



Gaseous nitrogen losses and ammonia volatilization measurement following land application of cattle slurry in the mid-Atlantic region of the USA

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Abstract

To provide locally-determined field data for extension and environmental management purposes, gaseous N losses were measured following cattle slurry application to an arable silty-loam soil in the mid-Atlantic region of the USA. The field had been cropped to no-till maize. NH_3 volatilization was measured with the micro-meteorological, integrated horizontal flux (IHF) method, and denitrification with a core incubation method using acetylene inhibition. An early-winter surface application (5 December 1996; $88 \text{ m}^3 \text{ ha}^{-1}$ supplying $91 \text{ kg NH}_4^+-\text{N ha}^{-1}$) was either unincorporated or immediately incorporated. NH_3 volatilization was measured from the unincorporated application, and denitrification from both slurry treatments and appropriate control soils. Total NH_3 loss from the unincorporated slurry application was 19% of applied NH_4^+-N ; temperatures were cool ($4\text{--}6^\circ\text{C}$), and 25 mm of rain fell within 24 h of application. For 3 months, enhanced denitrification occurred from the two slurry treatments, with generally higher rates from the incorporated slurry. Total net denitrification loss from the surface-applied and incorporated slurry treatments was, respectively, 11 and 17% of applied NH_4^+-N . Denitrification loss over the winter/early-spring period was appreciable but not substantial, even where NH_3 volatilization was restricted by immediate incorporation. From the spring application (30 April 1997, $39 \text{ m}^3 \text{ ha}^{-1}$ supplying $51 \text{ kg NH}_4^+-\text{N ha}^{-1}$), total NH_3 loss was 71% of applied NH_4^+-N . These NH_3 volatilization loss data and the similarity of climate suggest that NH_3 loss factors from recent NW European work are likely to be generally applicable in the mid-Atlantic region. NH_3 volatilization from the spring application was also measured using the Z-instrument (Z_{INST}) approach, and with a system of small wind tunnels. A comparative assessment of the three methods is reported.

Introduction

In the mid-Atlantic region of the USA (states of Delaware, Maryland, Pennsylvania, Virginia), dairy cattle are generally housed for at least six months each year. Nutrient budgets for dairy farms in the region show that large amounts of N are contained in collected manure (Bacon et al., 1990; Meisinger and Thompson, 1996), much of which is handled as a semi-liquid slurry. Until recently, common criteria for

land application of manures in the mid-Atlantic region were soil traffic bearing ability and manure storage capacity. To reduce nutrient loading of the Chesapeake Bay, livestock farmers are currently either being obligated or strongly encouraged to improve manure management practices, for which farm nutrient management plans are essential.

To accurately account for manure N in farm nutrient budgets, pertinent N loss data are required. Unlike NW Europe, where considerable work has been conducted since the mid-1980s (see Jarvis and Pain, 1990; 1997; Nielsen et al., 1991), there are very few directly

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measured data of gaseous N losses following applications of livestock slurries for this and other US regions (Thompson et al., 1997). Because of the considerable climatic variation between seasons and between regions, and differing management practices in the USA, locally determined gaseous N loss data are required for the development of accurate extension and environmental management advice (Thompson et al., 1997).

The recent NW European studies showed that large and variable losses by ammonia (NH_3) volatilization occur following surface application of cattle slurry (Jarvis and Pain, 1990; Pain and Thompson, 1988; van der Molen et al., 1990). Immediate incorporation after surface application can substantially reduce NH_3 loss (Klarenbeek and Bruins, 1991).

Denitrification can also cause appreciable loss of slurry N, with highly variable losses reported in different studies (Pain et al., 1989a; Thompson et al., 1987 cf. Rubæk et al., 1996; Schwarz et al., 1994). The largest accumulated losses have been observed over the winter/early-spring period, following late-autumn/early-winter applications in temperate humid climates with relatively mild winters (Myrold et al., 1992; Pain et al., 1989a; Thompson et al., 1987; Thompson, 1989; van den Abbeel et al., 1990). Management practices that considerably reduce NH_3 loss can appreciably increase denitrification loss (Pain et al., 1989a; Thompson et al., 1987).

The three most-commonly used field methods for direct measurement of NH_3 volatilization are: (i) the micro-meteorological (MM), integrated flux method (IHF) described by Denmead (1983), (ii) the MM, Z-instrument (Z_{INST}) method of Wilson et al. (1982), and (iii) the small wind tunnel (WT) system of Lockyer (1984), which are also referred to as dynamic chamber systems. The IHF method is considered to be the most accurate (Denmead, 1983; Wilson and Shum, 1992), but requires considerable equipment and analytical support. The Z_{INST} method requires much less equipment and analytical support, but makes more assumptions about profile shape (Denmead, 1983; Wilson et al., 1982, 1983). The large uniform field sites required by the IHF and Z_{INST} methods commonly preclude replication and treatment comparison. The small wind tunnel system of Lockyer (1984) uses small surface areas enabling replication and treatment comparison; however, in routine experimental work it is commonly used with a fixed air velocity (e.g. Moal et al., 1995; Pain et al., 1989a; Sommer and Olesen, 1991; Thompson et al., 1990a, b; Thompson and Mei-

singer, 2002). There are very few data quantitatively evaluating the use of the WT system, operated at fixed air velocity, against the IHF method to measure ammonia volatilization following land application of cattle slurry.

Quantitative N loss data, for cattle slurry applications, are required for the mid-Atlantic region to assess: (i) the magnitude and characteristics of NH_3 volatilization, and (ii) whether the relatively mild winters are associated with appreciable denitrification loss from late-autumn/early-winter applications, particularly where NH_3 volatilization loss is restricted.

Field studies were conducted to directly measure gaseous N losses following cattle slurry applications to an arable soil. Following an early-winter application, NH_3 volatilization and denitrification were measured from soil where slurry was surface-applied, and denitrification in soil where slurry was immediately incorporated following surface application. Ammonia volatilization was measured with the IHF method. Following a mid-spring application, NH_3 volatilization was measured using the IHF, Z_{INST} , and WT methods to compare results from the three methods.

Materials and methods

Field site

The field studies were conducted at the United States Department of Agriculture, Agricultural Research Service (USDA-ARS), Beltsville Agricultural Research Centre (BARC), in Beltsville, Maryland, USA. The soil at the site is classified as a moderately well-drained, Codorus silt loam (fine-loamy, mixed, active mesic, Typic Fluvaquent Dystrudepts). Some relevant soil properties (0–10 cm) are pH: 6.0 (1:1 in water), sand: 35%, clay: 20%, silt: 45%, total C: 11.1 g kg⁻¹, total N: 0.93 g kg⁻¹, CEC: 14.5 cmol kg⁻¹, and bulk density of 1.35 g cm⁻³. Soil water content at field capacity is 299 g kg⁻¹. During the experimental period, the surface soil was not waterlogged. All fields used had been cropped to no-till maize (*Zea mays* L.) during the previous (1996) cropping season.

For the winter application, two fields, 100 m apart were used. At the time of application, the maize residue provided a ground cover of 100%, and amounted to approximately 10 t dry matter ha⁻¹. On one field, a 40 m dia. circular plot of slurry was used for IHF measurement; on the other, which was adjacent

to the circular plot with respect to prevailing wind direction a 15 by 5 m rectangular plot was used for an incorporated slurry application.

For the spring application, the same circular plot was used as in the winter application. An additional plot, 150 m adjacent to the circular plot with respect to prevailing wind direction, was used for the wind tunnel measurements. At the time of the spring application, the maize residue provided a ground cover of 88%, and amounted to approximately 9 t dry matter ha⁻¹.

Slurry applications

The cattle slurry was collected, during the 24 h period prior to each application from housed dairy cattle at BARC. The cattle were fed a diet based on maize silage; small amounts of sawdust from bedding material were contained in the slurry.

Slurry was applied with a tractor-pulled, Houle EL 54-3600 tanker (Houle Co., Drummondville, QC, Canada) with a low trajectory spreading bar (40 cm above ground) using three equidistant nozzles. Slurry was applied in 4.6 m wide bands. The rate of slurry application was determined by weighing the slurry tanker before and after application.

The 40 m dia. circular plot was formed from nine adjacent 4.6 m wide bands. The three central bands were 40 m long; the lengths of the three other bands on either side of the circle were 36, 28, and 26 m. There was a 0.7 m overlap between the two outer bands on each side. Slurry application took approximately 30 min. The middle bands were applied first, so that the sample and anemometer masts could be positioned in the centre of the circular plot, enabling measurements to commence immediately after slurry application was completed.

Winter application

The slurry contained: 75 g kg⁻¹ dry matter, 3.0 g kg⁻¹ total N, and 1.0 g kg⁻¹ NH₄⁺-N. Slurry was applied on 5 December 1996 at a rate of 88 m³ ha⁻¹, which supplied 91 kg NH₄⁺-N ha⁻¹ and 272 kg total N ha⁻¹.

Slurry application to the 40 m dia. circular plot was completed at 1030 h, and NH₃ volatilization measurements began immediately. Slurry was then surface-applied to the 15 m by 5 m rectangular plot, which was then immediately incorporated using a rotovator to a depth of 10 cm.

Control soils for both slurry treatments were designated for denitrification measurement. For the surface

application, it was the untreated area surrounding the circular plot, hereafter termed the 'control soil'. For the incorporated slurry treatment, it was two 5 by 5 m areas at both ends of the rectangular plot, which were rotovated but did not receive slurry, hereafter termed the 'incorporated control soil'.

Spring application

Relevant characteristics of the slurry used were, dry matter content: 87 g kg⁻¹, total N: 3.6 g N L⁻¹, NH₄⁺-N: 1.3 g N L⁻¹ and pH: 7.0. Slurry was applied on 30 April 1997. Slurry was applied to the 40 m dia. circular plot at a rate of 39 m³ ha⁻¹, which supplied 51 kg NH₄⁺-N ha⁻¹ and 137 kg total N ha⁻¹. NH₃ volatilization measurements (IHF and Z_{INST} methods) commenced at 1030 h. The intended rate of slurry application for the circular plot was 80 m³ ha⁻¹; however, an error was made with the application rate from the slurry tanker.

For the wind tunnel measurements, 8 L of slurry was applied, using hand-held watering cans, to each of two 2.0 m by 0.5 m plots, at an application rate equivalent to 80 m³ ha⁻¹ which supplied 106 kg NH₄⁺-N ha⁻¹ and 286 kg total N ha⁻¹. Wind tunnel measurements commenced at 1050 h.

Ammonia volatilization measurement

Integrated-horizontal flux method

The principles of the IHF method are described by Denmead (1983). The basis of the methodology and method of calculation used were as described by Ryden and McNeil (1984).

The MM system consisted of three masts, two to support acid traps to sample atmospheric NH₃, and one with anemometers and a wind vane. A mast with acid traps, the 'treatment mast', was placed in the centre of a 40 m dia. circular plot. The mast with anemometers, the 'anemometer mast' was placed close to the treatment mast, within the circular plot. The other mast with acid traps, the 'background mast', was placed approximately 100 m upwind from the windward edge of the circular plot, to sample the background NH₃ concentration of air entering the treated area.

The treatment and background masts each consisted of a 3 m tall, 19 mm outer diam. metal alloy tube, held upright by sliding it over a 12.7 mm diam. iron rod, which had been driven vertically into the ground. The acid traps were held in place with laboratory clamps, with the inlets at the selected heights.

The anemometer mast consisted of a 3 m tall, 5.1 cm outer diam. metal alloy tube supporting 1.0 m long, 3.8 cm diam. aluminium tubes held horizontally in place at selected heights using scaffolding clamps (Nu-Rail, Cincinnati, OH, USA). The anemometers were positioned at the ends of the horizontal tubes. The anemometer cups were positioned at the same heights as the inlets of the acid traps on the measurement mast. Three metal cables were attached to the top of each mast and held taut with tent pegs.

For the winter application, the heights of the inlets of the acid traps on the treatment mast, and of the anemometer cups on the anemometer mast, were: 20, 40, 90, 140, 200, and 300 cm above the soil surface, while the inlets of the acid traps on the background mast were positioned at heights of 40, 90, 200, and 300 cm. For the spring application, the heights of the inlets of the acid traps on both the treatment and background masts, and of the anemometer cups, were: 25, 55, 90, 140, 200, and 300 cm.

The acid traps were 125 mL pyrex gas washing bottles containing 80 mL of 0.002 M phosphoric acid (H_3PO_4). Air was drawn through the acid solution by glass gas dispersion tubes. Each acid trap was connected by polyethylene tubing to a small pump and flow meter which controlled air flow at 5 L m^{-1} .

The cup anemometers used were Climatronic F460 anemometers (Climatronic Corp., Bohemia, NY, USA) for the lower two heights, which required more sensitive measurement, and Met One Model 010C anemometers (Met One Instruments, Grant Pass, OR, USA) for the upper four heights. A Met One 024A wind direction sensor was placed on a horizontal bar at a height of 3 m. All wind speed and direction data were recorded on a Campbell 21X data logger (Campbell Scientific, Logan, UT, USA).

After the prescribed exposure, the H_3PO_4 solutions were made up to known volume, and stored at 3°C prior to analysis for NH_4^+ -N with a flow injection analyser system (Lachat Instruments, Milwaukee, WI, USA), using the salicylate modification of the Bertholet method (Mulvaney, 1996).

For the winter application, the acid traps were changed after 4, 6, and 12 h on the first day, and thereafter 2–3 times per day. Measurements were made for 6 days. For the spring application, the acid traps were changed after 3, 6, and 12 h on the first day and thereafter 2–3 times per day. Measurements were made for 8 days.

All NH_3 volatilization data are expressed in units of total loss as kg N ha^{-1} , or rate of loss as kg

$\text{N ha}^{-1} \text{ h}^{-1}$ or $\text{g N ha}^{-1} \text{ h}^{-1}$. When presented graphically, NH_3 volatilization data are presented in the mid-point of the sampling interval.

Z_{INST} method

The Z_{INST} method estimates NH_3 flux using atmospheric NH_3 concentration and wind speed for a single height, and the surface roughness (Z_0) (Wilson et al., 1982, 1983). Using the procedure of Wilson et al. (1982), surface roughness was estimated to be 0.5 cm. The corresponding Z_{INST} height for the measurement of atmospheric NH_3 concentration and wind speed, for a 40 m dia. circular plot, was 90 cm (Wilson et al., 1982). Two acid traps were located at this height; mean values were used to calculate the NH_3 flux using the Z_{INST} method.

Measurements with the Z_{INST} approach were made for 12 days. The sampling intervals were the same as for the IHF method, except for the additional 4 days when the acid traps were changed once every 24 h.

Wind tunnel system

The system of small wind tunnels is described in detail by Thompson and Meisinger (2002). It was based on the system originally described by Lockyer (1984). Each wind tunnel unit consists of: (i) a transparent, inverted U-shaped, canopy covering an 1 m^2 ($2.0 \times 0.5 \text{ m}$) treated area of soil, and (ii) a 40 cm internal dia., circular steel duct containing an electrically-powered fan blade to draw air through the canopy. In the current study, two tunnel units were used, and air velocity was set at 1.0 m s^{-1} .

The NH_3 concentration of air entering and leaving each canopy was sampled with separate gas washing bottles, containing 0.002 M H_3PO_4 , each connected to a small pump and a flow meter (Thompson and Meisinger, 2002). Chemical analysis and the expression of results were as previously described for the IHF method.

Measurements commenced within 5 min of slurry application. The tunnel canopies remained in place throughout the study. Measurements were made for 5 days. The acid traps were changed after 3, 6, 12, and 24 h, and thereafter 2–3 times per day.

Denitrification measurements

Denitrification was measured with a core incubation system, using acetylene (C_2H_2) inhibition, very similar to that described by Ryden et al. (1987). The principles of this method and practical considerations are described in Mosier and Klemetsson (1994).

Minimally disturbed soil cores (4.1 cm diam., 15 cm length) were collected by hammering a steel soil-core sampler into the soil surface. Cores were collected inside plastic sleeves (4.1 cm internal diam., 15 cm length, 0.2 cm wall thickness) placed inside the soil sampler. Four parallel, equidistant slots (0.3 cm wide, 10 cm long) in the sleeve walls promoted gas exchange.

For each denitrification measurement from each of the four treatments, nine cores were collected from nine randomly selected locations in the corresponding treatment area. Three of these cores were placed in each of three 1920 mL volume glass fruit preserving jars. After placing the cores inside, the jars were sealed with a rubber gasket, a metal lid with two septum stoppers, and a screw band. Fifty cm³ of C₂H₂ was injected into each jar to give a C₂H₂ concentration of approximately 0.04 L L⁻¹. After twice 'pump-mixing' with a 60 mL syringe, the jars were vented to atmospheric pressure. The jars were incubated in the ground at the field site, in individual holes of slightly larger size; with a sheet of aluminium foil and foam insulation placed over the jars to prevent warming.

After 24 h, duplicate 4 mL gas samples were taken, at the field incubation site, using polypropylene syringes. The gas samples were taken from the headspace, above the soil cores, in each jar. Before removing gas samples, the gas contents of each jar were 'pump-mixed' twice using a 60 mL syringe. The gas samples were immediately transferred to 11 mL glass vials sealed with grey butyl rubber septa, which contained pure helium gas at atmospheric pressure. After introducing the gas samples, the septa were then immediately sealed with silicone sealing compound.

The gas samples were analysed for nitrous oxide (N₂O), within 24 h of collection, on a Shimadzu GC-8 gas chromatograph (Shimadzu America, Columbia, MD, USA) fitted with a ⁶³Ni electron capture detector (ECD). The methodology for the analysis N₂O in gas samples was very similar to that described by Mosier and Mack (1980). The measured N₂O concentration was adjusted for dilution by helium in the vial. The increased concentration of N₂O, in the air space, of each jar (above the ambient concentration) was related to the surface area of the three cores to calculate the flux of denitrification. Allowance was made for additional N₂O dissolved in soil water according to the procedure described by Tiedje et al. (1982).

Denitrification measurements were made during the period 12 December 1996 to 27 March 1997. Measurements were normally made on a weekly basis.

Bi-weekly measurements were made when the following dates of the weekly schedule were not sampled: 26 December 1996, and 16 January (frozen soil), 27 February, and 21 March 1997. Total denitrification loss for each treatment was estimated calculating the area beneath the daily flux curve. To facilitate this estimation, it was assumed (i) that the denitrification flux for 5 December 1996 was 37 g N ha⁻¹ d⁻¹ (the average flux from control plots during the measurement period) and (ii) that on 16 January 1997 when the soil was frozen there was no denitrification. The net loss for each slurry treatment was calculated by subtracting the total loss of the corresponding control treatment from the total loss of the slurry treatment.

Measurement of soil moisture and soil inorganic N

After removing gas samples, the soil in each jar was mixed. Gravimetric soil moisture was determined by drying at 105 °C for 48 h. Soil water-filled pore space (WFPS) was calculated as the average for all soil cores taken at an individual soil sampling date, assuming a bulk density of 1.35 g cm⁻³. Ammonium (NH₄⁺) and nitrate (NO₃⁻) were determined on filtered extracts (40 g of moist soil, 200 mL 2 M KCl), using a flow injection analyser system (Lachat Instruments, Milwaukee, WI, USA). Ammonium was determined using the salicylate modification of the Berthelot method (Mulvaney, 1996), and NO₃⁻ by the Griess-Ilosvay reaction following cadmium reduction (Mulvaney, 1996).

Measurement of environmental parameters

Data on rainfall (RF), soil temperature (7.5 cm depth), air temperature, and atmospheric relative humidity (RH) were collected throughout the studies. Rainfall was measured with a tipping bucket rain gauge (Model CS700-L, Campbell Scientific Inc. (CSI), Logan, Utah, USA), soil temperature with a thermistor (model 107B, CSI, Logan Utah, USA), and air temperature and atmospheric RH with a psychrometer model (CS500, CSI, Logan, Utah, USA). Soil and air temperature, and atmospheric RH were recorded at 15-min intervals, and RF at a one hourly interval. All data were recorded on a Campbell 21X data logger.

Environmental data presented with respect to NH₃ volatilization are average values for the corresponding time interval. Soil temperature and RF data presented with respect to denitrification are 24 h average temperature data, and 24 h total RF data.

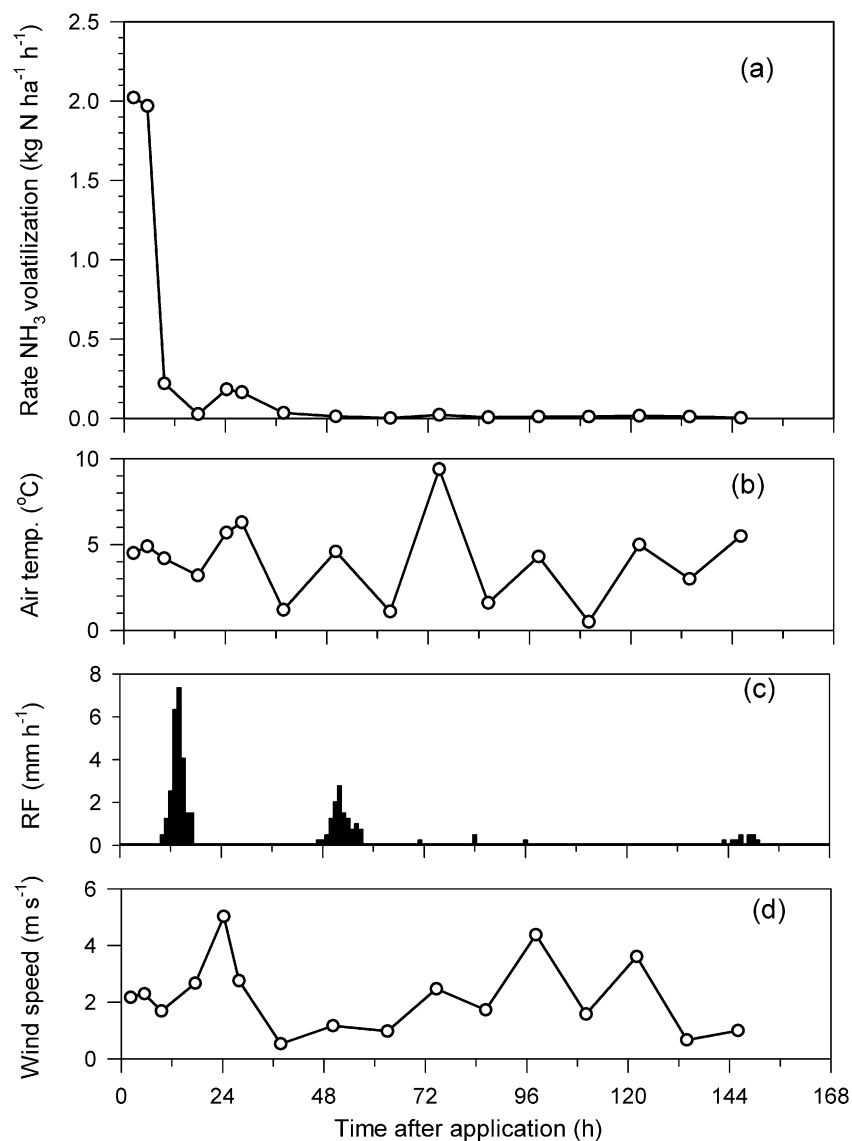


Figure 1. (a) Rate of NH₃ volatilization following application of cattle slurry (88 m³ ha⁻¹) to arable soil on 5 December 1996, and corresponding (b) air temperature, (c) hourly rainfall (RF), and (d) wind speed (height 1.4 m) data. Except for RF, data are averaged for each measurement interval, and are presented at the interval mid-point.

Statistical analysis

Uncertainty estimates were used to estimate data variability from the micro-meteorological measurements of NH₃ volatilization. Values of ± 10 –20% of the observed value were assigned as suggested by Denmead et al. (1977), Denmead (1983), Ryden and McNeil (1984), and Wilson and Shum (1992).

Uncertainty estimates were also used with the denitrification data, which were sub-sample measurements from large plots. These uncertainty estimates

were estimated from the between jar variation among the three incubation jars used for each measurement. Individual measurement estimates of variability (2 d.f.) were pooled for the 3.5-month measurement period giving an overall pooled uncertainty estimate for each treatment (22 d.f.). The variation among incubation jars is likely to have captured a large part of the total denitrification variability, because of the high degree of local spatial variability associated with denitrification (Parkin, 1987; Parkin et al., 1988).

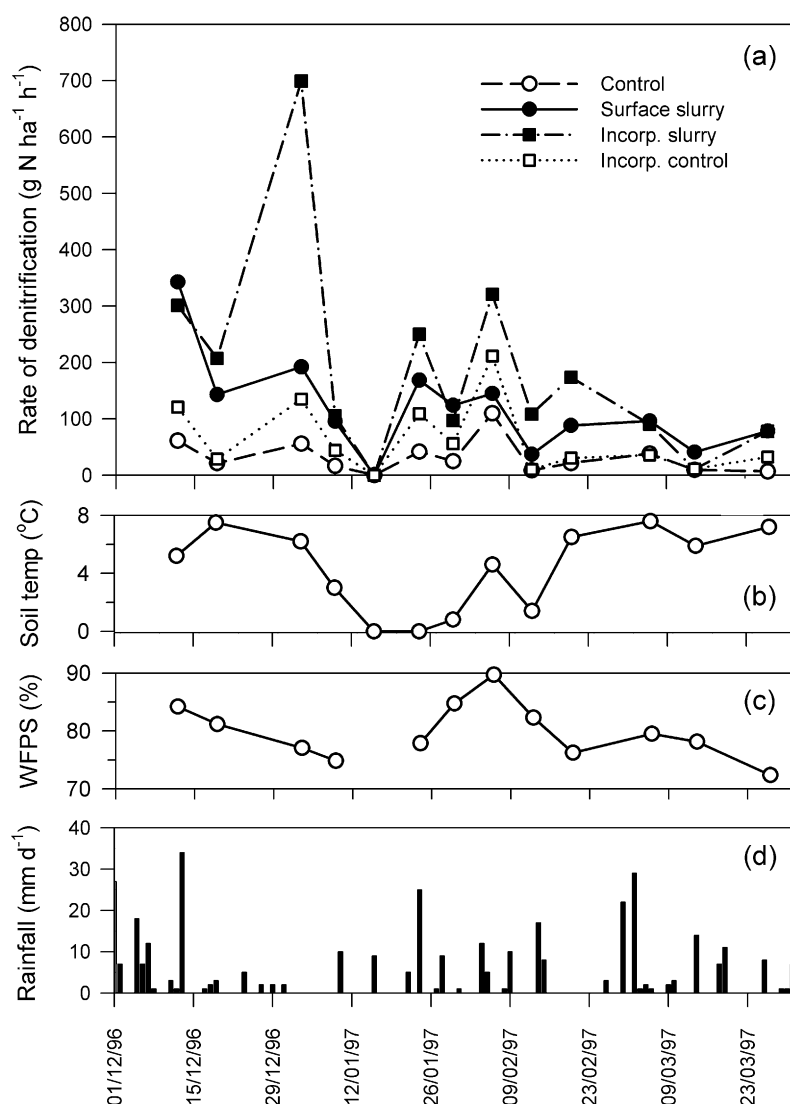


Figure 2. (a) Rates of denitrification in soil after surface application of cattle slurry, in soil with surface slurry application followed by immediate incorporation, in untilled control soil, and in tilled control soil. The corresponding uncertainty estimates are ± 33 , ± 93 , ± 22 , and $\pm 32 \text{ g N ha}^{-1} \text{ d}^{-1}$. Also presented are: (b) average soil temperature at 7.5 cm depth, and (c) average soil water-filled pore space, both for the corresponding sampling periods, and (d) daily rainfall amounts.

Conventional correlation analyses (Snedecor and Cochran, 1980) were conducted between denitrification rates and soil and climatic properties. A stepwise (step-up) regression analysis (Snedecor and Cochran, 1980; Statistical Analysis System, 1988) was used to assess which combination of these parameters was most strongly associated with the denitrification rate for each treatment. A parameter was included in the regression model at the significance level for entry ($P \leq 0.15$), and was retained if it then met the significance level for staying in the model ($P \leq 0.10$).

Results

Winter application

Ammonia volatilization

The average rate of NH_3 volatilization in the 6 h immediately after application was approximately $2.0 \text{ kg N ha}^{-1} \text{ h}^{-1}$ (Figure 1a). During the following 6 h, the average rate declined substantially to $220 \text{ g N ha}^{-1} \text{ h}^{-1}$. During the subsequent overnight period (2230 to 1030 h), the average rate was $28 \text{ g N ha}^{-1} \text{ h}^{-1}$. A small diurnal increase to

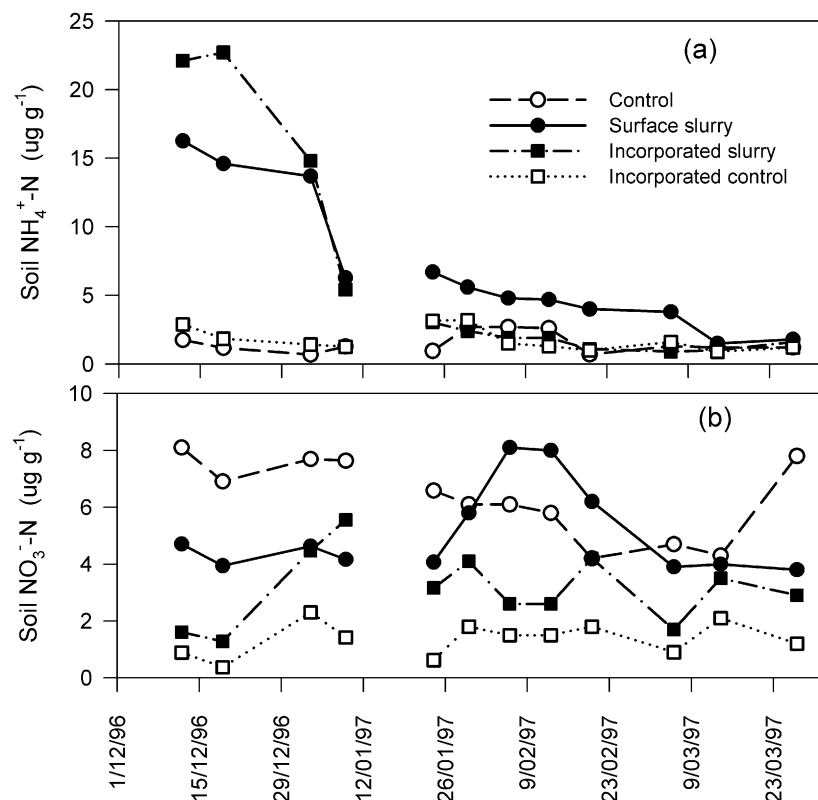


Figure 3. (a) Soil ammonium-N and (b) soil nitrate-N contents the 0–15 cm depth of soil following surface application of cattle slurry, surface application of slurry followed by immediate incorporation, in untilled control soil, and in tilled control soil. The sampling times correspond to the periods in which individual denitrification measurements were made.

$177 \text{ g N ha}^{-1} \text{ h}^{-1}$ occurred during the next day; thereafter, the rate of NH_3 loss remained $< 35 \text{ g N ha}^{-1} \text{ h}^{-1}$ for the remainder of the study. The total 6-day NH_3 volatilization loss was 17 kg N ha^{-1} , which represented 19% of applied slurry $\text{NH}_4^+\text{-N}$. Seventy-seven percent of the total loss occurred within the first 6 h after application, and 91% within the first 24 h.

On the night following slurry application, 25 mm of rain fell between 1800 and 0200 h, i.e. between 7.5 and 15 h after application (Figure 1c). After an additional 12 mm of rain between 0800 and 1800 h on the second day after application (7 December), no further diurnal variation was observed (Figure 1a). During the first 12 h after application, when most of the NH_3 loss occurred, air temperature was $4\text{--}6^\circ\text{C}$ (Figure 1b).

Denitrification

Enhanced denitrification relative to the corresponding control treatments was observed from the two slurry treatments until 6 March 1997 (Figure 2a). Denitrification rates from the two slurry treatments fluctuated considerably and in a similar manner over time. Gen-

erally higher rates were determined from the incorporated slurry treatment. Denitrification rates from the two control treatments exhibited similar fluctuations with time but at much smaller rates.

Rates of denitrification from the surface-applied slurry treatment, until 6 March 1997, were generally $90\text{--}200 \text{ g N ha}^{-1} \text{ d}^{-1}$ (Figure 2a). The average rate from the control treatment, during this period was $37 \text{ g N ha}^{-1} \text{ d}^{-1}$. The highest rate for the surface-applied treatment was $340 \text{ g N ha}^{-1} \text{ d}^{-1}$ on 12 December 1996. These peak denitrification rates could not be visually related to soil moisture (Figure 2c) or soil temperature (Figure 2b). On 14 March 1997, rates from both slurry treatments declined to $< 40 \text{ g N ha}^{-1} \text{ d}^{-1}$.

Denitrification flux from the incorporated slurry treatment, until 6 March 1997, was generally $90\text{--}320 \text{ g N ha}^{-1} \text{ d}^{-1}$ (Figure 2a). The average rate from the incorporated-only treatment, without slurry addition, during this period was $73 \text{ g N ha}^{-1} \text{ d}^{-1}$. The highest rates from the incorporated slurry of 700

Table 1. Total denitrification loss determined from surface-applied slurry, incorporated slurry, control and incorporated-only treatments. Net loss from the slurry treatments is the total loss minus the total loss from the appropriate control treatment

Treatment	Total denitrification loss (kg N ha ⁻¹)	Net denitrification loss (kg N ha ⁻¹)	Net denitrification loss as percent of applied NH ₄ ⁺ -N (%)
Surface-applied slurry	13.4	9.9	10.9
Incorporated slurry	22.0	15.1	16.6
Control	3.5	n.a.	n.a.
Incorporated only	6.9	n.a.	n.a.

n.a., not applicable

Table 2. Correlation coefficients ($n = 12$) for individual denitrification measurements against soil nitrate (0–15 cm), average soil temperature (7.5 cm), water-filled porosity (0–15 cm), and gravimetric water content (0–15 cm). Correlations significant at $P \leq 0.05$ when $r = 0.553$, and at $P \leq 0.10$ when $r = 0.476$. Correlations significant at $P \leq 0.05$ indicated with ***

Soil parameter	Treatments				Average of all treatments
	Surface-applied slurry	Incorporated slurry	Control	Incorporated only	
Soil nitrate N	-0.144	0.095	0.172	0.034	0.039
Soil temperature	0.013	0.100	0.011	-0.126	-0.001
Soil water-filled pore space	0.334	0.130	0.659***	0.533	0.414
Gravimetric soil water content	0.334	0.130	0.659***	0.533	0.414

and 320 g N ha⁻¹ d⁻¹ were determined on 3 January and 6 February, respectively. These peak rates corresponded to moderate soil temperatures (5–6 °C; Figure 2b), and relatively high soil nitrate contents (5–8 µg NO₃⁻-N g⁻¹; Figure 3b).

Total net denitrification loss (after subtracting total denitrification from the corresponding controls) for the incorporated and surface-applied slurry treatments was 15 and 10 kg N ha⁻¹, respectively, over the period 5 December 1996 to 27 March 1997 (Table 1). From the incorporated and unincorporated slurry applications, these losses represented, respectively, 17% and 11% of the applied slurry NH₄⁺-N. From 5 December 1996 to 27 March 1997, average daily soil temperatures during the 24 h incubation periods were < 8 °C (Figure 2b). Soil water-filled pore-space (WFPS) during this period was ≥ 70% (Figure 2c).

For individual treatments, there were no significant correlations ($P \leq 0.05$) between denitrification rate and the selected soil parameters for either of the two slurry treatments (Table 2). The only significant correlation was between denitrification rate and the two soil moisture parameters for the control treatment.

The stepwise regression analysis was unable to include more than one parameter in a statistically significant regression equation; the parameters identified as being the most influential and their levels of statistical significance were the same as for the correlation analysis. The uncertainty estimates for individual daily denitrification rate measurements were ± 93 g N ha⁻¹ d⁻¹ for the incorporated slurry, ± 33 g N ha⁻¹ d⁻¹ for the unincorporated slurry, ± 32 g N ha⁻¹ d⁻¹ for the incorporated-only soil, and ± 22 g N ha⁻¹ d⁻¹ for the control. Average coefficient of variations (CV), for triplicate incubation jars, were 47% for all measurements, and 40% for the two slurry treatments.

The rapid decline in soil NH₄⁺-N (Figure 3a) in the incorporated slurry treatment, which could not be related to an accumulation of soil NO₃⁻-N or to denitrification, suggested that appreciable immobilization of NH₄⁺-N occurred following incorporation of the no-till crop residues.

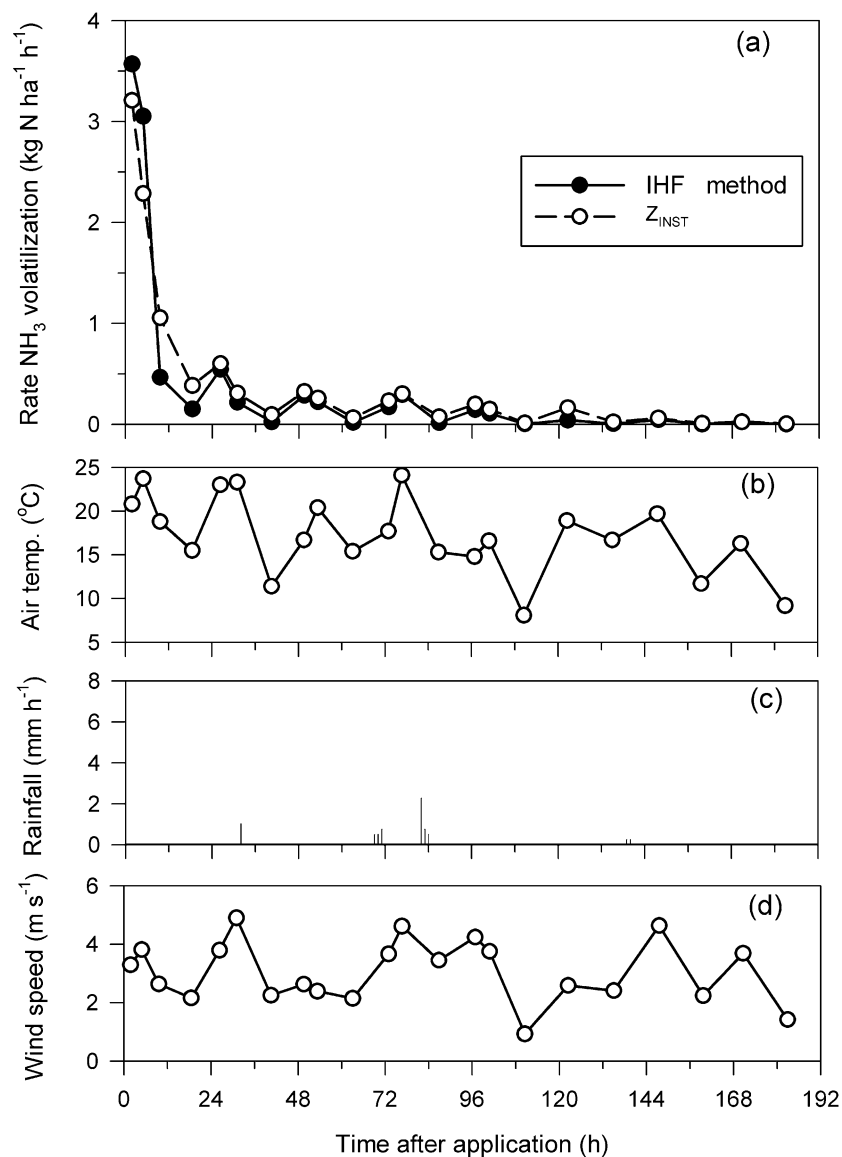


Figure 4. (a) Rate of NH_3 volatilization following application of cattle slurry ($39 \text{ m}^3 \text{ ha}^{-1}$) to arable soil on 30 April 1997, and corresponding (b) air temperature, (c) hourly rainfall (RF), and (d) wind speed (height of 1.4 m) data. Except for RF, data are averaged for each measurement interval, and are presented at the interval mid-point.

Spring application

Ammonia volatilization – IHF method

In the 6 h period following application at 1030 h on 30 April 1996, the average rate of NH_3 volatilization was $3.3 \text{ kg N ha}^{-1} \text{h}^{-1}$ (Figure 4a). Subsequently, the rate declined considerably to $466 \text{ g N ha}^{-1} \text{h}^{-1}$ for the following 6 h, then to $153 \text{ g N ha}^{-1} \text{h}^{-1}$ for the following overnight period between 2230 and 1030 h. During the following seven days, there was some diurnal vari-

ation, and night-time rates were $< 25 \text{ g N ha}^{-1} \text{h}^{-1}$. Rates of NH_3 volatilization during the day averaged 373 and $256 \text{ g N ha}^{-1} \text{h}^{-1}$ for 1 and 2 May (the first and second days following application), after which the diurnal peaks were progressively smaller. The diurnal peak on the seventh day after application (7 May) was $28 \text{ g N ha}^{-1} \text{h}^{-1}$. The following night-time rate, before measurements stopped the next day, was only $2 \text{ g N ha}^{-1} \text{h}^{-1}$.

The 8-day total loss was 36 kg N ha⁻¹ which represented 71% of applied slurry NH₄⁺-N. Fifty-eight percent of the total NH₃ loss occurred within 6 h, 67% within 12 h, and 72% within 24 h. During the 12 h period following application, air temperature was 18–24 °C (Figure 4b); during the rest of the experimental period it was 15–25 °C (Figure 4b). Small rainfalls of ≤ 3 mm each occurred on 1, 3, and 6 May (Figure 4c), but would have had little effect on NH₃ volatilization.

Ammonia volatilization – Z_{INST} method

The Z_{INST} method of calculating NH₃ volatilization gave generally similar rates to those obtained using the IHF approach (Figure 4a). The Z_{INST} method gave relatively lower NH₃ volatilization rates during 0–6 h after application when rates were high, and subsequently gave relatively higher rates, when the rates of NH₃ volatilization were low. The Z_{INST} values were appreciably higher 6–24 h after application; thereafter, the difference between the two MM methods was consistently small. Total eight-day loss using the Z_{INST} method was 45.2 kg N ha⁻¹ h⁻¹ (88% of applied slurry NH₄⁺-N), compared to 36.0 kg N ha⁻¹ (71% of applied slurry NH₄⁺-N) with the IHF method.

After 9 days, there was no discernible difference between the background and sample values for atmospheric NH₃ concentrations. Using the Z_{INST} approach, an additional 0.7 kg N ha⁻¹ was lost in the 24-hour period, between days 8 and 9.

The regression equation $y = 0.71x + 449$ ($R^2 = 0.95$), where y is the Z_{INST} rate and x is the IHF rate, described the relationship between rates measured with the two methods in the 0–24 h period ($n = 4$). The high intercept value and slope less than 1 reflected the lower Z_{INST} values for the 0–3 and 3–6 h intervals (during high-loss periods), and the higher Z_{INST} values for the 6–12 and 12–24 h intervals (during small-loss periods). After 24 h, ($n = 18$), the regression equation of $y = 1.06x + 44$ ($R^2 = 0.89$) showed good agreement.

Ammonia volatilization – wind tunnel method

Ammonia volatilization data measured with the wind tunnel system agreed qualitatively with that obtained with the IHF method (Figure 5a). Both showed a very rapid initial loss with slower losses thereafter, and similar diurnal variations for several days. However, because of the unintended difference in slurry application rates on the WT and IHF plots, only a relative comparison between these two methods is possible. Consequently, the percentage of applied slurry

NH₄⁺-N lost per hour is presented for both methods in Figure 5a. The relative rate of NH₃ volatilization measured with the IHF method was appreciably greater than measured with the WT during the first 6 h (Figure 5a). Thereafter, there was little difference between the two methods.

The large difference in relative rates of NH₃ loss between the IHF and WT measurements in the first 6 h is most likely related to air velocity. Whereas the air velocity in the WTs was fixed at 1 m s⁻¹, the average ambient wind speed (20 cm height) as measured on the MM site during the 0–6 h period was 2.8 m s⁻¹ (Figure 5b). After 6 h, the much higher wind speeds on the MM site had little effect on the relative rate of NH₃ volatilization presumably because a large percentage of the NH₃ loss had already occurred. The effect of the higher slurry application rate on the WT plots is discussed subsequently.

Discussion

Ammonia volatilization loss

The total loss of 71% of applied slurry NH₄⁺-N measured with the IHF method from the spring application indicate that, in the mid-Atlantic region of the USA, NH₃ volatilization losses following surface application of cattle slurry can account for much of the applied slurry NH₄⁺-N. The large quantity of surface crop residue, in this study, would have enhanced NH₃ loss, by reducing contact between slurry NH₄⁺-N and soil (Bless et al., 1991). Additionally, crop residues commonly have moderately alkaline pH values (e.g. McInnes et al., 1986), which could also contribute to enhancement of NH₃ volatilization. Given the favourable climatic and residue cover conditions for NH₃ volatilization, the value of 71% of applied NH₄⁺-N, can be regarded as an indication of the likely maximum spring NH₃ volatilization loss value for this region. This conclusion is consistent with data from NW Europe, where a total N loss by NH₃ volatilization of 70% is within the upper range of reported total loss values (e.g. Pain et al., 1989b; van der Molen et al., 1990; Sørensen et al., 2002). No till residue management is being increasingly used in maize production in the mid-Atlantic region of the USA.

The much smaller NH₃ loss from the winter surface application (19% of slurry NH₄⁺-N) is attributed to the combined effects of 25 mm of rain 7–15 h after application and the much lower temperatures in the

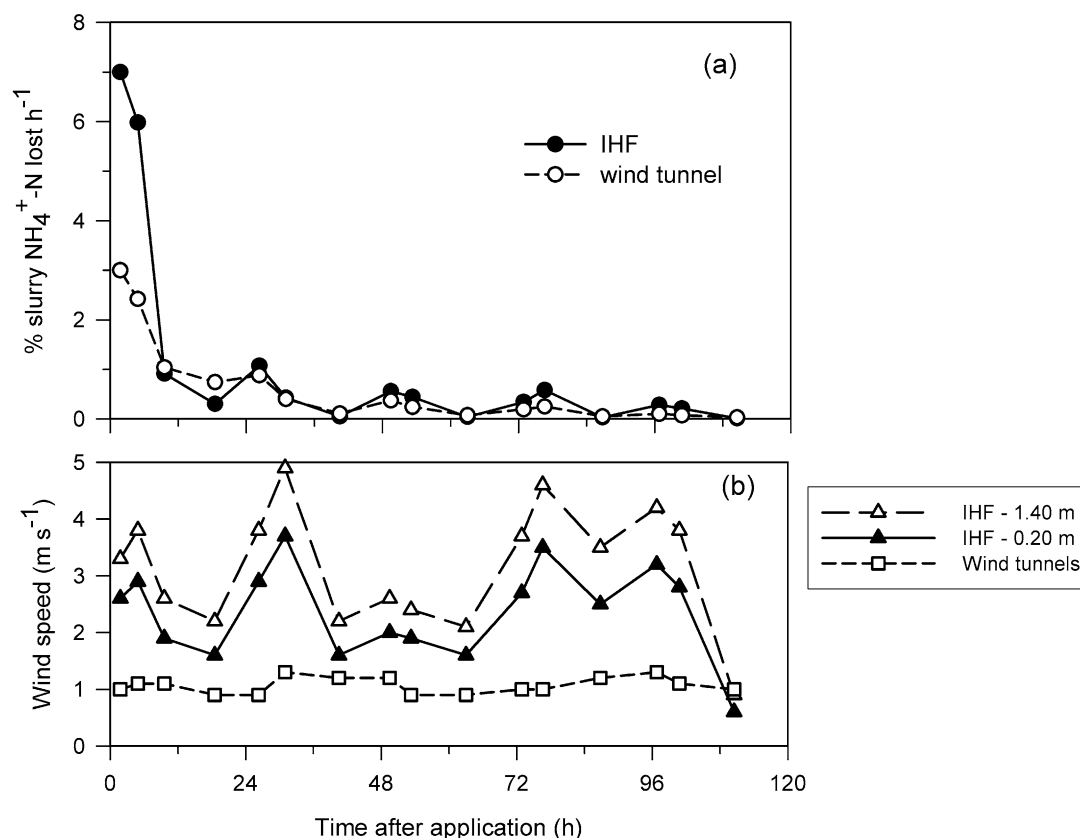


Figure 5. (a) Percent of applied NH_4^+ -N lost with time as measured with the IHF micro-meteorological and wind tunnel methods. Also presented are (b) wind speed data measured at heights of 20 and 140 cm during the micro-meteorological study, and the mean air velocities ($n = 2$) in the wind tunnels.

period after application. The heavy rainfall presumably washed slurry NH_4^+ -N into the soil enhancing contact with soil cation exchange sites. The much lower rates of NH_3 volatilization immediately after application and before the rain, compared to those from the spring application, despite a higher slurry application rate are presumably due to temperature differences. This suggests that, had there been no rain, the total NH_3 loss from the winter application would have been clearly less than from the spring application. Appreciably smaller NH_3 loss from winter compared to spring applications is also generally consistent with NW European observations (Moal et al., 1995; Sommer et al., 1991).

The NH_3 volatilization data from the present studies represent the range of total loss values that have generally been measured in recent NW European work using IHF methodology (e.g. Pain et al., 1989b; van der Molen et al., 1990). In a series of measurements with wind tunnels in the mid-Atlantic region

(Thompson and Meisinger, 2002), measured NH_3 volatilization losses were generally similar to those determined with similar methodology in NW Europe (Moal et al., 1995; Pain et al., 1989a; Sommer and Olesen, 1991; Sommer et al., 1991; Thompson et al., 1990a, b). The mid-Atlantic region of the USA and NW Europe have generally similar maritime climates, with summers being generally hotter and drier in the mid-Atlantic region (Thompson and Meisinger, 2002). The similarities in available NH_3 volatilization data and in climate suggest that, at least for the mid-autumn to mid-spring period, NH_3 loss factors, for slurry applications, derived from recent NW European data (e.g. Jarvis and Pain, 1993, 1997; Pain et al., 1989b; van der Molen et al., 1990; Sørensen et al., 2002) are generally applicable to the mid-Atlantic region of the USA. It is suggested that NH_3 volatilization is likely to generally account for 30–70% of cattle slurry NH_4^+ -N following surface applications in the mid-Atlantic region, with the larger losses occurring

from applications in warm climatic conditions to soils with plentiful crop residues. The data of Sørensen et al. (2002) suggest losses of 30–45% of NH_4^+ -N following surface application to bare soil.

Ammonia loss from the immediately incorporated slurry treatment was assumed to be very small on account of the effects of both immediate incorporation (Klarenbeek and Bruins, 1991; Thompson and Meisinger, 2002) and the heavy rainfall soon after application.

Denitrification loss

The denitrification data demonstrate that in the mid-Atlantic region: (i) enhanced denitrification can occur from slurry-treated soil throughout the winter period, (ii) immediately incorporating slurry after surface application, to reduce NH_3 volatilization, can increase denitrification loss from late-autumn/early-winter applications, and (iii) accumulated denitrification loss can represent an appreciable proportion of applied NH_4^+ -N. Similar observations have been made in NW Europe (Pain et al., 1989a; Thompson et al., 1987; Thompson, 1989; van den Abbeel et al., 1990), and in Oregon, USA (Myrold et al., 1992).

The heavy rainfall soon after slurry application presumably enhanced total denitrification loss from the surface-applied slurry treatment by retaining inorganic N, in the soil, that otherwise would have been lost by NH_3 volatilization. This rainfall event would have had relatively little effect on total denitrification loss from the incorporated slurry treatment, because much of the slurry NH_4^+ -N had been previously retained in the soil by incorporation with the rotovator.

Considerations concerning the methodology for denitrification measurement, in the present study, are (i) disruption of coupled nitrification-denitrification (Nielsen et al., 1996), (ii) the sampling depth of 0–15 cm, and (iii) the variability generally associated with denitrification measurement. The disruption of coupled nitrification-denitrification, by the inhibition of nitrification by acetylene (Nielsen et al., 1996), may cause notable underestimates of denitrification rate when appreciable nitrification is occurring. However, as soil NH_4^+ -N was appreciably increased in the slurry-treated soils for only 3 weeks (Figure 3a), the effect on the total denitrification loss is likely to be small. The sampling depth is unlikely to have appreciably influenced the results, as denitrification activity is usually concentrated in the surface soil (Aulakh et al.,

1992; Ryden et al., 1987). The CVs reported here (average value of 47%) are within the range commonly reported for denitrification measurement; for example, Duxbury and McConnaughey (1986) reported CVs of 50–60%, and Thompson et al. (1987) and Thompson (1989) reported CVs of > 100% when using a similar core incubation method but with two replicate jars per measurement. While the average CV reported here is appreciable, it is worth noting that consistent differences were maintained between treatments.

The silt-loam texture of the soil, and the soil WFPS which was generally 70–90% during the study (Figure 1c), were likely to favour denitrification, by providing both sufficient aerobic sites for rapid nitrification of slurry NH_4^+ -N, and sufficient anaerobic sites for denitrification. Considering the favourable nature of the soil conditions for denitrification, the results of the present study suggest that denitrification losses from late-autumn/early-winter applications of cattle slurry, to no-till arable soils, in the mid-Atlantic region whilst appreciable, are relatively small for both unincorporated and incorporated slurry, when compared to the likely NH_3 volatilization loss from surface applications.

Denitrification from the spring application was not measured in the current study. Despite the temperature differences, denitrification losses from slurry applications in the spring have been shown to be smaller than from late-autumn/early-winter applications because soils are usually drier and there is commonly strong competition for soil NO_3^- from growing crops (Myrold et al., 1992; Pain et al., 1989a; Thompson et al., 1987).

The presence of the maize residues from the preceding no-till crop may have indirectly influenced denitrification loss, particularly from the incorporated slurry treatment, by immobilising NH_4^+ -N applied in the slurry, before it could be nitrified. There is a need for comparative N balance studies determining N balances for slurry applications to tilled and no-till soils.

Measurement of ammonia volatilization

The comparison of the Z_{INST} and IHF rate of NH_3 volatilization estimates (Figure 4a) shows good general agreement, especially in light of the uncertainty in individual flux estimates of ± 10 –20%. The tendency for the Z_{INST} method to be lower than the IHF when rates of NH_3 loss were high, and higher when rates

were low cannot be considered conclusive due to the ± 10 –20% uncertainty associated with each method.

The 18% difference between the IHF and Z_{INST} methods in the present study is similar to the 16% difference reported by Klarenbeek et al. (1993). However, more commonly, better agreement between the two methods is reported (Pain et al., 1989b; Sommer et al., 1995; Wilson et al., 1983).

Compared to the IHF method, the Z_{INST} approach has considerable practical advantages. However, given the differences sometimes observed between the two methods, it is suggested that on-site evaluations against the IHF method be conducted before the Z_{INST} method is routinely used.

The comparison of the WT and IHF methods, suggested that in the period shortly after slurry application, when rates of NH_3 volatilization are very high, the fixed air velocity used in the WT modified the actual rate of NH_3 volatilization. Thompson et al. (1990b) and Sommer et al. (1991) reported that wind speed positively influenced NH_3 loss from slurry applications; with the effect being largest immediately after application, and then progressively smaller until 12 h, after which the effect was very small.

The smaller application rate on the plots used for the IHF measurement ($39 \text{ m}^3 \text{ ha}^{-1}$), would have moderately enhanced the relative NH_3 volatilization rate compared to that from the WT plots ($80 \text{ m}^3 \text{ ha}^{-1}$). Thompson et al. (1990b) reported that, after 7 h, the relative cumulative NH_3 volatilization loss from a $40 \text{ m}^3 \text{ ha}^{-1}$ application was 1.5 times that from an $80 \text{ m}^3 \text{ ha}^{-1}$ application. In the current study, after 6 h, the cumulative loss measured with the IHF system was 2.5 times that measured with the WT system. This suggests that the difference in application rates was responsible for only part of the difference observed between the two methods of measurement, and that the difference in air velocity/wind speed had an appreciable effect.

When used at fixed air velocities, and there is an appreciable difference between the tunnel air velocity and the ambient wind speed in the 12 h period following application, there is likely to be an error in the quantitative estimates of the initial rates of NH_3 volatilization. This difference in initial loss estimates will also be reflected in the total loss value.

The WT system used in this study has the capacity for manually adjusting velocity. Matching the air velocity to ambient wind speed considerably enhances the quantitative measurement of NH_3 volatilization (Ryden and Lockyer 1985; Braschkat, et al., 1993).

However, the labour requirements to regularly manually adjust wind speed (Ryden and Lockyer, 1985), and the technical complexity and cost required for automatic adjustment (Braschkat et al., 1993) are important practical considerations.

When used with fixed air velocities, the WT system qualitatively tracks NH_3 loss and enables semi-quantitative, replicated comparisons of different treatments. Its portability and its versatility, compared to micro-meteorological methods, enable it to be used in a wide variety of sites and studies.

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