
Toward a climate-dependent paradigm of ammonia emission & deposition

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Supplementary on-line material

S1 Spatial pattern of ammonia emissions and dominant sources in the UK.

Figure S1: Spatial variability in UK ammonia emissions based on Hellsten et al. (2008). A source type is labelled as dominant where it accounts for >45% of total emission; areas with annual emission <1 kg N ha⁻¹ are labelled ‘background’.
The spatial patterns of \( \text{NH}_3 \) sources in the UK are illustrated in Figure S1. The detailed sector breakdown for the UK shows how emissions from cattle dominate in the west of the country, with emissions from sheep dominating on less fertile uplands. In the east of the country, fertilizer/crop emissions form a background on which peak \( \text{NH}_3 \) emissions from clusters of large pig and poultry farms are superimposed. In the remote north west, apart from hotspots associated with seabird colonies (Wilson et al., 2004), emissions are mostly <1 kg N ha\(^{-1}\) yr\(^{-1}\).

**S2 Surface concentration and resistance controls on \( \text{NH}_3 \) bi-directional exchange**

![Figure S2](image)

*Figure S2*: Two views of the factors limiting \( \text{NH}_3 \) exchange, illustrated for upland moorland. Relationships of the canopy temperature with (A) the canopy surface concentration \( (\chi_{zo'}) \), where \( \Gamma = [\text{NH}_4^+]/[\text{H}^+] = 135 \), and (B) the bulk canopy resistance \( (R_c) \). The latter is only applicable for deposition fluxes, since it assumes zero surface concentration (from Flechard and Fowler, 1998). \( p_{\text{NH}_3} \) here is the theoretical \( \text{NH}_3 \) concentration according to the thermodynamic dependence fitted to the full dataset.
Figure S3: Environmental controls on NH$_3$ exchange: A) Dependence of the cuticular uptake resistance on canopy relative humidity ($h(z_0^{'})$) and vapour pressured deficit ($VPD(z_0^{'})$); B) air concentrations for events when the flux changed sign in relation to temperature (modified from Nemitz et al., 2004). The lines in B) represent least-square fits to the data according to the theoretical thermodynamic temperature dependence.

S3. Empirical approaches to simulating the climate dependence and timing of ammonia emissions from animal housing, manure storage and manure spreading

Research within the Danish Air Quality Monitoring programme has focused on reducing the uncertainty of NH$_3$ emissions in grid based models, for which empirical approaches have been used to disaggregate annual emissions temporally. In this context, Skjøth et al. (2004) found that temperature and windspeed (and hence building ventilation) were the most important environmental variables affecting emissions from animal buildings. For this purpose, where the source is active through the year, they estimated NH$_3$ emission from animal buildings at a given time ($E_t$) as:

$$E_t = C T_b^{0.89} V_b^{0.26}$$  \(\text{(S1)}\)

where $C$ is a constant based on the annual emission (a function of animal numbers and overall environmental conditions), $T_b$ is the temperature inside the buildings ($^\circ$C) and $V_b$ is the building ventilation rate. Parameterizations for $T_b$ and $V_b$ in relation to external conditions are given by Gyldenkærne et al. (2005). The parameterization applies above a building temperatures of 5 $^\circ$C, with $Q_{10}$ decreasing from 7.7 at 5 $^\circ$C to 1.3 at 35 $^\circ$C (mean $Q_{10}$ of 2).

A further modelling challenge is to distribute short-term emission events from manure spreading to fields over a longer temporal duration for incorporation in upscaled CTMs. To address this, Skjøth et al. (2004) and Gyldenkærne et al. (2005) applied a Gaussian distribution using the empirical temperature dependency of the ALFAM regression model (Søgaard et al.,
On this basis, they estimated the annual emission from short-term emissions \( E_i \) as a function of time \( (t) \), windspeed \( (u) \) and air temperature \( (T_a) \):

\[
E_i(t, W, T) = E_i \cdot \exp^{0.0237T_a} \cdot \exp^{0.0419u} \cdot \frac{1}{\sigma \sqrt{2\pi}} \cdot \exp \left[ \frac{-(t-\mu)^2}{2\sigma^2} \right]
\]

where the constants \( \mu \) and \( \sigma \) are values that determines the timing and duration of the short term activities (Gyldenkærne et al., 2005), which can be modified to fit local conditions and manure spreading regulations. These authors found that spring and autumn applications of manure to fields are linked to the timing of crop growth and harvest, and can be simulated using a combination fixed national values for \( \sigma \) and a spatial explicit crop growth model for \( \mu \) (Skjøth et al., 2004, 2011). A similar empirical approach has been applied by Skjøth and Geels (2012) to simulate the regional effect of future temperature scenarios on NH\(_3\) emissions from manure stores.

### S4. Seasonality of ammonia columns at different global locations

Retrievals from the IASI satellite were processed to examine the seasonal variability in estimated NH\(_3\) columns at different world locations characterized by contrasting dominant sources (Figure 2). The processed estimates are shown in Figure S4 for six locations including ground surface temperature and the regression relationship for the annual dataset with temperature.

Belgium and the Po Valley are both locations where NH\(_3\) emissions are strongly dominated by livestock sources, in north west and south central Europe, respectively. In the Delta area of the River Nile, NH\(_3\) emissions are aslo high, but dominated by field sources including spreading of fertilizers and livestock manures (Figure S4). In both the Po Valley and Nile Delta a strong seasonal cycle in NH\(_3\) columns is observed, while a much less clear seasonal cycle is seen for Belgium, with stronger spring peaks probably linked to spreading of animal manure. Strong seasonal cycles, with higher NH\(_3\) concentrations in warm conditions are seen in the USA Californian Central Valley (dominated intensive cropping and livestock farming) and in Parkistan (high density smallholder agriculture). By contrast, in a livestock-dominated area of eastern China, a weaker relationship with temperature is seen, including a peak NH\(_3\) concentration in February 2011. While these patterns of seasonality and in relationship to temperature require further exploration, it may be noted that the uncertainties in the monthly NH\(_3\) column estimates are highest for the Belgian and Chinese locations, while the locations with the smallest relative errors showed the closest relationship between NH\(_3\) levels and surface temperature. Short term snap-shots e.g. June 2011, did not show such a clear temperature dependence, which can be related to the coupling between temperature (increasing the NH\(_3\) column) and thermal mixing (diluting the column).
Figure S4. Variation in the relationship between NH$_3$ column concentrations with seasonality and ground temperature for six example world locations. (Error bars are standard deviations of monthly averaged daily values for surrounding 1 x 1 degree area)
S5. Further description of the GUANO model

The GUANO model (Generation of emissions from Uric Acid Nitrogen Outputs) has been developed by Blackall (2004) and Riddick (2012) as a process based description of NH₃ emissions from seabird colonies. The general principles, however, are applicable to any surface-based source of ammonia volatilization from excreted nitrogen.

The model is run for each seabird colony, considering bird species, population, nesting habitat and meteorological data. A bioenergetics model developed by Wilson et al. (2004) is used to calculate nitrogen excretion per breeding pair of seabirds, including corrections for the number of non-breeding adults and growth of chicks. Fresh excreta deposited in the bird colony contains both guano solids, including uric acid nitrogen, and water, which provide the starting point of the model. Calculation of the energy balance, including evaporation and inputs from precipitation allows calculation of the guano water volume and run-off (Figure S5). The rate of uric acid hydrolysis to Total Ammoniacal Nitrogen (TAN) is described empirically as a function of water volume (for moist conditions) and relative humidity (for dry conditions). Estimates of guano water volume combined with the total TAN content and estimate guano pH allow calculation of the surface NH₃ concentration, $\chi(z_0)$, from which the flux is calculated according to eq. (1) using a reference height for $R_a$ of 10 m. Given that $\chi(z_0) \gg \chi(10 \text{ m})$, the assumption that $\chi(10 \text{ m}) = 0$ has minimal effect on the calculated fluxes.

The model is set up to run on a hourly timestep, either through experimental campaigns (for comparison with measurements) or through several years (for global upscaling).

**Figure S5:** Summary structure of the GUANO model. TAN is total ammoniacal nitrogen.
S6. Seasonality of ammonia emissions in the OML model.

In the Danish modelling system (e.g., Gyldenkærne et al., 2005; Skjøth et al., 2008, Geels et al., 2012; Hertel et al., 2012) management, temperature and windspeed factors have been applied empirically to estimate the temporal distribution of NH$_3$ emissions. In this approach, the environmental and management relationships have been used to apportion previously-estimated annual emission totals through the year. Changes in animal numbers and fertilizer use, combined with the implementation of emissions abatement policies have led to a general decrease in the annual emission totals, while the modelled seasonality reflects major features of the measurements, as illustrated in Figure S3. Over the period shown (1989 to 2003) policies were implemented to limit manure spreading during a winter ‘closed period’. This led to an increased fraction of manure being spread on fields during spring, which can be seen in the relatively larger peak NH$_3$ values from during spring from 1996 onwards.

![Figure S6: Comparison of modelled (pink symbols) and measured (blue symbols) NH3 concentrations at a Danish station (Tang), highlighting the strong seasonal variation and a broad ability of the ACDEP model to capture this seasonal variation.](image_url)

S7. Sub-grid variability in regional models of atmospheric ammonia.

A number of sub-grid problems remain unresolved in regional modelling of ammonia. Application of bi-directional models relies upon an accurate simulation of NH$_3$ concentrations and other conditions just above the surface, with the result that exchange over emission hot-spots is very different to exchange in cleaner areas (Loubet et al, 2009). European to global scale CTMs typically have grid sizes of around 20-100 km, and even national-scale models with 1-5 km resolution cannot resolve the strong spatial gradients occurring within the first 10-100 m around a strong source (Loubet et al., 2009, Simpson et al., 2012). Such unresolved vertical gradients in concentrations and temperature near the surface have important implications for partitioning in the NH$_3$-HNO$_3$-NH$_4$NO$_3$ system (e.g. Nemitz and Sutton, 2004) and bi-directional exchange. When using low resolution models, underestimation of ground-level atmospheric NH$_3$ concentrations near sources can propagate to an underestimation of dry deposition to surrounding ecosystems (Dore et al., 2012) and an overestimation of ecosystem NH$_3$ emissions where these are driven by compensation points (Vieno, 2005).

Sub-grid calculations with CTMs may be adopted to reduce such errors. For example, many CTMs already include so-called ‘mosaic approaches’ for calculating dry-deposition over different land-cover types within a grid square (e.g. Simpson et al., 2012). Application of a full chemical system with a sub-grid module using fine-vertical and horizontal resolution is a clear design challenge, which will become easier to tackle as increasing computer processing capabilities allow simulations on finer grid sizes.
S8. Temperature parameterization of NH₃ emissions for global climate scenarios

The combination of measurements and modelling described in this study demonstrate the complexity of the climate dependence of NH₃ emissions. For volatilization-based sources, which account for around 90% of the global emission (Table 1), temperature is the primary controller according to the Henry and dissociation equilibria for NH₃ and NH₄⁺ (eq. 3). However, the actual temperature dependence is modified in practice by several interactions; the most important is water availability, which favours urea and uric acid hydrolysis to NH₃ (promoting NH₃ emission), while allowing dissolution in water pools, plant uptake and run-off (all suppressing NH₃ emission) (see e.g. Génermont et al., 1998; Garcia et al. 2013; Zhu et al., 2011). Given the temporal competition between the different NHₓ removal processes from the surface (emission, run-off, soil and plant uptake), faster emission may also increase the total fraction emitted as NH₃, suggesting that windy and convective conditions (reducing $R_a$ and $R_b$) also tend to increase total emissions.

In agricultural contexts, management factors further complicate the climate dependence of NH₃ emission. As illustrated in the main text, these include the potential for warming-induced growth-dilution of plant N pools (Figure 6), interactions between temperature, water and soil infiltration rates of liquid manure, and the extent of climatic control inside animal houses.

At present, the only process-model of NH₃ volatilization that has been verified by a global programme of measurements across contrasting climates is the GUANO model (Figures 8, 9). This has shown that temperature is the primary driver of differences in NH₃ emission rates, followed secondly by effects of precipitation and water availability (Riddick, 2012).

Process models have not yet been constructed or verified to quantify the climate effect on global NH₃ emissions from the main volatilization sources. Until this becomes possible, it is appropriate for global atmospheric and biogeochemical models to explore the likely response of NH₃ emissions to climate change using empirical functions, considering the range of temperature sensitivity observed in measured fluxes.

The smallest temperature responses have been noted here for NH₃ emissions from cut and fertilized grassland and for the application of liquid manure to agricultural land ($Q_{10}$ 1.4-2). By contrast, the NH₃ emission potential of semi-natural vegetation (Figures 3 and 4) followed theoretical thermodynamics (eq. 3), with $Q_{10}$ of 3-4. An empirical response for manure stores provided a response with $Q_{10}$ in the region 2-3. For the seabird colonies, simulations with the GUANO model incorporated the thermodynamic $Q_{10}$ of 3-4, while being offset by other factors (water availability, windspeed), giving an effective $Q_{10}$ of ~3, as shown also in the measurements (Figure 8). Finally, NH₃ emissions from the ocean surface are expected directly to follow the thermodynamic $Q_{10}$ of 3-4 (Johnson et al., 2008).

Based on these data, a preliminary operational response for global modelling of the climate change feedback on NH₃ emissions would be:

- For ocean and other water surface NH₃ emissions: apply the thermodynamic response based on Henry’s Law and NH₄⁺ dissociation (eq. 3);
- For all land-based volatilization sources: apply a nominal $Q_{10}$ of 2(1.5–3), based on reduction of the thermodynamic response in practice;
- For biomass burning, industrial and other combustion based emissions: the effect of climate change remains uncertain. It is assumed that NH₃ emissions from these sources are unchanged, although there may be an affect for biomass burning.

Strictly, the thermodynamic $Q_{10}$ is not constant with temperature, but decreases from 4.1 at -5°C to 2.9 at 35°C. By modifying eq. (3), the following general function can be applied to estimate regional NH₃ emissions under a future mean temperature, $E(T_f)$:

$$E(T_f) = E(T_p) \exp^{\alpha(T_f - T_p)}$$  \hspace{1cm} (S3)

where $E(T_p)$ is the emission under the present mean temperature ($T_p$), both temperatures are expressed in Kelvin, and $\alpha$ is the temperature sensitivity factor. The values of $\alpha$ given in...
Table S1 match to mean $Q_{10}$ values for the range of -10 to +40 °C (mean 15 °C) of 1.5, 2, 3 and 3.4. The variation of $Q_{10}$ values with temperature is shown in Figure S1.

**Table S1:** Values of the temperature sensitivity factor for empirical exploration of ammonia emission sensitivity to future climate change scenarios.

<table>
<thead>
<tr>
<th>Situation</th>
<th>$\alpha$</th>
<th>Mean $Q_{10}$ over temperature range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terrestrial volatilization sources</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mid estimate</td>
<td>-5700</td>
<td>2.0</td>
</tr>
<tr>
<td>Low estimate</td>
<td>-3340</td>
<td>1.5</td>
</tr>
<tr>
<td>High estimate</td>
<td>-9030</td>
<td>3.0</td>
</tr>
<tr>
<td>Marine &amp; freshwater volatilization sources (thermodynamic response according to eq. 3)</td>
<td>-10380</td>
<td>3.4</td>
</tr>
</tbody>
</table>

![Figure S7: Variation in temperature dependence of regional NH$_3$ emissions according to four values of $\alpha$ (see Table S1) based on eq. S1. These equate to mean values of $Q_{10}$ across the range -10 to +40 °C of 2(1.5-3) for the empirical functions (mid, low, high) for terrestrial volatilization, and 3.4 for the thermodynamic response.](image)

**S9. Effect of temperature and activity changes on future global NH$_3$ emissions.**

The simple empirical relationships from Table S1 are applied in Table S2 to indicate of how climate change may increase NH$_3$ emissions by 2100. For this purpose, a mean temperature increase of 5 °C is assumed, while the possible offsetting effects of altered precipitation / wetness patterns are subsumed in the lower value of $\alpha$ applied for terrestrial than for marine sources.

Table S2 points to a potential increase in global NH$_3$ emissions in response to climate change for this scenario by 42% (28%-67%). In the absence of any other changes in anthropogenic activities, this would estimate global NH$_3$ emissions for 2100 at 93(84-109) Tg N yr$^{-1}$. This uncertainty range for the climate scenario may be combined with the estimated uncertainty in baseline global NH$_3$ emissions of ±30% (Section 2) using the square root of sum of squares in the relative errors. This gives an overall uncertainty in NH$_3$ emissions in 2100 (including the effect of 5 °C warming combined with 2008 activity statistics) of 93 (64-125) Tg N yr$^{-1}$. 

Reference: [Climate dependent ammonia](#)
Table S2: Estimated effect of climate warming on NH$_3$ emissions by 2100, assuming 2008 activity levels, according to a 5 ºC warming scenario. These figures do not include the baseline uncertainty in NH$_3$ emissions or the effect of future increases in anthropogenic activities (see text).

<table>
<thead>
<tr>
<th>Year</th>
<th>Excreta from domestic animals</th>
<th>Agricultural soils &amp; crops (inc fertilizer applic)</th>
<th>Biomass burning</th>
<th>Industrial &amp; fossil fuel burning</th>
<th>Human population &amp; pets</th>
<th>Waste composting &amp; processing</th>
<th>Soils under natural vegetation</th>
<th>Excreta from wild animals</th>
<th>Oceans</th>
<th>Volcanoes</th>
<th>Total</th>
<th>% increase from 2008</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>8</td>
<td>25.2</td>
<td>4.4</td>
<td>1.3</td>
<td>3</td>
<td>4</td>
<td>2.4</td>
<td>2.5</td>
<td>8.2</td>
<td>0.4</td>
<td>59.4</td>
<td>42%</td>
</tr>
<tr>
<td>2008</td>
<td>8.7</td>
<td>28.3</td>
<td>5.5</td>
<td>1.6</td>
<td>3.3</td>
<td>4.4</td>
<td>2.4</td>
<td>2.5</td>
<td>8.2</td>
<td>0.4</td>
<td>65.3</td>
<td>28%</td>
</tr>
<tr>
<td>Mid T sensitivity</td>
<td>12.3</td>
<td>40.0</td>
<td>5.5</td>
<td>1.6</td>
<td>4.7</td>
<td>6.2</td>
<td>3.4</td>
<td>3.5</td>
<td>15.2</td>
<td>0.6</td>
<td>93.0</td>
<td>67%</td>
</tr>
<tr>
<td>Low T sensitivity</td>
<td>10.7</td>
<td>34.7</td>
<td>5.5</td>
<td>1.6</td>
<td>4.0</td>
<td>5.4</td>
<td>2.9</td>
<td>3.1</td>
<td>15.2</td>
<td>0.6</td>
<td>83.6</td>
<td></td>
</tr>
<tr>
<td>High T sensitivity</td>
<td>15.1</td>
<td>49.0</td>
<td>5.5</td>
<td>1.6</td>
<td>5.7</td>
<td>7.6</td>
<td>4.2</td>
<td>4.3</td>
<td>15.2</td>
<td>0.6</td>
<td>108.8</td>
<td></td>
</tr>
</tbody>
</table>

% increase from 2008: 42% (28% - 67%).

Notes: a, Temperature dependence based on mid (low and high) empirical estimates according to Table S1 and Figure S1; b, Temperature dependence based on the thermodynamics eq. (3) (Table S1, Figure S1); c, Climatic effect not included. Estimates for which no climate dependence is assumed are shown in italics. While biomass burning emissions are likely to be climate dependent, further work would be needed to specify the relationships.

Including the consequences of changing human population and consumption patterns leads to further increases in estimated future global NH$_3$ emissions (Lamarque et al., 2011; Fowler et al., 2013). According to the Representative Concentration Pathway (RCP) scenarios reported by Lamarque et al. (2011), increases in anthropogenic activity are expected to increase the direct anthropogenic component of NH$_3$ emissions according to Figure S5. Of these scenarios, the RCP4.5 is not considered reliable (not all anticipated agricultural changes were included). Based on the mean and standard deviation of the three other scenarios for 2100, this equates to an increase of 56% (44%-67%) compared with 2008. By applying these changes to the anthropogenic categories of Table S2, while assuming no direct anthropogenic increase in emissions from natural soils, wild animals, oceans and volcanoes, gives an overall direct anthropogenic increase in total global NH$_3$ emissions of 42% (33%-52%).

The combined effect of direct anthropogenic increases and climate change on the anthropogenic NH$_3$ emissions is illustrated in Figure S5 for the RCP8.5 scenario (excluding natural and marine sources). Combining the climate feedback on NH$_3$ emissions and the direct anthropogenic changes, including all sources listed in Table S2 and all sources of uncertainty, gives a total estimated NH$_3$ emission for 2100 of 132(89-179) Tg N yr$^{-1}$. This value is nearly a factor of 3 higher than included in the currently mapped EDGAR database (JRC/PBL, 2011), which is a consequence of here including: a) additional sources (Table 1), b) the effect the climate change feedback and c) the anticipated increase in anthropogenic activities.
Figure S8: Estimated relative change in projected anthropogenic NH₃ emissions over the period 2008 to 2100, based on Lamarque et al. (2100). These estimates are developed for the Representative Concentration Pathways (RCP) for use by the Intergovernmental Panel on Climate Change according to different warming scenarios of 2.6, 4.5, 6.0 and 8.5 W m⁻². The additional effect of the estimated climate feedback on anthropogenic NH₃ emissions is illustrated for RCP 8.5 according to a 5 °C warming by 2100 based on Table S2.

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Supplementary References


