Infiltration of slurry liquid and volatilization of ammonia from surface applied pig slurry as affected by soil water content

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SUMMARY

Ammonia (NH₃) volatilization may decrease the fertilizer efficiency of surface-applied slurry and may cause the unwanted deposition of nitrogen (N) in oligotrophic ecosystems. We studied the effect of soil water content on the infiltration of slurry liquid and how infiltration affected NH₃ volatilization. NH₂ volatilization was measured with dynamic chambers through which air was drawn continuously. Slurry spiked with bromide (Br⁻) to trace slurry infiltration was applied to a loamy sand in steel cylinders (diameter 67 cm and height 12 cm) adjusted to water contents of 0.01, 0.08, 0.12 and 0.19 g H₃O per g soil (g g⁻¹). At different time intervals after slurry application the soil columns were cut into slices and Br⁻, ammonium (NH₄⁺) and nitrate (NO₃⁻) concentrations were determined. At soil water contents $> 0.12 \text{ g g}^{-1}$ nitrate content increased significantly from 24 to 72 h, and at 96 h NO₃⁻ content was equivalent to 75–130% of the NH₄⁺ present at 0.5 h after slurry application. Nitrification may have contributed to a low NH_3 volatilization from 24 to 96 h by reducing NH_4^+ concentration and contributing to acidity, and most of the NH₃ volatilization occurred, therefore, during the first 24 h after application. Low soil water content enhanced the infiltration of slurry liquid and hence the mass transport of NH_4^+ into the soil. Transport of NH_4^+ by diffusion, on the other hand, was highest at the highest water content. Transport of NH_4^+ from the slurry at the soil surface down into the soil at 0.01 g g⁻¹ reduced NH₃ volatilization to c. 70% of the volatilization from slurry applied to soils at higher water contents. Diffusion of NH_4^+ into the soil did not significantly decrease NH₃ volatilization.

INTRODUCTION

In Denmark c. 214000 tonnes of nitrogen (N) are collected in animal manure and applied to agricultural soils each year (Kristensen & Kristensen 1997). It is assumed that up to 30 % of this volatilizes as ammonia (NH₃) and thereby lowers the value of the N for plant production (Buijsman *et al.* 1987; Asman 1992). Deposition of increasing amounts of N due to losses of NH₃ may adversely affect nitrogen limited ecosystems (Schulze *et al.* 1989).

In the last two decades, losses of NH_3 from animal slurries have been studied intensively. It has been shown that losses are related to environmental

* To whom all correspondence should be addressed. Email: SvenG.Sommer@agrsci.dk conditions, e.g. temperature, wind speed, and rain (Moal et al. 1995; Braschkat et al. 1997). There have been indications that infiltration of liquid from slurry may have a significant influence on losses (Sommer & Olesen 1991; Braschkat et al. 1997). A better understanding and description of the mechanism of infiltration, and the relationship between NH₃ volatilization and infiltration, may therefore be a useful tool for improving and adapting application techniques to soil conditions. Infiltration of the slurry liquid is influenced by the water-holding capacity of the slurry and the soil. A high viscosity or dry matter content of the slurry increases the water-holding capacity of the slurry and thereby decreases the transport of water from the slurry into the soil (Frost et al. 1990; Génermont et al. 1996; Sommer et al. 1997). The soil's water-holding capacity is mainly

affected by the water content and the porosity. A high soil water content will decrease the soil's ability to absorb liquid from the slurry.

In field experiments, NH₃ volatilization and infiltration of ammonium (NH_4^+) were studied by Beauchamp et al. (1982) and van der Molen et al. (1990). These studies showed that ammonium and nitrate (NO₃⁻) concentrations after slurry application to the soil are variable due to NH₃ emission, leaching and immobilization of NH4+ (Sørensen & Jensen 1995). The amounts of slurry applied in practice and in field experiments have been within the range of 30-50 t ha⁻¹, corresponding to 3-5 mm of liquid applied. Thus the slurry may only infiltrate the upper surface layers. Due to soil inhomogeneity it has been extremely difficult to quantify infiltration rates and maximal infiltration depth in field studies. Apart from the study of Beauchamp et al. (1982) few researchers have examined infiltration from slurry to the top soil layers and related infiltration to NH₃ volatilization. In their study NH_4^+ and NO_3^- in the soil were determined immediately and 5 days after slurry application. Ammonia loss rates were high immediately after slurry application and low 2-3 days later (Beauchamp et al. 1982; Moal et al. 1995). Thus there is a gap in our knowledge about slurry infiltration, NH₃ volatilization and nitrification in the soil and slurry mixture during the period when substantial NH₃ losses are occurring.

In laboratory experiments using small dynamic chambers for measuring NH_3 volatilization, we applied pig slurry onto repacked soil columns at four different soil water contents ranging from 0.01 to 0.19 g g⁻¹ to study how the soil water content influences the infiltration of water and ions and thereby NH_3 volatilization.

MATERIALS AND METHODS

Soil

The soil used in the experiment was a coarse loamy sand (Typic Hapludult) from Research Centre Foulum, Denmark, with 9.5% clay, 11% silt, 77% sand, and total C of 0.015 g g⁻¹. The soil was collected from the top 10 cm of an arable field, air-dried to 0.01 g H₂O per g soil (g g⁻¹) gravimetric soil water content and passed through a 2 mm sieve. Particle analysis was performed by hydrometer (Gee & Bauder 1986) and sieve, and organic matter (OM) determined by the loss of ignition method (Tabatabai & Bremner 1970).

For each of four water contents (0.01, 0.08, 0.12 and 0.19 g g⁻¹) the soil was packed at dry bulk density of 1.5 g cm⁻³ into 12 columns with a diameter of 6.7 cm and a height of 12 cm, so that each column contained 635 g oven-dry soil. The soil at 0.01 g g⁻¹ was packed into the columns without any pretreatment, i.e. 641 g air-dry soil at 0.01 g g⁻¹. For 0.08

Table 1. Amounts of pig slurry, total ammoniacal nitrogen (TAN) and Br^- applied to soil at four water contents

Soil water content	Slurry applied	TAN	Br ⁻ (g Br ⁻ m ⁻²)		
(g g ⁻¹)	(kg m ⁻²)	$(g N m^{-2})$			
0.010	2·78	9·89	7·53		
0.080	1·32	4·67	3·56		
0·120	2:95	10·48	7·98		
0·190	2:99	10·60	8·07		

and 0.12 g g^{-1} , water was added to the soil, and soil and water were carefully mixed and stored in a closed container for 14 days. During storage the soil was mixed each day. After adjusting soil water content, the amount of soil added to the columns was 685 g soil at 0.08 g^{-1} and 711 g soil at 0.12 g^{-1} . The soil at 0.19 g^{-1} was prepared by packing 641 g air-dry soil (0.01 g^{-1}) into each column, and placing the soil columns on a sandbox. Thereafter, water was added to the bottom of the soil columns and drained each day for 10 days. Although this treatment gave slightly higher water contents towards the bottom of the column this procedure was chosen because it was not possible to pack soil at 0.19 g^{-1} into columns.

Slurry application

At each water content, pig slurry was applied to the surface of 10 columns at a rate of 3 kg m⁻² (30 t ha⁻¹). The amount applied to the columns at 0.08 g g⁻¹ was by mistake about half of the amount of the others. The slurry was spiked by adding 0.001 g KBr per g slurry, giving the following slurry composition: dry matter 0.0659 g g⁻¹ (s.D. 0.0001 g g⁻¹), total ammoniacal nitrogen (TAN) 0.0036 g N g⁻¹ (s.D. 0.000003 g g⁻¹). The average amounts applied to soils at the different water contents are shown in Table 1. Experiments were run at 20 °C with an air humidity of 80–90 %.

Ammonia volatilization

The 10 slurry-treated soil cores and two untreated cores at each soil water content were placed in 12 cylindrical screw-top plastic jars (100 mm diameter, 165 mm height). The volume of the head space in each jar was 353 ml. Three input and output ports were placed on opposite sides of the jar directing air into the head space. Air was sucked into each jar by a suction pump (ASF 7010Z) at 3 litres min⁻¹, giving a volatilization rate similar to rates expected in the field (Sommer & Ersbøll 1996). Air flowing out of each jar passed through an NH₃ scrubber containing 50 ml 0.2 M H₃PO₄. The amount of ammonia absorbed in



Fig. 1. Concentrations of Br⁻ in repacked soil samples at (a) 0.5 h, (b) 24 h and (c) 96 h after slurry application at a rate of 3 kg m⁻² onto soils at 0.01 (\bullet), 0.12 (∇) and 0.19 g g⁻¹ (\bigtriangledown) and 1.3 kg slurry m⁻² at water content of 0.08 g g⁻¹ (\bigcirc).

each scrubber was determined colorimetrically on a flow injection analyser, QuickChem 4200 (Lachat Instruments, Milwaukee, WI) as described by Crooke & Simpson (1971). For each measuring period the amount of background NH_3 was subtracted from the amount obtained from treated soils to give the daily loss of NH_3 . Background NH_3 was determined by measuring the flow of NH_3 through the two dynamic chambers with untreated soils.

Soil analysis

After 0.5, 24, 48, 72 and 96 h from slurry application, the measurement of NH_3 volatilization was stopped in two columns which were then sliced for determination of infiltration of Br^{-1} and inorganic N. The columns were placed in a refrigerator at 4 °C with PVC foil enclosing the opening at the top. Within 0.5 to 1 h after stopping NH_3 measurements the soils were cut into slices of 0–0.5, 0.5–1, 1–1.5, 1.5–2, 2–3, 3–4, 4–12 cm after the slurry dry matter remaining on the surface was scraped off and collected. The cores were carefully pushed up through the columns with a piston, and the segments of soil cut off with a sharp steel plate.

 NO_3^- and NH_4^+ in the soil were extracted with 1.0 M potassium chloride for 0.5 h and determined by standard methods on a QuickChem 4200 flow injection analyser (Lachat Instruments, Wisconsin, US). Br⁻ was extracted in deionized water for 0.5 h and determined on a high pressure liquid

chromatograph with solvent delivery system from LDC Analytical (Florida, US) and conductivity detector from Dionex Corporation (California, US).

Statistics

The effects of treatments were tested in an analysis of variance using the general linear models procedure (SAS 1989).

RESULTS AND DISCUSSION

There was no Br⁻ in the soil before pig slurry application. Thus, traces of Br⁻ indicate that liquid from the applied slurry has leached to the depth at which the soil sample was taken for analysis. At a slurry application rate of c. 3 kg m⁻², Br⁻ infiltrated to maximum depths of 1.75, 0.75 and 1.75 cm at soil water contents of 0.01, 0.12 and 0.19 g g⁻¹, respectively (Fig. 1). The liquid infiltrated to maximum depth within 0.5-24 h after slurry application. The infiltration to greater depths at low soil water content is due to the high water potential of the soil enhancing mass flow of liquid from the slurry into the soil (Petersen & Andersen 1996). The rate of diffusion also increases with soil water content. At high soil water content (0.19 g s^{-1}) diffusion may therefore have caused infiltration to greater depth than at 0.12 g s^{-1} . In the treatment at 0.08 g s^{-1} where the slurry application rate was half of the other treatments by mistake, slurry liquid infiltrated the soil to a maximum



Fig. 2. Concentrations of NH_4^+ in repacked soil samples at (a) 0.5 h, (b) 24 h and (c) 96 h after slurry application at a rate of 3 kg m⁻² onto soils at 0.01 (\bullet), 0.12 ($\mathbf{\nabla}$) and 0.19 g g⁻¹ (\bigtriangledown) and 1.3 kg slurry m⁻² at water content of 0.08 g g⁻¹ (\bigcirc).



Fig. 3. Concentrations of NO₃⁻ in repacked soil samples at (a) 0.5 h, (b) 24 h and (c) 96 h after slurry application at a rate of 3 kg m⁻² onto soils at water content of 0.01 (\bigcirc), 0.12 (\triangledown) and 0.19 g g⁻¹ (\bigtriangledown) and 1.3 kg slurry m⁻² at water content of 0.08 g g⁻¹ (\bigcirc).

depth of 0.75 cm. The low infiltration depth may be due to both the low application rate and the low soil water content. Immediately after slurry application NH_4^+ concentration was in the range 2000–10000 mg NH_4^+ - N kg⁻¹ (dry matter) in the slurry layer (Fig. 2). Similar

Soil water (H_2O) (g g ⁻¹ soil)	Time application of slurry (h)										
	0.5		24		48		72		96		
	NH4 ⁺ -N	NO ₃ ⁻ -N	NH4 ⁺ -N	g NO ₃ ⁻ -N	NH4 ⁺ -N	NO ₃ ⁻ -N	NH4 ⁺ -N	NO ₃ ⁻ -N	NH4 ⁺ -N	NO ₃ ⁻ -N	
	(g N per column)										
0.01	12.8	1.9	6·6	0.5	6·5	0.47	5.2	1.6	6·4	1.3	
0.12	16.3	(2.0) 1.1 (0.2)	(1.0) 5.5 (0.2)	(0.2) 2.5 (1.7)	(0.4) 4.9 (0.2)	(0.04) 6.6 (1.5)	(0.7) 4.4 (0.7)	(2.3) 9.1	(0.01) 3.4	(0.8) 11.6 (2.6)	
0.19	(2.6) 16.0 (N.R.)	(0.3) 2.4 (N.R.)	(0.3) 13.2 (11.1)	(1.7) 3.8 (2.7)	(0.3) 3.9 (0.2)	(1.3) 10.7 (2.3)	(0.7) 4.1 (0.2)	(1.4) 11.4 (0.8)	(0.4) 2.8 (0.2)	(3.6) 18.3 (0.1)	

Table 2. The change in NH_4^+ and NO_3^- contents in repacked soil columns with time after shurry application at a rate of 3 kg m⁻². The data for NH_4^+ and NO_3^- are mean values with $\pm s.E.$ values in parentheses

N.R. = no replicates.

NH⁺ concentrations in the topsoil after dairy cattle slurry application were reported by Beauchamp et al. (1982). In contrast, the concentrations of NH_4^+ after incorporation of slurry were much lower due to the mixing of slurry and soil (from 200 to 800 mg NH₄+-N kg⁻¹ dry soil; Comfort *et al.* 1988; Paul *et al.* 1993; Sommer et al. 1996). Twenty-four h after slurry application, NH4⁺ concentrations were lowest in the slurry layer at 0.01 and 0.19 g g^{-1} due to infiltration and diffusion. From 24 to 96 h after application, NH₄⁺ concentrations varied from 200 to 1000 mg kg⁻¹. Concentrations of NH_4^+ at different depth were not related to Br- concentration. Immediately after slurry application, the NH4+ concentration was high at the surface and low at 0.75 and 1.25 cm in relation to Br-, because Br- readily infiltrated the soil (Figs 1 and 2). From 24 to 72 h, NH4⁺ would have diffused downward and the NH_4^{*+} : Br⁻ ratio was similar at different depths apart from in the slurry layer (-0.1 cm), where NH_4^+ was low due to volatilization of NH₃.

In the soils at 0.12 and 0.19 g g⁻¹, NO₃⁻ concentrations nearest the surface increased to between 3000 and 4000 mg NO₃⁻-N kg⁻¹ after 96 h (Fig. 3). The increase in NO₃⁻ was measured from 24 to 72 h in the soils at 0.12 and 0.19 g g⁻¹. At 0.01 and 0.08 g g⁻¹ nitrification did not increase the amount of NO₃⁻ significantly (P = 0.05). In the study of Paul *et al.* (1993) nitrification was not significantly affected by varying soil water contents from 0.18 to 0.28 g g⁻¹. Due to nitrification in the soils at 0.12 and 0.19 g g⁻¹, the NH₃⁻ content at 96 h after slurry application was equivalent to 75 to 130% of the NH₄⁺ present in the soil 0.5 h after slurry application (Table 2).

Ammonia loss rates were highest during the first 24 h after slurry application and declined thereafter (Fig. 4*a*). Thus, nearly all the difference in cumulated NH_a volatilization can be contributed to the loss



Fig. 4. Ammonium volatilization rate (a) and accumulated NH₃ volatilization (b) from slurry application at a rate of 3 kg m⁻² onto soils at water content of 0.01 (\odot), 0.12 (∇) and 0.19 g g⁻¹ (∇) and 1.3 kg slurry m⁻² at water content of 0.08 g g⁻¹ (\bigcirc).

during the first 24 h (Fig. 4*b*). Volatilization of NH_3 was significantly lower (P = 0.05) when slurry was applied to the soil at 0.01 and 0.08 g g⁻¹. For 0.08 g g⁻¹, a lower amount of slurry was applied, which explains

the low volatilization and, when the data are plotted as the percentage of applied TAN (Fig. 4b), only NH₃ volatilization from soils at 0.01 g g⁻¹ was significantly lower (P = 0.05) than the volatilization from soils at higher water contents. Therefore, measurement at 0.01 g g⁻¹ indicates that infiltration decreases volatilization. From slurry applied to the soil at 0.19 g s^{-1} , the emission seemed to be lower than at 0.08 and 0.12 g g⁻¹ (Fig. 4b), but the difference was not significant (P = 0.05), showing that in this experiment we could not associate low volatilization with diffusion of NH_4^+ into soils at higher soil water contents. Nitrification may have affected the volatilization pattern by reducing the NH₄⁺ concentrations, and by reducing pH as nitrification of one mole NH₄⁺ produces 2 moles of H⁺ according to the following equation:

$$NH_4^+ + 2O_9 \rightarrow NO_9^- + H_9O + 2H^+$$
.

The volatilization rate of ammonia after 24 h was low and did not change with time (P = 0.05). The low volatilization of NH₃ after 24 h could have been due to a low pH, as a parallel study in the field with slurry from the same slurry store showed an increase in pH immediately after slurry application and a decline in the days following slurry application. This decline has been attributed to volatilization of NH₃ adding H⁺ (Husted *et al.* 1991), but nitrification may also contribute significant amounts of acidity at 18 °C. Nitrification is high in soils at field capacity although the optimum temperature is between 30 and 35 °C (Whitehead 1995). After 24 h, NH₃ volatilization was low irrespective of the high concentration of NH_4^+ in the slurry at the soil surface. The low volatilization was due to a combination of factors including low pH, nitrification and absorption of NH_4^+ to clay and organic matter.

CONCLUSION

Transport of NH₄⁺ into the soil was high at low soil water content due to transport by mass flow of slurry liquid into the upper soil. The infiltration of slurry liquid at the low water content (0.01 g g^{-1}) lowered the total loss of NH_3 from c. 30 to 20% of applied TAN compared to losses at soil water contents of 0.12 and 0.19 g s^{-1} . Transport of TAN from the slurry into the soil increased when soil water content was increased from 0.12 to 0.19 g g⁻¹, because diffusion is highest at a high soil water content. Thus transport of NH_4^+ from the slurry layer into the soil at 0.19 g g⁻¹ was greater compared to intermediate water contents. The higher diffusion of NH4+ into the soil at high affect water contents did not significantly volatilization in this study.

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