Ammonia volatilization from nitric-acid-treated cattle slurry surface applied to grassland

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Abstract

Much research is being done to lower NH_3 volatilization from animal manure. In this study, reduction in NH_3 loss from HNO_3 treated cattle slurry, surface applied to grassland, was measured on different soil types throughout the Netherlands from 1989 to 1992. In total, 13 micro-meteorological mass balance and 10 small wind tunnel experiments were carried out. Amounts varying between 7–17 and 10–30 m^{-3} ha^{-1} were applied, respectively. Measurements were performed for 4 and 10 days, respectively. The pH of treated slurry ranged from 3.9 to 6.6. Acidified slurry was always compared with untreated slurry.

A mean total of 60% (range: 29–98%) of the NH_4–N from untreated slurry was volatilized in the mass balance experiments. A reduction in NH_3 volatilization of 85, 72 and 55% was achieved for acidified slurry with a respective pH of c. 4.5, 5.0 and 6.0. Approximately 55% (range: 7–91%) of the total loss from acidified slurry was measured on the day of application. A mean total of 66% (range: 21–90%) of NH_4–N from untreated slurry volatilized in the tunnel experiments. The reduction in NH_3 volatilization was 73% for slurry with pH 4.5. Approximately 27% (range: 6–91%) of the total loss from acidified slurry was measured on the first day. The lower reduction and the different pattern in NH_3 volatilization observed in the wind tunnel experiments might be the consequence of different climatic conditions in and outside the tunnels or they might be related to the higher rates of slurry application in these experiments.

Regression analysis indicated that high temperature, slurry pH, potential water evaporation and NH_4^+ concentration stimulated NH_3 loss in the mass balance experiments ($R^2 = 87\%$). It is suggested that the results obtained with acidified slurry were independent of the grassland soil type at the application levels employed.

Keywords: ammonia volatilization, cattle slurry, acidification, nitric acid, grassland, pH

Introduction

Livestock excreta are generally regarded as the main source of NH_3 input into the atmosphere (Apsimon *et al.*, 1987; Schlesinger & Hartley, 1992). Losses may arise

from grazing, housed livestock, slurry storage units and (surface) applied slurry. In Europe the largest losses are considered to result from surface applied slurry (Buijsman et al., 1987); ranging between 20 to 85% of the NH_4–N applied (Bless et al. 1991; Pain et al. 1989; Sommer et al. 1991). The large variation is due to differences in soil type, amount and composition of slurry (Sommer & Olesen 1991) and environmental conditions (Horlacher & Marschner, 1990; Sommer et al. 1991).

Decreasing NH_3 losses will improve the N fertilizer value of land-applied slurry and decrease the impact of NH_3 on eutrophication and acid deposition (Roelofs et al., 1985). Slurry injection and soil tillage immediately after surface application on arable land (Van der Molen et al. 1990; Horlacher & Marschner, 1990; Bless et al. 1991; Mulder & Huijsmans 1994) and slurry injection on grassland (Van der Meer et al., 1987; Thompson et al. 1987; Bussink & Bruins, 1992; Mulder & Huijsmans, 1994) proved to be efficient methods in reducing NH_3 losses. Because of the heavy application machinery and high draft requirement, injection on grassland is limited to light stone-free soils with a high bearing capacity. Under such conditions dilution of slurry or water irrigation after surface application (Sommer & Olesen, 1991; Bussink & Bruins, 1992) and band-spreading (Mulder & Huijsmans, 1994) are useful techniques.
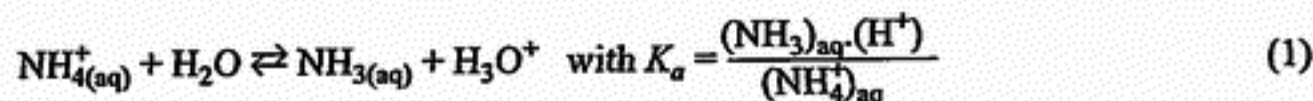
Acidification of slurry has also shown great potential in reducing of NH_3 losses (Stevens et al., 1989; Frost et al., 1990; Pain et al., 1990). A key factor in the reduction of NH_3 losses is slurry pH at application (Stevens et al., 1992).

In the Netherlands much research has been done with respect to NH_3 loss reducing potential, the technical implementation in practice, the economics and the environmental aspects of nitric-acid-treated cattle slurry. This study examines the NH_3 losses from acidified cattle slurry surface-applied on grassland. Nitric acid (HNO_3) was chosen because the anion is a valuable plant nutrient and by varying the amount of HNO_3 applied it is possible to meet the total N demand of grass. However, this will lead to variations in slurry pH and thus in NH_3 losses. Therefore the main emphasis was placed on the effect of slurry pH and NH_4^+ activity on NH_3 volatilization and on changes in slurry pH after application. Results from four years of experimentation, using the micro-meteorological mass balance method and small wind tunnels at various sites and environmental conditions are described. The results were used to predict pH requirement for target volatilization reduction levels.

Materials and methods

Theory of NH_3 volatilization
Up to 80% of the mineral N in slurry originates from urea, which rapidly hydrolyses into $(NH_4)_2CO_3$. The NH in the slurry is in equilibrium with NH_3 in the liquid and gas phases according to:

$$NH_{4(aq)}^+ + H_2O \rightleftarrows NH_{3(aq)} + H_3O^+ \quad \text{with } K_a = \frac{(NH_3)_{aq} \cdot (H^+)}{(NH_4^+)_{aq}} \tag{1}$$

$$NH_{3(aq)} \rightleftarrows NH_{3(g)} \quad \text{with } H = \frac{(NH_3)_g}{(NH_3)_{aq}} \tag{2}$$

where $(..)_{aq}$ and $(..)_g$ are the activity (M) of the species in solution and in air, respectively; K_a is the dissociation constant (M) and H is the Henry constant (M M^{-1}). K_a and H are temperature (T, °C) dependent. Using the temperature corrections of Emerson et al. (1975) for K_a and of Dasgupta & Dong (1986) for H/RT = K_h (M atm^{-1}, with atm = 1.103 * 10^5 Pa) and rewriting Equations (1) and (2) gives:

$$(NH_3)_g = \frac{K_a(NH_4)_{aq}}{K_h(H^+)} = (NH_4)_{aq} \, 10^{(4.117 + pH - 4507.053/(T + 273.15))} \tag{3}$$

By lowering the pH of the solution $(NH_3)_g$ decreases and thereby so does the potential for NH$_3$ losses. The relationship between $(NH_3)_g$, pH and T is shown in Figure. 1. For a slurry of average ionic strength (I) of 0.3 M and 2.2 kg NH$_4$–N m^{-3}, $(NH_4^+)_{aq}$ is 0.108 M (Vanysek, 1989), neglecting adsorption and complex formation. Lowering the pH from 7.5 to 4.5 gives a sharp decrease in $(NH_3)_g$ to values below background level in the atmosphere i.e. 5–25 µg NH$_3$–N m^{-3} in our experiment. Due to water evaporation, I and $(NH_4^+)_{aq}$ will increase. At a relative humidity of 75%, the osmotic pressure of the slurry will rise to −38 MPa before evaporation ceases (calculated according to Koorevaar et al. 1983). This agrees with I = 8.0 M, assuming a
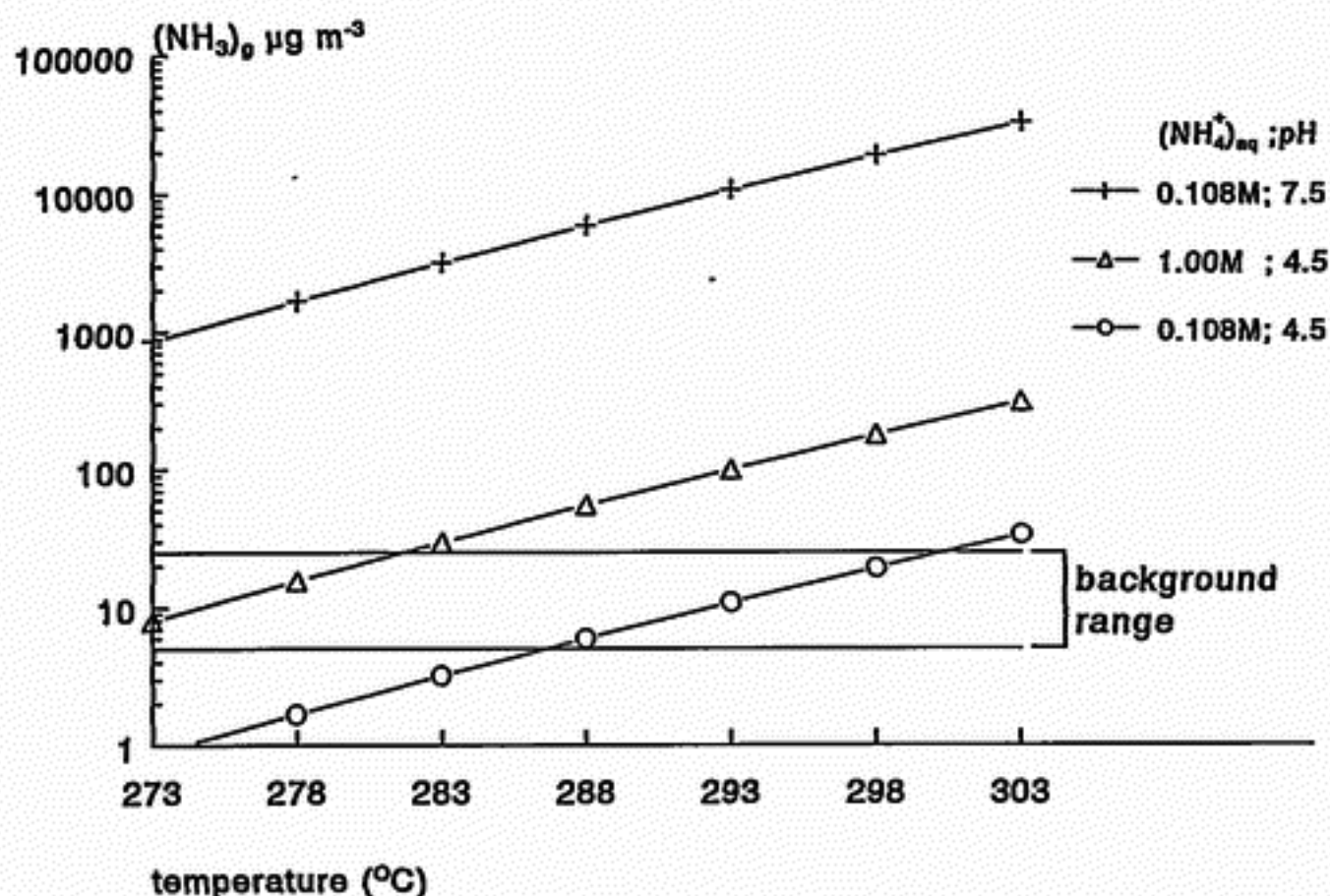

Figure 1. Equilibrium $(NH_3)_g$ concentration in air for a solution with NH$_4^+$ activity, (NH_4^+) of 0.108 and 1.0 M at different temperatures and solution pH's (1.0 M as example of the effect of water evaporation); background $(NH_3)_g$ range from 5 to 25 µg m^{-3}.

complete dissolution of the salts. As a consequence $(NH_4^+)_{aq}$ and $(NH_3)_g$ increase and, hence, NH_3 is released (Figure 1). In theory due to evaporation, there may be NH_3 volatilization at pH values as low as 4.5.

Description of sites and experimental treatments

Two separate data sets were available to analyse the effects of slurry acidification. One set of volatilization data had been obtained using the micro-meteorological mass balance method (Denmead, 1983) the other set using wind tunnel measurements (Lockyer, 1984).

All data originated from field experiments carried out at 5 sites, on clay soils near Swifterbant and Duiven, peat soil in Zegveld and sandy soils in Luttenberg and Wageningen. The location and soil characteristics of the sites are shown in Table 1. The well established swards contained perennial ryegrass as dominant grass species and had been intensively managed in previous years. In all experiments untreated cattle slurry was compared with HNO_3 treated cattle slurry at similar levels of slurry application. Wind speed, air temperature at 1.5 m, humidity and sunshine duration and radiation were recorded on all sites. Water evaporation data for the sites were obtained from the meteorological office.

In the experiments using the mass balance method, slurry was surface applied before noon using a tanker fitted with a splash plate. Working width varied between 2.5 and 8 m. By spreading in parallel passes varying in length over a pre-marked area, circular plots were achieved with a radius varying between 20 and 24 m. The pH of the acidified slurry ranged from 3.9 to 6.6.

In the experiments using small wind tunnels slurry was applied with a watering can. The pH of the acidified slurry was c. 4.5.

Measurement of NH_3 losses by mass balance
The micro-meteorological mass balance method assumes that the vertically integrated product of wind speed and the difference in air-NH_3 concentration, between the

Table 1. Location of the sites and characteristics of the 0–5 cm soil layer.

	location		soil type	pH-KCl	CEC mol_c kg^{-1} %	organic matter	CaCO$_3$ %	clay <2μm
	longitude	latitude						
Zegveld	4 52'	52 07'	peat	4.9	0.24	45.1	0	–
Luttenberg	6 21'	52 23'	sand	5.3	–	5.7	0	–
Duiven	6 01'	51 56'	heavy clay	5.2	–	13.7	0	44
Wageningen	5 40'	51 59'	sand	5.0	0.04	3.2	0	–
Swifterbant	5 40'	52 35'	clay	6.9	0.28	8.1*	6.4	18

* corrected for CaCO$_3$

centre and boundary of the plot, divided by the fetch (distance between upwind boundary and the centre of the plot) is equal to the NH_3 flux from the soil surface (Denmead, 1983).

As soon as the first half of the circular plots was covered with slurry (usually within 5 minutes) a mast supporting 7 to 8 NH_3 traps at heights between 0.25 and 3.30 m was placed in the centre of the plot. At the windward boundary of the plot, a mast was placed with 5 NH_3 traps at heights between 0.40 and 2.30 m. Fewer traps were placed at the boundary because the background concentration was low and essentially uniform with height. Each trap contained 20 ml 0.02 M H_3PO_4 or 0.02 M HNO_3 held in 100 ml collection tubes. Air was drawn through the acid via a sintered gas dispersion tube at rates of $2-4$ l min^{-1}, measured with flow meters. A correction was made for the measured pressure drop between the flow meter and the air inlet of the trap.

The measurements continued for at least 4 days after slurry application. Traps were replaced five times in the first 24 h when the highest NH_3 loss rates occurred. From day 2 to day 4 the traps were replaced in early morning and late afternoon. Wind speed was measured on a mast outside the plot, at six different heights, between 0.40 and 3.30 m. A total of 13 experiments were conducted (see Table 2 for details).

Measurement of NH_3 losses by wind tunnels

The design of the small wind tunnels followed essentially the description by Lockyer (1984). A U-shaped transparent tunnel of polycarbonate covers an experimental plot (2.0 x 0.5 m). The tunnel is connected to a circular steel duct housing an electrically powered fan. In principle the method consists of sampling a controlled airflow (generated by the fan) before and after it passes over the experimental plot in the tunnel. The difference in concentration between inlet and outlet multiplied by the airflow and corrected for the experimental area is equal to the NH_3 flux for a certain measurement period.

The NH_3 concentrations in inlet and outlet of the tunnel were measured by drawing air continuously via a sintered gas dispersion tube at a rate of 13 l min^{-1} through 0.3 M H_3PO_4 held in 100 ml collection tubes. These traps were usually replaced on a 24 h basis during a 10-day measurement period. Air passed through the tunnel at rates of 2 m s^{-1} in two experiments and 1 m s^{-1} in the other eight experiments (see Table 3 for details).

Analytical methods

The NH_4^+ concentration in the H_3PO_4 solutions was measured colorometrically (Weatherburn, 1967; Bietz, 1974), whereas ion-chromatography was used for analysis of the NH_4^+ concentration in the 0.02 M HNO_3 solution.

In the mass balance experiments 12 and 13 and in the tunnel experiments 4, 6, 8 and 10 slurry surface pH was measured after application using a flat-surface combined glass electrode after moistening the slurry with dionized water. Per plot three readings were obtained during the course of the experiment.

Table 2. Slurry composition and measured NH_3 volatilization on grassland using the mass balance method. (In experiments 11–13 slurry was acidified immediately prior to application.)

experiment nr.; date	measurement days	soil type	slurry composition pH	DM %	NH_4-N kg ha^{-1}	amount applied m³ ha^{-1}	NH_3-N loss % of NH_4-N applied	of 1st day % of total loss	reduction by acidification	T 1st day (°C)	T 2nd day (°C)	rainfall 1st day mm	rainfall 2nd day mm
1. 16-3-89	7	clay	7.5	–	2.7	10.0	28.5	98		4.5	3.3	3.0	7.1
			4.5	–	3.3	10.0	0.4	91	99				
2. 19-6-89	5	sand	7.5	–	3.0	10.0	97.9	89		21.9	21.1	0.0	0.0
			5.1	–	2.1	10.0	12.5	20	87				
3. 20-3-90	5	clay	7.3	8.0	2.3	6.5	42.3	95		13.0	10.7	2.5	0.5
			3.9	11.2	2.2	7.0	2.6	8	94				
4. 24-4-90	4	peat	7.5	7.3	2.2	10.2	58.3	92		12.2	12.4	0.0	0.0
			4.5	11.1	1.7	9.0	11.1	50	81				
5. 29-5-90	4	peat	7.1	8.3	2.3	9.8	44.2	87		12.3	15.1	0.0	0.0
			4.6	11.6	1.7	8.1	13.5	29	69				
6. 12-6-90	4	sand	7.2	8.3	2.3	9.9	33.9	88		12.0	12.4	0.0	0.0
			4.3	9.7	1.7	8.7	0.2	60	99				
7. 26-6-90	4	sand	7.4	8.3	2.3	9.8	51.1	98		19.2	19.7	0.0	20
			4.3	8.8	1.7	8.6	7.0	90	86				
8. 28-8-90	4	peat	7.1	7.3	2.0	12.7	52.0	72		20.3	22.8	0.0	0.0
			4.4	8.1	1.3	13.2	7.0	7	87				
9. 4-9-90	4	peat	7.4	7.6	2.3	9.6	49.7	91		15.7	13.9	0.0	0.0
			4.5	8.1	1.4	8.2	13.2	59	73				
10. 11-9-90	4	peat	7.3	7.3	2.1	8.7	58.1	85		13.5	13.9	2.2	0.4
			5.0	8.1	1.5	7.7	20.4	35	65				
11. 16-7-91	10	heavy clay	7.0	7.2	1.5	9.8	96.7	85		16.4	16.9	0.0	0.0
			6.0	7.5	1.6	10.1	46.5	73	52				
			5.8	7.6	1.3	10.3	47.8	62	51				
			4.9	7.9	1.4	10.2	20.6	50	79				
12. 10-3-92	3	heavy clay	7.4	6.6	2.1	17.3	85.8	96		7.4	5.9	0.0	2.1
			6.6	6.7	2.2	14.9	60.5	84	29				
			6.3	7.0	2.2	16.7	29.5	79	66				
			5.8	7.3	2.3	15.1	13.5	65	84				
13. 19-5-92	10	heavy clay	6.8	8.7	2.0	11.6	88.9	93		19.1	18.8	0.0	0.0
			5.7	9.1	2.2	13.0	46.1	60	48				
			5.6	9.3	2.3	12.0	41.3	77	54				
			5.2	9.6	2.4	15.8	38.0	62	57				

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Results

NH_3 losses from untreated slurry

The mass balance measurements showed a high NH_3 loss rate from untreated slurry during the first hours after application (Figure 2). The average total NH_3 loss was 60% (range: 29–98%) of the NH_4–N applied at an average slurry application of 10.4 (range: 6.5–17.3) m^3 ha^{-1} (Table 2). On average 90% (range: 72–98%) of the total losses were measured on the first day after application. One day after application the rate of loss decreased sharply.

Results obtained with the tunnel method were comparable to those obtained with the mass balance method. Total average loss was 66% (range: 21–90%) of the NH_4–N applied (Table 3) at an average slurry application of 24.1 (range: 9.9–30) m^3 ha^{-1}. On average 60% (range: 44–94%) of the total NH_3 loss was measured on the first day. Hence, volatilization continued longer in the tunnel than in the mass balance experiments (e.g. Figures 2 and 3).

NH_3 losses from acidified slurry

The mass balance experiments gave a reduction in NH_3 volatilization for acidified slurry of 29 up to 99% of that found with untreated slurry. Ammonia volatilization was strongly related to slurry pH (Table 2). A mean reduction in NH_3 volatilization of 85, 72 and 55% was achieved for acidified slurry with a respective pH of c. 4.5, 5.0 and 6.0. The NH_3 loss from acidified slurry was very low in the first hours after application, but increased later. On average, 55% (range: 7–91%) of the total NH_3 loss was measured on the first day with application rates averaging 10.8 (range: 7.0–16.7) m^3 ha^{-1}. The percentage of NH_4–N volatilized (%NH_4-loss) on the first day was strongly related to initial $(NH_3)_g$ (Equation 3; using the initial slurry pH, the average temperature of the first day at 1.5 m and using the initial NH_4^+ concentration instead of NH_4^+ activity) and soil type according to:

$$\%NH_4\text{-loss} = 5.42 \, (\pm 0.77) \times 10^7 \, (NH_3)_g + 4.25 \, (\pm 2.03) \times \text{peat} + 10.44 \, (\pm 2.74) \times (\text{heavy clay}) \tag{4}$$

with: $R^2_{adj} = 90.5\%$ and n = 19 (all treated slurries of Table 2)

It was tested that clay and sandy soil did not differ from each other. Peat and heavy clay showed higher volatilization rates for the same $(NH_3)_g$ than clay and sandy soil. Inclusion of (wind speed)×$(NH_3)_g$, (water evaporation)×$(NH_3)_g$ or (application level)×$(NH_3)_g$ did not improve R^2_{adj}. The total percentage of NH_4–N (%TNH_4-loss) volatilized during the experimental period was strongly related to initial $(NH_3)_g$, soil type and 4-day cumulative water evaporation ($cumE_p4$, mm), according to:

$$\%TNH_4\text{-loss} = (3.61 \, (\pm 1.68) + 1.58 \, (\pm 0.86) \times cumE_p4) \times 10^7 \, (NH_3)_g + 12.09 \, (\pm 2.96) \times \text{peat} + 17.87 \, (\pm 4.24) \times (\text{heavy clay}) \tag{5}$$

with: $R^2_{adj} = 87.4\%$ and n = 19

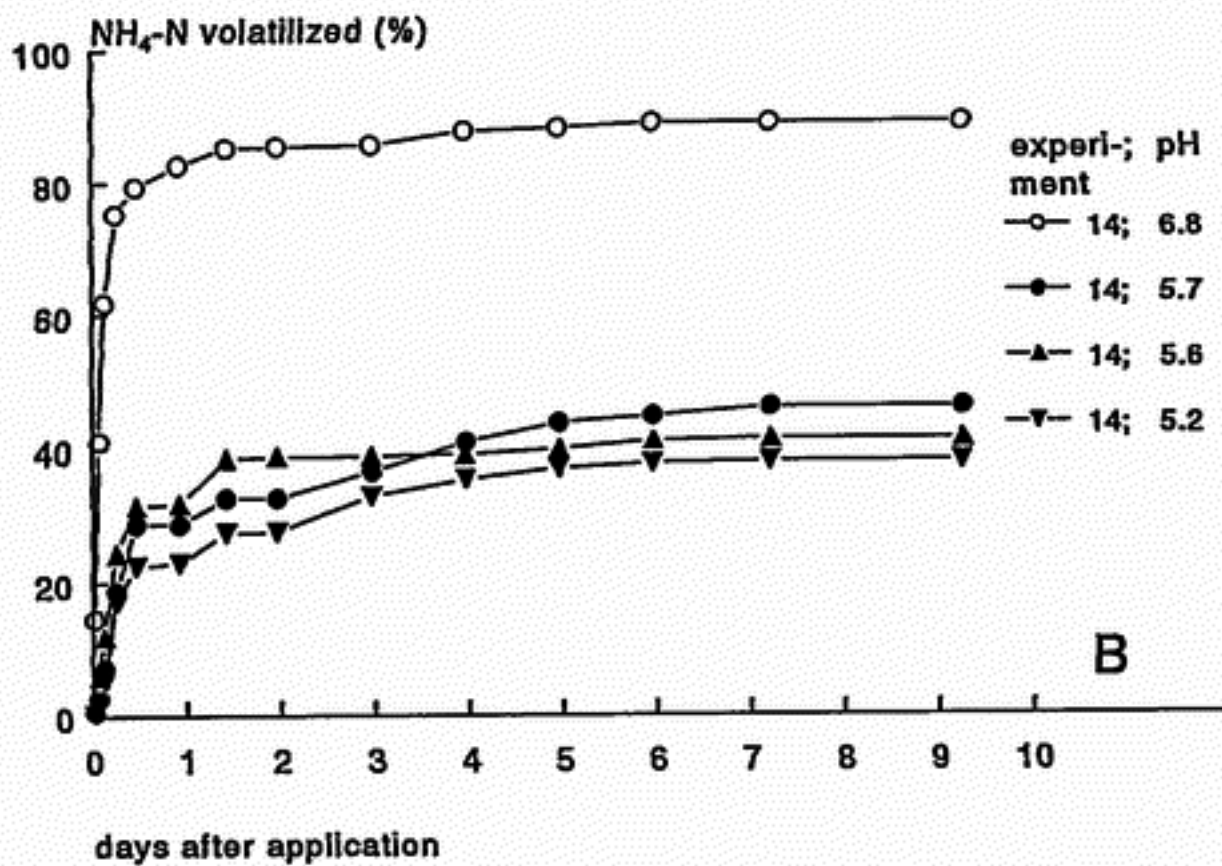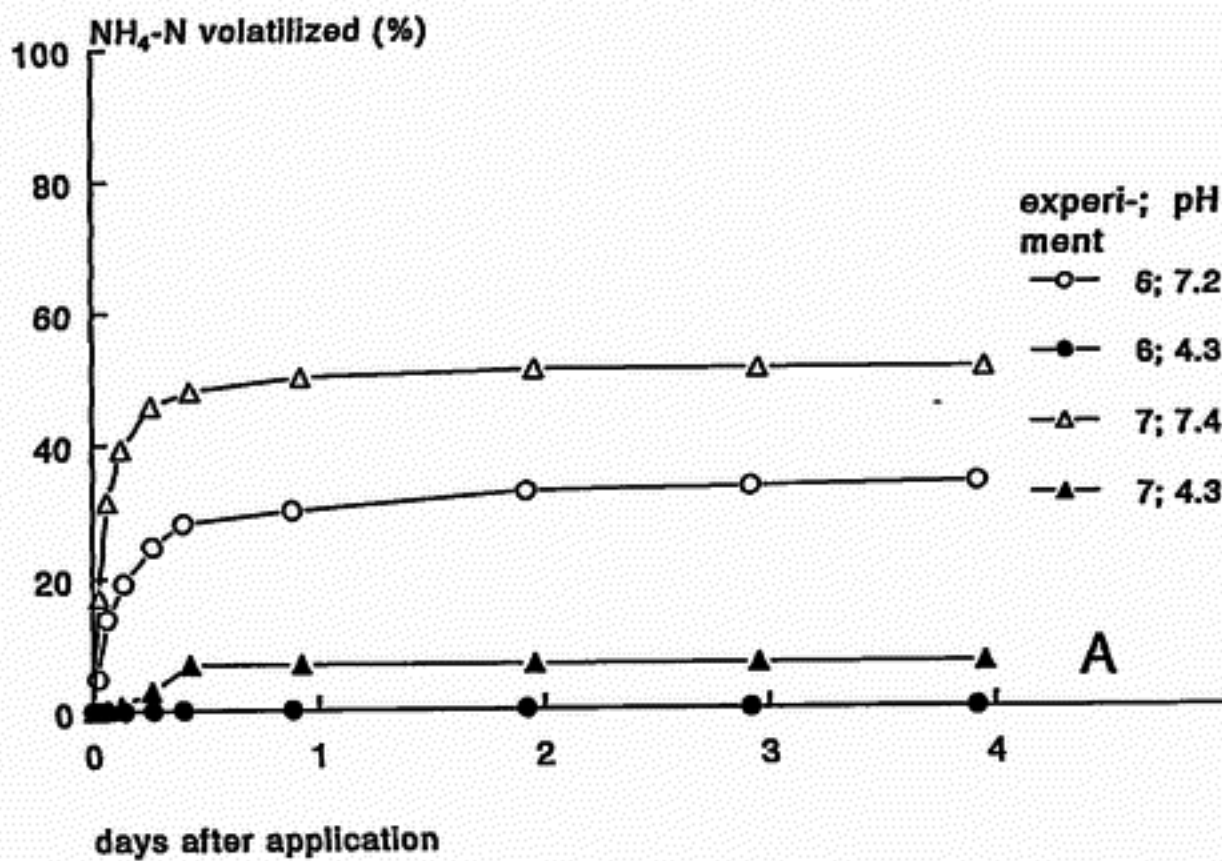The tunnel experiments also showed a reduction in NH_3 losses from acidified slur-

Figure 2. Pattern of NH_3 volatilization in the mass balance experiments 6 and 7 (A) on sandy soil and experiment 13 (B) on heavy clay soil.

Table 3. Slurry composition and the measured NH₃ volatilization on pasture using wind tunnels.

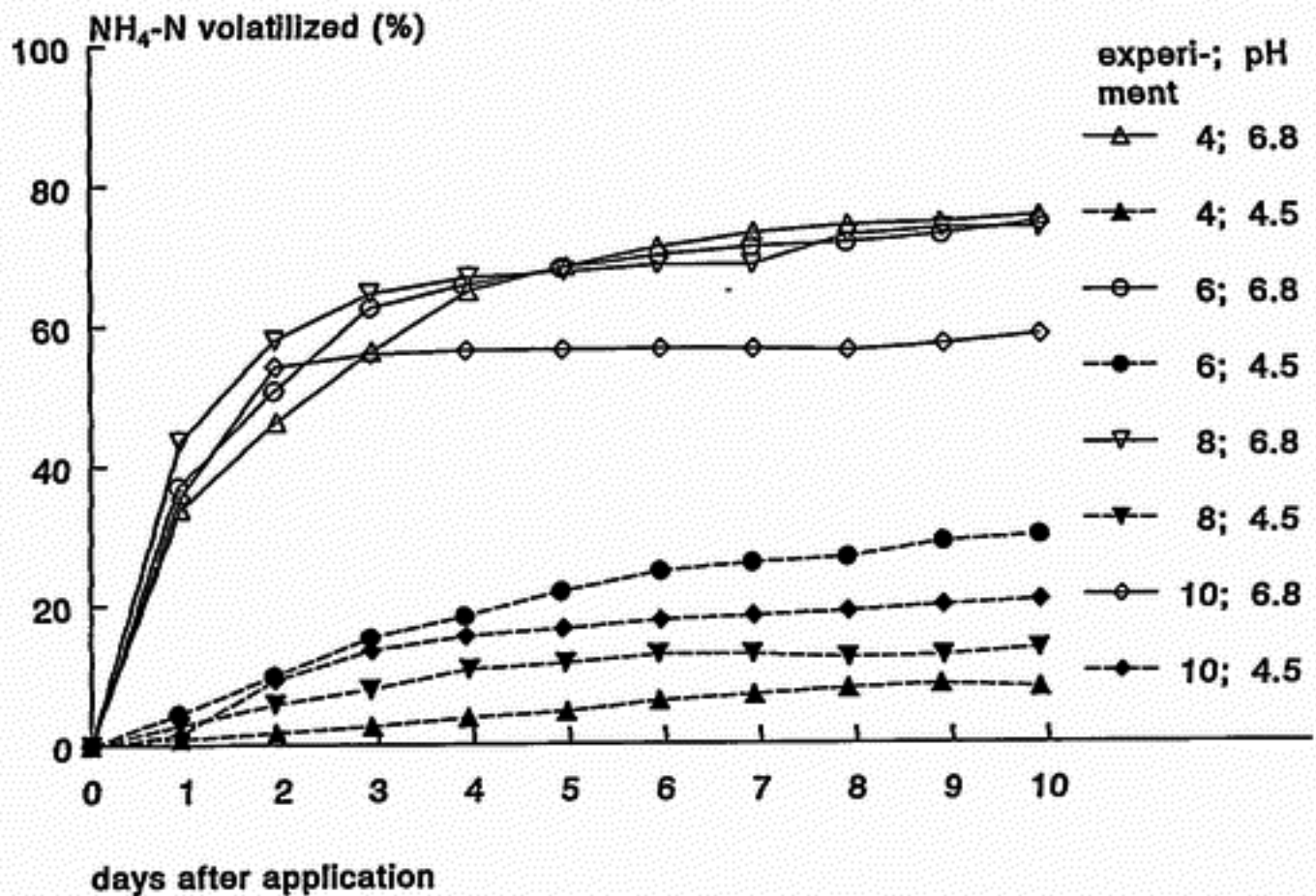| experiment nr.; date	measu rement days	soil type	slurry composition				NH₃-N losses			T		cumulative potential evaporation
			pH	DM %	NH₄-N kg ha⁻¹	amount applied m³ ha⁻¹	in % of NH₄-N applied	of 1st day in % of total loss %	reduction by acidi- fication (°C)	1th day (°C)	2nd day	
1. 16-3-89	7	clay	7.5	–	2.7	14.8	21	94		4.5	3.3	–
			4.5	–	3.3	10.6	1.5	16	93			
2. 26-6-89	5	sand	7.5	–	3.0	10.2	82	63		13.0	10.7	–
			5.1	–	2.1	9.9	9	91	89			
3. 26-3-91	10	sand	6.8	10.8	2.5	22	90	57		6.6	8.3	18.4
			4.5	–	2.5	22	3	81	97			
4. 16-4-91	10	sand	6.8	10.8	2.5	22	75	45		5.9	5.1	20.4
			4.5	–	2.5	22	8	11	89			
5. 2-4-91	10	sand	6.8	10.8	2.5	30	59	44		7.7	7.5	21.3
			4.5	–	2.5	30	30	6	49			
6. 14-5-91	10	sand	6.8	10.8	2.5	22	75	50		10.2	7.1	26.3
			4.5	–	2.5	22	30	15	60			
7. 28-5-91	10	sand	6.8	10.8	2.5	30	60	51		11.1	13.2	26.8
			4.5	–	2.5	30	33	12	46			
8. 11-6-91	10	sand	6.8	10.8	2.5	30	74	59		14.2	14.1	21.9
			4.5	–	2.5	30	14	20	82			
9. 25-6-91	10	sand	6.8	10.8	2.5	30	62	52		17.4	15.9	29.1
			4.5	–	2.5	30	15	8	75			
10. 9-7-91	10	sand	6.8	10.8	2.5	30	58	61		15.5	19.4	29.3
			4.5	–	2.5	30	20	7	65			

Figure 3. Pattern of NH_3 volatilization in the wind tunnel experiments 4, 6, 8 and 10.

ry of 46 up to 97% to that of untreated slurry (Table 3). At pH $\approx$ 4.5 the mean reduction with the tunnel (73%, range: 46–97%) was less, than with the mass balance method (85%, range: 69–99%). Furthermore, there was a difference in variation and volatilization continued longer in the tunnel experiments than in the mass balance experiments (Figures 2 and 3). On average 27% (range: 6–91%) and 68% (range: 48–100%) of the total NH_3 loss was measured during the first and up to the fourth day, respectively.

Surprisingly, %NH_4-loss on day one was not significantly related to $(NH_3)_g$ or any weather parameter. This is probably due to the low losses on day one and the constant initial pH of the slurry. Also, %TNH_4-loss was not related to $(NH_3)_g$, but only slightly to the 10-day cumulative E_p (cumE_p10, mm):

$$\%TNH_4\text{-loss} = 0.565 \, (\pm 0.097) \times cumE_p10 \quad (R^2_{adj} = 23.6\% \text{ and } n = 8) \tag{6}$$

for tunnel experiments 3–10 (1 and 2 are excluded because of differing experimental design).

Changes in slurry pH

In the mass balance experiments 12 and 13, there was a rapid increase in pH immediately after slurry application, followed by a decrease in pH (Figure 4). After several hours a small rise in pH was observed.

In the tunnel experiments the pH of acidified slurry increased steadily (Figure 5). Experiment 10 showed the largest pH increase with c. 1.5 units. This did however
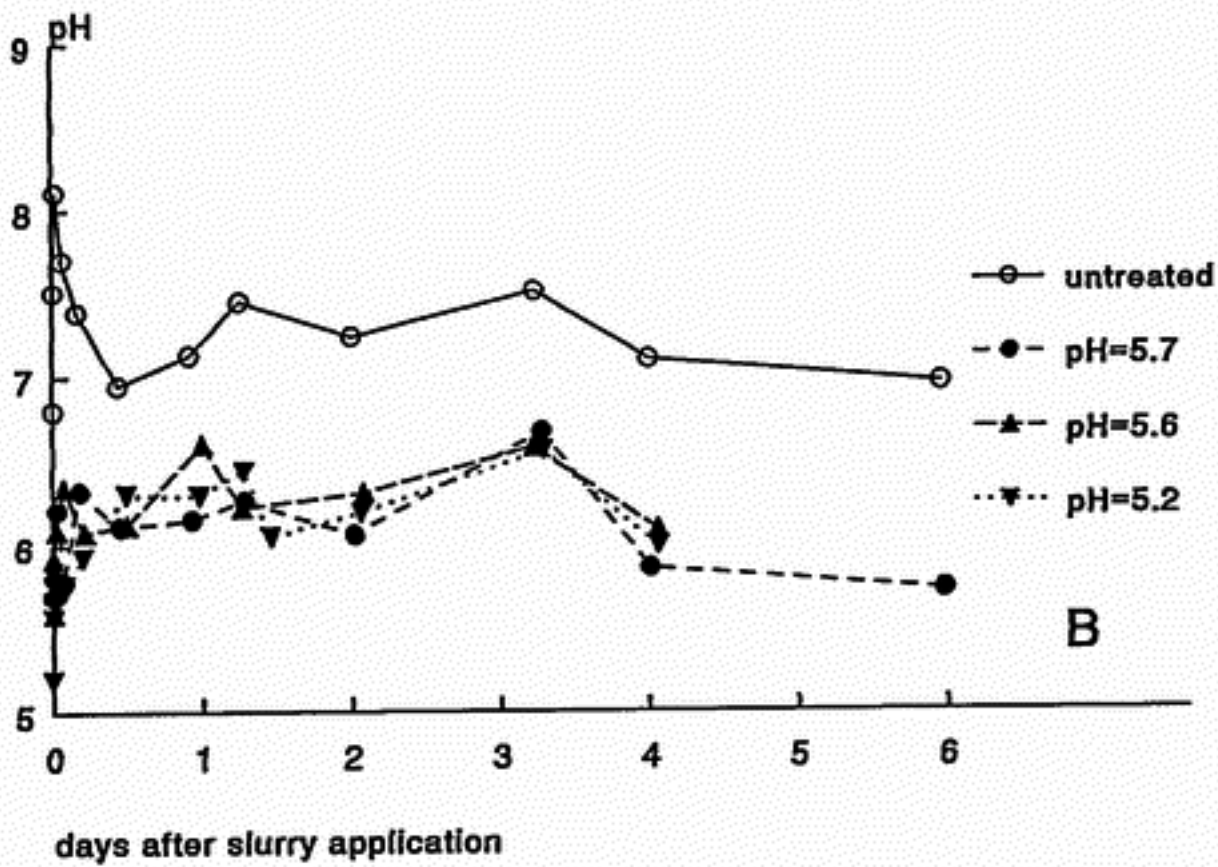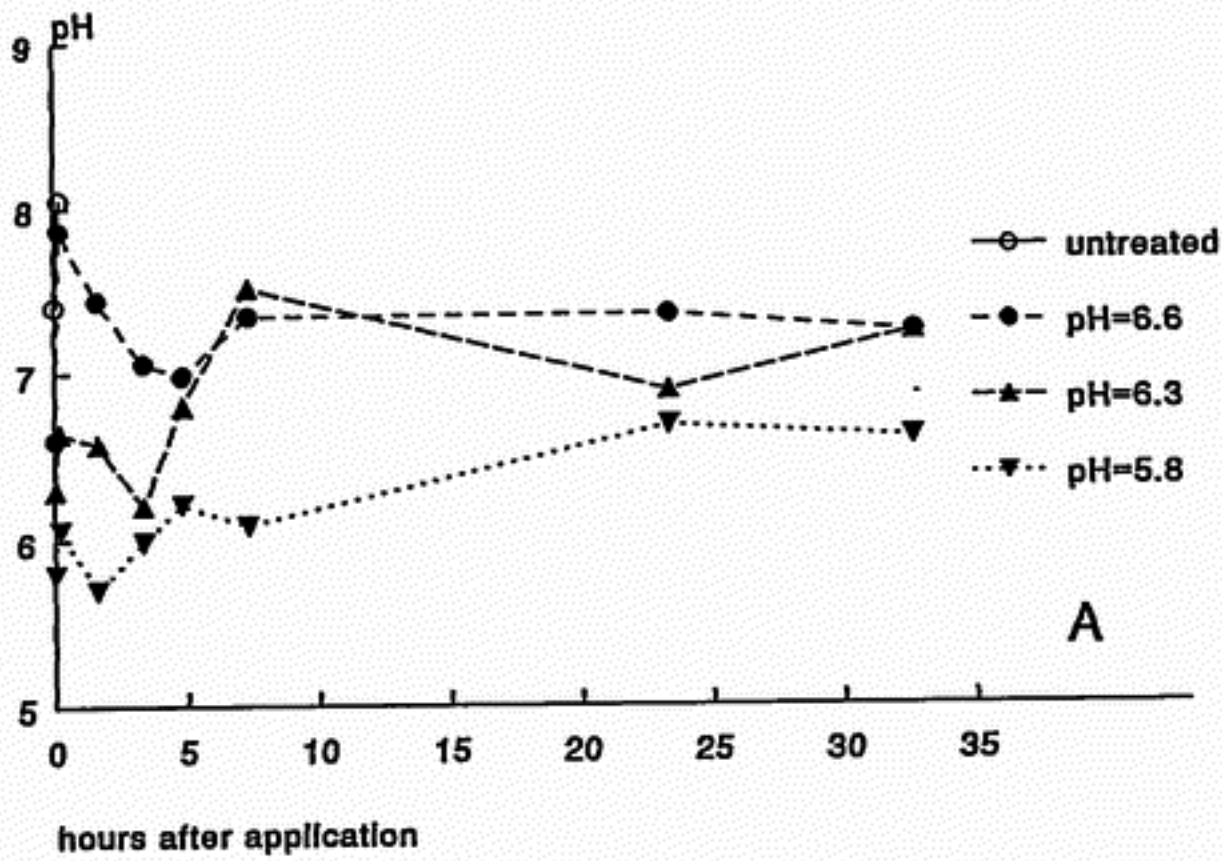
Figure 4. Slurry pH after application on heavy clay soil in the mass balance experiments 12(A) and 13(B).
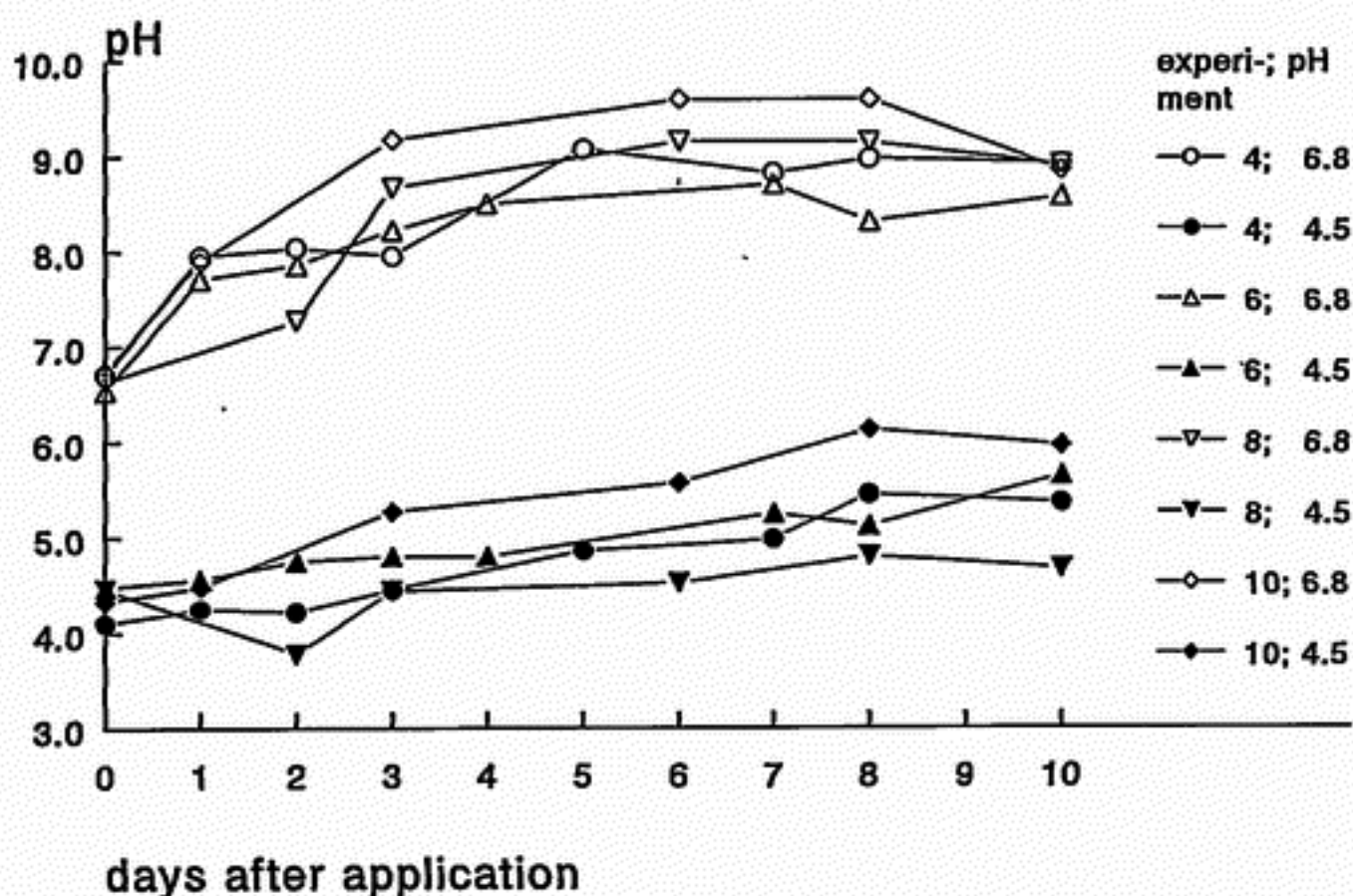
Figure 5. The pH of acidified slurry after application on sandy soil in the wind tunnel experiments 4, 6, 8 and 10.

not result in the highest NH_3 loss rate (Figure 3, experiment 6), despite the fact that $cumE_p10$ was also the largest (Table 3). Untreated slurry gave a sharp rise in pH.

Discussion

Effect of slurry acidification on NH_3 loss

Slurry acidification proved to be an efficient method of reducing NH_3 losses. The reduction achieved strongly depended on initial slurry pH and air temperature (Figure 1), which was confirmed by regression analysis (Equation 5). Ammonia losses increased progressively with increasing pH and temperature and according to Equation 5 NH_3 losses increased also with $cumE_p4$.

Other experiments also showed marked reductions in NH_3 loss due to acidification. In Northern Ireland, a slurry pH of 5.5, 6.0 and 6.5 resulted in a reduction of NH_3 loss of > 85% (Frost et al., 1990), 90% (Stevens et al., 1992) and 75% (Stevens et al., 1992), respectively. Our experiments showed lower reductions for these pH values (Table 2), e.g. pH values of 4.5 to 5.0 were needed in the mass balance experiments – and even lower pH values in the tunnel experiments – to obtain similar reductions. This might be attributed to (i) the used measurement technique in Northern Ireland (discontinues measurements using ventilated enclosures) which underesti-

mated NH_3 loss rate (Frost *et al.*, 1990) and (ii) the slightly higher temperature and evaporation in the Netherlands, which enhance NH_3 loss as observed from Figure 1. Consequently lower pH values are needed to obtain the same levels of reduction. Also the smaller amount of slurry applied (e.g. Döhler, 1991) and the high slurry DM content may stimulate NH_3 loss rate (Sommer & Olesen, 1991), in comparison to other experiments on grassland (Pain *et al.*, 1990; Frost *et al.*, 1990; Stevens *et al.*, 1989 & 1992).

Comparison of measuring techniques
Two factors may account for the higher loss rates and the continuing loss (Figure 3) in the tunnel experiments. Firstly, differences in conditions in and outside the tunnel may stimulate NH_3 volatilization. In tunnels any rainfall is intercepted and due to the continuous wind speed dew formation is possibly prevented and evaporation is possibly stimulated. These factors may lead to a lower infiltration of NH_4^+ into the soil and to an increase in $(NH_4^+)_{aq}$ and I. In a study of Ryden & Lockyer (1985) no difference was found between mass balance and tunnel measurements with urea fertilizer provided that there was no rainfall and that wind speed in the tunnel was adjusted to wind speed outside the tunnel at a height of 0.25 m. A lengthy NH_3 loss was also observed by Pain *et al.* (1990) where the tunnels were only moved to an adjacent area of the plots if more than 2 mm of rain fell within a 24 h period.

Secondly, the rate of of slurry application in most wind tunnel experiments was 2 to 3 times higher than in the mass balance experiments. This difference may have also created a more favourable environment for a prolonged volatilization.

Whatever the cause of the differences between techniques may be it seems wise to move tunnels at least twice a day to adjacent spots with the same treatment and to adjust windspeed in the tunnel to local conditions.

Changes in slurry pH
In the mass balance experiments 12 and 13, where the slurry was acidified shortly before application (Figure 4), a rapid increase immediately after application of up to 1.2 pH units was observed, especially for the higher pH values. This was caused by faster volatilization of CO_2 than of NH_3 (calculated with help of a chemical equilibria model; Keizer & Van Riemsdijk, 1994), probably enhanced by the fact that the freshly prepared acidified slurry had not reached a chemical equilibrium and much carbonate remained. Similar rapid pH increases due to a faster volatilization of CO_2 than of NH_3 were observed in aeration experiments performed by Husted *et al.* (1991) with HCl treated slurry. The initial pH values of experiments 12 and 13 and probably also of experiment 11, used in the regression analysis (Equation 4 & 5) were underestimated in contrast to the initial pH at lower values (Figure 5). Consequently this results in a different behaviour of the heavy clay soil in Equations 4 & 5, since all the freshly prepared acidified slurry with high pH values was applied on this soil type. On the peat soil a pH increase of the applied slurry with respectively 0.5 and 1 unit after 1 and 4 days may have caused the different behaviour in Equations 4 & 5 according to statistical analysis. This suggests some denitrification. However no pH or denitrification measurement data were available to confirm this.

In addition it is possible that NH_3 loss from acidified slurry at low application rates ($7-17 \ m^3 \ ha^{-1}$) to grassland, is independent of soil type, since it was observed that the slurry made almost no direct contact with the soil surface in dense grass swards. Equations 4 & 5, without the peat and heavy clay terms, may then be applied for all grassland soil types if the slurry is stable and almost free of carbonate, due to acidification.

In experiments 12 & 13 the rapid initial increase in pH is followed by a decrease during the next hours, due to NH_3 loss (Figure 2B). Thereafter a slow increase in pH is observed, followed by a sharp decrease after day 3. This increase in pH may be due to denitrification. Experiments conducted by Velthof & Oenema (1993) with acidified cattle slurry of pH 4.5 and 6.0, surface applied to grassland, gave N_2O-N losses of < 0.1 and 1.4% of applied nitrate. Taking into account that N_2O losses may be accompanied by substantial N_2 losses, then the pH increase of acidified slurry after the first hours (Figure 4) may result from denitrification. For pH values below 5.0 denitrification is probably lower, the more because N efficiency trials with acidified slurry of pH 4.5 (Schils; personal communication) showed an N recovery of applied mineral N which was similar to that of calcium-ammonium-nitrate fertilizer.

Treated slurry (Figure 5) in the tunnel experiments showed a slow uniform pH increase. This may be due to denitrification and or pH buffering by the soil.

Target slurry pH for various conditions

Because of the possible environmental impact of NH_3 losses, legislative targets have been formulated for the reduction of NH_3 losses from livestock, especially from manure application. In the Netherlands the target is 80% reduction by the year 2000. This target can be met by slurry acidification as follows.

The measured mean total loss in the mass balance experiments of untreated slurry was 61%. A loss of 12% is thus sufficient to meet the target reduction of 80%. By rearranging Equation 6 for the sandy and clay soil, the required pH can be estimated from Equation 7 as a function of initial NH_4^+ concentration, average T, $cumE_p4$ and maximum NH_3 loss (12%):

$$pH = \log(12) - \log((3.61 + 1.58 \times cumE_p4)*[NH_4^+]) - 11.117 + 4507.053/(T + 273.15) \tag{7}$$

As discussed it is likely that there is no difference between the four grassland soil types in NH_3 volatilization. Therefore Equation 7 is also used for peat and heavy clay soil. The pH needed to obtain the reduction target of 80% on grassland then ranges from 6.0 for an average temperature of 5 °C and $cumE_p4$ of 4 mm, whereas it has to be 4.5 for an average temperature of 20 °C and $cumE_p4$ of 16 mm (Figure 6).

Conclusion

Acidification of cattle slurry gave a marked reduction in NH_3 losses from surface applied slurry, irrespective of the method employed to measure NH_3 volatilization.

Key factors in determining the NH_3 loss rate are T, pH and potential evaporation.
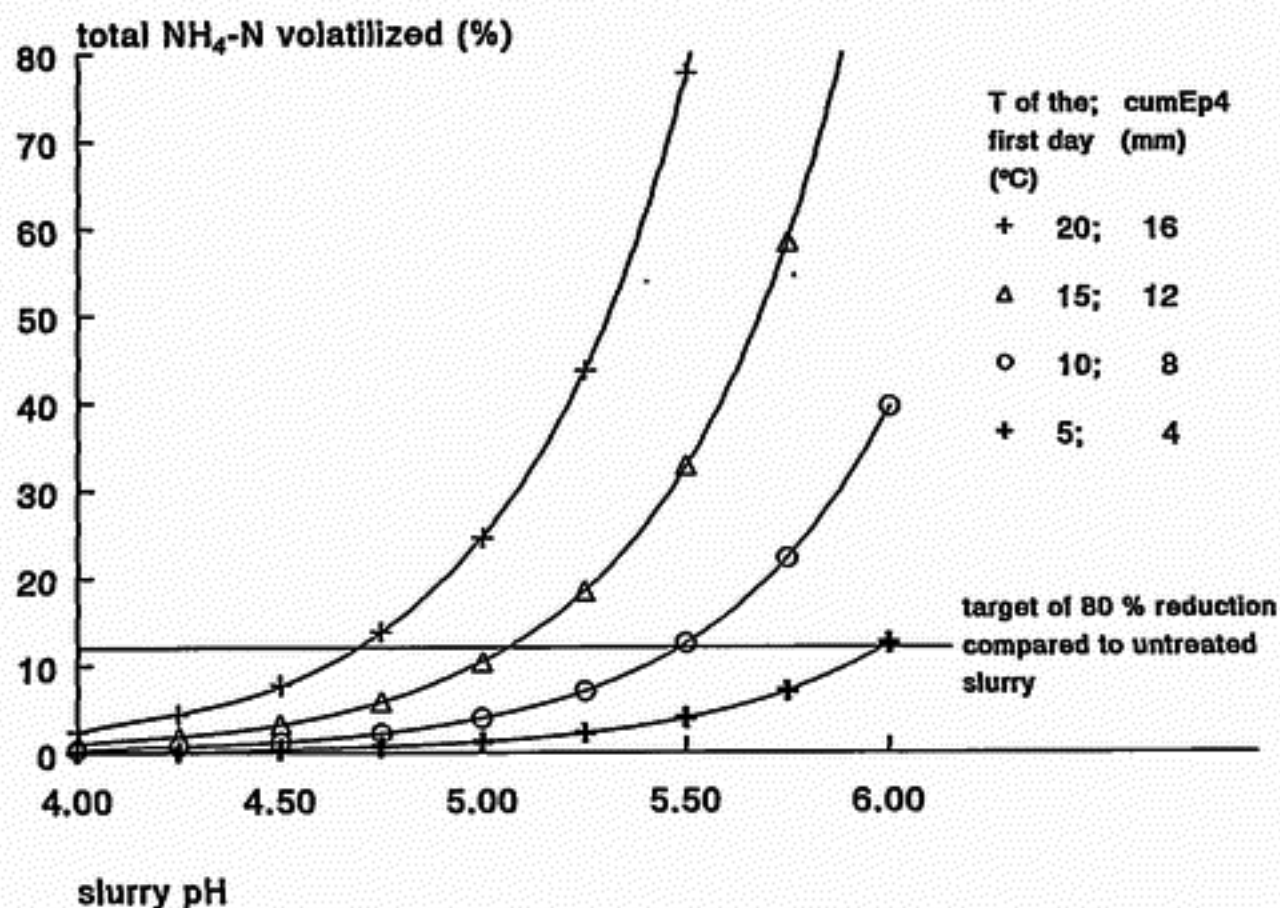
Figure 6. Expected rate of loss in total NH_3 for different pH, cumulative evaporations and temperature values according to Equation 5 for an initial NH_4^+ concentration of 0.157 M, assuming that peat and heavy clay soil do not differ from sand and clay soil.

To obtain a low volatilization by acidification all the carbonate should be removed from the slurry (via CO_2). It was hypothesized that the pH required to obtain a certain reduction in NH_3 loss was independent of the grassland soil type at the application levels used in the experiments, because of the limited contact of slurry with the soil. At low temperatures and water evaporation a pH of about 6.0 is needed to achieve a reduction in NH_3 loss of 80% of that of untreated slurry. At high temperatures and water evaporation this is approximately 4.5.

The measured rise in pH in the experiments with acidified slurry after the initial hours after application, is probably caused by denitrification of slurry with a pH between 5.0 and 6.0.

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