Contents

• Processes
• Model results
• Conclusions
Definitions

$\text{NH}_3$ (ammonia): gas

$\text{NH}_4^+$ (ammonium): found in particles

$\text{NH}_x = \text{NH}_3$ (ammonia) + $\text{NH}_4^+$ (ammonium)
Modelling = book keeping

During transport:
\[ \frac{dc}{dt} = \text{emission} - \text{deposition} +/\text{- reaction} \]
Emission
EMISSION-1

- No $\text{NH}_4^+$ emitted: all $\text{NH}_4^+$ has once been $\text{NH}_3$.
- Many scattered sources with low emission height.
- Partly influenced by meteorological conditions (that also influence deposition and atmospheric diffusion).
- Many different agricultural systems. Often no information on the distribution of different housing types, manure handling systems etc.

$\rightarrow$ The emission per animal is NOT the same everywhere!
EMISSION-2

For models emission rate needed:
• On a regular grid.
• With a temporal (diurnal/seasonal) resolution.
• Preferably: indication of uncertainty.

For administrators:
The emission calculations should be set up in such a way that scenarios for abatement and associated costs can be studied.
Seasonal variation Netherlands 1990
From ratio measured value/ modelled value with constant emission rate

![Graph showing seasonal variation of NH₄ aerosol and NHₓ precip. with function variation.](image-url)
EMISSION-3

Europe: try to get funding for a project that will make it possible to generate the NH$_3$ emission rate for use in atmospheric transport models.

It will include:

- Spatial distribution of agricultural systems and soil properties.
- Parameterizations for different agricultural systems.
- Dependence on the same meteorology as used in atmospheric transport model.
EMISSION-4

Co-dependence of emission, transport and dry deposition on meteorology:

At high wind speed:

- Higher $\text{NH}_3$ emission rate
- $\text{NH}_x$ deposited further away
Modelling emission after slurry application (Génermont and Cellier, INRA, France)
Reaction
Important types of reaction

One-way reaction:

\[ \text{NH}_3 + \text{H}_2\text{SO}_4 \text{ in particle} \rightarrow \text{NH}_4^+ \text{ in particle.} \]
No NH\(_3\) bound in this way can volatilise.

Two way reaction:

\[ \text{NH}_3 + \text{HNO}_3 \text{ (gas)} \leftrightarrow \text{NH}_4\text{NO}_3 \text{ containing particle} \]
\[ \text{NH}_3 + \text{HCl} \text{ (gas)} \leftrightarrow \text{NH}_4\text{Cl} \text{ containing particle} \]
NH\(_3\) can volatilise again (depending on temp., humidity, concentrations).

Remarks:

- Reaction with OH radical not so important.
- Europe: 10-30\% hour\(^{-1}\) decrease in NH\(_3\) conc.
Dry deposition $\text{NH}_3$
Dry deposition velocity ammonia

- Relatively high; diurnal variation (meteo).
- Vegetation: most ammonia not taken up by stomata, but deposited on wet leaves.
- A concentration is present in the surface (compensation point): flux depends not only on concentration in air, but also on concentration in surface:
  \[ F = -v_e (c_{\text{air}} - c_{\text{surface}}) \]
  
  \[ c_{\text{surface}} \] important for vegetation (crops), sea (can lead to emission).
- Depends on wind speed/atmospheric stability and wetness surface.
Models for dry deposition/exchange

\[ r_a = \text{aerodynamic resistance} \]

\[ r_b = \text{laminar boundary layer resistance} \]

\[ r_c = \text{surface resistance} \]

\[ r_{cut} = \text{cuticular resistance} \]

\[ r_{st} = \text{stomatal resistance} \]
Dry deposition of NH\textsubscript{3} is high close to sources, why?

• Concentrations are high, because low source height and plume is not yet diluted.

• Dry deposition velocity of NH\textsubscript{3} is relatively high.
Measured average $\text{NH}_3$ conc. vs. downwind distance east of a poultry farm (Fowler et al., 1998)
Fraction of emission dry deposited vs. distance

Source height: 3 m; neutral atmosphere; $u(60) = 4.8 \text{ m s}^{-1}$
Dry deposition ammonia

• Once it is vertically diluted (no large vertical gradient): removal rate is of the order of 1% h\(^{-1}\)
Dry deposition $\text{NH}_4^+$ (particles)
Dry deposition velocity ammonium containing particles

- Dry deposition velocity depends on particle size, humidity, wind speed and atmospheric stability
- Mostly not re-emitted after deposition
- If no vertical conc. gradient: removal rate of the order of 0.1% h\(^{-1}\)
Comparison:
Dry deposition NH$_3$ vs. NH$_4^+$
Dry deposition velocity $\text{NH}_3$ vs. $\text{NH}_4^+$

- $V_d$ at 5 m over sea/vegetation (m s$^{-1}$)

- Wind speed at 60 m over ground level (m s$^{-1}$)

- $\text{NH}_3$: high vegetation

- $\text{NH}_4^+$: high vegetation
Dry deposition velocity $\text{NH}_3$ vs. $\text{NH}_4^+$
Dry deposition velocity $\text{NH}_3$ vs. $\text{NH}_4^+$

$V_d$ at 5 m over sea/vegetation (m s$^{-1}$)

wind speed at 60 m over ground level (m s$^{-1}$)
Dry deposition velocity $\text{NH}_3$ vs. $\text{NH}_4^+$

$V_d$ at 5 m over sea/vegetation (m s$^{-1}$)

wind speed at 60 m over ground level (m s$^{-1}$)
Effect of limited vertical resolution in model:
Fraction emission dry deposited vs. distance

Fraction of emission deposited vs. downwind distance (km)

- NH$_3$
- NH$_4$
- NH$_3$
- NH$_4$

real situation 40 m layers
Dry deposition: additional conclusions

• A high vertical resolution is needed to model dry deposition NH$_3$ close to sources; or a correction factor.

• The dry deposition velocity of NH$_4^+$ << NH$_3$.

• Once NH$_3$ is converted to NH$_4^+$ it can travel over long distances (only removal by precipitation is an efficient mechanism).

• Local NH$_3$ sources can dominate local NH$_x$ deposition, but most emitted NH$_3$ travels as NH$_4^+$ over long distances!!!
Vertical concentration profiles of $\text{NH}_3$ and $\text{NH}_4^+$ in an area with high emission density.
Area with high emission density

- $\text{NH}_3$
- $\text{NH}_4$
Wet deposition of \( \text{NH}_3 \) and \( \text{NH}_4^+ \)
Wet deposition

in-cloud scavenging of ammonia and ammonium

below-cloud scavenging of ammonia and ammonium
<table>
<thead>
<tr>
<th>Process</th>
<th>Efficiency</th>
<th>Importance (efficiency*conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• in-cloud sc.</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>• below-cloud sc.</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>Ammonium</td>
<td></td>
<td></td>
</tr>
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</tr>
<tr>
<td>• below-cloud sc.</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Notes:

• *Importance for concentration in precipitation depends on airborne concentration.*
• *Ammonia conc. is low at cloud-level*
Wet deposition: Conclusions

- Cloud and raindrops are acidic. Therefore all NH$_3$ taken up by them is converted to NH$_4^+$
- Only models can calculate contributions of different processes to the NH$_4^+$ conc. in precipitation
- Most NH$_4^+$ in precipitation originates from in-cloud scavenging of NH$_4^+$ containing particles
- Removal due to in-cloud-scavenging is fast (order: 75% h$^{-1}$), but it rains only 5-10% of the time in NW Europe
Model results
Fate of ammonia emissions (whole lifetime)

Width of the arrows is measure of importance

NW Europe 1990; Calculated with TREND model
Cumulative deposition as a function of downwind distance (NW Europe, 1990)

- Dry $NH_3$
- Dry $NH_4$
- Wet $NH_3$
- Wet $NH_4$
- Total $NH_x$

Fraction deposited vs. downwind distance (m)
Ammonia emission Denmark (kg N ha\(^{-1}\) yr\(^{-1}\))
NH₃ conc.

ground-level

Resolution 5x5 km²
NH$_x$ wet deposition

Resolution
5x5 km$^2$
NH$_x$ total deposition (dry+wet)

In this area dry dep. of NH$_3$ dominates

Resolution 5x5 km$^2$
Ammonia emission Denmark (kg N ha\(^{-1}\) yr\(^{-1}\))

Horizontal gradient

Sea
Concentrations and depositions across Denmark
Modelled vs measured NH$_3$ conc.

Resolution

5x5 km$^2$
Modelled vs measured NH$_4^+$ conc.

Resolution

5x5 km$^2$
Modelled vs measured NH$_x$ wet deposition

Resolution

5x5 km$^2$
\( \text{NH}_3 \) conc. vs. \( \text{NH}_3 \) emission density (5x5 km\(^2\))

\[
\begin{align*}
\text{\( >90\% \) \ farmland} & & \text{\( <90\% \) \ farmland} \\
\end{align*}
\]
Ratio
dry/ total deposition

Close to areas with high emission density:
dry deposition dominates
NH₃: meas. vs. modelled conc. Netherlands with different model resolution

5x5 km²

75x75 km²
NH$_3$: meas. vs. modelled conc. Netherlands with different model resolution

5x5 km$^2$  
150x150 km$^2$
Ammonia emission (all sources)

NH$_3$ emission from all sources

Europe
Ammonia emission Europe (kg N ha\(^{-1}\) yr \(^{-1}\))

Denmark
Ammonia emission Denmark (kg N ha\(^{-1}\) yr\(^{-1}\))
Ammonia emission part of Vejle County

Resolution: 100x100 m²

Map made by Bernd Münier
Total N deposition part of Vejle county (from all European NH3 and NOx sources)

Transport model runs within GIS system

Resolution: 100x100 m²

Map drawn by Bernd Münier
Purpose

atmospheric transport models
Models can have different purposes

- Size of the area to be modelled (local effect of one farm or distribution of particles over the whole U.S.)
- Time scale: episodes or annual averages.
- Compound to be modelled (e.g. $\text{NH}_x$ deposition or fine particle concentration).

All these factors have influence on the spatial and temporal resolution of the model results and input data needed.
Is there one model that can describe all situations?
No. Computers have limited resources (speed, memory).
What to do then?
Optimize the model design for the required purpose:
• Adapt to spatial/temporal resolution.
• Describe some processes in detail, and others more generally.
Conclusions NH$_x$ modelling
NW Europe
Conclusions-1

NH$_x$ mainly deposited as:

- Dry deposition of NH$_3$ close to the source.
- Wet deposition due to in-cloud scavenging of NH$_4^+$ further away from the source.

The NH$_4^+$ particle conc.

- Originates mainly from distant sources, but not in coastal areas with dominant wind from the sea.
Conclusions-2

Model resolution:

*Deposition modelling* in areas with high NH$_3$ emission densities:

- high spatial resolution ($>1 \times 1 \text{ km}^2$) is needed to adequately model the large horizontal gradients.

*Deposition modelling in other areas and particle formation modelling:*

- High resolution not necessary, but correct modelling of dry dep. of ammonia near source still needed.
Conclusions-3: Examples of model types

Local modelling:

• High vertical resolution (plume dilution).
• High horizontal resolution.
• Limited chemistry.

Regional modelling:

• Limited horizontal and vertical resolution.
• Correction factor local NH$_3$ deposition.
• More complicated (photo)chemistry.
End
Diurnal variation Netherlands
Dry deposition velocity ammonium containing particles: **Sea** (continued)

\[ r_a = \text{aerodynamic resistance} \]
\[ r_b = \text{laminar boundary layer resistance} \]
\[ r_{vgd} = \text{resistance gravitational settling dry particles} \]
\[ r_{vgw} = \text{resistance gravitational settling wet particles} \]
Link emission <-> conc./deposition
Netherlands 1994-1997:
• Abatement: estimated 35% emission reduction
• No detectable trend measured ammonia conc.
• 10% reduction in measured ammonium wet deposition (model estimate:
• 29% reduction in measured ammonium aerosol concentration
Why?
• Maybe influence from parallel trends in sulphur dioxide and nitrogen oxides emission
• Maybe abatement not so effective as estimated
Link between ammonia emission changes and measured conc./depositions
Rothamsted, UK; line = modelled with hist. emission
Generation of emission as a function of time and space:

Use geographical distribution of:

- Number of animals, fodder, housing, storage, application techniques, grazing, use of fertilisers, soil properties, regulations

But:

Generate then the emission with a preprocessor or in the transport model, using process descriptions that are functions of the meteorological conditions.
Why?
Because the emission, diffusion and dry deposition depend on the same meteorological conditions.
Result: Higher wind speed => then more emission which is deposited further away.

Disadvantage for policymakers:
Emission shows interannual variations already due to variations in the meteorological conditions (if all other factors are the same).
Annually average dry NH$_x$ deposition vs. distance: as a function of the wind direction up to a factor of 5 difference!
Variation of dry deposition with wind speed

Ratio dry dep. at 2 m s\(^{-1}\)/4 m s\(^{-1}\) \( (r_c = 60 \text{ s m}^{-1}) \)
Variation dry deposition with dry deposition velocity $v_d$

ratio dry dep. at $v_d=0.0254/0.0127 \text{ m s}^{-1}$

![Graph showing variation in dry deposition ratio with downwind distance](image)
Vertical concentration profiles at two different dry deposition velocities

Distance from source: 200 m

\( v_d = 0.0127 \text{ m s}^{-1} \)  
\( v_d = 0.0254 \text{ m s}^{-1} \)
Variation of dry deposition with surface resistance $r_c$

ratio dry dep. at various $r_c$ vs. at $r_c = 60 \text{ s m}^{-1}$
Variation dry deposition with source height ratio dry dep. at 1 m/6 m \( (r_c = 60 \text{ s m}^{-1}) \)
Fraction of emission dry deposited vs. distance

roughness length (m)

- 0.025 (grass)
- 0.1 (wheat)
- 1.0 (forest)

Source height: 3 m; neutral atmosphere; $u(60) = 4.8 \text{ m s}^{-1}$
Vertical NH$_3$ flux as function of the distance to a farm with 500 pigs and influence of compensation point

compensation point (µg NH$_3$ m$^{-3}$)

0 1 2 5 10

flux (µg NH$_3$ m$^{-2}$ s$^{-1}$)

Emission

Deposition

x(m)
NH₃ flux North Sea found from measured concentrations

Emission

Deposition

[Graph showing monthly emission and deposition fluxes with bar charts for March to September, including sample numbers CH47 to CH61, with a peak off scale for August.]
Moorland-experiment
Measured horizontal NH$_3$ gradient

- Emission area
- Nature reserve

Concentration (µg NH$_3$ m$^{-3}$)

Distance from emission area (m)

Wind direction
Modelled horizontal NH$_3$ gradient (with different model options)
Measured vs. Modelled NH$_3$ conc.
Vertical NH$_3$ profiles in emission area (--) and nature area (- - -)
**NH₃ vs. NOₓ**

How large is the *global* emission of ammonia compared to that of nitrogen oxides (NO + NO₂)?

<table>
<thead>
<tr>
<th>Compound</th>
<th>tonnes N yr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>53.7×10⁶</td>
</tr>
<tr>
<td>Nitrogen oxides</td>
<td>41.8×10⁶</td>
</tr>
</tbody>
</table>

**Conclusion:**

Same order, but a larger fraction of ammonia comes from anthropogenic sources.
Geographical distribution global emission

The scale is the *same in all figures*!
Ammonia emission from fertiliser

NH₃ emission (g N m⁻² yr⁻¹)

0 - 0.05
0.05 - 0.1
0.1 - 0.5
0.5 - 1
1 - 2
2 - 3
> 3

NH₃ emission from synthetic fertilizer use
Ammonia emission from biomass burning

(deforestation, savanna burning, agr. waste burning)
Ammonia emission (all sources)

NH$_3$ emission from all sources

NH$_3$ emission (g N m$^{-2}$ yr$^{-1}$)

- 0.05
- 0.1
- 0.5
- 1
- 2
- 3
> 3
NH₃ conc. (µg NH₃ m⁻³)
NH₄ conc. (µg NH₄ m⁻³)
NH$_x$ dry deposition (mol ha$^{-1}$ yr$^{-1}$)

100 mol = 1.4 kg N
NH$_x$ wet deposition (mol ha$^{-1}$ yr$^{-1}$)

100 mol = 1.4 kg N
NH$_x$ total Deposition (wet + dry) (mol ha$^{-1}$ yr$^{-1}$)

100 mol = 1.4 kg N
Ratio
dry/ total deposition
NH$_x$ deposition
Kattegat sea area
(\text{kg N km}^{-2} \text{ yr}^{-1})
NO$_y$ deposition
Kattegat sea area
(\(\text{kg N km}^{-2} \text{ yr}^{-1}\))