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## Fine particles and their constituents in Germany - results of denuder filter measurements

Ulrich Dämmgen<sup>1</sup>

### Abstract

Ammonia in the atmosphere reacts with atmospheric acids such as nitric acid, hydrogen chloride and sulfuric acid to form ammonium salts, which form a major proportion of the atmospheric aerosol, in particular within  $PM_{2.5}$ . In contrast to the concentrations of other air pollutants, the concentrations of these so-called secondary aerosols did not decrease proportionally to the decrease of their precursor acids, in particular of  $SO_2$ , as their formation is in several ways closely linked to the availability of gaseous ammonia.

The paper presents and discusses measurements of the concentrations of ammonium salts in  $PM_{2.5}$  aerosols and their precursor gases made at several locations in northern Germany using denuder filter equipment.

Ammonia and sodium seem to neutralize the acids in the water soluble part of the aerosol totally. The annual cycle of the concentrations of these aerosol constituents can be interpreted as being a function both of the ammonia emissions in spring and air temperature.

Fluxes of nutrients and acidity with aerosols may contribute significantly to the respective overall fluxes into forest ecosystems. Any measures to reduce the areas endangered by acidification and eutrophication will have to make sure that the emission of the precursor gases of aerosols, especially of ammonia, will be reduced. This applies also to measures reducing the concentrations of air-borne particulate matter with respect to human health.

As ammonia originates almost entirely from agriculture, the reduction of the concentrations of aerosols will have effects on agricultural management practices.

*Keywords: aerosols,  $PM_{2.5}$ , ammonia, agriculture*

### Zusammenfassung

Das Spurengas Ammoniak reagiert mit atmosphärischen Säuren wie Salpetersäure, Chlorwasserstoff oder Schwefelsäure unter Bildung von Ammoniumsalzen, die einen wesentlichen Anteil am atmosphärischen Aerosol, insbesondere an  $PM_{2.5}$ , bilden.

Im Gegensatz zu den Konzentrationen anderer Luftverunreinigungen sind die Konzentrationen dieser sogenannten Sekundäraerosole nicht in dem Maße zurückgegangen, wie es die Verringerung der Konzentrationen der zu ihrer Entstehung beitragenden Säuren, insbesondere von  $SO_2$ , hätte erwarten lassen, da die Entstehung der Sekundäraerosole in mehrfacher Hinsicht mit der Anwesenheit von gasförmigem Ammoniak verknüpft ist.

Der Beitrag stellt Ergebnisse von Messungen zur Bestimmung der Gehalte von Ammoniumsalzen in Aerosolen ( $PM_{2.5}$ ) und ihren Ausgangsverbindungen vor, die an mehreren Orten in Norddeutschland unter Verwendung von Denuder-Filter-Apparaturen gewonnen wurden, und diskutiert sie.

Ammoniak und Natrium neutralisieren praktisch die gesamten wasserlöslichen Säuren im Aerosol. Der Jahresgang der Konzentrationen der genannten Aerosol-Bestandteile lässt sich über die Ammoniak-Emissionen im Frühjahr und die Lufttemperaturen deuten.

Die aus der Abscheidung von Aerosol herrührenden Flüsse von versauernden und eutrophierenden können insbesondere bei Waldökosystemen erheblich zur Gesamtbelastung beitragen. Alle Maßnahmen zur Verringerung der durch Versauerung und Eutrophierung gefährdeten Flächen müssen dafür Sorge tragen, dass die Emissionen der zu ihrer Bildung beitragenden Spurengase, vor allem die von Ammoniak, verringert wird. Dies gilt in gleicher Weise für die Verringerung der Aerosol-Konzentrationen im Hinblick auf die menschliche Gesundheit zu.

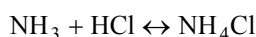
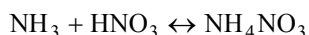
Da Ammoniak nahezu ausschließlich aus landwirtschaftlichen Quellen emittiert wird, werden Maßnahmen zur Verringerung der Aerosol-Konzentrationen Auswirkungen auf die landwirtschaftliche Praxis haben.

*Schlagwörter: Aerosol,  $PM_{2.5}$ , Ammoniak, Landwirtschaft*

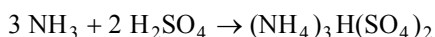
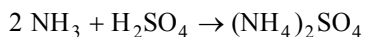
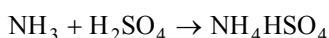
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## 1 Introduction

Agricultural sources are not only responsible for direct emissions of particles (emission of so-called primary particles), but also for the emission of precursor gases the atmospheric chemistry of which yields secondary particles: ammonia ( $\text{NH}_3$ ) emitted from animal and arable agriculture serves as base in atmospheric reactions with gaseous nitric acid ( $\text{HNO}_3$ ) or hydrogen chloride ( $\text{HCl}$ ) such as



or sulfuric acid ( $\text{H}_2\text{SO}_4$ ) in aerosol droplets



The first two reactions are fast and reversible. The equilibrium concentrations are within the range of concentrations generally observed in central Europe. The concentration product describing the maximum concentrations of gaseous reactants in the atmosphere is a function of both temperature and humidity: low temperatures and high humidities lead to increased particle concentrations, high temperatures result in thermolysis of particulate  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$ . At temperatures above 10 °C  $\text{NH}_4\text{Cl}$  is not existing in practice. Reactions between gases yielding solid or liquid particles normally presuppose the existence of condensation nuclei such as soot particles.

Atmospheric  $\text{H}_2\text{SO}_4$  is a reaction product of sulfur dioxide ( $\text{SO}_2$ ). The three reactions given above are irreversible.

Due to their formation process, secondary particles are normally (more or less) spherically shaped; they have typical aerodynamic diameters between 0.1 and 3  $\mu\text{m}$ . As a consequence, these particles are not subject to sedimentation and hence have long atmospheric half-lives, being capable of long range travelling, i.e. over more than 1000 km (see Garland, 2001, and literature cited therein), and contributing to acidification and eutrophication even in remote areas (Dämmgen and Sutton, 2001). However, if these particles are inhaled, they will pass the human nose, trachea and bronchial tubes and reach the alveoles, where they are deposited. For this reason they have gained specific interest in the past decade and are subject to national and international air pollution control.

Measurements of aerosol size distributions show that about two thirds to three quarters of the total suspended particulate matter (TSP) are in the fraction with aerodynamic diameters below 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ )

(c.f. Umweltbundesamt 2001). Although considerable effort has been made during the past decades to reduce the concentrations of particles, concentrations of this fraction of aerosols have not yet lessened proportionally, as can be shown by the concentration of S in particles (TSP) (figure 1).

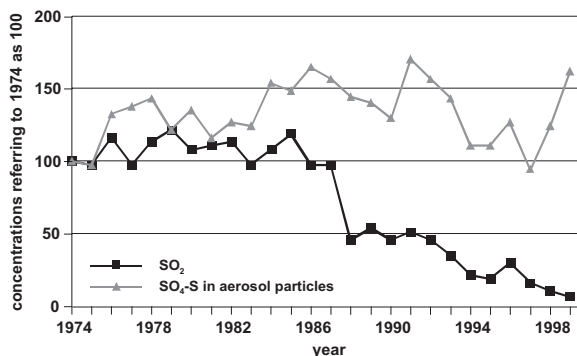


Figure 1: Effects of air pollution control in Germany: the drastic reduction in  $\text{SO}_2$  emissions is not reflected by S concentrations in aerosols (Umweltbundesamt 2001)

The reason for this is the fact that aerosol S concentrations are limited at least to a great extent by the availability of atmospheric  $\text{NH}_3$ : in non-urban central European atmospheres,  $\text{PM}_{2.5}$  particle masses are dominated by ammonium salts, their proportion typically being between 50 and 70 % of the total mass. In addition there is crustal material (a few %), so-called elementary or black carbon as well as organic carbon compounds and water. Ammonium salt proportions are highest for particle diameters around 1  $\mu\text{m}$  (c.f. Zinder et al., 1988, ten Brink et al. 1996, Harrison et al. 2002, Hass et al. 2002, Spindler et al. 2002). In the atmosphere, subsequent thermolysis of  $\text{NH}_4\text{NO}_3$  and  $\text{HCl}$  combined with chemical reactions of particulate salts with  $\text{H}_2\text{SO}_4$  as well as dry deposition of reactants and reaction products as outlined in figure 2, should lead to changes in the composition of aerosols: “old” aerosols are likely to be composed of sulfates, whereas “young” aerosols should consist mainly of nitrates.

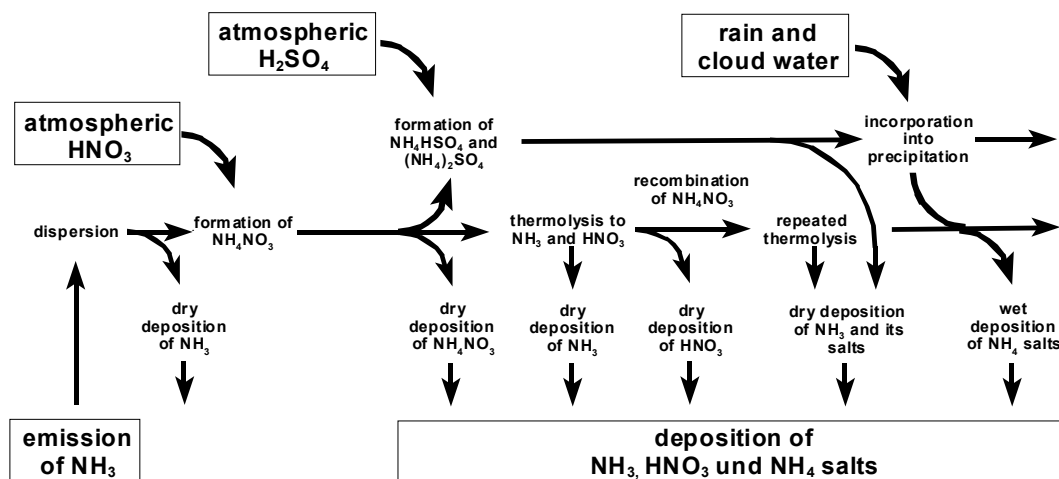


Figure 2:

Emission, atmospheric reactions and deposition processes determining the formation and transformation of aerosol ammonium salts (after Dämmgen & Erisman, 2002)

## 2 Material and methods

### 2.1 Sampling of aerosols for constituent determination

Analysis of aerosols is normally achieved by collection on filters with subsequent chemical analysis of the solution obtained when stripping the filter. However, the solutions gained have the same analytes as some gases, which might be collected on the filter at the same time, in particular NH<sub>3</sub>, HNO<sub>3</sub> or SO<sub>2</sub>, which then fake higher concentrations. At the same time, thermolysis may occur on the filters leading to reduced amounts of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>. Therefore the investigation of aerosol constituents has to make use of combined denuder filter samplers. Denuders strip the sampled air from reactive gases (c.f. Dämmgen 2001), so that artefact formation on the filters due to interaction of gases is avoided. The acid gaseous reaction products which stem from thermolysis on an inert (PTFE) filter, are collected on a second (nylon) filter which then allows the back-calculation of the losses on the PTFE-filter.

Combined denuder filter samplers facilitate the determination of the whole set of gases and particles, the concentrations of which are depending on one another as a consequence of chemical transformation, i.e. of gaseous SO<sub>2</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, HCl, NH<sub>3</sub>, and of NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup> as well as Na<sup>+</sup> in aerosols. However, operation of batch denuder filter samplers is time consuming, automation is very costly.

For our experiments, we used Kananaskis Air Pollutant Samplers (KAPS, three-stage denuder with PTFE and nylon filter, for details of set-up, operation, analytical procedures involved, and accuracy gained see Zimmerling et al., 1996a, 1997). The samples

taken can be analysed for constituents only. Due to potential losses during equilibration in the laboratory, it is (nearly) impossible to obtain filters which can be weighed for the determination of aerosol concentration directly. For such purposes additional sampling of size segregated PM using impactors and filters is necessary.

### 2.2 Locations of sampling

Since 1991, measurements have been performed of the concentrations of reactive nitrogen and sulfur species in ambient air at various locations

- 1991 to 1993: Rotenkamp near Braunschweig, above grassland
- 1995 to 1998: Müncheberg east of Berlin, above arable land (little animal agriculture)
- 1996 to 1998: Britz/Schorfheide northeast of Berlin, above forest
- 1997 to 1998: Wildbahn/Schwedt in the Oderbruch, in a forest partly influenced by industry and a town
- since 1999 at the FAL site near Braunschweig, above arable land (arable and animal agriculture)

Furthermore two additional sites have been operated at Augustendorf near Friesoythe (Frisia) above forest and Linden near Gießen (Hesse) above grassland since 2001. Results of all campaigns will be used in this paper.

At Melpitz, Saxony, atmospheric aerosol has been investigated using filter techniques since 1993 (Spindler et al. 2002). The results obtained there serve as comparison. No other long-term measurements have been published for Germany (Schaap et al. 2002).

### 3 Aerosol (PM<sub>2.5</sub>) constituents in northern Germany

#### 3.1 Composition and concentrations

Secondary aerosols are to a large extent composed of ammonium nitrate and sulfates, the ammonium of which stems almost entirely from agriculture. For this reason the total concentration (partial density) of PM<sub>2.5</sub> ammonium salts will be called the *agricultural aerosol concentration* {PM<sub>2.5</sub>} in this paper. It can be obtained from the partial densities of the constituents analysed.

For 2001, Na concentrations were available almost all of the time. The percentages of the composition are given in Table 1. The anions and cations determined under the assumption that all sulfate is existing as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> nearly always form neutral salts. A slight surplus of anions, i.e. the potential acidity, could be deduced from the linear regression ( $\Sigma e_{\text{cat}} = 0.97 e_{\text{an}} + 0.004$ ,  $r^2 = 0.924$ ). However, this is also well within the uncertainty caused by sampling and the analytical procedures involved (figure 3).

Table 1:

{PM<sub>2.5</sub>} concentrations at the FAL site, Braunschweig, in 2001, as calculated from water soluble constituents, and proportions of the respective mass contributions

species	unit	Apr - Sep	Oct - Mar	year
{PM <sub>2.5</sub> }	µg m <sup>-3</sup>	6.8	10.7	8.6
NH <sub>4</sub>	%	28	28	28
NO <sub>3</sub>	%	24	38	30
SO <sub>4</sub>	%	31	19	26
Cl	%	11	12	11
Na	%	5	3	4

Similar measurements had been performed at other locations in different years. A comparison of the results compiled in Table 2 has to be made with due care. However, it shows a reduction in overall concentrations for the one location where samples were taken in different periods: the summer means of PM<sub>2.5</sub> concentrations at the FAL site obviously decreased considerably. This corresponds with PM<sub>10</sub> measurements at Melpitz (Spindler et al. 2002).

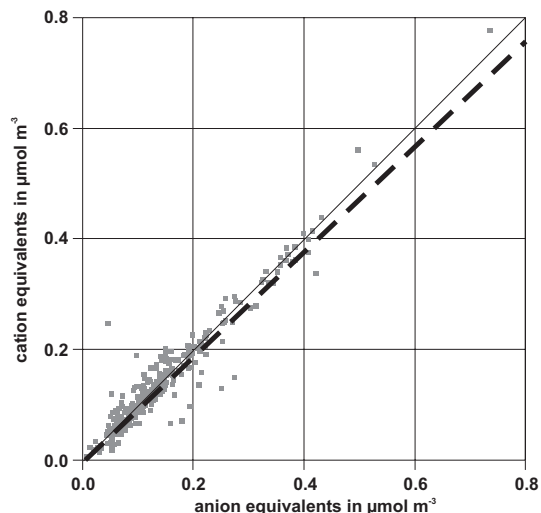


Figure 3:

Anion and cation equivalents in aerosols, denuder filter samples taken at the FAL site, 2001, including NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and Cl<sup>-</sup>. The dotted line illustrates the regression mentioned in the text

Table 2:

Mean {PM<sub>2.5</sub>} concentrations in µg m<sup>-3</sup> at various places in northern Germany, as calculated from water soluble constituents, and proportions of the respective mass contributions. Data from Zimmerling et al., 1996b, Zimmerling et al. 2001, and unpublished data

location	from	to	{PM <sub>2.5</sub> }
Rotenkamp	May 1991	Apr 1993	13.0
	Apr 1993	Aug 1993	10.7
Müncheberg	May 1995	Apr 1998	9.5
Britz	May 1996	Apr 1998	8.7
Wildbahn	Aug 1997	Jul 1998	10.1
FAL	Jan 2000	Dec 2001	8.6
	Apr 2001	Sep 2001	6.8
	Apr 1993	Aug 1993	13.9

At the FAL site, in the (roughly spoken) decade between the measurements in 1993 and 2001, mean concentrations of the precursor gases decreased from about 10 to 2 µg m<sup>-3</sup> for SO<sub>2</sub>, stayed more or less equal for HNO<sub>3</sub> (0.7 µg m<sup>-3</sup>) or increased considerably for NH<sub>3</sub> (summer 1993: 3.8 µg m<sup>-3</sup>, summers 2000/2001 6.9 µg m<sup>-3</sup>).

The parallel measurements in Brandenburg (Münchenberg, Britz and Wildbahn) reveal a difference between the remote forest site at Britz, the agricultural site at Müncheberg and the slightly polluted site at Wildbahn. Although these differences are small, they exceed the resolution of the measurements and are significant. The same order of difference can be seen for the summer period in 1993 when simulta-

neous measurements were performed east (Rotenkamp) and west (FAL) of Braunschweig in areas slightly influenced (Rotenkamp) and considerably influenced (FAL) by animal husbandry. Even in times of increased air pollution, the nearby steel works at Salzgitter and the city of Braunschweig do not emit articles to an extent which can be traced in the rural areas considered (Hartwig-Hanitz et al. 1996).

3.2 Annual and diurnal variation of the concentrations of PM<sub>2.5</sub> constituents

The annual variation of the species composition of PM<sub>2.5</sub> with regard to N, S and Cl species is shown in figure 4. The fact that summer concentrations fall below the mean as indicated in Table 2 can clearly be seen. The reduction can obviously be attributed to the decreased proportion of NH<sub>4</sub>NO<sub>3</sub>.

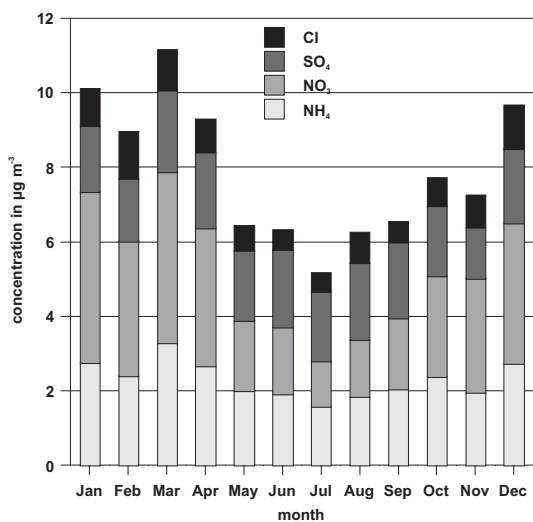


Figure 4: Annual variation of the concentrations (partial densities) of ammonium, nitrate, sulfate and chloride in PM<sub>2.5</sub>, monthly means for 2000 and 2001, FAL

A comparison of figures 4 and 5 clarifies that the concentrations of the precursor gases are not directly influencing the local concentrations. In particular does the presence of SO<sub>2</sub> in winter not result in a greater proportion of sulfate. Prior to the formation of ammonium sulfates, SO<sub>2</sub> has to be oxidized to form H<sub>2</sub>SO<sub>4</sub>. This process takes place within droplets; its rate is strongly pH dependent, and “hence the rate of sulfate production tends to be determined by the concentration of ammonia gas“ (Choularton and Bower, 2001). Nevertheless, even the comparatively small amount of HNO<sub>3</sub> present leads to effective particle formation.

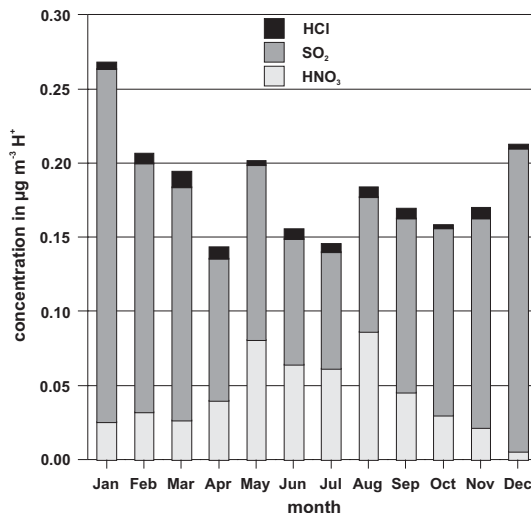


Figure 5: Annual variation of the concentrations (equivalents) of acid precursor gases for secondary particle formation (HCl, SO<sub>2</sub>, HNO<sub>3</sub>), monthly means for 2000 and 2001, FAL

Although there is no direct correlation at all between single concentrations of the aerosols and their precursor gases - correlation coefficients between the relevant pairs of species are typically below 0.2, (Zimmerling et al. 2000a) -, the diurnal variation of {PM<sub>2.5</sub>} is obviously related to the variation of the NH<sub>3</sub> concentrations in ambient air. figure 6 indicates that a “mixture” of the annual variations in NH<sub>3</sub> concentrations shown may serve as a key to interpret the annual variation of {PM<sub>2.5</sub>} with a maximum at the time of fertiliser application, again indicating the importance of regional rather than local atmospheric composition.

Obviously concentrations are below average during summer. This can be attributed to minor contributions of NH<sub>4</sub>NO<sub>3</sub> to overall {PM<sub>2.5</sub>}, most of which can be related to the increased temperatures and thus the increased vapour pressure of NH<sub>4</sub>NO<sub>3</sub> (figure 7).

Differences between the agricultural and the forest sites are greatest in March and April showing the influence of regional ammonia sources. This agrees with the interpretation of long-time monitoring results in the USA (Edgerton et al. 1992)

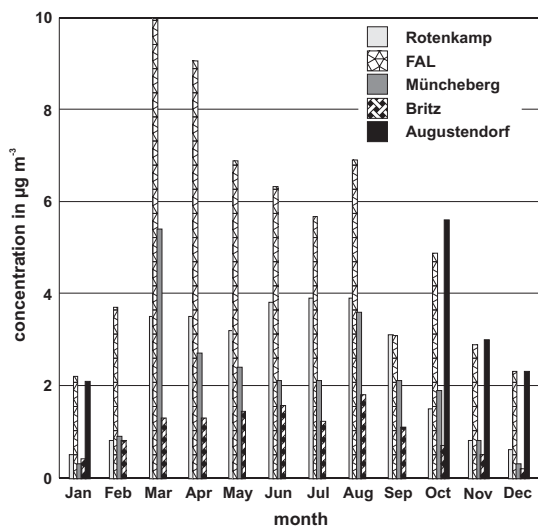


Figure 6: Annual variation of the concentrations (partial densities) of ammonia at different locations, monthly means for the periods given in Table 1, Augustendorf Oct 2001 to Feb. 2002

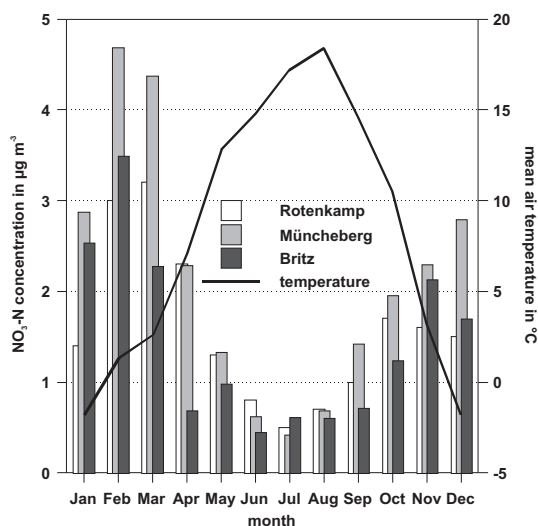


Figure 7: Annual variation of the concentrations (partial densities) of nitrate N at different locations, monthly means for the periods given in Table 1. Mean air temperature shown is for the Müncheberg region

In contrast to the gases measured, the aerosol constituents exhibit definitely less diurnal variation of their concentrations.

### 3.3 Concentration profiles and vertical fluxes

Vertical fluxes of gases and aerosols between the atmosphere and a canopy result in vertical concentration gradients, which - with roles reversed - can be

related to an atmospheric transport conductance to yield the amount of the vertical flux.

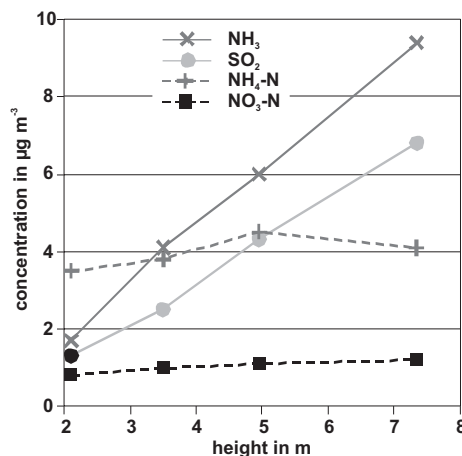
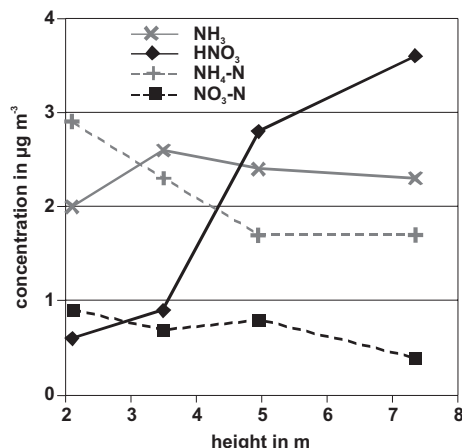


Figure 8: Vertical gradients of gas and aerosol constituent concentrations, measured at Rotenkamp. Upper half: night-time case study; lower half: daytime case study. Data from Zimmerling (1994)

As can be seen from figure 8, the reactive gases exhibit a strong gradient during night-time, indicating a deposition situation. However, due to the fact that the conductance is very low, no significant fluxes result. The concentration gradients of the aerosol constituents have the same “direction”, but are not distinctive.

The daytime profiles shown in figure 8 look different: the reactive gas HNO<sub>3</sub> has a strong gradient typical for deposition. NH<sub>3</sub>, however, reveals an ambiguous pattern, which in combination with those of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> and keeping in mind analytical errors, has to be interpreted in terms of a slight emission from the grassland vegetation and subsequent reaction with HNO<sub>3</sub> causing particle growth near the canopy.

The assessment of vertical fluxes of the aerosol constituents described here shows different behaviour for different types of vegetation. For aerosols and

their constituents, the deposition velocity (i.e. the ratio between flux and concentration of a given species) is strongly dependent on the roughness of the receptor system. Whereas fluxes of aerosol constituents are small for agricultural systems, they contribute significantly to the overall inputs of  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$  and  $\text{SO}_4\text{-S}$  in forests (Hesterberg et al. 1996, Erisman et al. 2001). They may even dominate inputs of eutrophying species into a forest (Zimmerling et al. 2000b).

#### 4 Conclusions

At present, European legislation aims at a reduction of the ecosystems and areas endangered by acidification and eutrophication (cf UN/ECE 2000, IIASA 2002) as well as a reduction in aerosol concentrations (EU 1999). The critical analysis of the composition of aerosols and their depositions clearly shows the importance of the ammonium in aerosols salts for all three fields.

Obviously the availability of atmospheric  $\text{NH}_3$  governs the process of particle formation and/or growth. Thus any measure to reduce acidity and nitrogen inputs into natural and semi-natural ecosystems, especially forest ecosystems, will be connected to reductions in  $\text{NH}_3$  concentrations. The same applies to reductions of fine particle concentrations in ambient air with regard to human health. As  $\text{NH}_3$  originates almost entirely from agriculture, the regulations and recommendations mentioned above will have to be based on a reduction of ammonia emissions, which will have an impact on agricultural production processes, in particular in animal husbandry.

In general, knowledge about aerosols and their constituents in central Europe is thought to be insufficient, which - amongst others - results in poor agreement of measured and modelled concentrations and fluxes of the respective aerosol constituents.

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