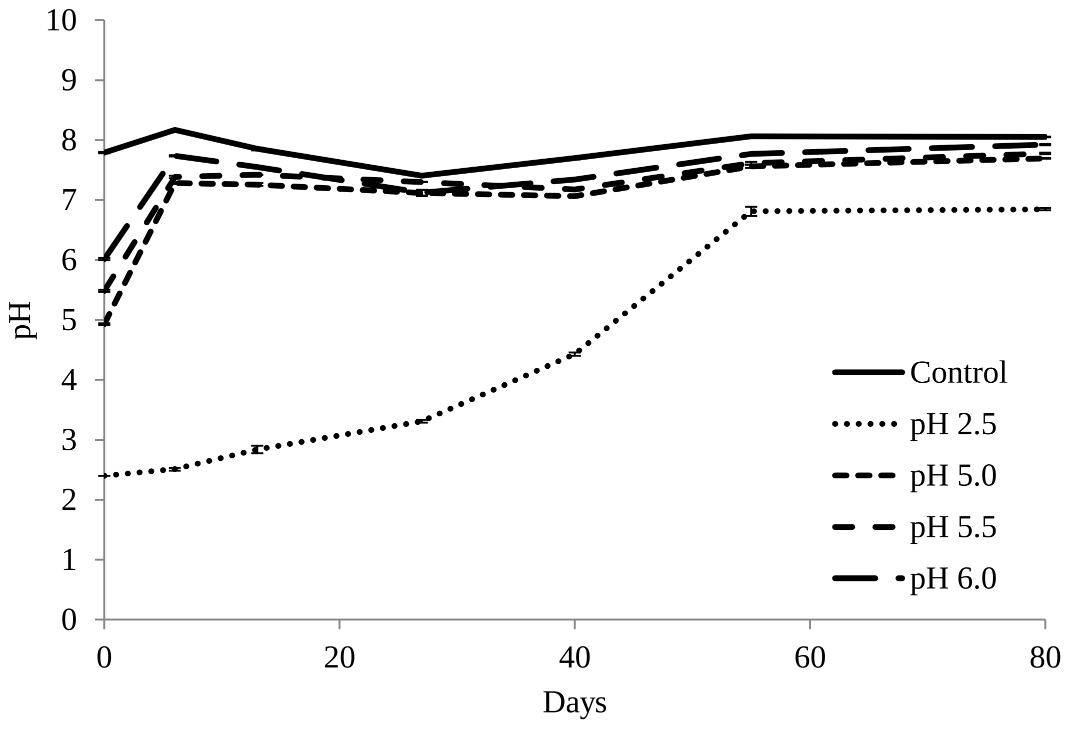

Figure 3: Changes in effluent pH following addition of sulphuric acid (error bars represent one SEM).

The result of this very short term effect on pH meant that cumulative N losses from these 3 acid treatments after 81 days' storage were not too different from the control treatment as described above. Multiple additions of acid to maintain a decreased pH in the stored effluent could increase N retention by lowering volatilisation. It is hypothesised that frequent additions of acid maintaining effluent pH at approximately 5-6 would be a more effective practice than a single dose and warrants further research. Multiple dosing would be especially important in a working pond as there are regular inputs of fresh effluent.

In the effluent lowered to pH 2.5 the pH did not return to control treatment levels during the 81 days of storage (Figure 3). This resulted in a greatly reduced N loss, 14% when compared with 62% in the control after 81 days. A pH of 2.5 arrested microbial and urease activity which slowed urea hydrolysis (Figure 4), this in turn delayed the production of NH_4-N (Figure 3).

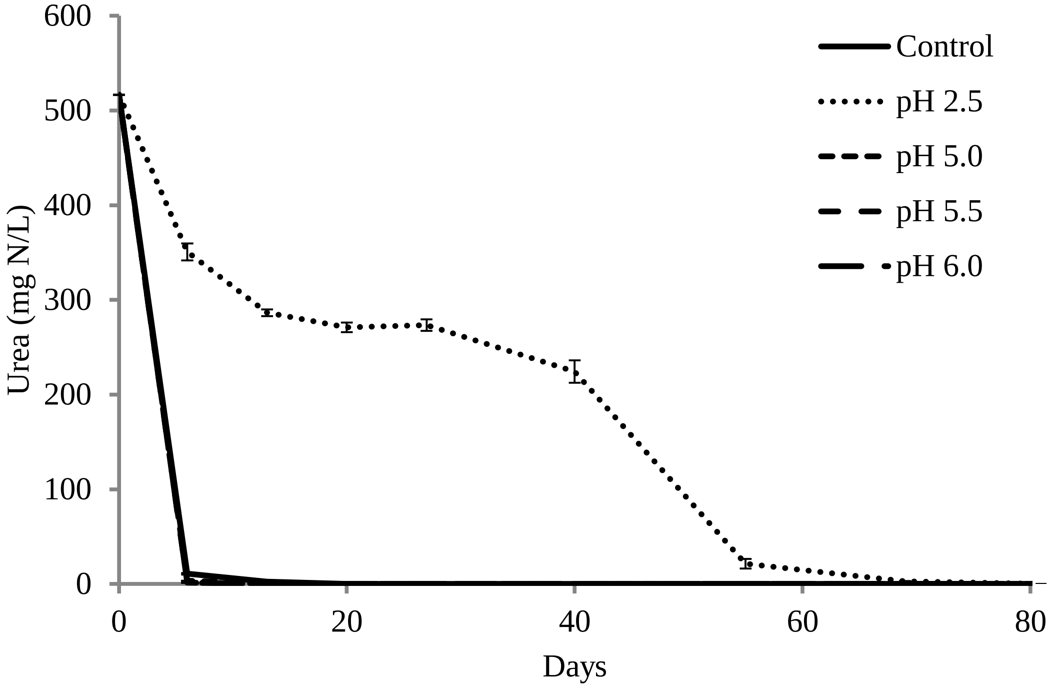

Figure 4: Changes in urea-N content over the 81 day storage period, as affected by addition of sulphuric acid (error bars represent one SEM).

By day 55, in the pH 2.5 treatments, the pH of the effluent reached levels where urea hydrolysis was able to occur more rapidly (Figure 3), therefore increasing ammoniacal N levels (Figure 2) and thus N loss through volatilisation. The reduced pH and reduced ammoniacal N production combined to make pH 2.5 by far the most effective treatment at reducing N losses. Further studies should be conducted to determine the optimal pH (lowest acid dosage) at which urea hydrolysis is significantly reduced in order to maximise N retention and minimise costs.

The increase in TKN content, above 100%, measured in the pH 2.5 treatments during the first 40 days of storage (Figure 1) is currently unexplained. It may have resulted from the low pH of the pH 2.5 treatments creating a sink for the N, especially NH_3, lost from the surrounding control and pH 5-6 treatments, creating some form of deposition. The increase in TKN is not accounted for in the ammoniacal N pool suggested it may be being deposited in an organic form and may be microbial in nature. It is not known whether this N deposition would still occur if this treatment was isolated from the other treatments (ones losing N). If this deposition was an interaction between effluent treatments it would result in an over-estimation of N preservation in the pH 2.5 effluent and this needs to be addressed prior in future research.

Conclusions

The trial data shows that acidification of dairy farm effluent increases N retention and helps maintain effluent N as a fertiliser resource when applied to land. Increasing the rate of acid addition reduces N losses slightly up to the point where the lowered pH not only reduces NH_3 volatilisation losses but also dramatically slows urea hydrolysis. The combination of these processes dramatically increased N retention (as seen in the pH 2.5 treatment), this point occurs somewhere between pH 5 and 2.5. Further study should be conducted to determine the lowest acid dosing required to significantly reducing urea hydrolysis, thus maximising N retention while minimising acid costs.

Acidification should also be further tested under more dynamic storage conditions, replicating regular additions of both effluent and acid in order to better simulate a working pond system. It is envisaged that the next step will require some further cost benefit analysis to help determine additive rate and frequency prior to assessing products in full field conditions i.e. operating effluent storage systems.

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