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# Preliminary validation of ammonia emission data using a combination of monitoring and modelling

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## Abstract

A method is presented to validate the ammonia emission data used as input in model calculations of ammonia concentrations. The method takes into account the uncertainty in model parameters and uses measured ammonia and ammonium concentration and wet deposition data. The calibrated emissions are subsequently used in the calculation of the spatial distribution of ammonia concentrations.

## 1. INTRODUCTION

Acidification is regarded as one of the major environmental problems in the Netherlands. To protect vegetation and groundwater from adverse effect, the Dutch Government has set a limit for potential acid deposition. In 2010 this should not exceed 1400 mol $ha^{-1}$ $a^{-1}$. For forested areas 400 mol $ha^{-1}$ $a^{-1}$ is the target[1].

The major contributing substances to potential acid deposition are oxidised sulphur and nitrogen compounds ($SO_x$, $NO_y$) and reduced nitrogen compounds ($NH_x$). In the Netherlands with its intensive livestock breeding the latter contributes to a rather high degree. For 1993 it was estimated that the deposition of $NH_x$ contributed about 45% to the potential acid deposition in that year, being 4000 mol $ha^{-1}$ $a^{-1}$.

The DEADM model [2] is used for the determination of the potential acid deposition. The distribution of wet deposition of $SO_x$, $NO_y$ and $NH_x$ is determined by interpolation of the wet deposition values determined for the 15 fixed stations of the Dutch Precipitation Chemistry Network. The dry deposition is determined by inference; for each 2-hour period the concentration field is multiplied with the appropriate deposition velocity which varies with space and time because of its dependence on surface characteristics and meteorological conditions. The distribution of the yearly dry deposition is then obtained by integrating the 2-hourly deposition fields.

For the oxidised sulphur and nitrogen compounds the required concentration fields are obtained from continuous measurements at some thirty fixed stations of the Dutch Air Quality Monitoring Network. For $NH_3$ however a different route is followed. A very dense network of measuring points would be required for the accurate assessment of the spatial distribution of $NH_3$ by interpolation. This is due to the many local sources of $NH_3$ emission, the low emission height and the atmospheric chemical behaviour of $NH_3$. Moreover, only recently an operational method for monitoring $NH_3$ concentrations became available. Consequently, the spatial distribution is calculated with an atmospheric dispersion and deposition model (OPS; [3]) using spatial detailed emissions of $NH_3$ as input. The annual mean $NH_3$ and $NH_4$

concentrations calculated with the OPS-model are subsequently used in the DEADM model to calculate depositions.

Though the application of the OPS model for $NH_3$ was validated by Asman & Van Jaarsveld [4] with data available those days, there has been no possibility until recently for routine validation of the model results because of the before mentioned lack of an operational monitoring method. Such a method has recently become available resulting in the establishment of an (interim) network for $NH_3$ mid 1992. In this paper measured and calculated values of $NH_3$ and $NH_4$ concentrations and of wet $NH_x$ deposition are compared. Subsequently, it is investigated whether the observed discrepancy between measured and calculated values of $NH_3$ can be explained by uncertainties in measured and/or calculated data. Lastly, a calibration procedure is applied in which the emissions are adapted in such a way that the deviations between measured and calculated values are minimised. Herewith the uncertainty in model parameters is taken into account. In this way information is obtained about the validity of the emissions.

## 2. MATERIALS AND METHODS

### 2.1. The monitoring network for $NH_3$ and $NH_4$

The monitoring network for $NH_3$ consists of 8 stations where the concentration is measured continuously with an annular denuder system [5]. Four of these stations are located in areas with high emission densities whereas the rest of the stations is located in regions with low to moderate emissions. Together with the establishment of the $NH_3$ network the number of stations where $NH_4$ aerosol is measured was increased from 2 to 5. Daily values of $NH_4$ aerosol are obtained by low volume sampling. In addition to concentration measurements wet deposition of $NH_3$ and $NH_4$ (together $NH_x$) is determined at 15 stations in the Dutch Precipitation Chemistry Network. For all 3 components data for 1993 were used in this study.

The location of the measurement stations is shown in Figure 1. The spatial distribution of emissions is also indicated in this figure.

### 2.2. Measurements on spatial representativity

Due to the very good characteristics of the measurement method employed [5] and the continuous monitoring, the annual mean values of $NH_3$ are regarded as very accurate values for the location where the samples are taken. However, when measurements are compared with model calculations the measured values should be representative for the grid cell surrounding the fixed station because the OPS model predicts averaged values for the 5 by 5 km area surrounding the receptor point.

In order to determine the spatial representativity of the (annual) $NH_3$ concentrations, measurements with a van were carried out around the fixed points. The number of reference points chosen is dependent on the emission strength in the surrounding area, decreasing from 8 in strong emission areas, via 6 in moderate emission areas to 4 in background areas. All reference points belonging to a certain fixed point were sampled at the same day during 15-20 minutes. For each fixed station the reference measurements were repeated several times

Figure 1. Locations of stations and spatial distribution of emissions.

emission (in tonnes):
0 -50 (617)
■ 50-100 (293)
■ 100-150 (308)
■ 150-300 (377)
■ >300 (56)

stations:
□ $NH_3$,$NH_4$, wet deposition
○ $NH_3$, wet deposition
◇ $NH_3$ only
△ $NH_4$ only
▽ wet deposition only

throughout the year, the number of repeats being dependent on the emission strength in the surrounding area.

## 2.3. Calculation of $NH_3$ and $NH_4$ concentrations and wet deposition with OPS

OPS is a Lagrangian dispersion, conversion and transport model which calculates the concentration and deposition of primary and secondary components in a receptor point due to each of the emission sources separately. It is thus linear with respect to the emissions. The model uses national mean values for roughness length, deposition velocity and conversion rate. Normally, also national mean values for meteorological conditions are used but in this study regionalised meteorological conditions were used because of the substantial influence on predicted concentrations [6,7]. The diurnal emission pattern used here was that according to Acharya [7].

The emission data for the Netherlands used in this study are the official emission data for 1992 as described by van der Hoek [8]. The emission data for the European countries were obtained from Asman [9].

## 2.4. Determination of the uncertainty of model predictions

One of the sources for uncertainty of the model results is the uncertainty in the model parameters. The uncertainty of the predicted $NH_3$ concentration was determined by simultaneous variation of parameters using the UNCSAM package [10]. The three parameters studied are the conversion rate of ammonia to ammonium ($a$), the surface resistance for ammonia ($r_c$) and the scavenging efficiency for ammonia and ammonium ($s$).For this study it was assumed that the value of each of these parameters was distributed homogeneously over the uncertainty region. The default values applied in the model and the boundaries of the uncertainty regions are listed in Table 1.

Table 1
Default value and uncertainty boundaries of some model parameters

| parameter | default | boundaries |
|---|---|---|
| $a$ (% per hour) | 28.8 | [10,50] |
| $r_c$ (s m$^{-1}$) | 30 | [10,100] |
| $s$ (-) | $1\cdot10^6$ | $[10^5,2\cdot10^6]$ |

## 2.5. The calibration method

Foreign emissions and industrial emissions were left out of the calibration procedure. The field of the remaining agricultural and household emissions was subsequently divided into 5 regions, 4 emission regions and the rest of the Netherlands. The determination of the emission regions was based on the amount of emission from manure per 5 by 5 km grid cell. Grid cells with emissions higher than 150 000 kg were selected. This resulted in 4 clusters of grid cells being the 4 emission regions (see Figure 2). Due to the linearity of the model with respect to the emissions the following equation applies to the model outcomes:

$$\mathbf{V}_c^p = \mathrm{ops}(\mathbf{E}_{ah,1}\cdot f_1) + \mathrm{ops}(\mathbf{E}_{ah,2}\cdot f_2) + ...... + \mathrm{ops}(\mathbf{E}_{ah,5}\cdot f_5) + \mathrm{ops}(\mathbf{E}_i) + \mathrm{ops}(\mathbf{E}_f) \tag{1}$$

where $\mathbf{V}_c^p$ is the vector with model outcomes ($NH_3$ and $NH_4$ concentrations, $NH_x$ deposition) for each of the measurement locations and parameter set p, $\mathbf{E}_{ah,n}$ is the vector of grid cell emissions for region $n$ and $f_n$ is the emission calibration factor for region $n$ with value 1 in the default situation. The calibration now consists of finding the values of $f_1$ to $f_5$ which minimise:

$$C^p = \left\| \mathbf{w}\cdot\left(\mathbf{V}_c^p - \mathbf{V}_m\right)\right\|_2^2 \tag{2}$$

where $\mathbf{V}_m$ is the vector with measured values and **w** is a vector with weighting factors which correct for the different order of magnitude between ammonia, ammonium and wet deposition (set at 1, 3 and 0.015 respectively in this study). This problem is solved analytically. If one of the values $f_1$ to $f_4$ becomes negative, the corresponding region is added to the rest of the Netherlands and the analysis is started again. Because the model parameters are also uncertain, it is subsequently searched iteratively for the values of **p** which minimise $C^p$.

The calibration procedure is carried out in 2 ways. The first method uses all stations in the analysis (for wet deposition only those stations where also the ammonium and/or the ammonia concentrations are measured). The second method uses all stations but one and the calibration is repeated as many times as there are stations (*m*), each time leaving out another station (jack-knife method). This procedure yields *m* values for the calibration factors and the model parameters. The inner *m-2* values are averaged and the standard deviation of the *m-2*

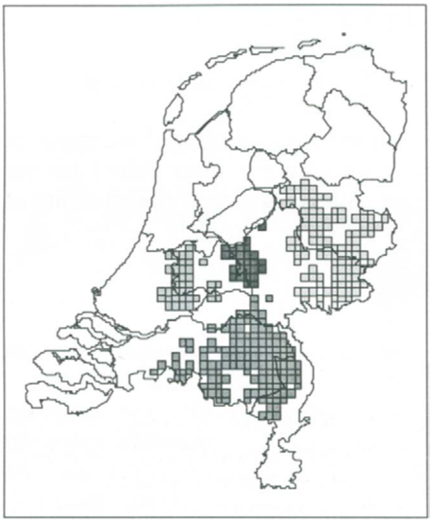


Figure 2. Partitioning of the Netherlands into 4 emission regions. The partitioning is based on the emission from manure per grid cell.

□ Eibergen region
▨ Zegveld region
■ Vredepeel region
■ Lunteren region

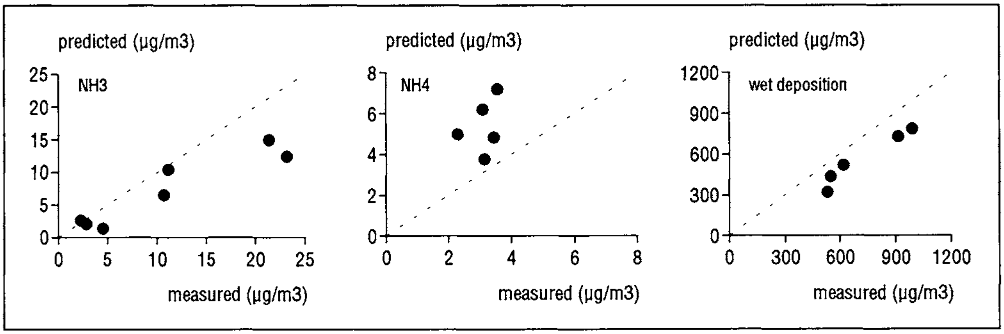
values is calculated. The jack-knife procedure was used as a way to 'validate' the results of the 'all stations' procedure.

## 3. RESULTS

### 3.1. Comparison between measured and calculated values

Figure 3 shows the comparison between measured and calculated values for the ammonium concentration, the ammonia concentration and for the wet deposition of $NH_x$. Though the correlation between calculated and measured values of $NH_3$ is reasonable, the calculated values for the stations in emission areas are much lower than the annual means from the measurements. For $NH_4$ aerosol there is hardly any correlation between calculated and

Figure 3. Comparison between measured and calculated values before calibration.



measured values and calculated values are much higher than the measured values. For wet deposition of $NH_x$ there is a fairly good correlation between calculated and measured values. However, the calculated values are somewhat lower than the measured values over the entire range of measured values.

It should be mentioned here that the poor correlation for $NH_4$ aerosol and the apparent underestimation of wet deposition of $NH_x$ may be caused by erroneous values for the measured data. Unlike $NH_3$ (next section) there has been no investigation of the reliability of measured values of $NH_4$ and wet $NH_x$ deposition.

### 3.2. Spatial representativity of measured values of $NH_3$

Figure 4 shows for each station the mean value of all reference measurements (averaged over space and time) and for comparison the mean value of all simultaneous measurements at the fixed point. Also indicated are the standard errors of the mean. From these measurements there is no indication of significant local influences on the fixed point. However, especially for the stations in areas with high emission density (131, 722 and 734) conditions with enhanced concentrations seem to be under represented in the reference measurements. This becomes evident when the mean value of the reference measurements at the fixed point is compared with the annual mean value of the continuous measurements at the fixed point. — using the same time window (11.00-19.00 h) as with the reference measurements to avoid diurnal variation effects.

### 3.3 Uncertainty in the model calculations of $NH_3$

The results of the UNCSAM analysis are shown in Figure 5. The dots represent the complete range of the model outcomes. The outer values of this range are less probable than the inner values. It can be concluded that although the uncertainties in the three model parameters studied give rise to an appreciable uncertainty in the predicted $NH_3$ concentration, the gap between predicted and measured values can not be closed by the uncertainty in the parameters only.

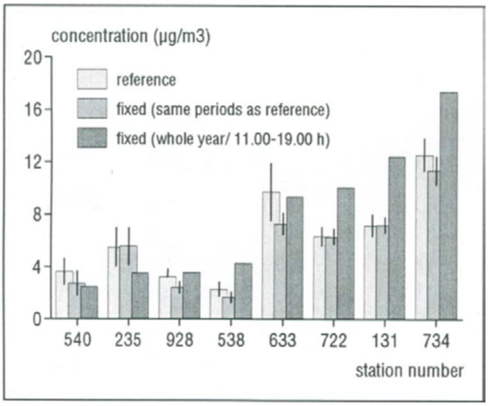


Figure 4. Comparison between mean value of measurements made at reference points and mean value of simultaneous measurements at fixed point. The annual mean at the fixed point is also indicated.

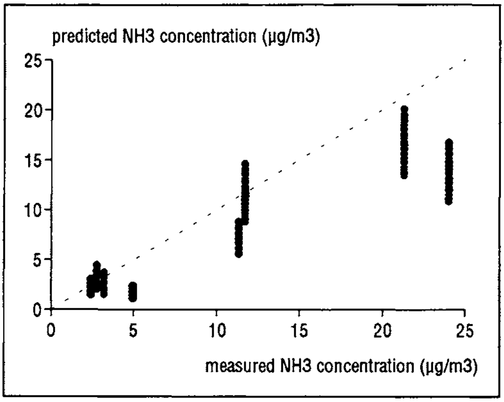


Figure 5. Uncertainty in the calculated $NH_3$ concentrations due to uncertainty in 3 model parameters (conversion rate, surface resistance and scavenging efficiency.

### 3.4. Calibration results

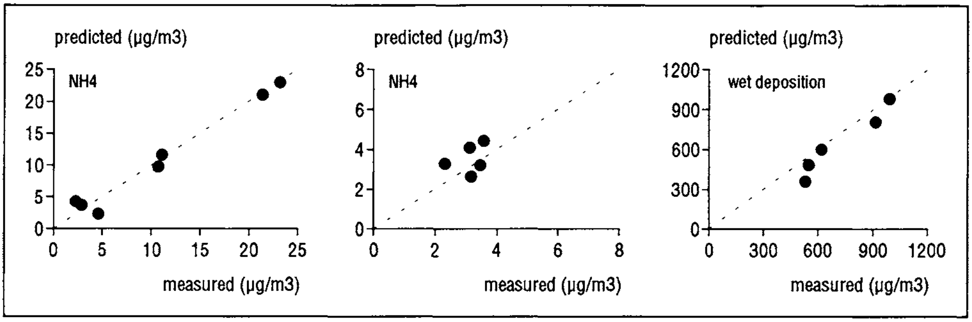
The first calibration runs in which the model parameters were also calibrated showed that the value of the conversion rate $a$ was consistently adjusted to its lowest possible value and that the value of the scavenging efficiency $s$ was always adjusted to its highest possible value. Therefore $a$ and $s$ were fixed at these boundary values in order to save computer time. Because the results of the jack-knife method compare very well with the results of the 'all stations' method only the results of the jack-knife method will be presented here. In Table 2 the results of the calibration analysis are listed.

When the model parameters are kept at their default values, the emissions of all four emission regions are increased by the calibration procedure. The highest adjustments are

Table 2
Calibration results with default and adapted parameter values.

| | with default parameter values | with adapted parameter values |
|---|---|---|
| $a$ | 28.8 | 10 |
| $r_c$ | 30 | 62 ± 11 |
| $s$ | $10^6$ | $2*10^6$ |
| $f_1$ (Eib) | 1.18 ± 0.03 | 0.80 ± 0.05 |
| $f_2$ (Lun) | 1.99 ± 0.04 | 1.56 ± 0.04 |
| $f_3$ (Vre) | 1.20 ± 0.02 | 1.13 ± 0.04 |
| $f_4$ (Zeg) | 1.79 ± 2.69 | 1.35 ± 0.32 |
| $f_5$ (rest) | 0.27 ± 0.56 | 1.06 ± 0.13 |
| $E_{tot}$ (ktonnes) | 123 | 178 |

Figure 6. Comparison between measured and predicted values after calibration.



needed for the Lunteren and the Zegveld regions (regions 2 and 4 respectively). However, simultaneously the emission of 'the rest of the Netherlands' is strongly decreased. Consequently, the national total $NH_3$ emission decreases from 166 ktonnes to 123 ktonnes. This result is regarded as very unlikely.

When $a$ and $s$ are set at their lowest respectively highest value and $r_c$ is allowed to change within certain limits, the calibration procedure doubles the value of $r_c$ in order to increase the ammonia concentration at the stations in the high-emission areas. Consequently, the emissions need not be increased that much as with the default parameter values. For the Lunteren region and the Zegveld region calibration factors are in the range 1.4-1.6 now. For the Eibergen region (region 1) the reported emissions are decreased with about 20%. The national total $NH_3$ emission increases from 166 ktonnes to 178 ktonnes with this calibration 'scenario'.

Figure 6 shows the comparison between measured and calculated values after calibration with parameter values allowed to change. Obviously, the calibration has resulted in a much better agreement for all components ($NH_3$, $NH_4$, wet deposition of $NH_x$).

Table 3 gives the national mean values for $NH_3$ concentration, $NH_4$ aerosol concentration, dry, wet and total deposition before and after calibration with adapted parameter values. As a result of increasing the emissions, decreasing the conversion rate and increasing the surface resistance, the ammonia concentration has increased by about 50% and the ammonium

Table 3
National mean values before and after calibration with adapted parameter values

| | before calibration | after calibration |
|---|---|---|
| $NH_3$ (μg $m^{-3}$) | 4.36 | 6.60 (+51%) |
| $NH_4$ (μg $m^{-3}$) | 5.25 | 3.42 (-35%) |
| wet deposition (mol $ha^{-1}$ $a^{-1}$) | 499 | 583 (+17%) |
| dry deposition (mol $ha^{-1}$ $a^{-1}$) | 1004 | 1024 (+2%) |
| total deposition (mol $ha^{-1}$ $a^{-1}$) | 1503 | 1607 (+7%) |

concentration has decreased by about 35%. Wet deposition has increased due to the increase in scavenging efficiency. Also the increased $r_c$ and therefore the increased ammonia concentration contributes to the increase in wet deposition. This becomes evident when the wet deposition data are not used in the calibration. In that case $r_c$ stays at its default value. Dry deposition is hardly influenced by the change in emissions and parameters. The increase in ammonium concentration is counteracted by the decrease in ammonia concentration and the increase in surface resistance. Consequently, also the total deposition has not changed much.

## 4. SUMMARY AND DISCUSSION

The calculated values of ammonia and ammonium concentrations using the emissions as reported by van der Hoek [8] and the default model parameters show considerable disagreement with the measured values. The calculated values for the concentrations of ammonia are lower than the measured ones, whereas for ammonium the opposite is valid. For wet deposition of $NH_x$ the calculated values are lower than the measured values. In spite of the use in this study of the measured data as they are now available, further investigation of the reliability of the ammonium concentrations and also the wet deposition of $NH_x$ is needed.

The deviations between measured and predicted values for ammonia cannot be explained by the uncertainty in either of these. Measurements of ammonia concentrations in the surroundings of the fixed point do not prevail local influences on the fixed point. However, conditions with high emissions are probably under represented. Therefore, local influences cannot be excluded. Considering the fact that the comparison measurements with a van are very time consuming, it is suggested to develop low-cost passive methods which integrate the ammonia concentrations over a certain time span and which should be applied a year long.

The uncertainties in the model parameters result in a quite large uncertainty in the calculated ammonia concentration, but not large enough to account for the difference in measured and predicted concentrations. The parameters studied are the conversion rate of ammonia to ammonium, the surface resistance for ammonia and the scavenging ratio for ammonia and ammonium. All three parameters describe the removal process and represent the main uncertainties. Not covered in this study are some additional uncertainties caused by (meteorological) parameters describing the dispersal process.

Calibration with the model parameters kept at their default value leads to a very unlikely best fit for the emission distribution. The emissions for the Zegveld and Lunteren area increase (up to a factor 2) whereas the emissions for 'the rest of the Netherlands' are substantially reduced. As a consequence, the total Dutch emission decreases from 166 ktonnes to 123 ktonnes. When the uncertainty in the model parameters is taken into account the required corrections of the emissions are smaller but still considerable (up to 1.6 for the Lunteren area). In that case the values for the conversion rate and the scavenging efficiency are invariably set at their lowest respectively highest possible value and the surface resistance is about doubled. Because the regions with the high corrections do not contribute that much to the total Dutch emission, the latter increases only slightly from 166 ktonnes to 178 ktonnes. This increase is within the 'normal' uncertainty of an emission estimate.

As a consequence of the adapted emission and model parameters the modelled national mean ammonia concentration increases with about 50%. However, the dry deposition of ammonia and ammonium is hardly affected because of the simultaneous decrease in the ammonium concentration (about 35%) and the increase of the surface resistance. The wet deposition increases lightly (17%) due to the increase in the scavenging efficiency but also resulting from the higher ammonia concentration. Following this, the total deposition of $NH_x$ increases with about 7%.

The results from this study are (probably) not independent of the way the emission field is partitioned. In a further study not the emissions of distinguished regions but the emission factors of the activities leading to emission of $NH_3$ will be calibrated.

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