Ammonia volatilisation from livestock slurries and mineral fertilizers

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Nitrogen, Phosphorus and Oxygen NPO-decade

(Overgård 1982; Sommer 1982)

- Nitrate bomb
- Blue babies
- NPO was the front runner of the Action Plan for the Aquatic Environment I to III (APAE-I-III, Vandmiljøhandlingsplaner).
Ammonium in rainwater (Sommer, 1984 & 2013). Idea for this work was provided by Eivind Hansen, Head of Centre for Terrestrial Ecology

- Acidification and eutrophication of natural ecosystems
- Airborne particulates that is a hazard
- UN have included NH3 in the Convention on Long-range Transboundary Air Pollution
- EU has set a limit – the NH3 ceiling – to the emission of NH3

![Graph showing deposition of N, kg N ha⁻¹ over years from 1920 to 1980. The graph indicates an increase in deposition over time, with red dots representing Ammonium and blue dots representing Nitrate.](image-url)
Example of EU regulations the Gothenborg protocol deals with ammonia

- Reduced NH₃ emission from 1990 to 2010, in pct. of emission in 1990
- Reduction targets

Countries: Netherlands, Belgium, Portugal, United Kingdom, Germany, Sweden, Austria
Ammonia emission - processes

From:
• Stored slurry
• Slurry applied in the field
• Mineral fertilizer in the field

They have the release and emission processes in common

\[
[TAN] = [\text{NH}_4^+ (aq)] + [\text{NH}_3 (aq)]
\]

\[
\text{NH}_3 (aq) = \frac{TAN(aq)}{1 + (H_3O^+ / K_N (Temp))}
\]
Understanding the system, slurry applied onto soil

\[ \text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) \uparrow + \text{H}_3\text{O}^+(aq) \]
Slurry applied onto soil
(*Sherlock, Sommer, Khan, Wood, Guertal, Freney, Dawson and Cameron, 2002; Sommer, Olesen and Christensen, 1991*)

- **Emission rate, kg NH$_3$-N h$^{-1}$**

  - Hours: $0, 48, 96, 144, 192$

- **Cumulated NH$_3$-emission, % of TAN**

  - Cumulated NH$_3$-emission from 0 to 192 hours

- **Surface pH**

  - Surface pH values from 7.4 to 8.8

- **NH$_3$(g)** and **CO$_2$(g)**

  - Atmosphere

  - Stagnant air interfacial layer

  - Stagnant liquid surface layer

  - Reactions:
    
    - $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(\text{aq}) \uparrow + \text{H}_3\text{O}^+(\text{aq})$
    
    - $\text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{CO}_2(\text{aq}) \uparrow + 2\text{H}_2\text{O}(l)$
The pH buffer system of animal slurry and anaerobic digested slurry

(Sommer and Husted, 1995)

\[
\text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \rightleftharpoons \text{CO}_2(aq) + 2\text{H}_2\text{O}(l)
\]

\[
\text{R} - \text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{RCOO}^-(aq) + \text{H}_3\text{O}^+(aq)
\]

Pig slurry

Buffer capacity, (meq L\(^{-1}\)) pH\(^{-1}\)

\[
\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)
\]
Electric charge of organic matter - particles
(Sommer and Husted, 1995)

**TAL**: Total Alkalinity is the amount of equivalents of hydrons (H⁺(aq)) that has to be added to the biomass to reduce pH to 4.5.
The negative charged particles may explain the low emissions after 24-48 h – i.e. only 15-20% of the TAN is lost.
Organic matter (Dry matter) in slurry may also reduce infiltration of slurry liquid containing TAN

(Sommer and Olesen, 1991)
Dry matter (DM) is an indicator of reduced liquid infiltration

*(Thygesen, Triolo and Sommer, 2012)*

- High viscosity
- Seal soil surface
- Increase water retention

\[ F(x) = 1.82 \cdot e^{0.606 \cdot x} \]

\[ R^2 = 0.83 \]
NH$_3$ volatilisation vs. infiltration
*(Sommer and Jacobsen, 1999)*

**NH$_3$ volatilisation**

- **Bromide infiltration**
  - Bromide, mg Br$^-$ kg$^{-1}$ (dry soil)
  - Depth, cm
- **TAN (NH$_3$+NH$_4^+$)** infiltration
  - TAN, mg TAN$^-$ kg$^{-1}$ (dry soil)
  - Depth, cm
- **NH$_3$ volatilisation**
  - NH$_3$, NH$_3$% of TAN
  - Time from start of experiment, h
  - Water content: 0.01, 0.12, 0.19 g(H$_2$O) g$^{-1}$ (soil)
Empirical emission model
(Sherlock, Freney, Bacon and van der Weerden, 1995; Sommer, Søgaard, Møller and Morsing, 2001)

\[ F = K \times u \times (\text{NH}_3, G - \text{NH}_3, A) \]

- **Wind** \((u)\) speed at 1 m above source
- **K** dependent on surface characteristic (Here bare soil)
- **Air temperature**
- **TAN** and **pH** in source surface

\[
\left[ \text{NH}_3, G \right] = \frac{1}{H} \cdot \frac{[\text{TAN}(\text{aq})]}{1 + [\text{H}_3\text{O}^+]/K_N}
\]
Atmospheric transfer model

\( (Olesen \text{ and Sommer, 1993}) \)

\[ F_A = \frac{1}{R_a + R_b + R_c} \cdot ([NH_3,g] - [NH_3,a]) \]

- \( R_a \): Turbulent air resistance
- \( R_b \): Laminar air layer resistance
- \( R_c \): Surface layer resistance

\[ R_a(x, t) = \frac{\ln \left( \frac{l}{z_0} \right)}{\kappa \cdot u_*(t)} \]
- \( l \): height of the internal boundary layer
- \( z_0 \): roughness length of the surface
- \( U_* \): friction velocity

\[ R_b = 6.2 \cdot u_*^{-0.67} \]

\( R_c \): measured resistance
Atmospheric emission model

(Olesen and Sommer, 1993)

\[ R_a = 18 \text{ s m}^{-1}; \text{ at } 8 \text{ m s}^{-1} \]
\[ R_a = 71 \text{ s m}^{-1}; \text{ at } 2 \text{ m s}^{-1} \]
\[ R_b = 9 \text{ s m}^{-1}; \text{ at } 8 \text{ m s}^{-1} \]
\[ R_b = 22 \text{ s m}^{-1}; \text{ at } 2 \text{ m s}^{-1} \]
\[ R_c = 10 - 230 \text{ s m}^{-1}; \]

\( R_c \) Manure store
- Uncovered: \( R_c = 18 \text{ s m}^{-1} \)
- Surface crust: \( R_c = 118 \text{ s m}^{-1} \)

\( R_c \) Fertilizer or manure in field
- Bare soil vs. high plants: \( R_c = 10 - 230 \text{ s m}^{-1} \)
Micrometeorological transfer model slurry store

(Sommer, Sibbesen, Nielsen, Schjøerring and Olesen, 1996)

Data
- Initial bulk TAN and pH
- Hourly climate data, air temperature and wind speed
- Diffusion/convection transport of TAN in slurry
- Rc set to =0

Assumed that effect of distance from slurry surface to rim of the tank may improve model performance?
Trail hose application of slurry

(*Thorman, Hansen, Misselbrook and Sommer, 2008*)

![Image of slurry application equipment and diagram showing emission relative to uncropped, pct with equation F(x)=-1.1+91.4x, r²=0.73.](image-url)
Effect of increasing infiltration – harrowing the soil before slurry application

(Sommer and Ersbøll, 1994)
Direct injection of slurry applied in field

(Hansen, Sommer and Madsen, 2003)
Acidification of slurry

(Kai, Pedersen, Jensen, Hansen and Sommer, 2008)

**Slurry storage**

- Whole year 12 mth.
- Winter 6 mth.

**Slurry applied in the field**

- Nitrogen loss, % of total N
- NH$_3$ emission, % of ammonium

Graph shows the comparison between untreated and acidified slurry in terms of nitrogen loss and ammonia emission.
Factors affecting ammonia loss – The ALFAM model  
(Søgaard, Sommer, Hutchings, Huijsmans, Bussink and Nicholson, 2002)

<table>
<thead>
<tr>
<th>Experimental factor</th>
<th>Effect on $\text{NH}_3$ volatilisation</th>
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<tbody>
<tr>
<td>Soil moisture</td>
<td>Wet soil 10% higher than dry soil</td>
</tr>
<tr>
<td>Air temperature</td>
<td>+2% per °C</td>
</tr>
<tr>
<td>Wind speed</td>
<td>+4% per m/sec</td>
</tr>
<tr>
<td>Slurry type</td>
<td>Pig slurry 14% less than cattle slurry</td>
</tr>
<tr>
<td>Dry matter content</td>
<td>+11% per % DM</td>
</tr>
<tr>
<td>TAN content</td>
<td>Positive</td>
</tr>
<tr>
<td>Manure incorp.</td>
<td>No incorp. 11 times higher than shallow cult. and injection</td>
</tr>
</tbody>
</table>

Link: WWW.ALFAM.dk
The ALFAM model – Validation

(Søgaard, Sommer, Hutchings, Huijsmans, Bussink and Nicholson, 2002)

Observed NH₃ volatilization, pct.

Predicted NH₃ volatilization, pct.

trail hose

Injection

r² = 0.596
Conclusion

• Efficient techniques to reduce emission are developed and in use
• Models estimating ammonia emission from stored and applied manure should be developed accounting for the environmental condition, manure characteristics, management and treatment
• We need to improve our understanding “source” surface pH

Perspective

• Animal production is increasing and production systems changes without adapting manure management. This lead to increased pollution – which has to be reduced by developing environmentally friendly manure management.