Atmospheric nitrogen dynamics in Hesse, Germany: Creating the data base
3. Monitoring of atmospheric concentrations of ammonia using passive samplers

Ulrich Dämmgen

Abstract

From 2002 to 2004, a monitoring network was operated in Hesse to determine atmospheric ammonia concentrations using passive samplers. Primary goal of the measurements was the assessment of a data set which could be used to check the validity of the atmospheric transmission and deposition model. In addition, these data were to provide information about the accuracy and spatial representativeness of such measurements.

Concentration levels of sites in forested regions could well be differentiated from those in rural regions (coined by agriculture) and urban sites. The concentrations of the latter were surprisingly high.

Small scale spatial variability could be observed near sources only. At sites distant from sources neither a horizontal nor a vertical variability could be measured.

Keywords: nitrogen balance, ammonia concentrations, passive samplers

Zusammenfassung

Atmosphärische Dynamik von Stickstoff in Hessen: Erstellung der Datenbasis
3. Monitoring atmosphärischer Ammoniak-Konzentrationen mit Hilfe von Passiv-Sammlern


Kleinräumige Variabilität war in unmittelbarer Nähe von Quellen zu beobachten, an quellfernen Orten jedoch weder horizontal noch vertikal.

Schlüsselwörter: Stickstoff-Bilanz, Ammoniak-Konzentration, Passiv-Sammler

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1 Ammonia concentration measurements within the Hessian initiative to balance atmospheric fluxes of reactive nitrogen

Within the Hessian atmospheric nitrogen balance programme, special attention was given to the role of ammonia (NH$_3$). In contrast to most other atmospheric nitrogen species, its atmospheric lifetime is in the order of magnitude of a few hours. The pattern of sources is highly variable with time and space. Depending on their nutrition status and the respective atmospheric concentration, most ecosystems can act both as sinks and sources. Thus, the spatial variation of NH$_3$ concentrations is likely to be high in comparison with other air pollutants.

It is planned to model these concentrations using detailed emission data in combination with an atmospheric dispersion and deposition model (see Figure 1). In order to check the validity of this model, the atmospheric NH$_3$ concentrations provided have to be compared with measured concentrations.

In Germany, NH$_3$ emissions stem mainly from agriculture (approx. 95%, Dämmgen and Erisman, 2006). The assessment of spatially resolved emissions relies on input data from a complete agricultural census. This took place in May 2003. The results of this inventory will be reported separately in Lüttich and Dämmgen (2007).

A network to measure NH$_3$ concentrations in ambient air was established in 2002 and was to operate for three years, in order to get information about the representativeness in time of the concentrations measured.

As the general information about NH$_3$ concentrations was unsatisfactory and a standard method not yet developed, measurements were planned for rural, forest and urban environments.

The use of passive samplers is the only way to obtain mean NH$_3$ concentrations. Even the use of “cheap” denuder systems is comparatively expensive. Continuously and reliably recording NH$_3$ monitors are not readily available yet.

The resolution in time was to be the same as for the bulk deposition measurements (Dämmgen, 2006), i.e. one month.

Figure 1:
Data fluxes in the Hessian atmospheric nitrogen dynamics project and related sequels of activities needed to establish the data set and the subsequent modelling activities (Grünhage et al., 2002, modified). Rectangles in the uppermost line illustrate the data sets needed. Concentration data dealt with in this paper are accentuated.
2 Sampling sites and sampling system

2.1 The sites

15 sites were chosen to establish a first network for the assessment of NH₃ emissions. Details are given in Figure 2 and Table 1. Table 1 also refers to the type of environment.

Table 1

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</table>

U: urban site; F: forest site; R: rural site

Most of the sites are situated close to so-called level II sites of the ICP forest programme (http://www.icp-forests.org/MonLvIV.htm). These sites are normally considered to be sinks for atmospheric NH₃. Here, they are to provide information on the typical regional background concentration. For these sites concentration gradients should show concentrations increasing with height. Thus, additional measurements of this kind were performed at Königstein.

Small scale spatial variation was considered in the setup at the Linden site. Here, NH₃ concentrations could be compared to those obtained with denuders (Dämmgen, 2007). In addition, measurements made at the FAL site near Braunschweig were evaluated to describe the variation in space close to major sources.

2.2 The sampling system

Passive samplers of the IVL type (Ferm, 1991) were used. Samplers of this type have been operated successfully by various institutions. They showed good results in intercomparisons with denuders (Kirchner et al., 1999; Zimmerling, 2000; Zimmerling et al., 2000; Lumpp, unpublished). However, passive samplers should be operated in connection with denuders as reference system (VDI 3869 Sheets 3 and 4) (v.i.).
In this project, four samplers were mounted together and under a protective roof at a height of 3.5 m according to Bundesminister des Innern (1983).

![Diagram of IVL type passive sampler](image)

Figure 3: Assembly of the IVL type passive sampler (exploded view). Both lids snap on the tube, keeping the impregnated filter, the PTFE membrane and the wire gauze in position, respectively.

2.2 Calculation of results

The theoretical treatment of the diffusion and absorption process makes use of the following relation:

\[
\rho_{\text{NH}_3} = \frac{c \cdot v}{t \cdot \alpha \cdot D} \left( \frac{l_R}{A_R} + \frac{l_F}{A_F} + \frac{l_G}{A_G} + \frac{l_{LBL}}{A_{LBL}} \right) \frac{M_{\text{NH}_3}}{M_N}
\]

where

- \( \rho_{\text{NH}_3} \): atmospheric concentration of NH\(_3\) (in \(\mu\text{g m}^{-3}\))
- \( c \): concentration of filter eluat (in \(\mu\text{g ml}^{-1}\) N)
- \( t \): duration of exposure (in d)
- \( v \): volume of filter eluat (in ml)
- \( \alpha \): time units conversion factor (\(\alpha = 86400 \text{ s} \text{ d}^{-1}\))
- \( D \): molecular diffusion coefficient (\(D_{\text{NH}_3} = 2.54 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}\) at 25 °C; Massman, 1998)
- \( l_R \): length of the tube (\(l_R = 0.010 \text{ m}\))
- \( A_R \): cross sectional area of the tube (diameter 0.020 m; \(A_R = 3.14 \times 10^{-4} \text{ m}^2\))
- \( l_F \): thickness of PTFE membrane (Millipore Fluorpore FALP02500; \(l_F = 0.175 \times 10^{-3} \text{ m}\))
- \( A_F \): cross sectional area of PTFE membrane (porosity 85 %; \(A_F = 0.85 A_R = 2.67 \times 10^{-4} \text{ m}^2\))
- \( l_G \): thickness of wire gauze (\(l_G = 0.16 \times 10^{-3} \text{ m}\))
- \( A_G \): cross sectional area of gauze (\(A_G = 0.47 \times 10^{-4} \text{ m}^2\))
- \( l_{LBL} \): thickness of the laminar boundary layer, depending on wind speed and design of the sampler (assumed: \(l_{LBL} = 0.0015 \text{ m}\))
- \( A_{LBL} \): cross sectional area of aperture (\(A_{LBL} = A_R\))
- \( M_{\text{NH}_3} \): molar weight of NH\(_3\) (in g mol\(^{-1}\))
- \( M_N \): molar weight of N (in g mol\(^{-1}\))

The diffusion coefficient recommended in Ferm (1991) does not agree with the present state of knowledge. According to Massman (1998) \(D\) should be in the order of magnitude of 0.20 to 0.21 for prevailing temperatures in Hesse.

2.3 Preparation and analysis

Filter papers (cellulose) are washed with demineralized water (60 min, ultrasonic bath), dried in a desiccator and impregnated with 50 \(\mu\)l citric acid solution in acetone (\(c = 2 \%\)). After 10 min drying in a dessicator the passive samplers are mounted and stored in an air tight container till they are exposed (normally a few days later).

After exposure, these filters are eluated with 5 ml demineralized water (60 min, constant shaking). After microfiltration, the solution is analyzed using either segmented flow analysis or ion chromatography (DIN 38 406). Blanks are measured regularly. The mean of blanks is equivalent to an atmospheric concentration of 0.28 \(\mu\text{g m}^{-3}\) NH\(_3\).

2.4 Data availability

With the exception of Riedstadt (06), Königstein (12), Zierenberg (14), Kleiner Feldberg (15) and Witzenhausen (16), sampling started in July 2001. Sampling at Königstein commenced in October 2001, at Zierenberg in November 2001, and at Riedstadt, Witzenhausen and Kleiner Feldberg in January 2002. As a rule, monthly samples were taken. Due to bad weather conditions, sampling was impossible in February 2002. This resulted in a 2 months’ sample. At Bad Arolsen (11), no samples were collected in April 2002. Only once a single filter was missing. Thus, the overall coverage of the sampling period was very good.

2.5 Data quality

Calibration

Passive samplers should be used after calibration with denuders (VDI 3869 Sheet 3). Such an intercomparison was made at the Braunschweig FAL site (see Figure 4).
As in other such experiments, IVL samplers are likely to overestimate concentrations by about 20%, and a calibration factor of about 1.2 should be used (Lumpp, unpublished). Although a direct intercomparison between Linden denuder and passive sampler data could not be made, as sampling intervals were not identical, the results obtained for a "rough estimate" are similar and suggest a correction factor of about 10%.

For the results presented in this paper, a calibration factor of 1.2 was used.

In principle, the diffusion process resulting in a deposition of NH$_3$ on the impregnated filter is temperature dependent. It could be shown by Zimmerling (2002) that the correction is irrelevant. Furthermore, it is impossible in practice.

**Standard deviation and standard errors**

For each site and month, the four replicates were used to derive the mean and the standard deviation. Obvious outliers were removed. The frequency distribution of the standard deviations is shown in Figure 5. A mean monthly deviation $\sigma_{m,1}$ of 0.15 to 0.20 µg m$^{-3}$ results in a standard error $G$ of about 0.5 µg m$^{-3}$, if one assumes $G = 3 \sigma_{m,1}$. This is not satisfactory. However, an error propagation calculation shows that the standard deviation of annual means of all sites is 0.10 µg m$^{-3}$, and thus the error 0.3 µg m$^{-3}$. This seems a reasonable accuracy.

![Figure 4: Calibration of IVL passive samplers using KAPS denuder. Data obtained at FAL using monthly means of the daily denuder measurements. Calibration factor $x_{IVL} = \rho_{IVL}/\rho_{denuder} = 1.19; R^2 = 0.94.$](image)

![Figure 5: Standard deviations of 4 replicates taken at measurements in the entire network, 696 data sets. Bin width 0.05 µg m$^{-3}$.

**3 Results of concentration monitoring – means and annual variation**

Mean annual concentrations $\rho_{NH3}$ and their standard errors $G_{NH3}$ are listed in Table 2. Both the table and Figure 6 show the difference between forest sites on the one hand and rural and urban sites on the other.

![Figure 6: Mean annual variation of the ammonia concentrations measured at the forested, rural and urban sites.](image)

As expected, the rural sites show a pattern with two peaks in spring and summer, reflecting the application of manures and fertiliser. The forested sites still show this pattern, albeit on a much lower level. The high concentrations at Limburg and Bebra were unexpected. Recent discussion reveal that similar concentrations were observed on other urban sites. The explanation has not yet been given. Urban traffic (three way catalytic converters) as well as humans might be the sources.
### Table 2:
Annual mean concentrations of ammonia $\rho_{\text{NH}_3}$ and their standard error $G_{\text{NH}_3}$

<table>
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<th>Nr.</th>
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<th>$G_{\text{NH}_3}$</th>
<th>$\rho_{\text{NH}_3}$</th>
<th>$G_{\text{NH}_3}$</th>
<th>$\rho_{\text{NH}_3}$</th>
<th>$G_{\text{NH}_3}$</th>
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<td>0.9</td>
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</table>

U: urban site; F: forest site; R: rural site

### 4 Representativeness in time and space

Long time series of NH$_3$ concentration measurements do not exist in Germany. The few data available have the same order of magnitude as the Hessian urban, rural and forested sites (Figure 7) and fit the ranges given in Dämmgen and Sutton (2001).

Measurements also indicate the high spatial variability of NH$_3$ concentrations. Figure 8 shows exemplary concentration measurements downwind from animal houses. The figure shows relative concentrations related to the highest concentrations as obtained between the animal houses lessened by the background concentration. The distance after which concentrations half is less than 200 m. Concen-
Concentrations increase slightly after 300 m, apparently due to emissions from the fields surrounding the animal houses.

Small scale variability was also under examination at the Linden site, where three sets of samplers were exposed from years after February 2004 to December 2006. Here, set A was mounted in the centre of the experimental site of the Linden experimental station (Grünhage et al., 1996; Jäger et al., 2003). Sets B and C were located 120 m east of the centre, the distance between B and C was 25 m.

As shown in Figures 9 and 10, the overall agreement between the sets is satisfactory. Major deviations occur for single months such as May 2005 and November 2005. The four parallels indicate “correct” measurements. Reasons for both deviations cannot be reconstructed. As this may also be the case when field measurements are made, the Linden measurements can be used to obtain the order of magnitude of the potential error. If the mean of the concentrations obtained from the three sets is taken to be true, then standard errors can be calculated from the standard deviation (Table 3).

![Figure 9](image-url)

**Figure 9:**
Time series of simultaneous concentration measurements at Linden using three sets of passive samplers

**Table 3:**
Annual mean concentrations $\rho_{\text{NH}_3}$ for the Linden sets A, B and C, as well as the standard error $G_{\text{NH}_3}$ (in µg m$^{-3}$ NH$_3$)

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<td>$G_{\text{NH}_3}$</td>
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</table>

Set A was mounted close to the denuders described in Dämmgen (2007). Here, the mean concentration for 2004 was 2.0 µg m$^{-3}$, the mean for 2002 to 2004 was 2.4 µg m$^{-3}$.

These results indicate the necessity of replications rather than the assumption of a standard error when mean regional concentrations are to be assessed.

The tower at Königstein was used to investigate the variation with height of NH$_3$ concentrations. Earlier measurements in typical rural areas had shown distinct vertical gradients close to the ground or vegetation. Modelling of deposition normally makes use of a concentration at a height of 25 m, to which a deposition velocity is applied.

![Figure 10](image-url)

**Figure 10:**
Simultaneous concentration measurements using three sets of passive samplers, deviations from the mean concentration

No systematic difference between the three exposure heights could be detected. Apart from the results obtained for August 2003, all concentration differences are within the error bars. This is also reflected by the data given in Table 2. Königstein is a site without any direct influence of NH$_3$ sources. However, the typical peaks in spring and summer can be observed here as well, though on a comparatively low level. These concentrations are close to the
socalled NH₃ canopy compensation point (i.e. the atmospheric concentration, which is equal to the concentration immediately above the leaves; this concentration is influenced by i.a. the NH₄ concentrations in the apoplast and therefore by nutrient status and the physiological activity of the plants).

5 Discussion and future activities

The Hessian experiment showed that passive samplers are a means to establish mean concentrations with an adequate accuracy. However, this can only be achieved with replicate measurements at each site. The method is not suitable to identify mean gradients above a system which should act as a permanent sink. It had been shown that the method cannot be used for this purpose whenever bidirectional fluxes can be expected (Dämmgen et al., 1996).

In order to gather more experience, some sites are operated until December 2007 (01 Limburg, 03 Linden (three sets), 04 Bebra, 06 Riedstadt, 07 Spessart, 09 Wasserkuppe and 11 Fulda).

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