

Atmospheric nitrogen dynamics in Hesse, Germany: Creating the data base

2. Atmospheric concentrations of ammonia, its reaction partners and products at Linden

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Abstract

Within the Hessian atmospheric nitrogen dynamics project, concentration measurements of gaseous ammonia, nitrous acid, nitric acid and sulphur dioxide as well as of ammonium, nitrate, sulphate, chloride and sodium in particles (PM₃) were made at Linden near Giessen, Hesse, between November 2001 and December 2004. The primary goal was the establishment of a data set that could be combined with a soil vegetation atmosphere transfer (SVAT) model to assess the vertical fluxes. Weekly measurements of mean day and night concentrations were made using denuder filter equipment. In order to obtain information about the typical diurnal variation of these concentrations, another programme was established at the site of the Federal Agricultural Research Centre near Braunschweig. Here, a set of eight samplers was used to derive correction factors for three-hourly periods.

When compared with other measurements in Germany and Europe, concentrations indicated a moderately polluted countryside situation. As usual, ammonia concentrations followed the annual pattern of agricultural emissions. Nitric acid concentrations reflected the overall photochemical activity. Sulphur dioxide emissions were determined by energy consumption and peak in winter. The spatial and temporal variabilities of the concentrations of nitrogen and sulphur species in atmospheric particles were definitely smaller than for gases. Both ammonium and nitrate concentrations exhibited a maximum in spring and seemed to be related with ammonia emissions. Chloride and sodium concentrations indicated their common origin in sea spray.

Keywords: nitrogen balance, denuder-filter measurements, ammonia, nitrous acid, nitric acid, sulphur dioxide, particulate ammonium, particulate nitrate, particulate sulphate

Zusammenfassung

Atmosphärische Dynamik von Stickstoff in Hessen: Erstellung der Datenbasis

2. Atmosphärische Konzentrationen von Ammoniak, seinen Reaktionspartnern und -produkten in Linden

Innerhalb der Arbeiten zur Schließung der atmosphärischen Stickstoff-Bilanz über Hessen wurden in Linden bei Gießen Konzentrationsmessungen von Ammoniak, salpetriger Säure, Salpetersäure und Schwefeldioxid in der Gasphase sowie von Ammonium, Nitrat, Sulfat, Chlorid und Natrium in Partikeln (PM₃) vorgenommen. Die Messungen dauerten von November 2001 bis Dezember 2004. Wesentliches Ziel war die Bereitstellung eines Datensatzes, der in Kombination mit einem Soil-Vegetation-Atmosphäre-Transfer-Modell (SVAT-Modell) die Bestimmung vertikaler Flüsse erlauben sollte. Hierzu wurden wöchentliche Messungen (getrennt für Tag und Nacht) unter Verwendung von Denuder-Filter-Sammlern vorgenommen. Um näheren Aufschluss über die zeitliche Auflösung der Konzentrationen zu erhalten, wurden auf dem Gelände der Bundesforschungsanstalt für Landwirtschaft bei Braunschweig zusätzlich Denuder-Filter-Messungen vorgenommen, die es erlauben, Korrekturfaktoren für acht Dreistunden-Abschnitte eines Tages zu gewinnen.

Im Vergleich mit anderen deutschen und europäischen Messstellen stellt Linden eine mäßig verunreinigte Umland-Messstelle dar. Wie üblich, folgte der Jahresgang der Ammoniak-Konzentrationen dem der landwirtschaftlichen Emissionen. Die Salpetersäure-Konzentrationen spiegelten die photochemische Aktivität der Atmosphäre wider. Die Schwefeldioxid-Konzentrationen waren durch die Energiebereitstellung geprägt und hatten im Winter die höchsten Werte. Die räumliche und zeitliche Variabilität der Staub-Inhaltsstoffe war deutlich geringer als die der Gase. Sowohl Ammonium- als auch Nitrat-Gehalte waren im Frühjahr am höchsten und offenbar auf die Ammoniak-Emissionen zurück zu führen. Chlorid- und Natrium-Konzentrationen ließen den gemeinsamen Ursprung in der Gischt der Ozeane erkennen.

Schlüsselwörter: Stickstoff-Bilanz, Denuder-Filter-Messungen, Ammoniak, salpetrige Säure, Salpetersäure, Schwefeldioxid, Ammonium in Partikeln, Nitrat in Partikeln, Sulfat in Partikeln

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1 The Hessian initiative to balance atmospheric fluxes of reactive nitrogen – the emphasis on reduced nitrogen species

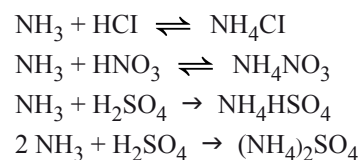
Fluxes of reactive nitrogen compounds contribute to acidification and eutrophication of ecosystems. Whereas the risk of acidification has been reduced considerably during the past decades due to politically induced programmes in particular for large combustion sources, eutrophication has remained a problem for almost all natural and semi-natural ecosystems in Central Europe.

Within the initiative taken by the Hessian Agency for the Environment and Geology (HLUG) in cooperation with the Institute of Agroecology of the Federal Agricultural Research Centre (FAL) and the Institute for Plant Ecology of the Justus-Liebig University, Giessen (Grünhage et al., 2002; Dämmgen, 2006), special attention was given to the quantification of dry deposition on reactive nitrogen species. As it is not feasible to measure such fluxes, they have to be obtained from models. It is customary to obtain the necessary concentration data from emission inventories and meteorological modelling (see Figure 1). Much is known about concentration fields of the oxidized nitrogen species nitric oxide (NO) and nitrogen dioxide (NO₂). Far less is known about concentrations of nitric and nitrous

acids (HNO₃ and HNO₂), about reduced nitrogen (ammonia, NH₃) and the contribution of aerosol constituents (ammonium, NH₄, and nitrate, NO₃) in aerosol particles.

A special problem is the treatment of NH₃, as it is highly reactive, and the determination of NH₃ concentrations that are representative in time and space is difficult. The determination even of NH₃ concentrations in ambient air is still not trivial. Measurements have to rely on enrichment procedures and wet chemical analysis; continuous monitoring of concentrations with a high resolution in time is still very costly or even impossible.

Furthermore, the concentration dynamics of NH₃ can only be understood if its reaction partners and reaction products



are analyzed from the same air sample. Of these reactions, those with hydrochloric and nitric acids are reversible, whereas the latter two are irreversible. The reaction with hydrogen chloride is normally insignificant.

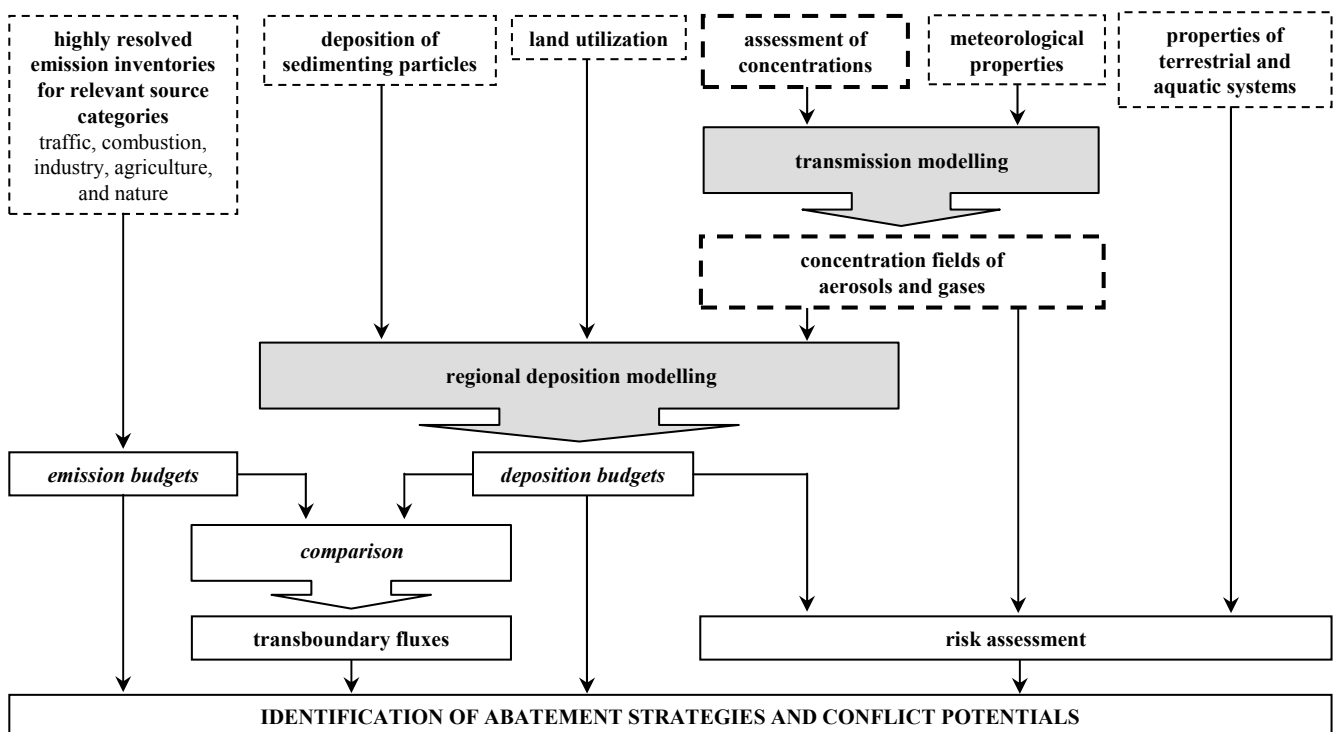


Figure 1:

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 Locations, methods and data quality

2.1 Locations

In order to check the viability of the concentration field modelling, a *concentration monitoring* of ammonia, its reaction partners and the reaction products was performed at Linden near Giessen at the Environmental Monitoring and Climate Impact Research Station Linden (50°32'N 8°41.3'E, 172m a.s.l., Grünhage et al., 1996; Jäger et al. 2003) using denuder filter equipment.

Normally, the modelling of vertical fluxes requires data sets with a resolution in time of about 0.5 h. As such data could not be provided with the technique involved, typical diurnal variations of the concentrations mentioned above had to be determined. Therefore, a second experiment was performed at the FAL site in Braunschweig aiming at the provision of correction factors with which typical diurnal variations can be described.

Measurements of *diurnal variation of concentrations* were conducted at the experimental field of the Institute of Agroecology of the Federal Agricultural Research Centre west of Braunschweig (52°18'N 10°26' E, 79 m a.s.l., Weigel and Dämmgen, 2000) from April 2004 until March 2006. The site is surrounded by grassland and fields. Animal houses of the experimental farm are more than 500 m southwest of the set up. Both fertilizing activities and the emissions from the nearby farm influence NH_3 concentrations significantly.

2.2 The sampling system

Air sampling for NH_3 concentrations using denuders is considered to be the standard procedure recommended in Germany (VDI 3869).

Both at Linden and Braunschweig, KAPS* denuder filter samplers were used. KAPS are "trains" of annular denuders and a filter pack which are arrayed as shown in Figure 2.

The air inlet is at a height of 3.5 m in accordance with German standards (Bundesminister des Innern, 1983). The air passes a cyclone to remove coarse particles. The air flow through the "train" and the auxiliary air flow are adjusted so that only particles with diameters below 3 μm enter the "train".

Denuders are coated tubes. If air passes them in a laminar flow, gases can be deposited on the walls, whereas particles pass them without being deposited. Thus, the disadvantages of impregnated filters (simultaneous deposition of gases and particles with the same analyte gaseous SO_2 , HNO_3

and NH_3 and particulate SO_4 , NO_3 and NH_4 , respectively can be avoided. As NH_4NO_3 captured on the PTFE filter is liable to thermolysis, the nylon filter is used to sample the gaseous reaction product HNO_3 (and HCl).

Three coated denuders in a series followed by two filters remove the air constituents under consideration completely. Imperfect depletion of the air in denuder 1 would be indicated by denuder 2.

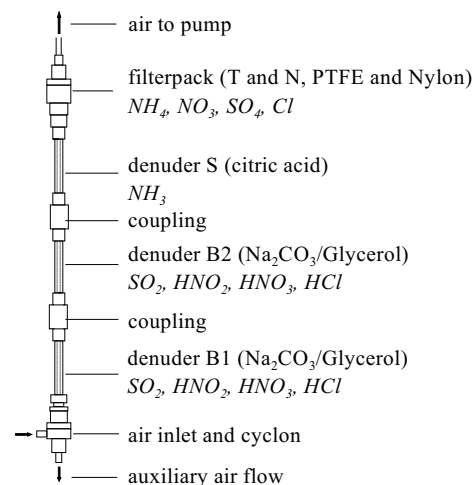


Figure 2:

Arrangement of denuders and filters in the KAPS denuder filter sampling system, and the species collected and deposited at the various denuders and filters.

Concentration monitoring at Linden

The distance of 300 km between Linden and the laboratory at Braunschweig did not allow for daily measurements. Instead, two denuders were run seven days at daytime and two over night, reflecting the different formation and destruction processes in particular for HNO_2 and HNO_3 (cf Zimmerling and Dämmgen, 2000). Two replicates were run to avoid losses and to check data quality.

As illustrated in Figure 3, a constant air flow through the "trains" is achieved by critical orifices. Solenoids switch the air flow according to time. One pump would be sufficient to create the necessary vacuum; again, two pumps were operated for security reasons. The flow rate was controlled using a flow meter before and after exposure. As a rule, the ventilation rate was 6 to 7 m^3 of air per week.

Diurnal variation measurements

Eight KAPS were mounted in an arrangement similar to that shown in Figure 3. They were exposed for one week, but switched on for 3 hours per day only (0 – 3hrs, 3 – 6 hrs, 6 – 9 hrs, etc.). Samples were taken every second week for two years. Thus, a mean diurnal variation could be established with a resolution of three hours.

* Kananaskis Air Pollutant Samplers

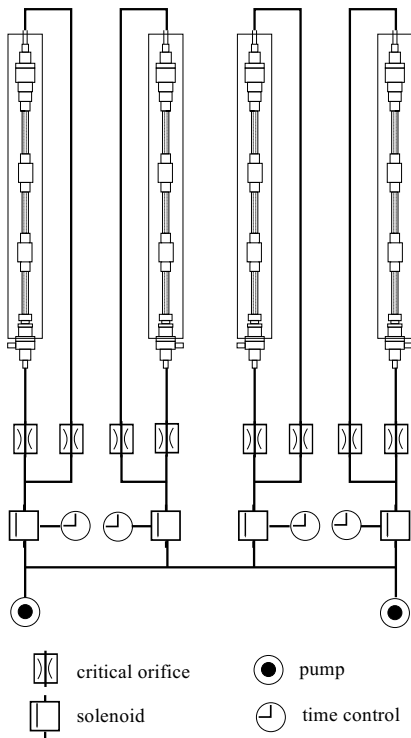


Figure 3:
Experimental setup to operate KAPS samplers at Linden (replicated sampling during night and day)

Table 1:
Analysis and subsequent calculation of results for KAPS samples

Species	analyte	calculation
denuders B1 and B2		
HNO ₂	NO ₂ -N	$(m_{B1} - m_{B2}) V^{-1}$
HNO ₃	NO ₃ -N	$(m_{B1} - m_{B2}) V^{-1}$
SO ₂	SO ₄ -S	$(m_{B1} - m_{B2}) V^{-1}$
HCl	Cl	$(m_{B1} - m_{B2}) V^{-1}$
denuder S		
NH ₃	NH ₄ -N	$m_S V^{-1}$
filters T and N		
NH ₄ -N	NH ₄ -N	$(m_T + e_N) V^{-1}$
NO ₃ -N	NO ₃ -N	$(m_T + m_N) V^{-1}$
SO ₄ -S	SO ₄ -S	$m_T V^{-1}$
Cl	Cl	$(m_T + m_N) V^{-1}$
Na	Na	$m_T V^{-1}$

m_{B1} and m_{B2} : amount of analyte recovered from denuders B1 and B2
 m_S : amount of analyte recovered from denuder S
 m_T : amount of analyte on filter T
 m_N : amount of analyte on filter N
 e_N : sum of equivalents of NO₃-N and Cl deposited on filter N
 V : air volume sampled

2.3 Preparation and analysis

Denuders were extracted with 15 ml demineralized water. Filters were eluted with 20 ml water (ultrasonic bath, 40 °C). Both solutions were analyzed by ion chromatography (NH₄-N, NO₃-N, SO₄-S, Cl; European standard EN ISO 10304-1) and segmented flow analysis (NH₄-N, NO₂-N; German standard DIN 38 406 E5). Na was determined occasionally (AAS, German standard DIN 38 406, E14). Details can be found in Table 1.

2.4 Data availability

Concentration monitoring at Linden

Apart from a few weeks, when breakages occurred during posting, only few samples were lost due to loose couplings, blockage of critical orifices, or power cuts. In most cases only one of the two replicates was lost. However, the overall availability was satisfactory. With the exception of Na measurements, the coverage of the three years was almost complete (Table 2).

Table 2:
Data availability, 2002 to 2004, in % of potential samples

	night-time	day time	weekly means
NH ₃	95.9	99.3	100.0
HNO ₂	93.9	96.6	99.3
HNO ₃	93.9	97.9	98.6
SO ₂	93.2	97.9	98.0
NH ₄ -N	94.6	98.6	98.6
NO ₃ -N	94.6	97.9	98.0
SO ₄ -S	94.6	97.9	98.0
Cl	94.6	97.9	98.0
Na	31.1	32.2	31.8

Diurnal variation measurements

No sampling losses occurred. However, the volume of the air samples did not allow for an adequate interpretation of HCl concentrations.

2.5 Quality of the data obtained at Linden

The two replicates allow for a quality assessment of the concentrations determined. Figures 4 to 7 illustrate the scatter of the results. Potential sources of the lack of identicalness are uncertainties in the flow or volume analyzed, and in the analytical procedures.

The accuracy of the flow meter is in the order of 2 %. Thus, deviations would not be significant. However, flows were only measured at the beginning and end of the

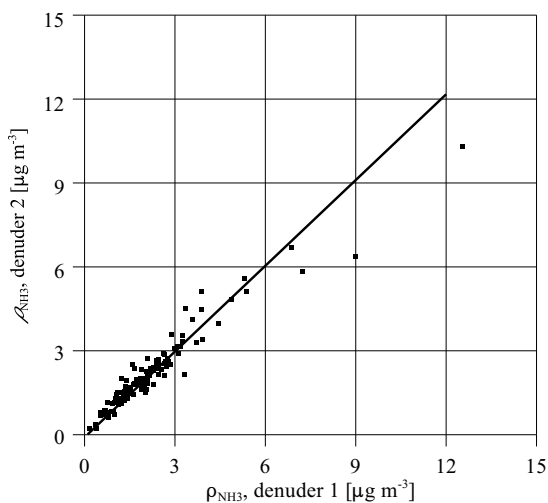


Figure 4:
Comparison of NH₃ concentrations measured in parallel at day time. 114 measurements

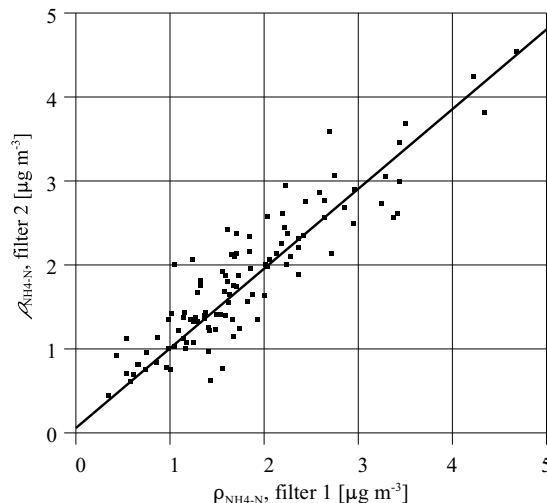


Figure 6:
Comparison of NH₄-N concentrations measured in parallel at day time. 106 measurements

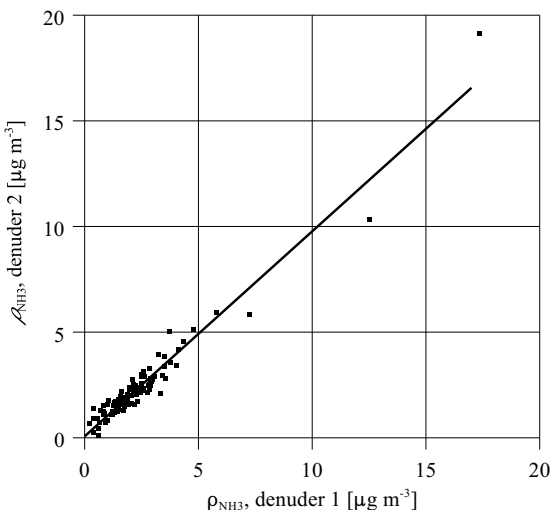


Figure 5:
Comparison of NH₃ concentrations measured in parallel at night time. 103 measurements

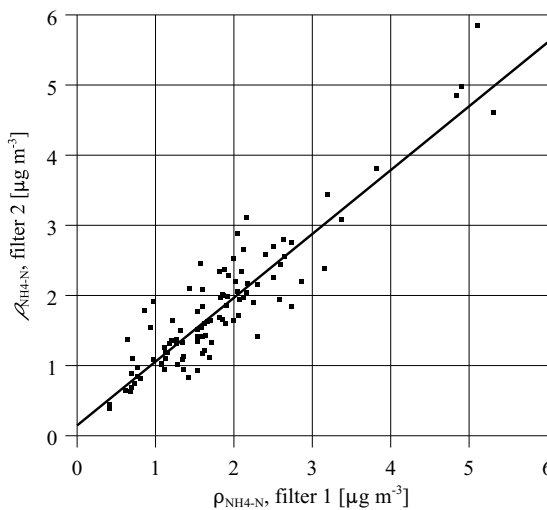


Figure 7:
Comparison of NH₄-N concentrations measured in parallel at night time. 100 measurements

exposure. Any events changing the flow rate during sampling could not be traced.

The small concentrations in ambient air of the species of interest result in solutions the concentrations of which are close to the limits of detection (Zimmerling, 1994).

Table 3 summarizes the results of a comparison of concentration replicates. For each species, about 100 pairs could be compared.

In principle, the slope of the regression line

$$\rho_{\text{denuder 2}} = a \cdot \rho_{\text{denuder 1}} + b$$

should be close to 1.00 and the intercept close to 0.00. However, with few exceptions, the slope deviated by 5 to 15 %. Regression coefficients R^2 for the nitrogen species were above 0.85. The standard deviation was normally about 20 % of the mean concentration. All values indicated that CI-measurements were too unreliable to be used. For all other species, integration over time resulted in mean concentrations which are likely to be “correct” for a season, i.e. within an error of $\pm 0.2 \mu\text{g m}^{-3}$.

Since the emission inventories have a resolution in time of a year – or are disaggregated to monthly values – and

an uncertainty of about 20 %, the concentration measurements are considered adequate.

Further plausibility checks could be made for the composition of particles, in particular of the Cl-Na and the $\text{NH}_4\text{-NO}_3\text{-SO}_4$ ratios. These will be considered in chapter 3.

Table 3:

Quality indicators for denuder filter concentration measurements (comparison of weekly measurements)

		slope a	inter- cept b $\mu\text{g m}^{-3}$	R^2	ρ_{mean} $\mu\text{g m}^{-3}$	σ $\mu\text{g m}^{-3}$
NH_3	day	1.02	- 0.09	0.901	2.1	0.3
	night	0.97	0.07	0.946	2.4	0.4
HNO_2	day	0.92	0.11	0.847	0.7	0.2
	night	0.91	0.10	0.855	1.0	0.2
HNO_3	day	0.93	0.04	0.846	1.2	0.2
	night	0.90	0.11	0.724	0.8	0.2
SO_2	day	0.93	0.09	0.891	2.0	0.3
	night	1.00	0.04	0.889	1.7	0.3
$\text{NH}_4\text{-N}$	day	0.95	0.06	0.824	1.8	0.2
	night	0.91	0.15	0.839	1.8	0.3
$\text{NO}_3\text{-N}$	day	0.95	0.09	0.857	0.8	0.2
	night	0.88	0.05	0.801	0.8	0.2
$\text{SO}_4\text{-S}$	day	0.87	0.08	0.764	1.1	0.2
	night	0.87	0.17	0.814	1.1	0.2
Cl	day	0.86	0.13	0.689	0.7	0.2
	night	0.74	0.19	0.480	0.8	0.2

2.6 Calculation of monthly means

The weekly mean night time and day time concentrations were averaged to form mean weekly concentrations. These were then aggregated to form mean monthly concentrations which are the weighted means of the respective weeks.

3 Results of concentration monitoring – means and annual variation

3.1 Concentrations of gases

Since concentrations were often close to or below the limits of determination, results had to be aggregated to allow for a meaningful interpretation. The complete set of monthly means (usually derived from the 16 measurements per month) is listed in Table 4.

Concentrations at Linden were compared with data obtained at the FAL site (Dämmgen, in preparation) and above a forest near Augustendorf (Schaaf et al., 2005) in the “pig and poultry belt” near Cloppenburg (northwest Lower Saxony,

cf. Meesenburg and Mohr, 2005) as well as with the remotely located Oberbärenburg (Ore Mountains).

NH_3 concentrations at Linden were typical for agricultural regions without intensive cattle production (Dämmgen and Sutton, 2001). Their annual variation is shown in Figure 8. It was obvious that peak concentrations in spring and summer coincided with the application of fertilizers, slurry and manure.

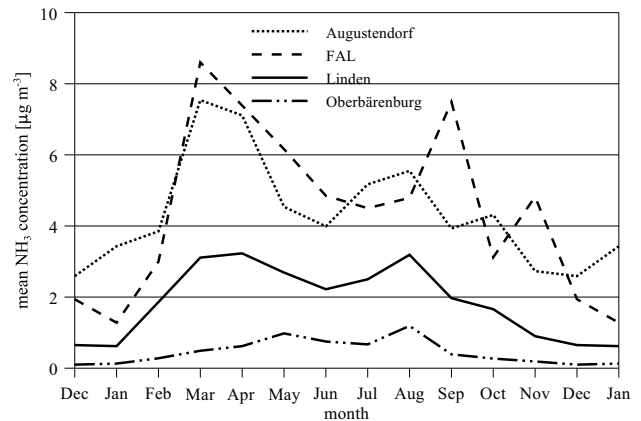


Figure 8:

Annual variation of NH_3 concentrations at Linden (2002 – 2004), FAL (2002 – 2004; Dämmgen, unpublished), Augustendorf (2002 – 2003; Schaaf et al., 2005) and Oberbärenburg (Ore Mountains, 2002; Plessow et al., 2005)

Concentrations were highest on the FAL field site. The forest site near Augustendorf is sheltered with respect to local NH_3 emissions. At Linden, both the concentrations as well as the ratio between highest and lowest concentrations were comparatively low. Oberbärenburg is a background station. Although concentrations were low at Linden, the annual pattern remains the same. It is yet unclear to what extent these concentrations are representative in time. For their representativeness in space see Dämmgen (2007).

As Figure 9 exemplifies, HNO_3 concentrations correlate with sunshine intensity (formation from nitrogen oxides) and temperature (thermolysis of NH_4NO_3). Wherever high NH_3 concentrations are observed, HNO_3 concentrations decrease (most significantly at Augustendorf) due to the formation of NH_4NO_3 .

SO_2 concentrations have decreased considerably during the past decades. As emissions are dominated by high sources, variability in space of SO_2 has become small. Linden exhibited the same concentration and seasonal pattern as FAL and Augustendorf. Concentrations in Oberbärenburg were obviously governed by long range transport of polluted air masses from fossil fuel combustion both in Saxony and Bohemia (Figure 10).

Table 4:
Monthly mean concentrations at Linden (in $\mu\text{g m}^{-3}$)

		gases					aerosol constituents				
		NH ₃	HNO ₂	HNO ₃	SO ₂	HCl	NH ₄ -N	NO ₃ -N	SO ₄ -S	Cl	Na
2001	Nov	1.3	1.2	0.1	2.3	0.2	1.8	1.0	1.0	1.1	
	Dec	0.5	1.1	0.3	3.9	0.3	0.8	0.4	0.4	0.3	
2002	Jan	0.6	1.9	0.7	6.1	0.2	2.4	1.3	1.2	0.9	
	Feb	1.3	0.5	0.6	2.8	0.5	1.2	1.0	1.0	1.0	
	Mar	3.4	0.8	0.9	2.9	0.3	2.5	1.3	1.4	0.8	
	Apr	4.0	0.6	1.3	3.2	0.4	3.7	1.7	2.3	0.6	
	May	2.3	0.4	1.6	1.3	0.4	2.4	0.6	1.2	0.7	
	June	2.9	0.4	1.6	1.3	0.4	1.7	0.4	1.1	0.5	
	July	2.2	0.6	1.2	1.1	0.3	1.6	0.3	1.4	0.5	
	Aug	2.5	0.5	1.6	1.1	0.1	2.2	0.4	1.8	0.5	
	Sep	2.4	0.9	1.0	1.2	0.2	1.9	0.6	1.4	0.4	0.2
	Oct	2.4	0.7	0.6	2.0	0.4	1.8	0.8	0.9	0.6	0.0
	Nov	0.7	1.3	0.3	2.0	0.2	2.3	1.1	0.8	1.0	0.4
	Dec	0.9	1.3	0.6	3.3	0.2	2.5	1.0	1.3	0.6	0.3
2003	Jan	0.6	1.3	0.5	2.8	0.2	2.5	1.3	1.2	0.7	0.4
	Feb	3.4	2.2	0.5	3.4	0.1	4.0	2.7	1.7	0.7	0.0
	Mar	3.7	0.6	0.5	1.5	0.2	1.8	1.2	0.8	0.5	0.3
	Apr	3.4	0.3	1.0	1.3	0.5	1.3	0.4	0.6	0.6	0.3
	May	4.1	0.5	1.6	0.9	0.2	1.7	0.6	0.9	0.8	0.5
	June	2.0	0.2	1.1	1.2	0.3	1.1	0.3	1.0	0.6	0.2
	July	3.5	0.6	1.8	2.1	0.2	1.1	0.3	1.0	0.4	0.2
	Aug	4.7	0.7	1.4	1.2	0.3	1.2	0.5	1.2	0.7	0.6
	Sep	1.6	1.1	1.5	1.3	0.3	0.7	0.5	0.7	0.4	0.3
	Oct	1.1	0.8	0.4	1.6	0.4	1.4	0.7	0.7	0.7	0.4
	Nov	1.2	1.5	0.4	1.3	0.3	1.4	0.8	0.8	0.5	
	Dec	0.4	0.8	0.7	1.9	0.5	0.8	0.5	0.4	0.7	
2004	Jan	0.6	1.0	1.0	2.6	0.7	1.9	1.2	0.8	2.3	
	Feb	1.0	1.3	0.7	3.4	0.5	3.6	2.0	1.5	1.6	
	Mar	2.2	0.7	1.2	2.2	0.7	2.9	1.6	1.2	1.1	
	Apr	2.4	0.5	1.4	1.5	0.7	2.2	0.8	0.9	1.6	
	May	1.7	0.5	1.0	0.9	0.5	1.4	0.8	1.1	2.0	
	June	1.8	0.7	1.2	0.7	0.3	2.2	0.7	1.0	1.3	
	July	1.9	0.6	1.7	2.6	0.4	2.6	0.4	0.9	1.2	
	Aug	2.4	0.2	1.6	1.3	0.4	2.3	0.4	0.9	1.9	
	Sep	1.9	1.0	0.9	1.7	0.4	1.2	0.4	0.8	0.7	
	Oct	1.5	1.2	0.5	1.5	0.4	2.0	0.8	0.9	0.9	
	Nov	0.8	1.7	0.4	3.0	0.6	3.1	1.5	1.4	1.1	
	Dec	0.6	2.7	0.6	3.7		3.6	1.6	1.8	1.1	
mean	Jan	1.4	1.4	0.7	3.8	0.3	2.3	1.3	1.1	1.3	
	Feb	1.3	1.3	0.6	3.2	0.4	2.9	1.9	1.4	1.1	
	Mar	0.7	0.7	0.9	2.2	0.4	2.4	1.4	1.1	0.8	
	Apr	0.5	0.5	1.2	2.0	0.5	2.4	1.0	1.3	0.9	
	May	0.5	0.5	1.4	1.1	0.4	1.8	0.7	1.1	1.2	
	June	0.5	0.5	1.3	1.0	0.4	1.7	0.5	1.0	0.8	
	July	0.6	0.6	1.6	1.9	0.3	1.8	0.4	1.1	0.7	
	Aug	0.5	0.5	1.6	1.2	0.3	1.9	0.4	1.3	1.0	
	Sep	1.0	1.0	1.2	1.4	0.3	1.2	0.5	1.0	0.5	
	Oct	0.9	0.9	0.5	1.7	0.4	1.8	0.7	0.8	0.7	
	Nov	1.5	1.5	0.4	2.1	0.3	2.3	1.2	1.0	0.9	
	Dec	1.6	1.6	0.6	3.0	0.4	2.3	1.1	1.2	0.8	
overall mean	year	2.0	0.9	1.0	2.1	0.4	2.1	0.9	1.1	0.9	

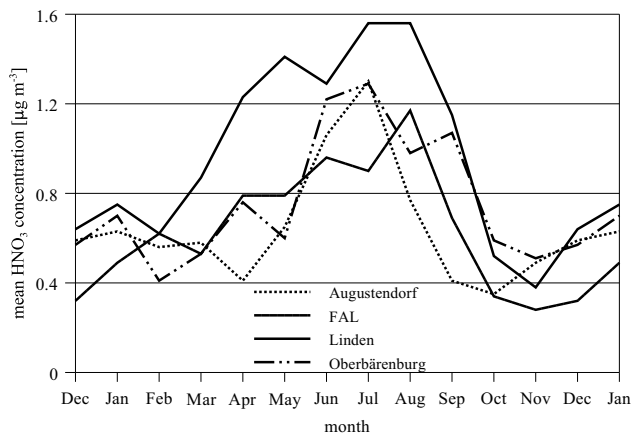


Figure 9: Annual variation of HNO₃ concentrations at Lindens (2002 – 2004), FAL (2002 – 2004), Augustendorf (2002 – 2003) and Oberbärenburg (Ore Mountains; 2002). For sources see Figure 8.

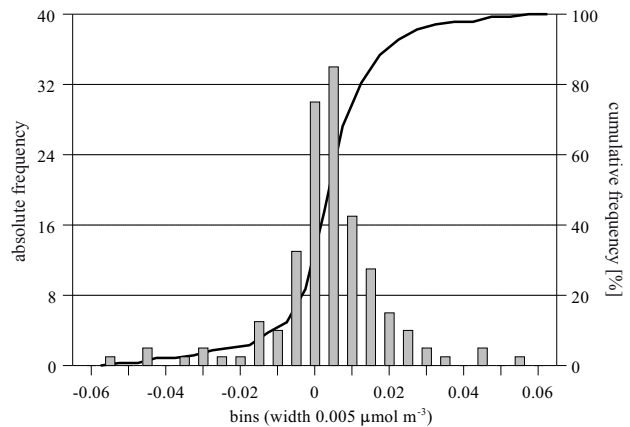


Figure 11: Frequency distribution of the difference of Cl and Na concentrations ($\rho_{Cl} - \rho_{Na}$, in $\mu\text{mol m}^{-3}$) at Lindens, measurements (March 2003 – March 2004)

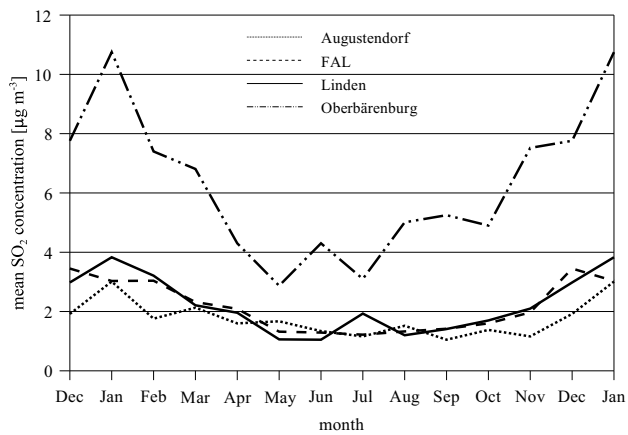


Figure 10: Annual variation of SO₂ concentrations at Lindens (2002 – 2004), FAL (2002 – 2004), Augustendorf (2002 – 2003) and Oberbärenburg (Ore Mountains, 2002). For sources see Figure 8.

3.2 Sodium and chloride in particles

During 12 months, sodium (Na) concentrations were measured at Lindens. For most of the time, concentrations were close to or below the limits of determination. The accuracy of these data is doubtful.

However, if one eliminates outliers, the mean difference of the concentrations of both Cl and Na in particles was zero. The frequency distribution showed that the deviations from zero are usually quite small (Figure 11). It is reasonable to assume that Na and Cl exist as NaCl in most cases. However, some events indicate that Cl was neutralized by NH₄.

3.3 Ammonium, nitrate and sulphate in particles

Due to their extended atmospheric lifetime, the spatial variability of the concentration of aerosol constituents is less pronounced than for gases. For NH₄-N, the concentrations at Lindens and FAL were almost the same. The overall source strength in the Weser Ems Region with Augustendorf resulted in higher levels of pollution with NH₄ salts. Concentrations are highest where NH₃ and SO₂ emissions were highest, resulting in a spring and a winter peak. At Lindens, the large NH₃ emissions in August were not neutralized by HNO₃ or the reaction products of SO₂ to form particles (Figure 12).

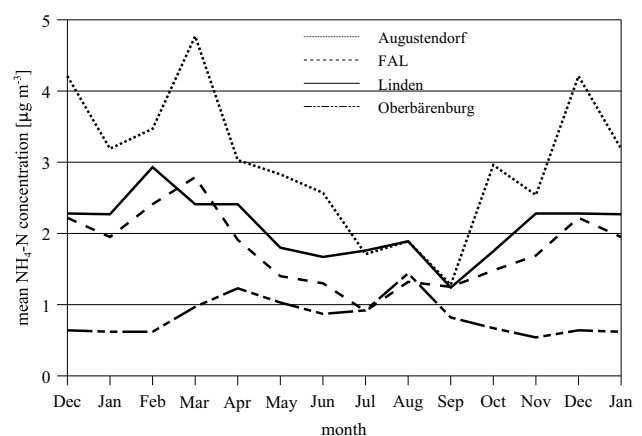


Figure 12: Annual variation of NH₄-N concentrations at Lindens (2002 – 2004), FAL (2002 – 2004), Augustendorf (2002 – 2003) and Oberbärenburg (Ore Mountains, 2002). For sources see Figure 8.

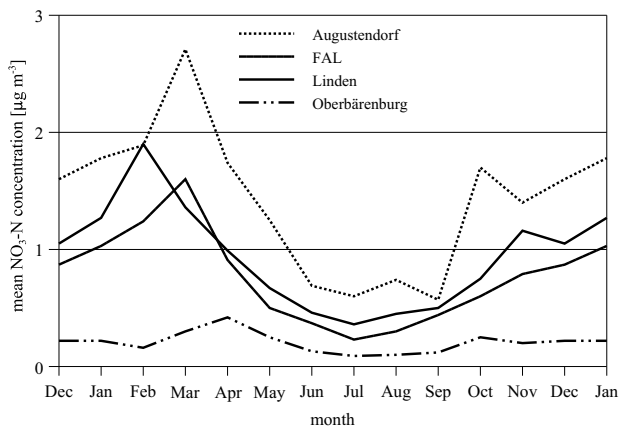


Figure 13: Annual variation of NO₃-N concentrations at Linden (2002 – 2004), FAL (2002 – 2004), Augustendorf (2002 – 2003), Oberbärenburg (Ore Mountains, 2002). For sources see Figure 8.

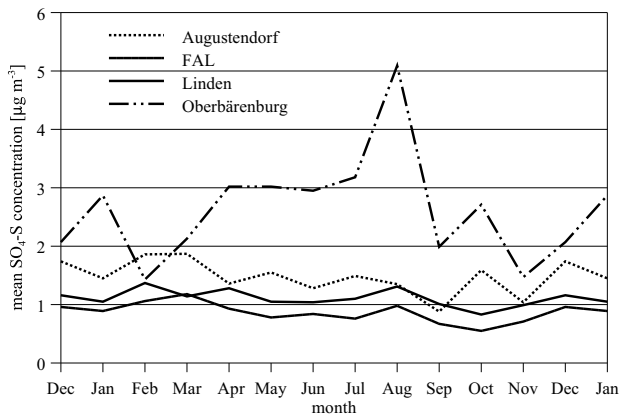


Figure 14: Annual variation of SO₄-S concentrations at Linden (2002 – 2004), FAL (2002 – 2004), Augustendorf (2002 – 2003) and Oberbärenburg (Ore Mountains, 2002). For sources see Figure 8.

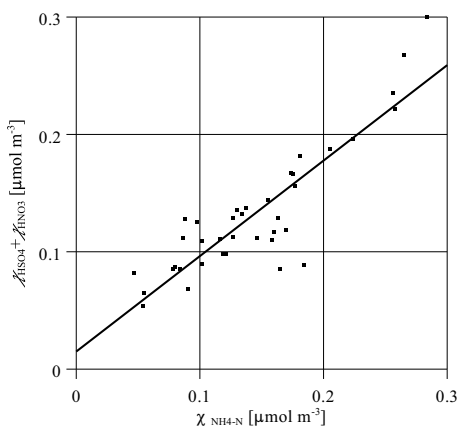


Figure 15: Neutralization of NH₃ with HNO₃ and H₂SO₄ (formation of NH₄HSO₄), comparison of monthly means of the equivalents. Linden (2002 – 2004). R² = 0.78.

NO₃-N concentrations reflect the influence of high NH₃ emissions in spring at comparatively low temperatures; they are inversely correlated with temperatures (Figure 13).

SO₄-S concentrations at Linden, FAL and Augustendorf are very similar. For Oberbärenburg, the situation is clearly different. The peak in August coincides with a peak in NH₄-N concentrations. However, these explain the high concentrations only partly (Figure 14).

If one assumes complete neutralization of H₂SO₄ and no interaction of Cl (see above) for the Linden site, then almost all NH₃ reacts with HNO₃ and H₂SO₄ (see Figure 15).

Similar relations were observed by Zimmerling and Dämmgen (2002), Vogt et al. (2005) and Herrmann et al. (2006).

4 Diurnal variation of concentrations

The diurnal patterns obtained at the FAL field site were aggregated to derive mean monthly or seasonal patterns which were to be used in flux monitoring if only long term measurements were available. The data obtained for FAL were then compared with the day and night data measured at Linden.

4.1 Ammonia

NH₃ emissions from fertilisation are temperature dependent and should result in peak emissions at noon (Sutton et al., 2006). In addition, diurnal variation of concentrations should be observed during the periods of fertiliser and manure applications. However, the raw data listed in Table 5 cannot be interpreted in a way that represents an annual

Table 5:

Relative diurnal variation of NH₃ concentrations at the FAL site, **raw data**.

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Jan	0.8	1.1	1.0	1.1	0.8	0.6	1.2	1.3
Feb	0.9	1.0	1.0	0.9	0.7	0.7	1.2	1.5
March	0.9	0.9	1.0	1.3	0.9	1.0	1.1	1.0
April	1.2	0.9	0.8	0.8	0.9	1.0	1.1	1.3
May	1.1	0.9	0.9	1.0	1.2	0.9	1.1	0.9
June	1.2	1.0	0.9	0.8	0.9	0.8	1.1	1.3
July	1.1	1.1	0.9	1.0	0.9	0.9	0.9	1.2
Aug	0.9	0.8	1.1	0.9	0.9	0.8	1.3	1.3
Sep	0.9	0.8	1.1	1.0	0.8	0.8	1.2	1.5
Oct	1.0	0.9	1.0	1.1	0.8	0.9	1.2	1.1
Nov	0.8	0.8	1.0	1.2	1.1	0.9	1.1	1.1
Dec	1.1	0.8	0.9	0.8	0.8	0.9	1.8	1.0

variation of the diurnal variation (Table 6). The diurnal variation rather reflected the atmospheric exchange properties resulting in higher concentrations over night.

It is recommended to derive „high resolution“ data from weekly means using the factors given in Table 6.

Table 6:

Correction factors proposed for the derivation of the diurnal variation of NH₃ concentrations from daily mean concentrations

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
All months	1.0	0.9	1.0	1.0	0.9	0.9	1.1	1.2

A comparison of these factors would explain the difference between the Linden day and night means (day night ratio calculated and found for Linden: 0.93 to 1.07)

4.2 Nitrous acid

Gaseous HNO₂ is rapidly photolyzed forming NO and HO radicals:



However, agricultural fields are likely to be a permanent source of HNO₂, therefore, concentrations never become zero, even in periods of intensive sunshine.

This should result in both a diurnal and an annual variation, as is illustrated in Table 7.

Table 7:

Relative diurnal variation of HNO₂ concentrations at the FAL site, **raw data**.

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Jan	1.3	1.0	1.0	0.9	0.6	0.8	1.2	1.1
Feb	1.3	1.0	1.1	0.9	0.6	0.6	1.2	1.3
Mar	1.4	1.3	1.3	0.7	0.6	0.5	0.9	1.3
April	2.0	2.1	1.2	0.3	0.4	0.1	0.2	1.7
May	1.4	1.6	1.2	0.8	0.6	0.5	0.6	1.3
June	1.4	1.5	1.2	0.7	0.7	0.5	0.6	1.5
July	1.8	0.9	1.1	0.4	0.4	0.5	1.4	1.4
Aug	1.7	0.9	1.0	0.5	0.4	0.4	1.0	2.1
Sep	1.5	1.4	1.3	0.5	0.3	0.6	0.9	1.5
Oct	1.2	1.2	1.2	0.9	0.7	0.6	1.1	1.1
Nov	1.2	0.9	1.2	1.0	0.6	0.7	1.2	1.3
Dec	1.0	0.8	0.8	0.8	0.6	1.1	1.4	1.4

In principle, the duration and intensity of sunshine should be the major variables governing the correction factor. This was found to be valid for the interpretation of the measurements and is reflected in the proposed correction factors (Table 8). Within the accuracy of HNO₂ measurements, the Braunschweig data reflect the situation in Linden well.

Table 8:

Correction factors proposed for the derivation of the diurnal variation of HNO₂ concentrations from daily mean concentrations

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Dec Jan	1.2	0.9	0.9	0.9	0.6	1.0	1.3	1.3
Nov Feb	1.2	1.0	1.1	0.9	0.6	0.7	1.2	1.3
Oct Mar	1.3	1.3	1.3	0.8	0.6	0.6	1.0	1.2
Sep April	1.8	1.7	1.3	0.4	0.4	0.3	0.5	1.6
Aug May	1.6	1.3	1.1	0.6	0.5	0.5	0.8	1.7
July June	1.6	1.2	1.2	0.5	0.5	0.5	1.0	1.5

4.3 Nitric acid

The formation of nitric acid occurs both at daytime (final product of NO and NO₂ oxidation) and at night time (so called dark reaction, see Zimmerling and Dämmgen, 2000). During summer days, the thermolysis of NH₄NO₃ will also contribute to HNO₃ concentrations. The presence of NH₃ in spring is unlikely to influence correction factors. In the winter months, two concentration peaks per day can be clearly identified (Table 9).

The overall correction table (Table 10) should reflect the annual variation of the photochemical activity and temperature. The four seasons are used to differentiate between correction factors.

Although formation, atmospheric chemistry and deposition are likely to differ between Braunschweig and Linden, the ratio between mean night and day concentrations was still similar (Braunschweig: 1.14 to 0.86; Linden: 1.06 to 0.94). Keeping in mind that the concentrations were very low, the Braunschweig corrections may well be used for flux modelling in Linden.

Table 9:

Relative diurnal variation of HNO₃ concentrations at the FAL site, **raw data**.

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Jan	0.8	0.4	1.0	0.6	1.9	0.8	0.6	1.9
Feb	0.8	0.6	0.7	0.6	1.6	0.9	0.6	2.2
Mar	1.3	0.6	0.8	0.6	1.7	0.4	1.0	1.6
April	0.6	0.0	0.7	0.8	2.1	0.8	0.9	2.0
May	0.9	0.3	0.7	1.1	1.4	1.3	0.6	1.7
June	0.4	0.2	0.4	1.1	2.3	1.5	0.8	1.2
July	0.7	0.5	0.5	1.1	2.2	1.4	1.0	0.7
Aug	0.4	0.3	0.6	1.2	2.3	1.4	0.6	1.3
Sep	0.5	0.6	0.7	1.4	2.0	1.2	0.6	1.1
Oct	0.6	1.2	1.0	1.4	1.5	0.9	0.7	0.7
Nov	1.4	0.7	0.6	1.1	1.3	0.9	0.7	1.3
Dec	0.6	0.4	0.6	1.3	1.5	0.9	0.4	2.3

Table 10:

Correction factors proposed for the derivation of the diurnal variation of HNO₃ concentrations from daily mean concentrations

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Dec								
Jan	0.7	0.5	0.8	0.8	1.7	0.9	0.5	2.1
Feb								
Mar								
April	0.9	0.3	0.7	0.8	1.7	0.8	0.9	1.8
May								
June								
July	0.5	0.3	0.5	1.1	2.3	1.4	0.8	1.1
Aug								
Sep								
Oct	0.8	0.8	0.8	1.3	1.6	1.0	0.7	1.1
Nov								

4.4 Sulphur dioxide

Both in Braunschweig and Linden, SO₂ is not emitted from local sources to an extent which needs to be considered. It is emitted from high stacks and liable to long-range transport. High resolution measurements at Braunschweig indicated that SO₂ concentrations peak after sunrise were caused by vertical mixing after the boundary layer has become deep enough (Grünhage et al., 1992, 1996). The same effect can explain the diurnal variation observed in the measurements described here (Table 11).

Attempts to obtain high resolution data from the SO₂

monitors installed at Linden failed, due to their inadequate limit of detection. The table of proposed corrections (Table 12) separates the season of large emissions in winter from the rest of the year. The major difference between the spring, summer and autumn factor is the time of sunrise.

Table 11:

Relative diurnal variation of SO₂ concentrations at the FAL site, **raw data**.

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Jan	1.1	0.7	1.1	1.0	1.4	1.0	1.0	0.8
Feb	1.1	0.9	1.0	1.1	1.2	1.1	0.8	0.9
Mar	0.9	1.0	1.0	1.2	1.1	1.0	1.0	0.8
April	0.9	0.7	1.2	1.4	1.0	0.9	0.8	1.1
May	1.1	0.9	1.2	1.4	1.4	0.6	1.1	1.0
June	0.7	1.4	1.3	1.4	1.0	1.1	0.5	0.6
July	1.2	0.9	1.9	1.1	1.0	0.7	0.6	0.5
Aug	0.8	0.6	1.2	1.3	1.1	0.9	0.9	1.2
Sep	0.8	0.5	0.9	1.7	1.2	1.1	1.0	0.8
Oct	0.9	1.0	1.1	1.3	1.2	0.9	0.8	0.8
Nov	1.1	0.8	0.9	1.1	1.3	0.9	0.9	1.0
Dec	1.0	1.0	1.0	0.9	0.9	1.1	1.1	1.1

Table 12:

Correction factors proposed for the derivation of the diurnal variation of SO₂ concentrations from daily mean concentrations

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Nov								
Dec								
Jan	1.1	0.9	1.0	1.0	1.2	1.0	0.9	0.9
Feb								
Mar								
Apr	0.9	0.8	1.1	1.4	1.1	1.0	0.9	0.9
Sep								
Oct								
May								
June,	0.9	0.9	1.4	1.3	1.1	0.8	0.8	0.9
July								
Aug								

4.5 Sulphate and chloride in particles

The atmospheric lifetime of particulate matter by far exceeds that of the reactive gases dealt with above. This results in a “damped” diurnal variability. Both sulphate and chloride do not undergo chemical reactions (Cl is almost always correlated to Na, ammonium sulphates do not thermolyze.) The raw data provided in Tables 13 and 14 do not

show any distinctive pattern. Since the situation in Linden is similar to that in Braunschweig, no correction factors are proposed.

Table 13:

Relative diurnal variation of $\text{SO}_4\text{-S}$ concentrations in particulate matter at the FAL site, **raw data**.

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Jan	1.0	1.0	1.1	1.0	0.9	1.0	1.1	1.0
Feb	1.2	1.2	1.0	0.9	0.8	1.0	1.0	0.9
Mar	1.1	1.1	0.9	1.0	1.0	1.0	1.0	0.9
Apr	0.9	0.9	0.8	1.1	1.0	1.2	1.1	1.0
May	0.9	1.2	1.0	1.2	1.0	1.0	0.8	0.9
June	0.8	0.9	1.0	1.2	1.2	1.0	1.0	0.9
July	1.0	0.9	1.1	1.2	1.1	1.0	0.8	0.8
Aug	0.9	0.7	0.9	1.2	1.2	1.4	0.8	0.8
Sep	0.8	1.0	0.9	1.2	1.1	1.0	0.9	1.1
Oct	0.9	0.9	0.8	1.2	1.2	1.2	0.9	1.0
Nov	1.0	1.1	1.1	0.9	1.0	0.9	1.0	0.9
Dec	1.0	0.9	1.0	1.1	1.1	1.1	1.0	0.9

Table 14:

Relative diurnal variation of Cl concentrations in particulate matter at the FAL site, **raw data**.

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Jan	1.2	0.9	0.7	1.0	1.2	1.0	1.1	0.9
Feb	1.1	0.9	0.7	1.0	1.0	1.1	1.1	1.0
Mar	1.6	1.6	0.5	1.0	0.9	0.6	0.8	0.9
Apr	1.4	1.0	0.8	0.8	0.9	1.3	0.9	1.0
May	0.8	1.3	0.9	1.0	1.0	1.0	1.2	0.9
June	1.0	1.0	1.3	1.0	1.0	0.8	0.9	1.1
July	0.8	1.3	1.0	0.8	1.0	1.0	0.9	1.1
Aug	0.9	0.9	1.2	1.1	1.3	0.9	0.9	0.9
Sep	0.9	0.9	1.0	1.3	0.8	1.2	1.0	1.0
Oct	0.9	0.7	0.8	1.2	1.0	1.1	1.1	1.1
Nov	1.0	0.8	1.0	1.0	1.2	1.3	0.9	0.8
Dec	1.0	0.9	1.0	1.0	1.2	1.1	0.9	1.0

4.6 Nitrate in particles

In contrast to sulphate and chloride and as a consequence of thermolysis, nitrate in particles should have a typical diurnal variation with minimum concentrations in the afternoon. As shown in Table 15, this effect was observed in all seasons. The corresponding correction factors in Table

16 are grouped according to the duration of sunshine and similar temperatures.

Highest concentrations were observed in the early morning hours, lowest in the afternoon. The months with increased NH_3 emissions were identified with large factors for the late morning. Braunschweig and Linden showed the same pattern.

Table 15:

Relative diurnal variation of $\text{NO}_3\text{-N}$ concentrations in particulate matter at the FAL site, **raw data**.

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Jan	1.1	1.1	1.1	1.0	0.9	0.9	1.0	0.9
Feb	1.2	1.3	1.0	1.0	0.8	0.8	1.0	1.0
Mar	1.3	1.4	1.3	1.1	0.6	0.6	0.8	0.8
Apr	1.4	1.3	1.0	1.1	0.7	0.8	0.7	1.1
May	1.2	1.7	1.2	0.8	0.8	0.7	0.6	0.9
June	1.1	1.3	1.4	0.9	0.8	0.7	0.8	0.9
July	1.4	1.4	1.1	0.9	0.9	0.8	0.7	0.8
Aug	0.8	1.0	1.6	1.0	1.0	0.9	0.8	0.9
Sep	0.9	1.3	1.5	1.4	0.6	0.7	0.8	0.9
Oct	0.9	1.1	0.9	1.2	1.0	0.9	0.8	1.1
Nov	0.9	1.1	1.1	1.1	0.9	0.9	0.9	1.0
Dec	1.0	1.0	1.0	1.1	1.0	1.0	1.0	1.0

Table 16:

Correction factors proposed for the derivation of the diurnal variation of $\text{NO}_3\text{-N}$ concentrations in particles from daily mean concentrations

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Dec	1.0	1.0	1.0	1.1	0.9	1.0	1.0	1.0
Jan	1.0	1.0	1.0	1.1	0.9	1.0	1.0	1.0
Nov	1.1	1.2	1.0	1.0	0.9	0.9	1.0	1.0
Feb	1.1	1.2	1.0	1.0	0.9	0.9	1.0	1.0
Oct	1.1	1.2	1.1	1.2	0.8	0.8	0.8	1.0
Mar	1.1	1.2	1.1	1.2	0.8	0.8	0.8	1.0
Sep	1.2	1.3	1.2	1.2	0.7	0.7	0.8	1.0
Apr	1.2	1.3	1.2	1.2	0.7	0.7	0.8	1.0
Aug	1.0	1.3	1.4	0.9	0.9	0.8	0.7	0.9
May	1.0	1.3	1.4	0.9	0.9	0.8	0.7	0.9
July	1.2	1.4	1.3	0.9	0.8	0.7	0.7	0.9
June	1.2	1.4	1.3	0.9	0.8	0.7	0.7	0.9

4.7 Ammonium in particles

In particles, NH_4 is the cation neutralizing NO_3^- , HSO_4^- , and Cl^- . As a consequence, any diurnal variation should

be small. However, as indicated in Table 17, no substantial variation could be observed. Even a combination of months with similar sunshine intensity and temperatures did not result in correction factors. Braunschweig and Linden data look similar, so the use of the mean concentrations is proposed for Linden.

Table 17:

Relative diurnal variation of $\text{NH}_4\text{-N}$ concentrations in particulate matter at the FAL site, **raw data**.

A: 0 – 3 hrs; B: 3 – 6 hrs; C: 6 – 9 hrs; D: 9 – 12 hrs; E: 12 – 15 hrs; F: 15 – 18 hrs; G: 18 – 21 hrs; H: 21 – 24 hrs

	A	B	C	D	E	F	G	H
Jan	1.1	1.1	1.1	1.0	1.0	0.9	1.0	0.9
Feb	1.1	1.1	1.1	1.0	0.9	0.9	1.0	0.8
Mar	1.2	1.1	1.0	1.1	0.9	0.9	1.0	0.8
Apr	0.9	1.2	0.9	1.1	0.9	1.0	0.9	1.0
May	1.0	1.4	1.0	1.1	0.9	0.8	0.8	0.9
June	1.0	1.1	1.2	1.1	1.0	0.9	0.8	0.9
July	1.0	1.1	1.1	1.1	1.1	1.0	0.8	0.9
Aug	0.9	0.9	1.1	1.0	1.2	1.1	0.9	0.9
Sep	1.0	1.1	1.2	1.3	1.0	0.9	0.8	0.8
Oct	0.8	1.1	1.1	1.2	0.9	1.0	0.9	1.0
Nov	1.0	1.1	1.0	1.2	0.9	1.1	0.9	0.9
Dec	0.9	0.9	0.9	1.1	1.0	1.0	1.1	1.1

5 Conclusions

Concentration measurements of gaseous and particulate reactive nitrogen and sulphur species in ambient air rely on the use of denuder filter techniques. At the time of the measurements described, the application of denuders was not an established procedure. Therefore an independent quality check was achieved at least for NH_3 by parallel concentration measurement using passive samplers. This comparison was satisfactory. Passive samplers were also used to obtain information about the spatial variability of NH_3 concentrations in Hesse (Dämmgen, 2007).

Meanwhile the use of denuders represents the German reference method for the determination of NH_3 concentrations (VDI 3869), and KAPS denuders in particular were tested successfully in the respective intercomparisons (Lumpp). Thus, the concentration data measured at Linden can be considered valid.

Concentration measurements with a low resolution in time can be used to establish fluxes successfully (Dämmgen and Zimmerling, 2002; Mohr et al., 2005). If micro-meteorological data are available to describe the atmospheric resistivities, assumptions have to be made for the diurnal variation of the concentrations. For Linden, cumulative annual fluxes will be established using the corrected

mean concentrations and the SVAT model PLATIN (Grünhage and Haenel, 2007).

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References

- Bundesminister des Innern (1983) Bundeseinheitliche Praxis bei der Überwachung der Emissionen und Immissionen. Gem Ministerialbl 76-81
- Dämmgen U (2006) Atmospheric nitrogen dynamics in Hesse, Germany : creating the data base. I. Bulk deposition of acidifying and eutrophying species. *Landbauforsch Völkenrode* 56(3-4):117-138
- Dämmgen U (2007) Atmospheric nitrogen dynamics in Hesse, Germany : creating the data base. III. Concentrations of ammonia as obtained with passive sampling. *Landbauforsch Völkenrode*, in preparation
- Dämmgen U, Sutton MA (2001) Die Umwelt-Wirkungen von Ammoniak-Emissionen. *KTBL-Schrift* 401:14-25
- DIN 38 406 E5 (1983) Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (Gruppe E) : Bestimmung des Ammonium-Stickstoffs (E 5). Berlin : Beuth
- DIN 38 406, E14 (1992) Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung. Kationen (Gruppe E) : Bestimmung von Natrium mittels Atomabsorptionsspektrometrie (AAS) in der Luft-Acetylen-Flamme (E14). Berlin : Beuth
- EN ISO 10304-1 (1995) Wasserbeschaffenheit. Bestimmung der gelösten Anionen Fluorid, Chlorid, Nitrit, ortho-Phosphat, Bromid, Nitrat und Sulfat mittels der Ionenchromatographie : Teil 1. Gering belastete Wässer. Berlin : Beuth
- Grünhage L, Dämmgen U, Haenel H-D, Jäger H-J (1992) Vertikale Flüsse von Spurengasen in der bodennahen Atmosphäre. *Landbauforsch Völkenrode* SH 128:201-245
- Grünhage L, Hanewald K, Jäger H-J, Ott W (1996) Auswirkungen dynamischer Veränderungen der Luftzusammensetzung und des Klimas auf terrestrische Ökosysteme in Hessen. II. Umweltbeobachtungs- und Klimafolgenforschungsstation Linden: Jahresbericht 1995. *Umweltplanung, Arbeits- und Umweltschutz* 220
- Grünhage L, Dämmgen U, Erisman JW, Lüttich M, Hanewald K, Jäger H-J, Freitag K, Baltrusch M, Liebl K (2002) Atmospheric nitrogen dynamics in Hesse, Germany : the challenge and its potential solution. *Landbauforsch Völkenrode* 52(4):219-228
- Grünhage L, Haenel H-D (2007) PLATIN (PLant-ATmosphere INTERaction) - a flux estimation programme for latent and sensible heat, trace gases and aerosol constituents. *Landbauforsch Völkenrode*, in preparation
- Herrmann H, Brüggemann E, Franck U, Gnauk T, Löschau G, Müller K, Plewka A, Spindler G (2006) A source study of PM in Saxony by size-aggregated characterisation. *J Atmos Chem* 55:103-130

- Jäger H-J, Schmidt SW, Kammann C, Grünhage L, Müller C, Hanewald K (2003) The University of Giessen free air carbon dioxide enrichment study : description of the experimental site and of a new enrichment system. *J Appl Bot* 77:117-127
- Lumpp R, LUBW Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Württemberg, unpublished results
- Meesenburg H, Mohr K (2005) Die Untersuchungsstandorte im ANSWER-Projekt. *Landbauforsch Völkenrode SH* 279:17-22
- Mohr K, Schaaf S, Horváth B, Meeseburg H, Dämmgen U (2005) Stoff- und Energieflüsse der im ANSWER-Projekt untersuchten Waldbestände. *Landbauforsch Völkenrode SH* 279:69-94
- Plessow K, Spindler G, Zimmermann F, Matschullat J (2005) Seasonal variations and interactions of N-containing gases and particles over a coniferous forest, Saxony, Germany. *Atmos Environ* 39:6995-7007
- Schaaf S, Dämmgen U, Mohr K, Meeseburg H (2005) Witterung, Spurengas- und Schwebstaub-Inhaltsstoff-Konzentrationen in der Umgebungsluft und in den Beständen des ANSWER-Projekts. *Landbauforsch Völkenrode SH* 279:57-68
- VDI-KRdL – VDI-Kommission Reinhaltung der Luft : Messen von Ammoniak in der Außenluft : Probenahme in beschichteten Diffusionsabscheidern (Denudern) ; Photometrische bzw. ionenchromatographische Analyse. VDI 3869, Blatt 3. Berlin : Beuth, in preparation
- Vogt E, Held A, Klemm O (2005) Sources and concentrations of gaseous and particular reduced nitrogen in the city of Münster, Germany. *Atmos Environ* 39:7393-7402
- Weigel H-J, Dämmgen U (2000) The Braunschweig Carbon Project : atmospheric flux monitoring and Free Air Carbon Dioxide Enrichment (FACE). *J Appl Bot* 74:55-60
- Zimmerling R (1994) Denuder-Filter-Messungen zur Bestimmung von Konzentrationen und vertikalen Flüssen von S- und N-Spezies in der bodennahen Atmosphäre über landwirtschaftlichen Nutzflächen. *Clausthal-Zellerfeld : Papierflieger*, 297 p
- Zimmerling R, Dämmgen U (1999) Sources, atmospheric transport and sinks of tropospheric nitrous and nitric acids. In: Agrawal SB, Agrawal M (eds) *Environmental pollution and plant responses*. Boca Raton : Lewis, pp 259-294
- Zimmerling R, Dämmgen U (2002) Concentrations of air-borne acidifying and eutrophying species in the Schorfheide Nature Reserve in Brandenburg, Germany. *J Appl Bot* 76:52-61