Ammonia volatilization from surface-applied livestock slurry as affected by slurry composition and slurry infiltration depth

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SUMMARY
Volatilization of ammonia (NH₃) from slurry applied in the field is considered a risk to the environment and reduces the fertilizer value of the slurry. To reduce volatilization a better understanding of the slurry–soil interaction is needed. Therefore, the present study focuses on measuring NH₃ volatilization as affected by differences in infiltration. Livestock slurries with different dry matter (DM) composition and viscosity were included in the experiments by using untreated cattle and pig slurry, pig slurry anaerobically digested in a biogas plant and pig slurry anaerobically digested and physically separated. NH₃ volatilization was measured using dynamic chambers and related to infiltration of the livestock slurries in the soil by measuring chloride (Cl⁻) and Total Ammoniacal Nitrogen (TAN = ammonium (NH₄⁺) + NH₃) concentrations in soil at different depths from 0.5 to 6.0 cm from the soil surface. The slurries were applied to sandy and sandy-loam soils packed in boxes within the chambers. There were no significant differences in relative volatilization of NH₃ from untreated cattle and pig slurries, but anaerobic digestion of pig slurry increased volatilization due to increases in pH. However, physical separation of the digested slurry reduced the volatilization compared with untreated slurry, due to increased infiltration. In general, the volatilization decreased significantly with increased infiltration. The present study shows that NH₃ volatilization from applied slurry can be related to infiltration and that infiltration is related to slurry composition (i.e. DM content and particle size distribution) and soil water content. The infiltration of liquid (measured by Cl⁻ infiltration) was affected by soil water potential, therefore, Cl⁻ infiltrated deeper into the sandy loam soil than the sandy soil at similar gravimetric soil water values. Dry matter (DM) and large particles (>1 mm) of the slurry reduced infiltration of liquid. A high proportion of small particles (<0.025 mm) facilitated infiltration of TAN.

INTRODUCTION
Ammonia (NH₃) volatilization from animal slurry is considered a major source of atmospheric NH₃ (ECETOC 1994). The volatilized NH₃ is partly deposited locally as NH₃ or as ammonium (NH₄⁺) in particles and partly transported far from the source before being deposited (Asman et al. 1998). Deposited NH₃/NH₄ may cause undesirable changes in natural ecosystems (Schulze et al. 1989). Therefore the UN and EU are considering NH₃ to be a Long-Range Transboundary Air Pollution gas component (EEA 1999) and in Europe directives have set country-specific NH₃ volatilization limits. Ammonia volatilization reduces the fertilizer nitrogen (N) efficiency of animal slurry and increases the degree of uncertainty in predictions of availability of the manure N to the crops.

A substantial proportion of the slurry produced in Denmark is applied to crops during spring (Hutchings et al. 2001), when conventional trail hose application of livestock slurry has a low efficiency in reducing NH₃ volatilization (Braschkat et al. 1997;
Hansen et al. 2003). Shallow direct injection techniques could be used, but the effectiveness of these techniques may be poor if the soil is moist and compacted, and the slot remains open (Klarenbeek & Bruins 1991; Phillips et al. 1991). Alternatively, the \( \text{NH}_3 \) volatilization may be reduced in a less energy-consuming way than slurry injection by reducing viscosity and dry matter (DM) of the slurry and thereby increasing infiltration of the slurry into the soil (Thompson et al. 1990; Sommer & Olesen 1991; Petersen & Andersen 1996).

There are few studies on the relationship between infiltration as affected by slurry DM content and viscosity, soil texture and \( \text{NH}_3 \) volatilization. Therefore, the main objective of the present study was to contribute to a better understanding of \( \text{NH}_3 \) volatilization related to slurry characteristics and soil. In the laboratory, \( \text{NH}_3 \) volatilization from surface-applied cattle slurry, pig slurry, anaerobically digested pig slurry and physically separated pig slurry was estimated by a dynamic chamber technique. Slurry infiltration was characterized by tracing chloride (\( \text{Cl}^- \)) and Total Ammoniacal Nitrogen (TAN = \( \text{NH}_3 + \text{NH}_4 \)) in the soil layers below the slurry string.

**MATERIALS AND METHODS**

In the laboratory, \( \text{NH}_3 \) volatilization from livestock slurry (Table 1) surface-applied to sandy and sandy-loam soils (Table 2) was measured using the dynamic chamber technique. The infiltration and volatilization experiments were performed on the two soils packed in boxes. Cattle, pig, digested pig and separated digested pig slurry (Table 1) were applied to the soil surface of both soil types at an application rate of 10.9 kg/m\(^2\), corresponding to about 30 t/ha, as slurry applied with trail-hoses typically covers 0.25–0.30 of the surface. The volatilization of \( \text{NH}_3 \) from each soil was measured in two experimental series. Four slurries were applied, in replicate, to a sandy soil in Expt. 1 and to a sandy-loam soil in Expt. 2. For both soil types the two replicated measurements of \( \text{NH}_3 \) volatilization from the four slurries were carried out using eight dynamic chambers. In addition to each of the two \( \text{NH}_3 \) volatilization experiments, the four slurries were also applied either to the sand or the sandy-loam for soil sampling and infiltration studies using four boxes containing the sandy soil and four boxes containing sandy-loam soil. Two samples were taken from each soil for analysis of infiltration.

**Soil**

The two soils used in the experiments were a sandy soil from Research Station Jyngevad, Denmark and a sandy-loam soil from Research Centre Bygholm, Denmark. The soils were collected from the top 10 cm
of an arable field, air-dried, and moistened to 170–180 g/kg gravimetric soil water content. The physical and chemical properties of the two soils are listed in Table 2. The particle analysis was performed by hydrometer (Gee & Bauder 1986) and sieve, organic matter (OM) determined by the loss of ignition method (Tabatabi & Brenner 1970), and CEC by saturation with ammonium acetate. Each of the two moistened soils was packed at a dry bulk density of 1.45 g/cm³ for 24 h at 80 °C. Total N was analysed using the Kjeldahl method, ammonium-N with MgO, total P with the vanadomolybdophosphoric acid colorimetric method and total K with flame-emission spectroscopy (Greenberg et al. 1992). Slurry viscosity for the three types of pig slurry was measured with a rotational viscometer (DV–II + P Viscometer, Brookfield) at a slurry temperature of 10 °C. The size distribution of particles in the manure was determined by sieving the manure in a water-jet sieving device, in which a spraying arm with 34 nozzles is forced to rotate over each sieve due to the jet created by water pressure (Retsch 1997). Sieves with 1.00, 0.50, 0.25, 0.10, 0.05 and 0.025 mm mesh sizes were used. The liquid, consisting of water and effluent, was collected in a tray at the bottom of the sieving device. After filtration, the amount of DM in each fraction was determined by drying the sieves for 24 h at 80 °C.

**Physico-chemical slurry analysis**

Slurry pH was determined with a standard electrode (704 pH meter, Radiometer, Copenhagen) and DM content was determined gravimetrically after oven drying at 80 °C for 24 h. Total N was analysed using the Kjeldahl method, ammonium-N by distillation with MgO, total P with the vanadomolybdophosphoric acid colorimetric method and total K with flame-emission spectroscopy (Greenberg et al. 1992). Slurry viscosity for the three types of pig slurry was measured with a rotational viscometer (DV–II + P Viscometer, Brookfield) at a slurry temperature of 10 °C. The size distribution of particles in the manure was determined by sieving the manure in a water-jet sieving device, in which a spraying arm with 34 nozzles is forced to rotate over each sieve due to the jet created by water pressure (Retsch 1997). Sieves with 1.00, 0.50, 0.25, 0.10, 0.05 and 0.025 mm mesh sizes were used. The liquid, consisting of water and effluent, was collected in a tray at the bottom of the sieving device. After filtration, the amount of DM in each fraction was determined by drying the sieves for 24 h at 80 °C.

**Ammonia volatilization**

Ammonia volatilization was measured simultaneously in replicate from four slurries applied to both soils with eight dynamic chambers (height 14.5 cm, width 26.5 cm, length 34.8 cm). The head-space above the soil in the dynamic chamber was 4.0 litres and three input and output ports were placed on opposite sides of the chamber, directing air into the headspace. Air was sucked into each chamber by a suction pump (Miele Electronic s438i, s-class) at an average rate of 65 litres/min, corresponding to 16 air changes/min, which ensured that the airflow was not a limiting factor for ammonia volatilization (Kissel et al. 1977). After passing through the chamber, a sub-sample of the air stream passed through an NH₃ scrubber containing 75 ml 0.2 M H₂SO₄. A diaphragm pump (ASF Thomas. TF5W, Germany) provided suction and a critical orifice adjusted the airflow through the NH₃ scrubber to exactly 2 litres/min. The amount of NH₃ absorbed in each scrubber was determined colorimetrically by the indophenol reaction (Weatherburn 1967) with a spectrophotometer (Shimadzu. UV–120–01). Cl⁻ was determined colorimetrically by Merck Spectroquant® (Spectroquant®, NOVA 60, Merck).

<table>
<thead>
<tr>
<th>Soil</th>
<th>Clay (2–63 μM)</th>
<th>Silt (63–2000 μM)</th>
<th>Sand (&lt;2 μM)</th>
<th>Total carbon</th>
<th>Cation exchange capacity (CEC) (mmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy</td>
<td>41</td>
<td>51</td>
<td>884</td>
<td>14</td>
<td>56</td>
</tr>
<tr>
<td>Sandy-loam</td>
<td>190</td>
<td>311</td>
<td>446</td>
<td>31</td>
<td>226</td>
</tr>
</tbody>
</table>

**Infiltration**

Replicate soil samples were taken 4 h after slurry application by pushing a steel column (97.5 cm diameter, 80.0 cm height) into the soils from each of the eight treatments (boxes not used for volatilization studies). The columns were carefully pulled up and the soil cores were immediately pushed up carefully through the columns with a piston. Segments of soil were then cut off with a sharp steel plate (Sommer & Jacobsen 1999). Each soil core was sliced into 12 slices of 0.0–0.5, 0.5–1.0, 1.0–1.5, 1.5–2.0, 2.0–2.5, 2.5–3.0, 3.0–3.5, 3.5–4.0, 4.0–4.5, 4.5–5.0, 5.0–6.0 and 6.0–8.0 cm after the slurry DM remaining on the surface was scraped off and collected. The soil slices were extracted with 20 ml demineralized H₂O for 20 min and TAN was determined colorimetrically using the indophenol reaction (Weatherburn 1967) with a spectrophotometer (Shimadzu. UV–120–01). Cl⁻ was determined colorimetrically by Merck Spectroquant® (Spectroquant®, NOVA 60, Merck).
were 0–0.5, 0.5–1, 1–2, 2–4, 4–7, 7–24, 24–48, 48–72 and 72–96 h.

**Calculations and statistics**

For assessment of infiltration, the amount-weighted average depth of infiltration ($Z_{inf}$, cm) was calculated for both Cl$^{-}$ ($Cl_{inf}$) and TAN ($TAN_{inf}$) with the following equation:

$$Z_{inf} = \frac{\sum_{Z=Z_1}^{Z_{12}} C_Z \times V_Z \times Z}{\sum_{Z=Z_1}^{Z_{12}} C_Z \times V_Z}$$  

(1)

where $C$ is the concentration of the ions (g/litre), $V$ the volume of soil water (l) in the layer and $Z_1$ to $Z_{12}$ (cm) are the depths of the layers expressed as the depths of the midpoints between the upper and lower boundaries of the layers.

Multiplicative models of the following type were used to test whether NH$_3$ volatilization was related to potential explanatory variables available from the measurements made during the experiments:

$$Y = b_0 \times b_1^{X_1} \times b_2^{X_2} \times \ldots \times b_n^{X_n}$$  

(2)

where $b_1$, $b_2$, ..., $b_n$ are model parameters, $X_1$, $X_2$, ..., $X_n$ are potential explanatory variables, characterizing soil/slurry and $Y$ is NH$_3$ volatilization. To ensure that the residuals were Gaussian-distributed, log-transformed versions of the model were used when estimating the model parameters. A similar procedure is explained in more detail in the appendix to the article of Søgaard et al. (2002). Table 3 depicts the results of the statistical analyses of NH$_3$ volatilization from the slurry. Among the potential explanatory variables, only those with a significant effect on NH$_3$ volatilization ($P<0.10$) were kept in the model behind these results.

In addition, the linear relationship between infiltration and soil/slurry factors was analysed statistically (Table 4).

**RESULTS**

Cattle slurry differed significantly from pig slurry in having a higher DM content and a large number of particles >1 mm (Table 1 and Fig. 1). Digestion of pig slurry increased pH from 7.4 to 8.1 and TAN content from 3.3 to 4.1 g N/kg. Digested pig slurry had a higher viscosity than separated digested pig slurry, and untreated pig slurry had a lower viscosity than either of the digested pig slurries (Table 1). The size distribution of the DM in untreated and digested pig slurry was identical (Fig. 1). Viscosity of the cattle slurry was not measured, due to interference of pieces of straw in the liquid.

Accumulated NH$_3$ volatilizations after 96 h varied from 4.9 to 15.2% of the TAN applied in manure (Fig. 2b). A factorial analysis of data showed a significant effect of time from slurry application on the NH$_3$ volatilization rate ($P<0.0001$). The volatilization rates declined with increasing time from slurry application apart from the measuring periods at 1–2 h and 2–4 h, probably due to a temperature increase at midday when measurements in the period 1–2 h and 2–4 h were carried out. The volatilization from untreated cattle and pig slurries was not significantly different ($P>0.15$), but anaerobic digestion increased volatilization ($P<0.002$) from pig slurry. Volatilization of NH$_3$ from slurry applied to the sandy soil was significantly higher than from slurry applied to sandy loam ($P<0.001$). Further analysis (Table 3) showed that volatilization of NH$_3$ significantly declined at increased infiltration, as shown by the relation to $Cl_{inf}$ and by increasing content of small slurry particles.

**Table 3. Statistical analysis of the relationship between NH$_3$ volatilization and soil and slurry variables and time elapsed from slurry application using a multiplicative model (Eqn 2). The analyses are based on 141 observations of NH$_3$ emission**

<table>
<thead>
<tr>
<th>Experimental factor</th>
<th>Effect on NH$_3$ emission (significance in parentheses)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time from application</td>
<td>* ($P&lt;0.001$)</td>
</tr>
<tr>
<td>Manure TAN</td>
<td>+74% per extra g N/kg ($P&lt;0.001$)</td>
</tr>
<tr>
<td>Proportion slurry particles &lt;0.025 mm</td>
<td>−0.02 per extra % ($P&lt;0.001$)</td>
</tr>
<tr>
<td>$Cl_{inf}$</td>
<td>−62% per extra cm ($P&lt;0.001$)</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.775</td>
</tr>
</tbody>
</table>

* The emission declined with time until 48 h from slurry application, except for the periods 1–2 and 2–4 h.

**Table 4. Statistical analyses of infiltration of TAN and Cl$^{-}$ related to soil and slurry characteristics. Infiltration depth of chloride and TAN expressed as $Cl_{inf}$ or $TAN_{inf}$, i.e. amount weighted average depth (Eqn 1)**

<table>
<thead>
<tr>
<th>Experimental factor</th>
<th>$Cl_{inf}$ P-value</th>
<th>$TAN_{inf}$ P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandy soil v. Sandy-loam</td>
<td>0.011</td>
<td>0.094</td>
</tr>
<tr>
<td>DM content</td>
<td>NS</td>
<td>0.063</td>
</tr>
<tr>
<td>Amount of large slurry particles (&gt;1 mm)</td>
<td>0.01</td>
<td>0.052</td>
</tr>
<tr>
<td>Amount of small slurry particles (&lt;0.025 mm)</td>
<td>NS</td>
<td>0.058</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.865</td>
<td>0.938</td>
</tr>
</tbody>
</table>
The analysis of data showed a significant effect ($P < 0.05$) of soil type and amount of large slurry particles on $\text{Clinf}$ (Table 4, Fig. 3). More $\text{Cl}$ was retained in the surface soil layers when slurry was applied to the sandy soil than to the sandy-loam soil at similar gravimetric water content and $\text{Cl}$ added to the soil in cattle slurry infiltrated less deeply into the soil than pig slurry.

$\text{TANinf}$ was significantly related to soil, DM and small and large particles ($P < 0.1$, Table 4). $\text{TAN}$ infiltration significantly increased with increased content of small particles in the slurry and to greater depths in the sandy soil than the sandy-loam soil.

**DISCUSSION**

Digested pig slurry had a higher viscosity than separated digested pig slurry because viscosity of a colloidal suspension increases with increasing DM content (Chen 1986). Despite a high DM content, the untreated pig slurry had a lower viscosity than either of the digested pig slurries. The similar size distribution of the slurry DM of pig slurry and digested pig slurry indicates that other factors such as the shape or charge of the particles may have caused interaction between the particles and thereby influenced the viscosity.

The Michaelis–Menten equation could not be fitted to $\text{NH}_3$ volatilization estimates, as in earlier studies (Søgaard et al. 2002). This could be due to the use of the dynamic chamber technique, which exposes the slurry to more turbulent air than in the open. In this study anaerobic digestion increased volatilization probably due to an increased $\text{NH}_3$ volatilization potential caused by the increased pH (Table 1). In contrast, earlier studies have shown that improved
infiltration may compensate for the high pH of digested slurry, resulting in similar volatilization rates from digested and untreated slurry (Pain et al. 1989; Rubæk et al. 1996). Separation of the digested slurry reduced the volatilization compared with untreated slurry ($P < 0.05$) because of better infiltration of slurry liquid. Volatilization is positively related to TAN concentration of the slurry, which is the source of NH$_3$. Therefore, in NH$_3$ volatilization models TAN is one of the input variables together with pH and temperature (Hutchings et al. 1996; Génermont & Cellier 1997).

Liquid infiltration is enhanced by the soil water potential (suction), therefore more Cl$^-$ was retained in the surface of the sandy soil than in the surface of the sandy-loam soil, because suction of the sandy-loam soil was lower than that of a sandy soil at similar gravimetric soil water content. Cattle slurry particles $>1$ mm were probably deposited on the soil surface. The particulate DM on the soil surface may retain slurry liquid (Petersen & Andersen 1996; Sommer et al. 2003); therefore cattle slurry with a large fraction of particles $>1$ mm infiltrated less deep than pig slurry, in consequence Cl$^-$ applied to the soil in cattle slurry infiltrated less deeply into the soil than pig slurry (Fig. 3). TAN, in contrast to Cl$^-$, is adsorbed to negative charges in the soil (CEC) and to slurry DM (Fleisher et al. 1987; Sommer et al. 2003); therefore TAN infiltrates to greater depths in the sandy soil with a low CEC than in the sandy-loam soil with a high CEC. The large particles deposited on the soil surface retain water and have an adsorption capacity, thus increasing amounts of TAN are retained in the top layer at increasing DM content of the slurry. High contents of small particles in the slurry enhanced infiltration of TAN: this may be an effect of TAN being adsorbed to the small particles subjected to colloidal transport into the soil. NH$_3$ volatilization is related to TAN in the slurry surface (Sommer & Olesen 2000), and infiltration reduces surface TAN. The present study indicates that important parameters for TAN infiltration algorithms may be slurry DM and particle size distribution of the slurry DM.

Animal slurry is anaerobically digested in biogas plants with the purpose of producing energy. Further, slurry may be separated into a solid and a liquid fraction to enhance transport of plant nutrients in slurry and thereby improve parity between crop demand and addition of plant nutrients in manure. A reduction in NH$_3$ emission from animal slurry applied to crops is a positive side-effect of these treatments, which does not increase treatment costs. Separation of animal slurry reduced NH$_3$ volatilization in contrast to anaerobic digestion that increased NH$_3$ volatilization.

There are a number of important conclusions from the current work. Ammonia volatilization was related to slurry and soil type, infiltration of slurry liquid and particle size distribution. The infiltration of slurry liquid was related to soil type and slurry DM particle size distribution. Liquid from cattle slurry with large particles infiltrated less deeply than pig slurry. The present study indicates that infiltration of TAN is enhanced by colloidal transport of TAN adsorbed to small DM particles ($<0.025$ mm). Liquid from the slurry infiltrates more deeply into a sandy-loam soil adjusted at lower soil water potential than a sandy soil, but adsorption of TAN to soil and to slurry particles retained on the soil surface significantly reduces TAN infiltration into sandy-loam soils. It is proposed that modelling NH$_3$ volatilization from applied slurry may be improved by including algorithms calculating the effect of these variables.
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