Comparison of modelled and measured NH_3 concentrations for 108 locations in Flanders

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Abstract

Over the period October 1997 - November 1998, NH_3 concentrations were measured at 108 locations in Flanders using diffusion tube samplers. The measurement averaging time was three to four weeks allowing the representation of temporal agricultural phenomena like periods of manure application, maize plantation and periods of prohibition of manure application. The results of the measurement campaign were compared with NH_3 concentrations obtained by the Operational Priority Substances (OPS) model. Model results show concentrations that are systematically lower than the measurements, especially in areas with high emissions. The statistical analysis shows a better comparison in summer time (full emission load) than in wintertime (no manure applications). A significant improvement in the comparison was found when only locations were considered where the distance from (potential) sources was more than 500 m. It was concluded that a large part of the measurements was carried out too close (<500 m.) to the local sources in order to give a *representative* picture of the dispersion and concentration distribution of NH_3 over Flanders as provided by OPS based on 1 km x 1 km area emission sources. Furthermore the model results seem to indicate that emissions from live stock stables are probably underestimated in wintertime at some locations.

1. Introduction

NH_3 concentrations in Flanders are of the highest in the world, with measured annual averaged concentrations ranging from 7,8 to 35 $\mu g/m^3$. This is comparable with NH_3 concentrations measured in livestock areas in the Netherlands (1-35 $\mu g/m^3$) [1], but much higher than NH_3 concentrations

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measured in livestock areas in Canada (2-8 µg/m³) [2], Scotland (1,4 µg/m³) [3] or Hungary (±1µg/m³) [4].

Although NH_3 itself does not have direct health effects, it may contribute considerably to the formation of aerosols like ammonium nitrate and ammonium sulphate. These aerosols may have an important effect on the respiratory functions of sensitive human individuals. Compared to the directive related to the protection of ecosystems, which provides a value of 8 µg/m³ as a critical level, these levels are exceeded in almost all locations where measurements have been carried out. NH_3 contributes considerably to acidification and eutrophication in Flanders. It is estimated that in 2010, NH_3 will be responsible for more than 50% of the acidification and more than 70 % of the eutrophication due to atmospheric deposition [5].

In this study a comparison is made between measured and modelled NH_3 concentrations over Flanders from October 1997 to November 1998. The measurement technique and measurement strategy are briefly described in section 2.1. The regional air quality model that is used to compute the NH_3 concentrations is described in section 2.2. Section 2.3 describes the various situations and periods that are compared, taking into account the model resolution, the variation in distances between emission sources and receptor locations and the period of the year, i.e. periods of low and high intensity of manure applications respectively. The statistical evaluation procedure to compare model results and measurements is given in section 2.4. In section 3 the results are presented in the form of scatter plots and tables showing the statistical evaluation parameters. The results are discussed in section 4.

2. Methodology

2.1 Measurements

For the period October 1997 – November 1998, NH_3 measurements were carried out with diffusion tube samplers at 108 locations in Flanders [6]. The measurements were distributed over 12 areas of 5 km x 5 km. In 11 of the 12 areas 8 diffusion tubes were placed, whereas in one area 20 diffusive samplers were installed. The areas were selected to obtain a representative picture that includes areas with sensitive ecosystems, back ground areas and areas with a high livestock density. The objective of the measurement campaign was to obtain an idea of the variability of NH_3 concentrations over the Flanders region.

The passive or diffusive sampling measurement technique is based on the diffusion of ammonia through a tube at which end a solution of concentrated H_2SO_4 is impregnated [1]. By comparing the net loading of NH_4^+, $M_{sampler}$ with the loading of a blank, M_{blank}, the NH_3 concentration C can be obtained from

$$C = \frac{M_{sampler} - M_{blank}}{Q \cdot T} \cdot \frac{MW_{NH3}}{MW_{NH4+}} \tag{1}$$

Where

Q : absorption velocity of the samplers as determined under laboratory conditions ($Q = 1,34 \cdot 10^{-4}$ m³/h)

T : the sample time (h)

MW_{NH3} : the molecular weight of NH_3 (17 g/mole)

MW_{NH4+} : the molecular weight of NH_4^+ (18 g /mole)

The sampling tubes are a few centimetres long and were placed at a height of ± 2,5 meters. The geographical position of the samplers was determined using a corrected GPS system obtaining an accuracy of a few meters. The averaging time for each tube was three to four weeks. In total 12 measurement periods were defined between 27/10/1997 and 12/11/1998. The detection limit was determined for each measurement period and varied between 0.3 and 1.8 µg/m³.

2.2 Modelling

The NH_3 concentrations were computed using the Operational Priority Substances (OPS) model [7]. OPS is a Lagrangian trajectory model for long-term simulations, ranging from a few days to several years. The model computes concentrations and dry and wet depositions for primary (SO_2, NO_x, NH_3) and secondary (SO_4, NO_3, NH_4) acidifying components. It uses a climatological database with statistical values for 18 meteorological parameters. The climatological database is constructed by a meteorological pre-processor using hourly observations of wind direction and wind speed (measured at two heights), global radiation, temperature, precipitation intensity and precipitation amount. Other input data are related to the receptor characteristics (roughness length) and the emission sources (co-ordinates, dimensions, source strength). The model has been implemented and validated for the Flanders region [8].

The NH_3 concentrations were computed at the locations where the samplers have been placed. The accuracy of the model results was ± 0.1 µg/m³. The climatological database for the measurement period consisted of hourly meteorological data from a 114-m. high meteorological tower in Mol. The emission data for this period were derived from a detailed (1 km x 1 km) NH_3 emission inventory for the Flanders region containing four categories of agricultural emissions sources: cattle, pigs, poultry and other sources. Outside of Flanders, emission data from EMEP [9] were used, in combination with the NUTS-3 distribution of the emissions as provided by CORINAIR.

2.3 Comparisons

The comparison between modelled and measured NH_3 concentrations was carried out for four different cases described in this section.

2.3.1 Influence of the spatial resolution of emission source data
The NH_3 emission in Flanders are represented on a uniform grid of 1 km x 1 km (14702 area sources) and 5 km x 5 km (1192 area sources) respectively. The

effect of this difference in spatial resolution with respect to the representation of NH_3 emission data is evaluated by comparing for the two cases the computed concentrations with the measurements at the 108 locations as averaged over the whole measurement period.

2.3.2 Influence of the source – receptor distance

The measurement data were split into two data sets. The first data set contained all monitoring sites for which the distance between receptor and possible sources (pig stables, cattle grazing, manure spreading on pastures, etc.) was smaller than 500 m. In the second data set this distance was more than 500 m. A distance of 500 m. was found to be the minimum to avoid direct influence of the NH_3 emissions on the measurements, as found by Fowler et al. [10].

2.3.3 Influence of the measurement period

Two measurement periods were compared for which the intensity of the manure applications were considerably different. During the first selected period (1/12/1997 – 13/01/1998) no manure applications were allowed, following the Flemish manure directive of 23 June 1991 being in force at that time. In this period only emissions from stables were considered. In the second period (6/08/1998 – 11/09/1998) intense manure applications were expected and confirmed by the measurements, since this is a period just before the directive was applicable. In this case there is an increase in emissions due to the intensive manure spreading and additional contributions from cattle grazing on pastures. For this period the NH_3 emissions were calculated from:

$$E_{total} = E_{stable} + E_{manure} \frac{365}{X} + E_{grazing} \frac{365}{Y} \tag{2}$$

Where

$\quad E_{total}$: total NH_3 for the period
$\quad E_{stable}$: NH_3 emissions from stables
$\quad E_{manure}$: NH_3 emissions from manure applications
$\quad E_{grazing}$: NH_3 emissions due to cattle grazing
$\quad X$: number of days for which the manure directive is not
                 applicable $(X = 181)$
$\quad Y$: number of days on which cattle are brought outside $(Y = 182)$

2.3.4 Influence of spatial averaging over the measurement area

In each of the 12 measurement areas (5 km x 5 km) the measured NH_3 concentrations were spatially averaged to compensate for the lack of precision in the emission data. Since the individual emission sources have immediately been attributed to the source areas, the specific impact of local (point) sources within the measurement areas can consequently not be reproduced anymore by the model. Using the 1 km x 1 km emission data set, the NH_3 concentrations were computed and compared with the measured NH_3 concentrations, averaged spatially over each of the 12 measurement areas and averaged in time over the whole measurement period.

2.4 Statistical evaluation

Scatter plots were used to compare the observed with the calculated NH_3 concentrations. In case of a perfect agreement the data points coincide on the diagonal and a correlation coefficient of $CORR = 1.0$ is obtained. Besides the correlation coefficient, the ratio predicted/observed R_{po} was used, calculated as:

$$R_{po} = \frac{\overline{C_p}}{\overline{C_o}}$$

(3)

Where $\overline{C_p}$ is the averaged predicted or modelled concentration and $\overline{C_o}$ the averaged observed or measured concentration. For a perfect match between the data sets $R_{po} = 1.0$.

A further statistical evaluation was carried out by calculating the relative root mean square error $RRMSE$, as

$$RRMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{C_{p,i} - C_{o,i}}{C_{o,i}}\right)^2}$$

(4)

With N the number of compared data points (N=108). The smaller the value of $RRMSE$, the stronger the data sets would resemble each other. The $RRMSE$ has also been used to assess the uncertainties of the OPS model results: for the computation of yearly averaged concentrations a $RRMSE = 15\%$ is reported [7]. For the monthly averaged concentrations a $RRMSE = 30\%$ is expected [7].

In eqn (4) all errors are weighted proportionally. This overemphasises the contribution of errors for the smaller concentration values that are close to the detection limit and for which the relative model accuracy is lower. Therefore the normalised mean square error $NMSE$ was evaluated as well:

$$NMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\frac{\left(C_{p,i} - C_{o,i}\right)^2}{\overline{C_p}\cdot\overline{C_o}}}$$

(5)

3. Results

3.1 Influence of the spatial resolution of emission source data

Figure 1 shows a scatter plot in which the computed NH_3 concentrations are compared with measurements for all 108 monitoring locations. Figure 2 shows the comparison within each of the measurement areas, as separated by the vertical lines. Section 1 in Table 1 shows the statistical evaluation parameters for the two results.
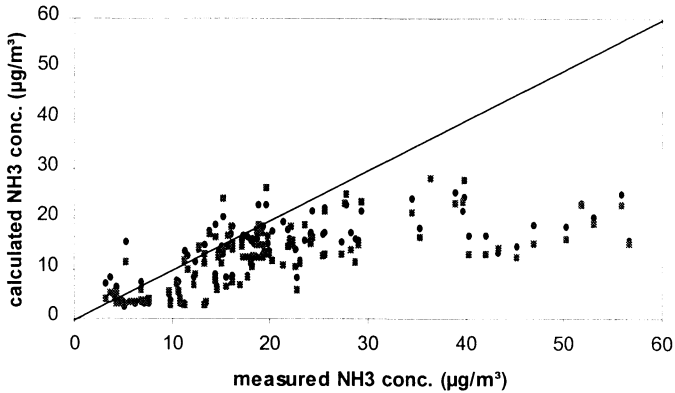
Figure 1: Measured and computed NH$_3$ concentrations for emission data with a resolution of 1 km x 1 km (dots) and 5 km x 5 km (squares).
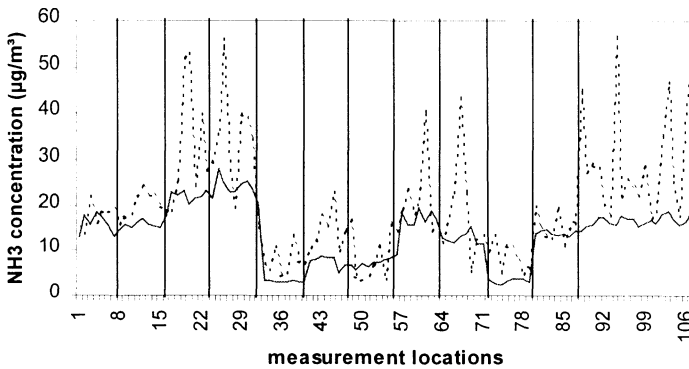
Figure 2: Comparison between measured (dotted line) and computed (full line) NH$_3$ concentrations per measurement area, using the 1 km x 1 km resolution emission data.

3.2 Influence of the source – receptor distance

The scatter plots for source-receptor distances smaller than 500 m. and for source-receptor distances larger than 500 m. is shown in Figure 3. Results for the statistical evaluation parameters can be found in the section 2 of Table 1.

3.3 Influence of the measurement period

The scatter plots for the winter period without manure applications and for the summer period with intense manure applications are given in Figure 4. Section 3 in Table 1 shows the results for the statistical evaluation parameters.
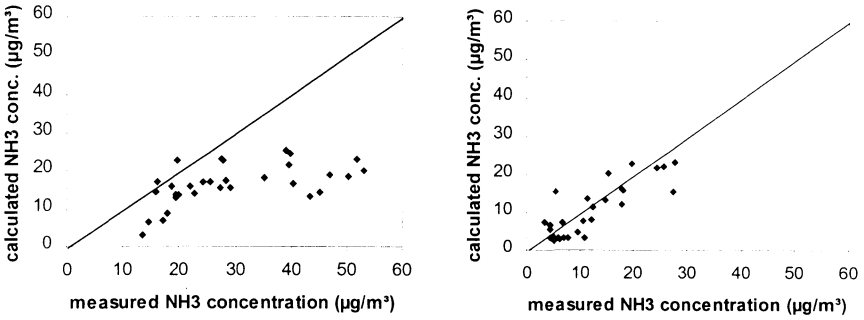
Figure 3: Scatter plots for the source-receptor distance smaller than 500 m. (left) and larger than 500 m. (right), using 1 km x 1 km emission data.
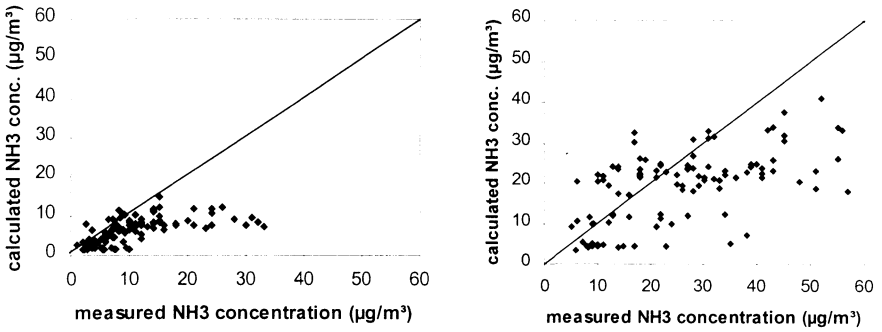
Figure 4: Scatter plots for the winter period without manure applications (left) and for the summer period with intense manure applications (right), using 1 km x 1 km emission data.
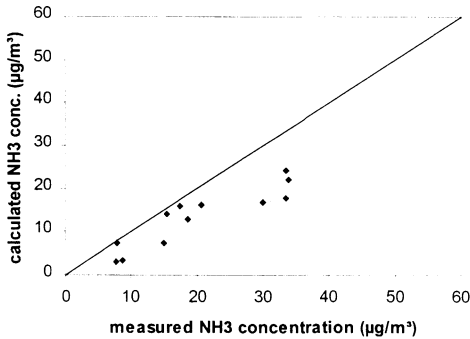
Figure 5: Scatter plot after averaging over the measurement areas (5 km x 5 km)

Table 1: Results for the statistical evaluation parameters

	$CORR$	R_{PO}	$RRMSE$	$NMSE$
1.				
5 km x 5 km emission resolution	0.653	0.612	0.441	0.245
1 km x 1 km emission resolution	0.682	0.672	0.458	0.160
2.				
Source-receptor distance < 500 m.	0.559	0.560	0.451	0.345
Source-receptor distance > 500 m.	0.840	0.869	0.534	0.020
3.				
Low manure application period	0.500	0.564	0.522	0.307
Intensive manure application period	0.604	0.738	0.430	0.062
4.				
Averaged over measurement area	0.907	0.664	0.383	0.171

3.4 Influence of spatial averaging over the measurement area

After averaging over the measurement areas (5 km x 5 km) a scatter plot as shown in Figure 5 is obtained. The statistical evaluation parameters for this case are shown in section 4 of Table 1.

4. Discussion

The results in Figure 1 show that the measured NH_3 concentrations are systematically higher than computed concentrations, especially for the higher concentrations. Increasing the resolution of the emission data, presented as area sources, has only very little effect, as can be seen from the statistical evaluation parameters in Table 1.

The subdivision into a data set with sources close to the receptor points (< 500 m.) and a data set with sources far from the receptor points (> 500 m.) clearly shows the importance of the influence of the source-receptor distance. It indicates that the model has problems in representing the direct influence of emissions and that some receptor points were selected too close to possible emission sources in order to avoid this direct influence and give a more representative picture of the dispersion and concentration distribution of ammonia in Flanders. However, the OPS model was designed for representing

the *transport* and *dispersion* of pollutants, rather than the direct influence of emissions. The direct influence of the emission sources was not excluded during the measurements. This was not only due to the presence of stables in the vicinity (< 500 m.) of the receptor points as could be seen from geographical maps, but also from to the fact that some receptor points were located close to pastures and / or crop fields where manure was spread. The model does not take that into account and only considers the emissions to be distributed uniformly over surface areas of 1 km x 1 km (or 5 km x 5 km). The model can therefore not represent the variability within such an emission area. Unfortunately, more detailed emission data are not made available because of reasons of confidentiality.

In the period of intensive manure applications a better agreement is found than in the period where manure applications are prohibited. Since only emissions from stables are taken into account in this period, the results could indicate that these emissions are possibly underestimated. During the period of intensive manure applications the peak concentrations are not well predicted. This is probably caused by emission sources (pastures) in the close vicinity of the receptor points.

From the results for the comparison of the NH_3 concentrations averaged over the 12 measurement areas, one can see that the model better approximates the measured concentrations. With a *RRMSE* of 38%, this is close to what can be expected and has been reported earlier [7].

5. Conclusions

From the results presented in section 3 and discussed in section 4 it can be concluded that at many of the locations the measurements were carried out too close to the sources in order to give a *representative* picture of the dispersion and concentration distribution of NH_3 in Flanders. Due to the limitation in the spatial resolution of the emission data sets (1 km x 1 km), the OPS model is not able to correctly represent the concentration variability within the measurement area (5 km x 5 km). The effect of individual (point) sources (stables, manure applications on certain pastures, etc.) cannot be represented. Unfortunately these data are not made available. However, when averaged over the measurement areas (5 km x 5 km), the regional scale model gives results that are within the expected uncertainty range.

Acknowledgement

References

[1] Thijsse, Th.R., Duyzer, J.H., Verhagen, H.L.M., Wyers, G.P., Wayers, A. & Mols, J.J., Measurements of ambient ammonia with diffusion tube samplers, *Atmospheric Environment*, **32**, No 3, pp. 333-337, 1998.

[2] Barthelmie, R.J. & Pryor, S.C., Implications of ammonia emissions for fine aerosol formation and visibility impairment – A case study from the Lower Fraser Valley, British Columbia, *Atmospheric Environment*, **32**, No 3, pp. 345-352, 1998.

[3] Burkhardt, J., Sutton, M.A., Milford, C., Storeton-West, R.L. & Fowler, D., Ammonia concentrations at a site in southern Scotland from 2 years of continuous measurements, *Atmospheric Environment*, **32**, No 3, pp. 325-331, 1998.

[4] Horváth, L. & Sutton, M.A., Long-term record of ammonia and ammonium concentrations at K-Puszta, Hungary, *Atmospheric Environment*, **32**, No 3, pp. 339-344, 1998.

[5] Mensink, C. & Beirens, F., Emission reduction scenarios for nitrogen compounds and their impact on acidification, eutrophication and ozone formation in Flanders, *Environmental Pollution* **102**, S1, pp 641-647, 1998.

[6] De Fré, R. & Swaans, W. *Screening ammonia concentrations in Flanders (1997-1998)* (Screening ammoniakconcentraties in Vlaanderen (1997-1998)), VITO-report 1998/DIA/216, 1998 (in Dutch).

[7] Jaarsveld J.A. van, *An Operational atmosferic transport model for Priority Substances; specification and instructions for use*, RIVM report nr. 222501002, 1990.

[8] Mensink, C. & Dumont, G., Comparisons of model results with observations for acid depositions and acidifying air pollutants over Flanders, *Air Pollution V, Monitoring, Simulation and Control*, eds. H. Power, T. Tirabassi & C.A. Brebbia, Computational Mechanics Publications: Southampton, pp. 395-404, 1997.

[9] Mylona, S., Storen, E. & Grini, A., *EMEP Emission data*, Status report 1999, Norwegian Meteorological Institute, Research Report no 26, EMEP/MSC-W: Oslo, 1999.

[10] Fowler, D., Pitcairn, C.E.R., Sutton, M.A., Flechard, C., Loubet, B., Coyle, M. & R.C. Munro, The mass budget of atmospheric ammonia in woodland within 1 km of livestock buildings. *Proceedings of the First International Nitrogen Conference*, eds. K.W. Van der Hoek et al., Elsevier: Amsterdam pp 343-348, 1998.