

AMMONIA AND ACIDIFICATION

EURASAP SYMPOSIUM



Bilthoven 13 -15 April 1987

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AMMONIA AND ACIDIFICATION

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**Symposium of the European Association for the Science
of Air Pollution (EURASAP) held at the National Institute
of Public Health and Environmental Hygiene, Bilthoven,
The Netherlands, 13–15 April 1987**

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editors**

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INTRODUCTION

The EURASAP Symposium "Ammonia and Acidification" was held in Bilthoven, The Netherlands during April 13-15, 1987, as presumably the first international symposium entirely devoted to the atmospheric behaviour of ammonia and ammonium. In the past attention had been paid to ammonia and ammonium because these components are of importance to the global nitrogen cycle (Söderlund and Svensson, 1976; Böttger et al., 1978) and to the possible interaction of sulphur dioxide and ammonia (Van den Heuvel and Mason, 1963; Adewuyi and Carmichael, 1982).

Moreover, it was noticed that ammonium was an important component in aerosols at ground level and in precipitation. The knowledge of the atmospheric behaviour of ammonia and ammonium was, however, very incomplete compared to that of sulphur dioxide and nitrogen oxides and reaction products. At the most semi-quantitative information was available.

At the moment our knowledge on ammonia and ammonium is expanding rapidly. This is probably caused by the fact that it was found that deposition of ammonia and ammonium can result in acidification of the soil (Van Breemen et al., 1982). In the Netherlands relatively much attention has been paid to ammonia, which is caused by the fact that the Netherlands has presumably the highest emission density of ammonia in the world, which leads to deterioration of natural ecosystems. It seems therefore appropriate that this first symposium on the atmospheric behaviour of ammonia was held in the Netherlands.

The picture we have at the moment is still incomplete, but I would use this opportunity to draw some personal conclusions. Looking at the information presented at the symposium from a modellers point of view the following remarks can be made:

Emission

The estimated ammonia emission rate in Europe (in equivalents) is only 20% of the emission rate of the acid precursors sulphur dioxide and nitrogen oxides. (The major part of the emission of acid precursors exists of sulphur dioxide.) This is a low percentage. At ground level the acid in aerosols and precipitation at many sites in N.W.-Europe is neutralized by ammonia to a large extent. Not many measurements are available at some height above ground level, so it cannot be excluded that averaged over the whole mixing layer the acid is neutralized to a lesser degree than at ground level. Moreover, sulphur dioxide is generally converted to sulphate at a much lower rate than ammonia is converted to ammonium. As a consequence the fraction of the emission of sulphur dioxide converted to sulphate is lower than the fraction of the emission of ammonia converted to ammonium. In this way part of the discrepancy between the relatively low emission rate of ammonia and the high degree of neutralization of aerosols and precipitation at ground level can be explained. An other part can, however, not be explained. It seems therefore not unreasonable to assume that the ammonia emission rate in reality is higher than has been estimated until now.

Dry deposition

The dry deposition velocity for ammonia in flat natural terrain outside emission areas seems to be rather well established. Information on the dry deposition velocity for ammonia for forests is almost absent. Information on the dry deposition velocity of ammonia or better said the frequency of occurrence and magnitude of a net flux to the surface in agricultural areas is lacking. A strong gradient of NH_4^+ in throughfall is found in forest edges, which is not yet reproduced by models. This reflects the problems of

dry deposition in inhomogeneous terrain. At the moment not enough information is available of the importance of a compensation point for ammonia for the deposition flux. In natural terrains in the Netherlands no indications of the existence of a compensation point were found at ammonia concentrations well below $1 \mu\text{g m}^{-3}$ (Diederer, 1987).

Conversion of ammonia to ammonium

In models the conversion of ammonia to ammonium is often described by a pseudo-first order reaction constant which is found by tuning some of the model parameters to fit the measured concentrations of NH_3 , NH_4^+ aerosol and NH_4^+ aerosol and NH_4^+ in precipitation. This is a rather critical procedure. If other model parameters get a somewhat different value, a different value for the reaction constant is found. Methods to measure the conversion rate have failed because too many assumptions have to be made to calculate the conversion rate. It would be better to use a model which takes all processes into account which lead to conversion; i.e. turbulent diffusion which causes mixing of ammonia with air containing acidic components, diffusion of ammonia to aerosols and reaction of ammonia at the surface of aerosols. As ammonia is mainly released at or near the earth's surface it is necessary to use at least multi-layer models to describe the upward flux of ammonia and subsequent reaction adequately.

Measurements

Measurements can be made to study processes, e.g. emission, deposition, reaction or scavenging. There is an urgent need for continuous measurement techniques for NH_3 and NH_4^+ aerosol to study such processes. Measurements can also be made to verify model results. The time-resolution of the models is mostly not so large that the concentration of these components has to be

monitored continuously. NH_3 concentrations in agricultural areas are closely related to local emissions and are not representative of the concentration in larger ($>5 \times 5 \text{ km}^2$) areas. As a result measurement of NH_3 concentrations are only useful for model validation, if the local emission rate can be estimated relative to the emission rate in other areas for which concentrations should be computed. The relation between emission rate and concentration found can then be used in models to describe the concentration pattern over a larger area.

There are a few sites in Europe for which long term NH_4^+ aerosol concentrations are known. So additional measurements are useful. This not because the dry deposition of NH_4^+ is important for the NH_x budget, but because knowledge of the NH_4^+ aerosol concentration pattern can improve the tuning of the model.

The NH_4^+ concentration in precipitation is measured at rather many sites in Europe, however the sites are not equally distributed. In southern and eastern Europe there are not many stations. Moreover, measurement artefacts are of importance. The measurements can be influenced by dry deposition of NH_3 in the open collectors and by micro-organisms if the collection bottles are not protected against light.

No models are available which are able to describe the gradients in throughfall of NH_4^+ in forest edges. This is partly caused by uptake of NH_4^+ by vegetation.

Effects

Only up to about 50 m from stables the ammonia concentration can be so high that on the long run direct effects on vegetation can be observed. For scientists studying the indirect effects of deposition it is not important to know the deposition during episodes. The information they need is the seasonally or yearly averaged deposition. In the Netherlands much research

has been done on the effects of ammonia (Roelofs et al., these proceedings). In other countries, especially in the Scandinavian countries one is also aware of the possible effects of NH_x deposition (Nilsson, 1986). But much is still uncertain. Some effects have been attributed to NH_x deposition but this has not yet been proven. This reflects the problems with biological systems which can be influenced by many factors at the same time.

Epilogue

I believe that these proceedings give a useful overview of the current knowledge of the atmospheric behaviour of ammonia and ammonium. Certainly much work has to be done before our knowledge on ammonia is as good as that of sulphur dioxide and nitrogen oxides. To facilitate contacts between scientists a list of participants is included in these proceedings.

I wish to thank Nicoline van Woudenberg (RIVM) for her help before, during and after symposium. Without her organizational talents this symposium would simply not have been possible.

Bilthoven, June 1987.

Willem A.H. Asman

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AMMONIA EMISSION CALCULATION

- fiction and reality -

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ABSTRACT

In 1985 the first European ammonia emission inventory was presented. The countries involved were 26 European and 1 Asian country. Sources considered were livestock wastes, fertilizers and fertilizer and related plants. The total ammonia emission is approximately 6.4 Mt of $\text{NH}_3 \text{ a}^{-1}$ with a major contribution (81%) from livestock wastes.

As a result of the uncertainties in ammonia emission factors it is concluded that the emissions could be higher by a 25 to 35%.

Much effort is spent to carry out field experiments in which ammonia emission from livestock wastes is measured. Thereby hoping to derive generalized emission factors. However, as a result of the many variables influencing ammonia emission from livestock wastes, it is concluded that the use of simple theoretical emission models will probably give more realistic and generally valid emissions.

INTRODUCTION

Since the early 1980s atmospheric ammonia has become a serious environmental issue.

Soon it became apparent that an accurate quantitative description of the atmospheric ammonia cycle was impossible to give because of lacking knowledge. Thus, one of the first things to do was to give a quantitative description of the start of the ammonia cycle: the emission of ammonia.

An European ammonia emission inventory was published in 1985 (Buijsman et al., 1985). Nevertheless, there is still a discussion going on about the reliability of our emission estimates, especially after several researchers had developed long range transport models for ammonia in which our emission estimates were used.

After presenting the most important results of our ammonia emission inventory, some remarks will be made about the reliability of our estimates and possible ways to improve our and future ammonia emission estimates.

AMMONIA EMISSION INVENTORY FOR EUROPE

Important sources of atmospheric ammonia are considered to be: livestock wastes, fertilizers and some industrial activities (Böttger et al., 1978; Bonis et al., 1980; Söderlund and Svensson, 1976; Cass et al., 1982).

Sources of minor importance include: traffic (Harkins and Nicksic, 1967; Bonis et al., 1980), natural soils (Böttger et al., 1978), coal combustion (Freyer, 1978), cats and dogs (Cass et al., 1978), human respiration (Larson et al., 1977), sewage sludge (King, 1973; Beauchamp et al., 1978) and wild animals (Söderlund and Svensson, 1976). A detailed overview of ammonia sources has also been published by the National Research Council (1978).

Global emission estimates have been presented by Robinson and Robbins (1970), Söderlund and Svensson (1976), Böttger et al. (1978) and Mészáros (1981). European emissions were calculated by Bonis et al. (1980), while Söderlund (1977) considered the NW part of Europe.

Emission inventories for smaller areas, but with detailed information about the geographical distribution of sources, were published by Cass et al. (1982) for California (USA) and by Buijsman et al. (1984) for the Netherlands.

Although most authors opinions about the absolute value of the emissions differ, they all consider livestock wastes and fertilizers to be responsible for 90% or more of the anthropogenic ammonia emission.

In our European emission inventory we considered ammonia emissions from livestock wastes, fertilizers and fertilizer and related plants.

As an example N-production and N-NH₃ emissions for livestock wastes from different kind of animals are shown in Figure 1.

The emission inventory includes 27 countries: 26 European countries, of which of the U.S.S.R. only the W part is considered, plus Turkey.

Calculations have been made for grid elements in two grid systems: the IE grid (grid size approximately 75 x 75 km² at 60° N) and the EMEP grid (grid size approximately 150x150 km² at 60° N).

Ammonia emission as well as ammonia emission densities for the countries considered are listed in Table 1.

Emissions in the IE grid system are shown in Figure 2.

Table 1. Total anthropogenic NH₃ emissions in Europe in the early 1980s

Country	Livestock waste	Fertilizers	Industrial* sources	Total ¶	Emission density †
Albany	16	4	< 1	21	1.7
Austria	62	9	1	72	1.7
Belgium	74	4	4	82	5.3
Bulgaria	91	31	4	126	4.7
Czechoslovakia	127	39	4	170	2.4
Denmark	87	23	1	111	3.8
Finland	38	4	1	44	0.7
France	569	130	9	709	4.4
F.R.G.	329	35	6	371	2.4
G.D.R.	159	42	6	207	3.2
Greece	69	25	2	95	2.2
Hungary	83	42	4	130	1.9
Ireland	110	5	1	117	1.9
Italy	252	101	7	361	2.0
Luxemburg	4	< 1	0	5	3.4
Netherlands	128	12	8	150	6.4
Norway	27	7	2	36	0.3
Poland	317	80	7	405	2.1
Portugal	38	7	1	47	4.0
Romania	237	53	11	301	1.9
Spain	177	49	5	232	1.1
Sweden	46	6	1	52	1.1
Switzerland	49	4	< 1	53	4.5
Turkey	632	47	4	683	0.9
U.K.	307	90	7	405	2.1
U.S.S.R.#	1046	210	(61)†	1256†	1.6
Yugoslavia	167	29	2	198	1.9
Europe	5241	1091	102†	6434	

All data in $10^3 \text{ t NH}_3 \text{ a}^{-1}$, except the emission densities ($\text{NH}_3 \text{ km}^{-2} \text{ a}^{-1}$).

* Emission from ammonia, fertilizer and related plants.

¶ Differences can occur due to rounding.

† Industrial emissions in the U.S.S.R. not taken into account.

‡ Defined as: agricultural emissions/agricultural area.

Not completely considered.

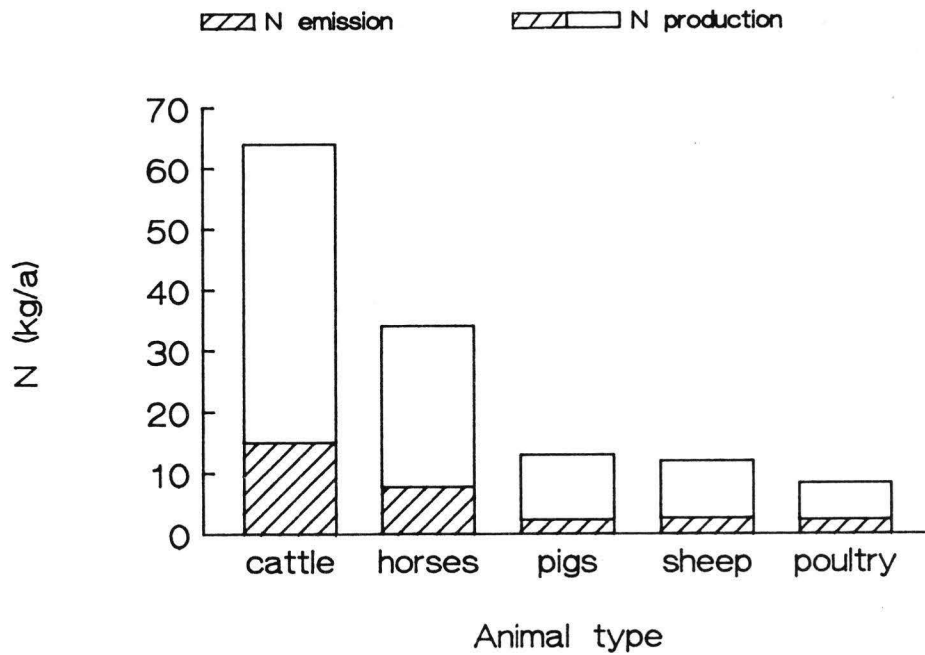


Figure 1: Total N production and N-NH₃ emission by different kind of animals. Please note: N data for poultry x10!

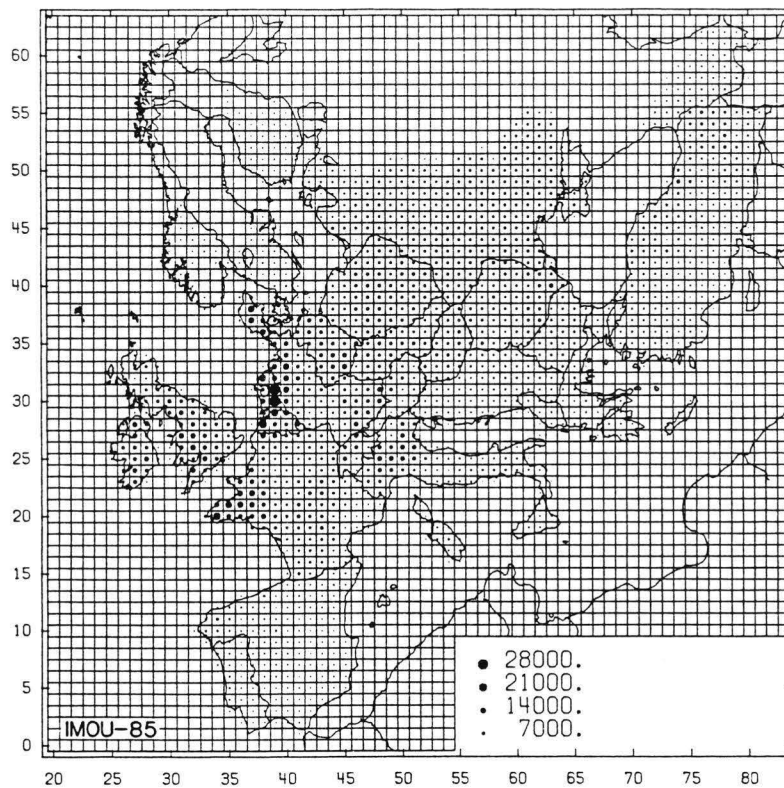


Figure 2: Total anthropogenic ammonia emission in the early 1980s (Buijsman et al., 1986)

UNCERTAINTIES IN CALCULATING AMMONIA EMISSIONS

Geographical aspects

The accuracy of the emission calculations is affected by several factors. First the livestock statistics used; not only as to the subdivision in the different animal categories, i.e. an accurate specification of the actual number of animals in the different age and/or weight classes, but also with regard to the geographical aspect.

Because of the fact that we make calculations for a grid system, it is obvious that the larger the number of areas in country for which statistical data are available, the more accurate our calculations for grid elements will be. Our method of calculating emissions is of course inherently inaccurate, because the number of animals in an area is redistributed over the relevant grid elements in a way proportional to the areas occupied by the different grid elements.

For that we define a national spatial accuracy ratio (NSAR) as the number of areas in country for which statistical data are available, divided by the number of (IE) grid elements in that country.

It is obvious that a high NSAR is preferable. For our inventory the NSAR ranges from 160 (Switzerland) to 0.03 (USSR). If we require a minimum NSAR value of 4, this condition is fulfilled for only 9 out of the 27 countries considered.

The conclusion here is straightforward: substantial improvement of the (geographical) accuracy can be achieved.

An overall emission factor?

The second problem is more serious: which values of the ammonia emission factors for livestock wastes should be used? However, comparing relevant literature reveals that we apparently have to deal with a very complex system (see e.g.: Stewart, 1970; MacDiarmid and Watkin, 1972; Luebs et al., 1973; Luebs et al., 1974; Denmead et al., 1974; Adriano et al., 1974; Giddons and Rao, 1975; Lauer et al., 1976; Ball et al., 1979; Brogan, 1981; Hoff et al., 1981; Beauchamp et al., 1982; Hutchinson et al., 1982; Vallis et al., 1982; Ryden and MacNeill, 1984; Sherlock and Goh, 1984; Hall and Ryden, 1986; Nilsson, 1986; Ryden, 1986).

Although attempted by several authors it is in fact impossible to give an overall ammonia emission factor for a certain animal type, especially when calculating emissions for a large area such as Europe.

So the figure presented by Christensen (1986) is indeed quite suggestive (see figure 3a), but a closer examination of the underlying literature reveals that we have to deal with a number of experiments which are hardly comparable. And if we reduce Christensen's figure by removing the urine data we cannot draw any conclusion at all (see figure 3b).

But even by doing it the other way around, that is by using for instance only data from experiments with liquid cattle manure no coherent picture can be obtained.

Thus a conclusion could be: it is of no use to look for one overall emission factor. Experiments are often not comparable, or even worse, the results are contradictory.

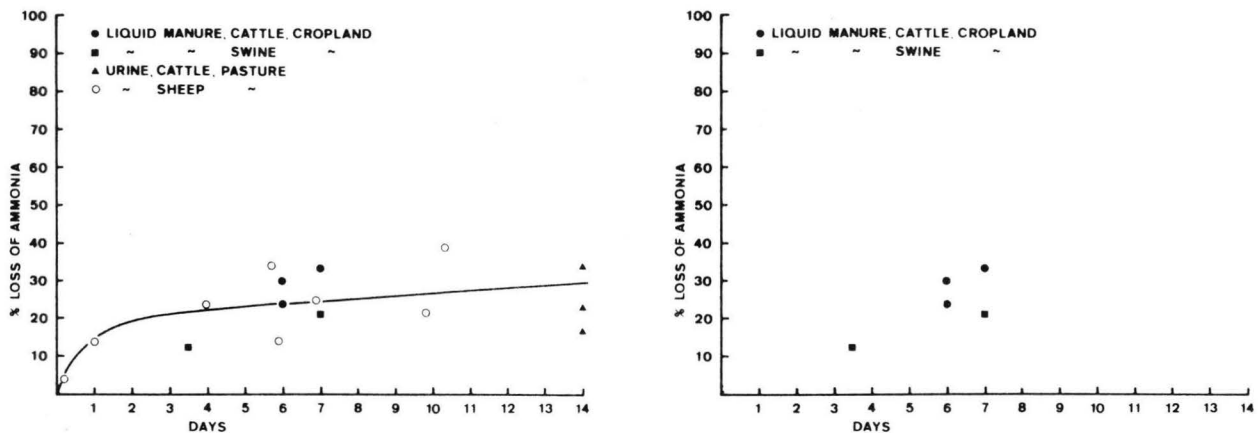


Figure 3: a (left): Ammonia emission as derived from field studies (from Christensen, 1986)

b (right): As figure 3a after removing urine data (▲, 0)

Original references:

● : Beauchamp et al. (1982)

■ : Hoff et al. (1981)

▲ : Vallis et al. (1982)

○ : Sherlock and Goh (1984)

Anyone who wants to make an ammonia emission inventory, has to use, one way or the other, ammonia emission factors. And if we compare the emission factors used by different authors in the field of inventories, we find little agreement (table 2).

It is clear that this wide range in emission factors, reflects the wide range of ammonia emission data observed under field conditions.

Table 2: Ammonia emission factors for cattle

author(s)	ammonia emission (kg N a ⁻¹)
- Böttger et al. (1978)*	23-33
- Cass et al. (1982)	42
- Buijsman et al. (1985)	18
- Kruse et al. (1986)	19

* also used by: Bonis et al. (1980), Závodský and Mitosinková (1984), Fisher (1984).

Illustration of the problem

The matter gets even more frustrating if we look at the actual routes of N production by cattle, because then it becomes clear why it is so difficult to define an overall ammonia emission factor (Figure 4). Cattle produce N in the housing period [N(o)], which gives directly or during storage NH₃ losses.

After some time the (liquid) manure will be applied on agricultural surfaces. The amount of N at that moment is N(t). A part of the mineral fraction of N(t), N(m) escapes as ammonia.

When the animals are at grass, N is produced in urine [N(u)] and in faeces [N(f)], again giving rise to ammonia emission.

The total ammonia emission by cattle can now be calculated according to the scheme shown in Figure 5.

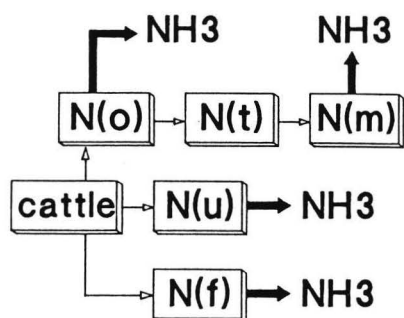


Fig. 4: N production routes
and ammonia emission

storage losses

$$F1 \times N(o)$$

application losses

$$F2 \times F3 \times F4 \times N(o)$$

losses at grass

$$F5 \times N(u) + F6 \times N(f)$$

Fig. 5: Calculation scheme for
the ammonia emission by
cattle

Now, if we go to the heart of the matter, the real problem is still: how to come to generalized emission factors? In my opinion it is impossible to use only one emission factor for a certain animal type which covers the whole wide range of agricultural practices and meteorological conditions throughout Europe. Summing up variables that are, more or less, influencing the ammonia emission, makes it clear why this statement must have a germ of truth (Figure 6, table 3).

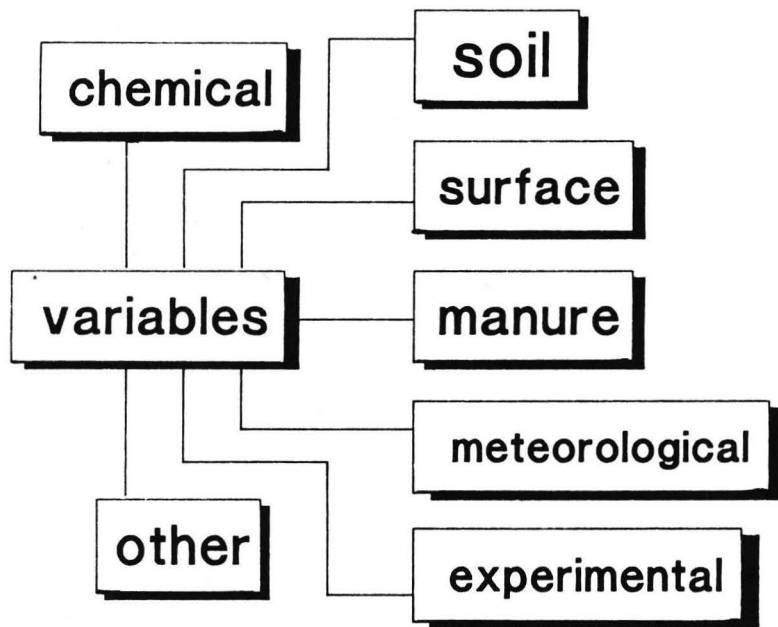


Figure 6: Main groups of variables influencing the ammonia emission from livestock wastes.

Table 3: Variables related to ammonia emission from livestock wastes.

<u>Surface</u> - vegetation type - wetness - slope of terrain - snowcover	<u>Manure</u> - pH - N content - NH_4 content - urea content - water content - surface roughness - temperature - microbiological activity
<u>Soil</u> - pH - chemical composition - physical status - water content - morfological condition	<u>Chemical</u> - solubility - Henry's law constant - temperature - dissociation constants
<u>Meteorological</u> - temperature - wind speed - turbulence - atmospheric stability - relative humidity - rainfall - freezing/thawing cyclus	<u>Other</u> - losses through other routes - ambient ammonia concentration
<u>Experimental</u> - experimental set-up - analytical techniques	

Reconsidering emissions

After the publication of our ammonia emission inventory several remarks have been made by modellers. In general they were of the opinion our emission estimates were too low (see for instance the papers by Asman and Janssen, by Derwent and by Fisher in this volume).

However, from the beginning we have stated that our emission estimates should be considered as conservative ones.

Thus, if we speculate that all N that has been lost during the storage of (cattle) manure, was lost as ammonia the emission by cattle increases by 16% and consequently the total anthropogenic emission by 9%. Assuming that cattle at grass produces the same amount of N as in the housing period, the losses at grass increase by 29% and consequently the total emission by 16%. There is some support for these assumptions and extending these assumptions to other animal types, the total anthropogenic ammonia emission in Europe could be higher by 25 to 35%.

TO CONCLUDE

Much effort has been spent in the past in measuring ammonia emissions from livestock wastes. Much more effort will be spent in future, at least in the Netherlands where the ammonia problem is a tricky matter.

However, in view of the foregoing and seen from the viewpoint of those working on (or with) ammonia emission inventories or other approach looks more promising.

My plea is: develop and use (simple) theoretical models in which the main variables (temperature, windspeed, N-content of manure, pH) are incorporated.

Furthermore, those models should be supported by the results of experiments. Preferably laboratory experiments, because then you can to a certain extent control your variables.

Illustrations of this approach can be found for instance in Steenhuis et al. (1979) and Muck and Steenhuis (1982).

And finally, use the model to derive locally valid emission factors.

ACKNOWLEDGEMENTS

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DETERMINATION OF NH₃ VOLATILIZATION FROM SURFACE-APPLIED CATTLE SLURRY USING PASSIVE FLUX SAMPLERS

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Abstract

A new passive flux sampler has been used to determine the NH₃ volatilization from cattle slurry applied to a grass ley. The slurry was applied on May 12 1986 at a rate of 30 t/ha. The first measuring period covered the spreading phase and the following 24 h, while the second period covered the succeeding 7 days period.

Horizontal NH₃ fluxes in the air through the four edges of a quadratic field (20 x 20 m) were estimated at 4 heights (0.75, 1.50, 2.25 and 3.00 m above the soil surface) both before and after the air had passed the experimental plot.

Vertical NH₃ losses from the plot were calculated from differences in the horizontal fluxes of the air. During the spreading phase and the following 24 h, 41 % (22.3 kg NH₃-N/ha) of the applied ammonium was lost; losses during the succeeding week accounted for 12 % (6.6 kg NH₃-N/ha).

Introduction

Livestock production is one of the most important sources of atmospheric NH_3 in Europe. Surface-applied animal manure may lose a considerable part of its ammonium contents by NH_3 volatilization (Christensen 1986). If direct injection of liquid manure is practised, NH_3 losses can be much reduced. The volatilized NH_3 plays an important role in atmospheric chemical reaction by regulating the pH in condensed phases. NH_3 is the only important atmospheric basic compound. When deposited to the soil it can be acidifying if it is oxidized to NO_3^- . Too much NH_3 can also cause problems to N-deficient ecosystems. It has been suggested as an additional explanation to the forest die back (Nihlgård, 1985). It seems, therefore, important to study the ammonia volatilization, the mechanisms which regulate it, atmospheric-chemical reactions and transport ways in air. This paper describes a new approach to measure volatilized NH_3 in the field.

Methods to measure the NH_3 volatilization from soil

The NH_3 volatilization can usually not be determined from analysis of the soil, because there are reactions in the soil that produce and remove NH_3 .

The NH_3 volatilization from soil or manure is rapid and the rate is determined mainly by the transport rate through the air-soil interface. The transport resistance in the air above the soil is

often so high that it can be used to determine the evaporation rate. The ammonia gradient or rather the concentrations at two or more heights (H) are then measured and the NH_3 volatilization $\emptyset\text{NH}_3$ (amount per unit time and area) calculated from:

$$\emptyset\text{NH}_3 = K \frac{\Delta \text{NH}_3 \text{ air}}{\Delta H} \quad (1)$$

K is the turbulent diffusivity between the heights in question and can be determined from wind speed and temperature gradients. The method has, however, several disadvantages. It requires stable wind and uniform fields and rather expensive equipment. It has successfully been used by several investigators (e.g. Denmead et al 1976, Beauchamp et al 1982, Harper et al 1983).

The volatilization rate can also be described by equation 2:

$$\emptyset\text{NH}_3 = h ([\text{NH}_3]_{\text{eq}} - [\text{NH}_3]_{\text{air}}) \quad (2)$$

in which $[\text{NH}_3]_{\text{eq}}$ is the gaseous concentration of NH_3 in equilibrium with the soil. $[\text{NH}_3]_{\text{eq}}$ is a function of several parameters as the free NH_4^+ concentration in the soil solution, the temperature and the pH of the soil solution. The equilibrium concentration can be determined by using the chamber technique (Ferm 1983). $[\text{NH}_3]_{\text{air}}$ is the ammonia concentration in the air above the thin (ca 1 mm thick) laminar air layer above the soil. Several methods to measure the NH_3 concentration have been developed. At low concentrations a denuder technique is preferable (e.g. Ferm 1979). h is the surface transfer coefficient,

which depends on several parameters as wind speed, air turbulence, etc. (Bouwmeester and Vlek 1981). It should be possible to estimate h if the rate of water evaporation $[H_2O]_{eq}$ and $[H_2O]_{air}$ is known. h has earlier been estimated inside chambers in this way using an artificial surface (wet filter paper) (Denmead 1979). h for water must be close to h for NH_3 as the two compounds have similar diffusion coefficients in air. This way of estimating the NH_3 loss has, however, never been used.

Further one possibility of estimating the NH_3 volatilization exists. The horizontal NH_3 flux in the air before and after the wind has passed the field can be measured.

The flux differences are summed up to a height at which it is negligible. Fluxes have earlier been estimated from wind speed and concentration measurements during stable wind (Denmead et al 1977, Beauchamp et al 1978 and Wilson et al 1983). The flux can, however, also be measured directly by letting the kinetic energy of the wind force it through a sampler with low air resistance. The flow through the sampler must then be proportional to the wind speed. Such flux samplers have earlier been used to collect airborne particles (Steen 1977). A drawback with the equipment is that the flux through the samplers decreases rapidly with the angle between the wind and the samplers (Steen et al 1981). The NH_3 flux can, however, be measured with rotatable samplers that always face the wind if they are placed in the middle of a circular field and the incoming NH_3 flux is negligible (Leuning et al 1985).

In this project a new version of flux samplers was used, in which the angular dependence of the measured flux is small. The advantage with the method is that the background flux of NH_3 does not have to be negligible. Rectangular fields can be used and the technique can also be used to measure the deposition of NH_3 .

Description of the method

The samplers measuring the horizontal NH_3 flux are made of pyrex (Figure 1). They consist of 4 glass tubes internally coated with oxalic acid (the shaded parts). The internal and outer diameters are 7 and 10 mm, respectively. They are 100 mm long, of which 20 mm is uncoated and are assembled by silicon tubing in two pairs. Each pair has a probe consisting of a thin (0.05 mm) stainless steel washer with a 1.0 mm hole.

If the wind direction and speed are represented by the vector U (see Figure 1) NH_3 is collected in the samplers B1 and B2 but not A1 or A2. If α is 180° B1 and B2 will receive the same amount of NH_3 . When α decreases B1 receives an amount which decreases more rapidly with α than $\cos \alpha$ and B2 receives an amount which decreases slower with α than $\cos \alpha$ does. The mean value of the amounts in B1 and B2 as a function of α resembles, however, approximately $\cos \alpha$. The flux through an area perpendicular to the tubes can, therefore, be measured .

The flux can be described by the equations 3

$$\bar{\phi}_{\text{NH}_3} = \frac{1}{(t_2-t_1)} \int_{t_1}^{t_2} [\text{NH}_3] U \cos \alpha dt = \frac{k}{(t_2-t_1)} \left(\frac{A_1+A_2}{2\pi r^2} - \frac{B_1+B_2}{2\pi r^2} \right) \quad (3)$$

The sampler has been tested in a wind tunnel containing about 1 ppm of NH_3 . The wind speed and angle were regulated and the gaseous NH_3 concentration was measured using a denuder. The NH_4^+ amounts in tubes A1 and A2 were determined by leaching the tubes in water and analysing the NH_4^+ concentration by an electrode (Orion 95-10), i.e. in the same way as the denuder was analysed.

The average amount in the tubes divided by the sampling time and the area of the hole in the washer is plotted as a function of the wind speed along the tube axis in Figure 2. As can be seen from the figure the proportionality is fairly good and rather independent of α . The regression line has, however, a slope (corresponding to k in eq. 3) of 0.7. This is due to the turbulence created by the flat washer. If instead a conical entrance is used the slope will be close to 1 but the angular dependence will not resemble $\cos \alpha$.

Experimental

The experiment, set up to test the samplers, was carried out on a grass ley field situated at Askov Experimental Station. The experimental plot (20 x 20 m) was cut and the cut grass removed

before manure was applied. Cattle slurry was surface-applied on May 12 1986 using a special hand-held aggregate. The slurry had a pH of 7.5 and contained 6.5 % dry matter, 0.352 % total-N and 0.179 % $\text{NH}_4\text{-N}$. The application rate was 30 t/ha corresponding to 106 kg total-N/ha or 54 kg $\text{NH}_4\text{-N}$ /ha.

The first measuring period covered the manure spreading phase and the following 24 h; the second period covered the succeeding week.

Sampling strategy and results

The samplers were mounted on 4 m high wooden masts dug into the soil. The masts were mounted around the field as shown in Figure 3.

The total loss during each sample time can actually be estimated by leaching all tubes facing the field together (2x16 tubes) and all tubes facing the surroundings together (also 32 tubes). Because this was the initial experiment and because we wanted to check if the flux increase at the highest altitude was small, all tubes were analysed separately (Tables 1 and 2). Most of the NH_3 at the field edge escaped below 3 m altitude during the first sampling, while relatively more of NH_3 was found at this height after the second sampling period (Table 3).

During the first and second sampling period, 22.3 and 6.6 kg $\text{NH}_3\text{-N/ha}$ were volatilized, respectively, corresponding to 41 and 12 % of the ammonium applied in slurry. Precipitation was 4.3 mm and 11.2 mm during the first and second sampling period, respectively. Mean daily temperatures varied between 8 and 13°C.

The NH_3 volatilization losses observed in the present experiment agree reasonably well with values obtained in similar studies (see Christensen 1986).

Conclusions

This initial attempt to measure NH_3 loss to the atmosphere by the use of passive flux samplers appears encouraging. The method has several advantages. Volatilization is not affected by the sampling, background concentrations of NH_3 are taken into account (which may be significant and variable in agricultural areas), the wind speed and wind direction may vary during the sampling period and sampling equipment does not require electricity. Further experiments must, however, be carried out in order to estimate the accuracy and test the limits of the method. An important aspect is a comparison with other methods, e.g. the gradient method.

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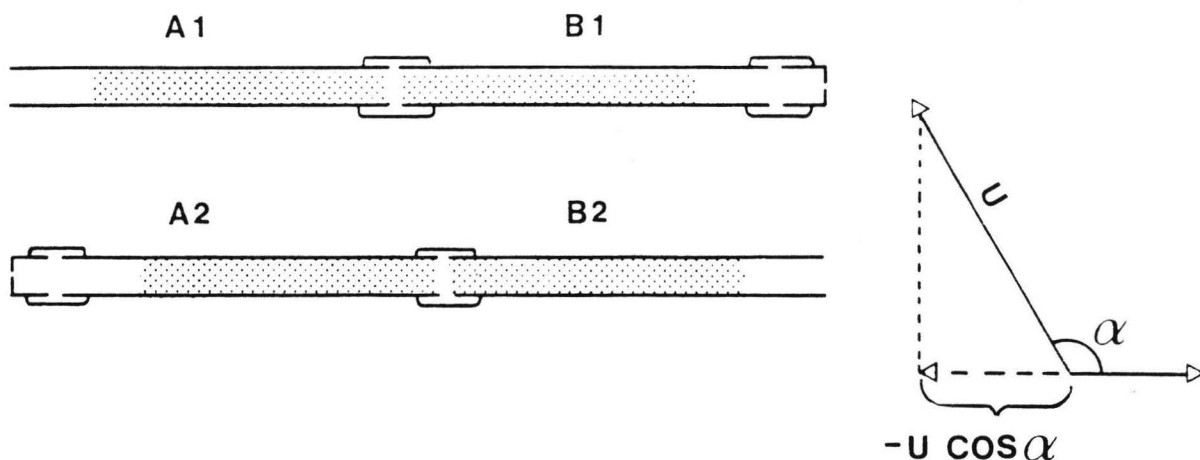


Figure 1. Two pair of tubes for estimating the NH_3 flux through one or the other side of a vertical area. The vector diagram is referred to in the text.

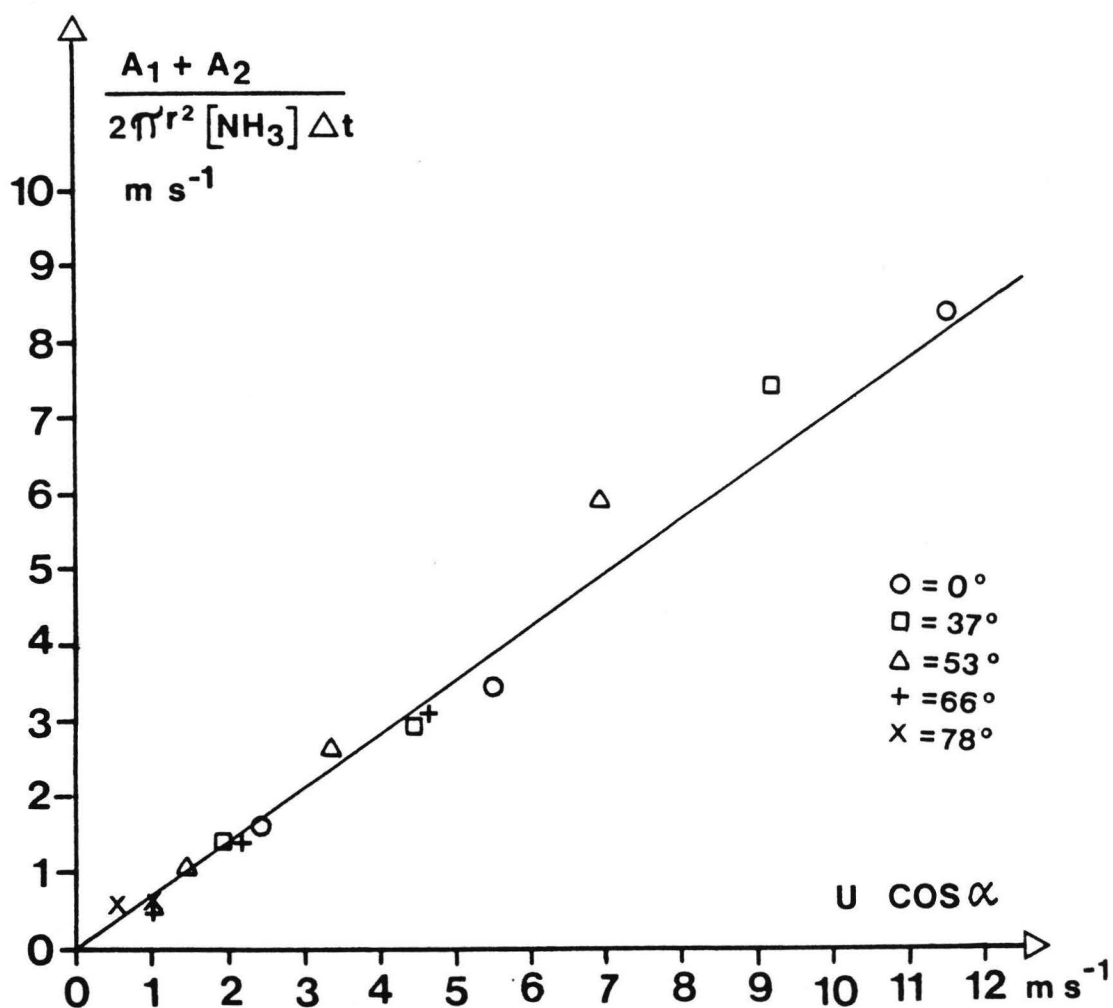
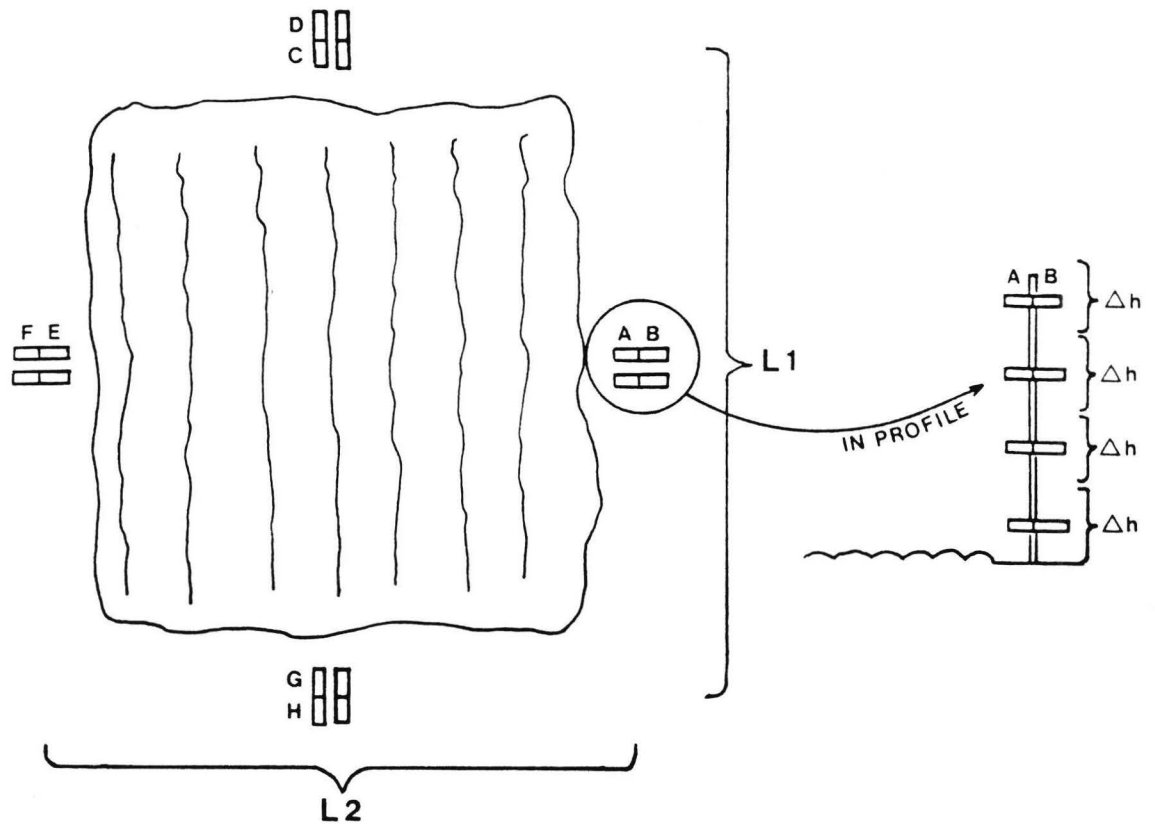


Figure 2. Measured NH_3 flux divided by the NH_3 concentration as a function of windspeed along the axis of the sampler. The measurements were performed with stable wind in a wind tunnel. The symbols represents different values on the angle α .



$$\text{The NH}_3 \text{ loss} = L1 \sum_h (\phi_A + \phi_E - \phi_B - \phi_F) \Delta h + L2 \sum_h (\phi_C + \phi_G - \phi_D - \phi_H) \Delta h$$

Figure 3. Sampling strategy used in the field experiments.

Table 3. Total amount of NH₃ (g) that has escaped from the field as a function of height at the field edge.

Height	12-13 May	13-20 May
3	55	45
2.25	107	27
1.50	200	72
.75	722	176
Sum	1084	320

Table 1. Measurements performed May 12-13 1986. The figures are given in ug NH₃ per tube. The flux in g NH₃ m⁻² is obtained by multiplying the figures for a pair of tubes by 0.91. Each tube pair (one with probe and one open) represents an area of 16.5 m². The total emission is thus 1084g or 27.1 kg NH₃/ha.

Height	End	North		East		South		West		Sum
NH ₃ from Field										
or Surroundings:										
		S	F	S	F	S	F	S	F	(F-S)
3	Probe	0	1.6	0	.6	.3	0	1.5	.4	.8
3	Open	.2	1.2	.8	3.1	.4	.1	.9	.8	2.9
2.25	Probe	.1	3	.2	1.9	.2	0	.7	.3	4
2.25	Open	.2	2.3	.1	2.4	.6	0	.9	.2	3.1
1.50	Probe	.2	4.8	0	3.1	.3	.1	.7	.6	7.4
1.50	Open	.2	1.5	.2	5.3	.4	.1	.9	.7	5.9
.75	Probe	.1	10.5	.1	11.4	.2	.1	.9	.7	21.4
.75	Open	.1	13.7	.8	15.1	.3	.1	1.3	.3	26.7
Sum		1.1	38.6	2.2	42.9	2.7	.5	7.8	4	72.2

Table 2. Measurements performed May 13-20 1986. The figures are given in ug NH₃ per tube. The flux in g NH₃ m⁻² is obtained by multiplying the figures for a pair of tubes by 0.91. Each tube pair (one with probe and one open) represents an area of 16.5 m². The total emission is thus 320g or 8.0 kg NH₃/ha.

Height	End	North		East		South		West		Sum
NH ₃ from Field										
or Surroundings:										
		S	F	S	F	S	F	S	F	(F-S)
3	Probe	.1	3.1	.2	1.3	1.4	.1	1.4	.2	1.6
3	Open	.2	2.9	.4	2.6	2.7	.1	1.5	.6	1.4
2.25	Probe	.1	2.6	.2	2	1.3	.1	1.8	.3	1.6
2.25	Open	1.4	3.6	.4	2.3	2.5	.1	2.1	.6	.2
1.50	Probe	.1	2.6	.2	2.6	1.2	.1	1.4	.3	2.7
1.50	Open	.2	3.3	.3	2.7	2.1	.1	2.1	.7	2.1
.75	Probe	.1	5	.3	4.2	.9	.1	1.2	.3	7.1
.75	Open	.9	2.6	.3	4.9	1.4	.2	1.2	.7	4.6
Sum		3.1	25.7	2.3	22.6	13.5	.9	12.7	3.7	21.3

AMMONIA EMISSIONS FROM LIVESTOCK OPERATIONS IN THE NETHERLANDS

J.V. Klarenbeek *).

1. Introduction.

The effects during the last decade of acid rain in Europe have become impressive. In the North and Western regions large areas of forest are dying or at least in a deplorable condition. The impact of this phenomena is well illustrated by the fact that in Germany one has created a new expression in daily conversation called 'Waldsterben'. This is best translated by 'the dying of forest'.

It has been thought for quite some time that acid rain was one of the major causes of soil acidification. Aerial precipitation with a pH lower than its natural value of 5.6 is caused by emissions of acidifying oxides like SO_x and NO_x. The first is related to the activities of coal and oil fired power plants while the latter is due to traffic and general combustion processes. However, research results published by van Breemen et al. (1982) indicate ammonia as a third major component of soil acidification. It can be concluded from their work that;

- the presence of NH₄-ions accelerates the deposition of SO₂-ions and vice versa,
- due to the nitrification of NH₄ in the soil, the import of acidifying components is more than can be calculated from the pH or SO₄ concentration of the rain,
- ammonia emissions are closer related to the topic of soil acidification than has been thought before.

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2. Sources of ammonia.

The presence of micro organisms on earth is the main course for atmospheric ammonia. In a continuous process performed by several species of bacteria and fungi organic material is converted to CO₂, H₂O and NH₃. The annual ammonia emission in the Netherlands is estimated at 130,000,000 kg (Buijsman; 1984). Of this, 114,000,000 kg originates from (liquid) manure. The remainder is related to the use of nitrogenous fertilizers, industrial processing and the presence of living creatures like man and animals.

The emissions originating from liquid manure in Holland are related to the present agricultural views on professional animal husbandry. As a result of labour saving considerations, the greater part of all farm animals are kept in confinement buildings. In most cases the animals excrements are stored as a liquid underneath the (slatted) building floor. The anaerobic degradation which takes place during storage produces a certain amount of ammonium (Miner et al.; 1975). Part of this is released to the atmosphere as ammonia.

Due to the potential soil acidifying capacity of ammonia much of the national attention has recently been focused on agriculture. This has resulted in a increased interest of governing authorities in the ammonia emissions of livestock operations. In most cases attention turned to single livestock buildings or small clusters near a particular nitrogen sensitive landscape. In some cases the emission of all buildings in a specified geographical region was needed as part of a general environmental study.

In some studies the results of research programs on the emissions of livestock houses were used in order to make accurate estimations. Since the aim of the various research programs on emissions of pigs (Klarenbeek et al., 1982), laying hens (Klarenbeek et al., 1985) and broilers (van Ouwkerk, 1984) has been to reveal the differences in emissions of housing systems, misinterpretation of research results with respect to the estimated absolute levels occurred. In order to obtain a more realistic and comprehensive view on the ammonia emissions of livestock operations by systematic analyses of all relevant data a specialised working party was formed. All members of this party (see appendix 1) were well-informed on modern animal husbandry and environmental hygiene.

3. Calculation of ammonia emissions.

Since all available data on ammonia emissions of livestock buildings exhibit a relative nature, absolute emission levels were the object of the working party. In order to achieve this goal it was decided to treat livestock buildings as a nitrogen input-output model. Figure 1 shows the various nitrogen flows. During the process of modeling it was realized that within the general model two subsystems existed. One on the animal and

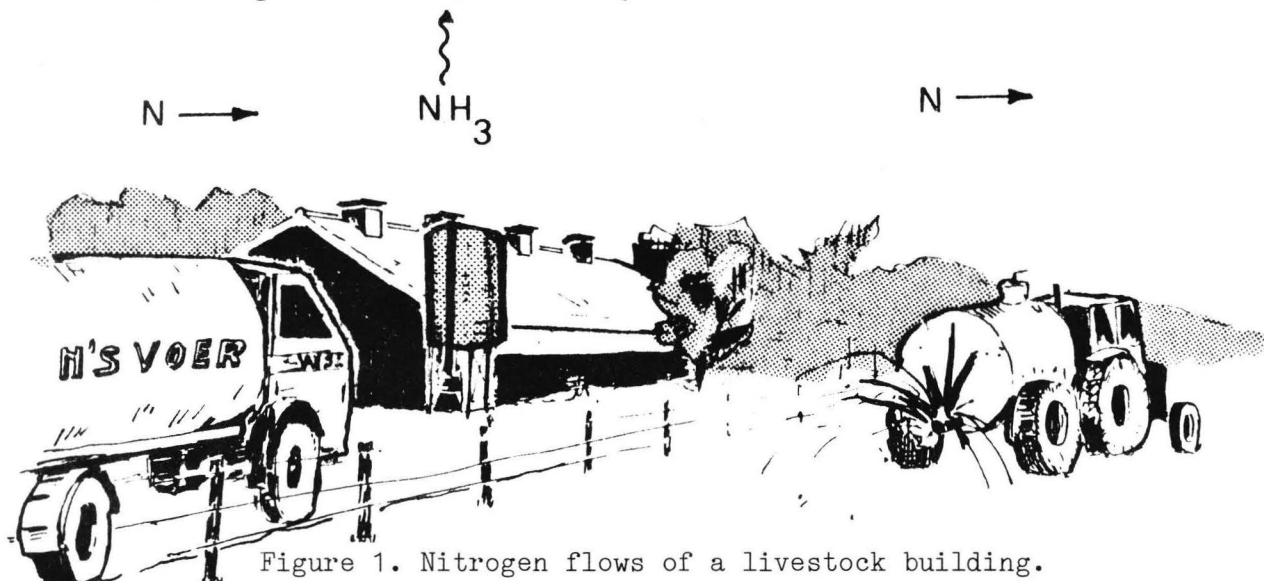
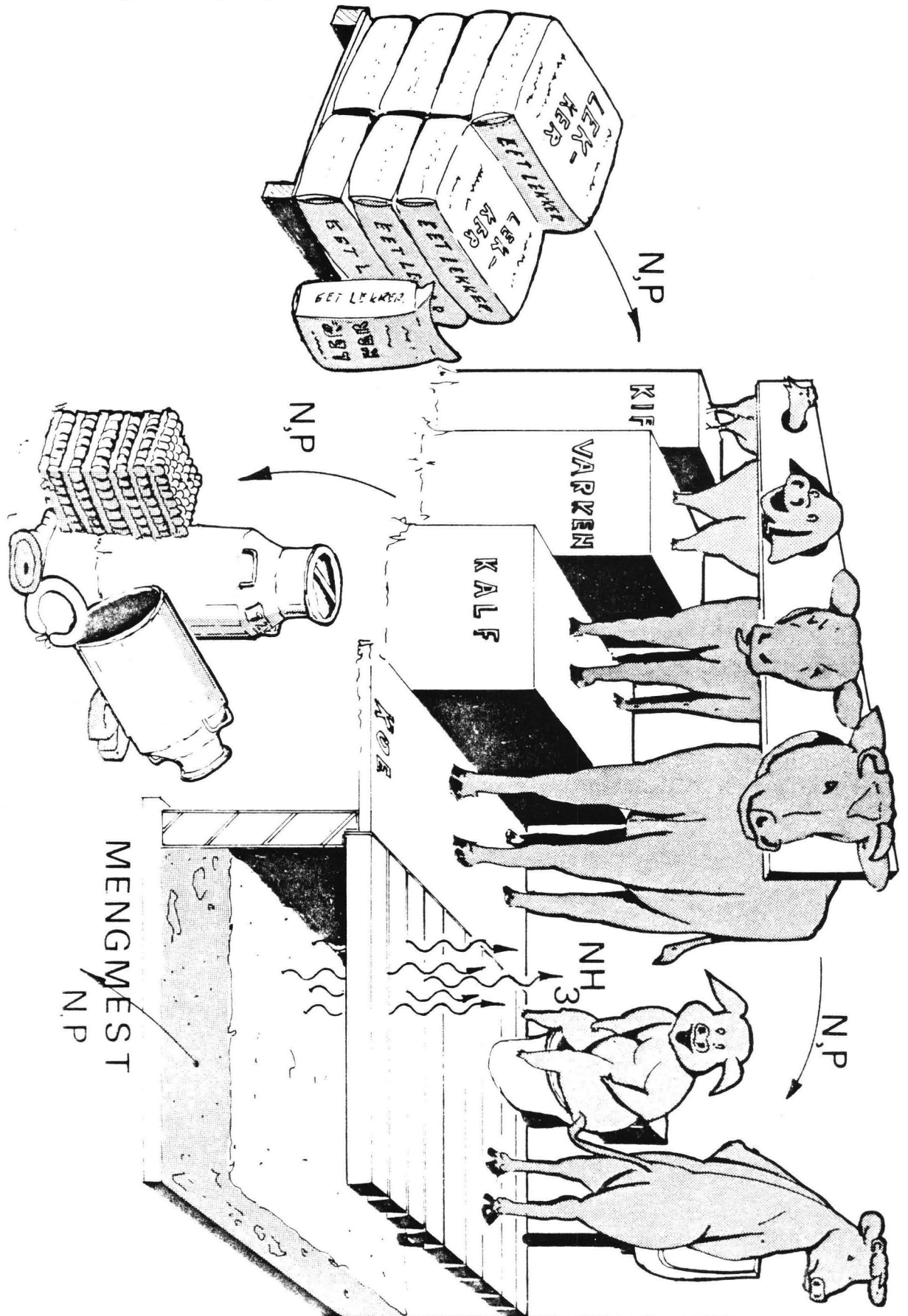


Figure 1. Nitrogen flows of a livestock building.

one on the manure storage (fig. 2). Due to nutritional research of the past decades nitrogen flows of livestock are well known and documented. In contrast with foregoing no information is available on the nitrogen flows of the manure system. Only the outcome of the system is known due to the fertilizing value of manures. Estimation of the nitrogen losses during storage by subtracting the nitrogen value of stored manure from that of freshly voided manure is therefore the only feasibility. However this is only possible when the effects on nitrogen concentration of (liquid) manure by dilution and evaporation processes during storage are taken into account. This makes nitrogen losses dependent upon uncertain factors like housing, ventilation and feeding systems.

In order to make up for all uncertainties a tracer was looked for. As a result of recent regulations for the land application of manure, which are based upon the total phosphorus supply to the soil, P_{205} contents of manures are well documented in the Netherlands. Since phosphorus is not

Figure 2. Nitrogen and phosphorus flows in livestock buildings.



effected by the process of manure storage, P205 concentrations of the manure were chosen as a tracer. By calculating the N-P ratios of the various stages of the emission model it is now possible to calculate the ammonia emissions of livestock operations. Using the schematics of figure 2 the following applies.

The excreted nitrogen and phosphorus $Ex(N,P)$ can be calculated by subtracting the N and P in the animals yield $Y(N,P)$ such as egg, meat and milk from that of the feedstuffs $F(N,P)$ used.

$$Ex(N,P) = F(N,P) - Y(N,P) \quad (1)$$

Together with (spilt) water and/or other products like bedding materials etc, the excrements make up the (liquid) manure which is stored underneath the (slatted) floor until needed for land spreading purposes.

The N and P values at the end of the manure storage period $M(N)$ and $M(P)$ can be taken from data published by specialized laboratories and other institutes. However it should be realised that as a result of microbial activities during the manure storage part of the nitrogen is released to the air $Em(N)$ (Miner, 1975).

$$M(N) = Ex(N) - Em(N) \quad (2)$$

As stated phosphorus is not effected by storage processes. The ratio $Ex(P):M(P)$ therefore reflects the change in dry matter content of manure which has occurred during storage. In order to match the N-P ratio of the manure with known values on nitrogen flows of livestock, changes in dry matter content of the manure should be taken into account.

$$Ex(N) : Ex(P) = M(N) : M(P) \quad (3)$$

Substitution of (1) and (2) in (3) generates an equation describing the nitrogen losses to air which has been taking place during the storage period of manure. Since most of the nitrogen released to air is ammonia, molecular differences should be taken into account. The final equation for calculating the ammonia emissions of livestock operations $Em(NH_3)$ knowing $M(N,P)$ and $Ex(N,P)$ is the following;

$$Em(NH_3) = 17/14((M(N) \times M(P)) \times Ex(P) - Ex(N)) \quad (4)$$

It should be noted that eq. 4 describes the general ammonia emission in case of a specified species of farm animal. As stated the various systems used for housing livestock differ in ammonia emission. In order to make up for these differences a more detailed approach was used for further discrimination. The following example on the calculation of pig housing emissions illustrates the approach.

Using eq. 4 the general ammonia emission of fattening pigs in 1985 is estimated at 1.787 kg per pig. With an average occupation of 88% and 2.7 fattening rounds per year the emission is 2.027 kg NH₃ per animal place per year. However research results published by Klarenbeek (1982) show differences caused by housing systems. This implies that a general figure for the ammonia emissions of pig houses is not applicable.

After analyses by the the working party of Klarenbeeks data it was concluded that differences in ammonia emissions of pig housing systems originate from differences in manure surface area. Since the surface area of manure varies proportionally with the slatted floor area, the latter was taken as relevant parameter. Furthermore it was decided by the working party that pig houses could be divided into two main groups as far as floor type is concerned. Table 1 shows the ammonia emissions.

Table 1. Ammonia emissions of major pig housing systems in 1980-1981.

Floor type	Average ammonia emission per pig	Emission per pig place
Partially slatted floor area	2.60 kg NH ₃	7.79 kg NH ₃
Fully slatted floor area	5.20 kg NH ₃	15.95 kg NH ₃

In comparison with the calculated emission level for 1985 the ammonia emissions per pig place in table 1 are considerably higher. This can be explained by the following. Due to restrictions put by the farmers the sampling of the ventilation air during the research period was carried out

in the afternoon while pigs were fed. It was concluded by the working party that as a result of higher ventilation rates and ammonia concentrations arising from feeding activities a systematic overestimation of the ammonia emission had taken place.

Furthermore it should be noted that nitrogen levels of feedstuffs in both years differ slightly. This too contributes to the difference in absolute emission levels. Therefore ammonia emissions of different housing systems were denoted as relative levels.

In order to obtain a realistic view on the 1982 ammonia emissions of Dutch pig housing systems an estimation was made of the total number of pig houses belonging to each of the classes. Together with the total ammonia emission calculated by using eq. 4 and the relative emissions of table 1, real emissions per housing system were established. Finally the ammonia emissions per pig place per year with respect to housing systems were calculated.

Knowing the emission of various housing systems true emissions in any year can now be calculated by estimating the distribution of the housing types and combining this with the general emission obtained from eq. 4.

4. Ammonia emission of various livestock operations.

In order to calculate the ammonia emission of modern animal husbandry emission factors have been established by the working party. This was achieved by using eq. 4 as well as the available data on $Ex(N,P)$ obtained from the Central Advisory Service for Forage and Livestock Feeding in the Netherlands and data on $M(N,P)$ from the Laboratory for the Analyses of Soil and Crops. After establishment of the general emissions distinction had to be made regarding the various housing systems. For this purpose data published by Klarenbeek et al. (1982), Klarenbeek et al. (1985), van Ouwkerk (1984) as well as unpublished data on previous and current research programs executed by the Institute of Agricultural Engineering have been screened on usefulness. Using the major part of all available data ammonia emissions per animal in specific housing systems have been calculated. Table 2 shows the results.

By using the emission data of table 2 it is now possible to calculate the ammonia emission of an entire geographical region. However by interpreting the results of such calculations it should be realized that

the major part of the ammonia emission factors of table 2 are based upon estimations combined with great deal of practical knowledge on modern animal husbandry. Since the major part of all present research programs on emissions of ammonia will be terminated within the next two years upgrading of table 2 is foreseen in the near future.

Table 2. Ammonia emission factors.

Category	Annual ammonia emission kg/(year.animal place)	
<u>A. Cattle.</u>		
1. Dairy cows	8.8	(1)
2. Heifers till 2 year	3.9	(1)
3. Fattening calves (0 - 6 month)	1.5	
4. Fattening bulls (incl. other fattening cattle) till 2 year	5.7	
<u>B. Pigs.</u>		
1. Sows with litter (0 - 25 kg)	8.1	(2)
2. Gilts (25 kg - 7 month)		
2.1 on fully slatted floor	1.9	
2.2 on partially slatted floor with oversized manure storage	1.9	
2.3 on partially slatted floor with proportional manure storage	0.9	
3. Gilts (7 months - first service)	4.2	
4. Young breeding boars (25 kg - 7 month)	see fattening pigs	
5. Breeding boars (7 months and older)	5.5	
6. Fattening pigs (incl. young boars)		
6.1 on fully slatted floor	2.2	
6.2 on partially slatted floor with oversized manure storage	2.2	
6.3 on partially slatted floor with proportional manure storage	1.1	

Table 2. Ammonia emission factors (contd).

Category	Annual ammonia emission kg/(year.animal place)
<u>C. Chickens.</u>	
1. Pullets and cockerels of laying breeds (until 18 weeks)	
1.1 on step deck batteries with open manure storage	0.165
1.2 on vertical tiered batteries with natural ventilation and closed manure storage	0.021
1.3 on vertical tiered batteries with mechanical ventilation and closed manure storage	0.097
1.4 on step deck batteries with manure drying by forced air movement	0.208
1.5 on vertical tiered batteries with manure drying by forced air movement	0.016 (3)
1.6 on deep litter	0.096
2. Laying hens (incl. breeding birds)	
2.1 on step deck batteries with open manure storage	0.308
2.2 on vertical tiered batteries with natural ventilation and closed manure storage	0.039
2.3 on vertical tiered batteries with mechanical ventilation and closed manure storage	0.181
2.4 on step deck batteries with manure drying by forced air movement	0.386
2.5 on vertical tiered batteries with manure drying by forced air movement	0.030 (3)
2.6 on deep litter	0.178

Table 2. Ammonia emission factors (contd).

Category	Annual ammonia emission kg/(year.animal place)
3. Pullets and cockerels of fattening breeds less than 18 month	0.128
4. Parent birds of fattening breeds	0.300
5. Broilers	
5.1 on non-insulated floor	0.160
5.2 on insulated floor	0.110

(1) Emission applies to the winter period from october to may.

(2) If a deep litter housing system is applicable the emission of the stored manure with bedding material is includede.

(3) If dried droppings are stored on the premises underneath a simple roof the calculated emission should be multiplied by two.

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Appendix 1. Members of the working party on ammonia emissions of livestock operations in the Netherlands.

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Hygiene,
Directorate of Air Quality, Division of Process
Emissions.

FIELD MONITORING OF NH_3 EMISSION FROM BARE SOIL AFTER ANIMAL MANURE
HAS BEEN SURFACE-APPLIED, PLOWED IN, OR INJECTED

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Keywords: NH_3 emission, field monitoring, micrometeorological mass
balance approach

Animal manure is considered to be the most important source of NH_3 emission in The Netherlands so far. Nevertheless remarkably little information is available about the extent of this type of emission. The field monitoring described here is part of a more extensive study which aims to analyse the factors which determine the magnitude of NH_3 emissions after application of manure and based on this analysis to indicate how NH_3 emissions can be minimized.

In order to monitor NH_3 emission in the field, micrometeorological measurements are preferred in principle since they do not disturb the environmental or surface processes which affect the exchange of NH_3 ; they permit continuous monitoring, thus facilitating the investigation of environmental effects; and they provide a measure of the average

flux density over a large area. A disadvantage is that micrometeorological techniques commonly used for measuring atmospheric gas transfer are difficult to employ for ammonia because they require large experimental areas, extending over hundreds of metres, and very accurate and sometimes very rapid measurement of small gas concentrations.

Several authors have recently discussed a more appropriate micrometeorological technique suitable for smaller experimental areas, extending over tens of meters, which has less stringent measurement requirements. Based on mass balance, it equates the vertical flux of gas into the atmosphere from a treated area of limited upwind extent with the horizontal flux of the gas across a vertical plane at a known distance downwind. Assuming a concentration of zero in the air passing the windward boundary, the flux F is given by:

$$F = \frac{1}{x} \int_{z_0}^{z_p} \overline{uc} \cdot dz \quad (1)$$

where u and c are the instantaneous wind speed and NH_3 concentration, respectively, \overline{uc} is the time-averaged horizontal flux at any particular height z in the vertical plane and x the fetch. The integration limit z_0 is the roughness height and z_p is the height at which the concentration of the gas has decreased to its background value, i.e. the height of profile development.

Writing u and c as the sums of means, \bar{u} and \bar{c} , and fluctuations about those means, u' and c' , equation (1) becomes

$$F = \frac{1}{x} \int_{z_0}^{z_p} (\overline{uc} + \overline{u'c'}) . dz \quad (2)$$

The first term within the integral is the flux due to horizontal convection while the second is that due to horizontal turbulence. Wind tunnel experiments (Raupach and Legg, 1984) indicate that the the flux due to horizontal turbulence may be about 10% of the convective flux, and so probably can be neglected in many cases. Assuming that this turbulence term can be neglected, equation (2) becomes

$$F = \frac{1}{x} \int_{z_0}^{z_p} \overline{uc} . dz \quad (3)$$

For a gas such as NH_3 which has a finite concentration in air, the practical solution to equation (3) requires the determination of profiles of wind speed and NH_3 concentration above the windward and leeward boundaries of an experimental area from which the profile of horizontal flux (wind speed x NH_3 concentration) is calculated.

In order to determine the above-mentioned profiles of wind speed and NH_3 concentration, the centre of a circular plot of 20 m radius is chosen as the leeward boundary. The upward boundary corresponds to a position in the wind direction at the edge of the circular plot (circular plots are used to make the fetch independent of wind direction).

At these two positions air is collected in orthophosphoric acid traps (0.02M) at various heights above the soil surface. A wind profile is measured outside the circular plot and is assumed to be valid at both positions.

The results obtained by this method are compared with a new type of ammonia flux sampler devised by Leuning et al. (1985). This 'shuttle' sampler has been designed to sample the mean total horizontal NH_3 flux, i.e. determination of \overline{uc} in equation (2), which obviates the need to determine the wind speed and NH_3 concentration profiles. NH_3 in the air is collected in the oxalic acid coated on a spiral surface located within the sampler.

To measure the NH_3 emission after application of manure, experiments will be carried out under different conditions and farm practices. Since the highest emissions are expected to occur in the simplest case, i.e. after spreading manure on the land, this situation was studied the first year of this research (1986). Experimental details and results from this research can be shown upon request.

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ATMOSPHERIC AMMONIA: DISTRIBUTION, EQUILIBRIUM WITH AEROSOLS AND CONVERSION RATE TO AMMONIUM

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ABSTRACT

Daily ammonia and ammonium measurements at five different sites in the Netherlands showed a strong seasonal variation for ammonia, with a maximum in early spring. Monthly averaged concentrations of NH_3 reached from $0.2 \mu\text{g NH}_3/\text{m}^3$ during a period with westerly winds in a coastal area up to $35 \mu\text{g NH}_3/\text{m}^3$ in the South-Eastern part of the Netherlands, an area with intensive livestock breeding. Ammonia concentrations showed a very strong gradient over an area with little or no ammonia emission, downwind of an area with very high ammonia emissions. Ammonia concentrations were halved after 600 m.

Vertical concentration profile measurements of ammonia, ammonium and related compounds showed a strong decrease of ammonia concentrations with increasing height. Equilibrium calculations for ammoniumnitrate were in good agreement with the concentration products of ammonia and nitric acid at relative humidities below 80% and temperatures above 0°C . The overall pseudo first-order reaction rate constant for the reaction of gaseous

ammonia to particulate ammonium was calculated to be $6 \times 10^{-4} \text{ (s}^{-1}\text{)}$ for daytime periods and $4 \times 10^{-4} \text{ (s}^{-1}\text{)}$ for nighttime periods.

INTRODUCTION

To obtain a better understanding of the behaviour of ammonia (NH_3) and ammonium (NH_4^+) in the atmosphere different types of measurements were undertaken by the Institute for Meteorology and Oceanography of the State University of Utrecht, in co-operation with the Netherlands Energy Research Foundation. In this lecture the most important results will be presented concerning daily NH_3 and NH_4^+ measurements, measurements of the horizontal NH_3 and NH_4^+ concentration gradients over an area with very little or no NH_3 emission and vertical profile measurements of NH_3 , NH_4^+ and related components in the lower 200 m of the atmosphere.

NH_3 AND NH_4^+ CONCENTRATIONS OVER THE NETHERLANDS

During two years concentrations of NH_3 and NH_4^+ were measured daily, first at three and later at 5 sites in the Netherlands (see Figure 1) (Erisman et al. 1986A). The sites were chosen thus that the concentrations obtained would be representative for area's with different emission patterns. Futhermore information would be available on NH_3 concentration levels in areas sensitive to soil acidification. Petten is clearly a background station, especially during westerly winds. Bilthoven is situated in an area with little NH_3 emission, whereas Eibergen, Vredepeel and Houtakker are situated in areas with intensive livestock breeding.

NH_3 was collected on a denudertube coated with H_3PO_4 . NH_4^+ particles were retained on a filter, also coated with H_3PO_4 . It was estimated that 97% of the NH_3 -gas was absorbed in the denuder. The sampling times were 24 hours. The NH_4^+ measurements were unreliable, mostly because of the long transport times. At Petten, however, the filters were directly analysed by ECN after sampling, these results are trustworthy.

The monthly mean NH_3 concentrations (Figure 2) reached from $0.2 \mu\text{g NH}_3/\text{m}^3$ at the coast during westerly winds, up to $35 \mu\text{g NH}_3/\text{m}^3$ in the South-Eastern

part of the Netherlands. Day to day variations were even higher, 0-250 $\mu\text{g NH}_3/\text{m}^3$. From Figure 2 it can be seen that there is a distinct seasonal trend with a maximum in early spring, probably due to large scale spreading of the winter stock of animal manure. In figure 3 the monthly mean NH_4^+ concentrations are given for Petten. There is a much lesser seasonal difference for NH_4^+ than for NH_3 . Petten is clearly a background station when westerly winds dominate. The concentration levels are then for NH_3 : $0.8 \mu\text{g}/\text{m}^3$ and for NH_4^+ : $2.8 \mu\text{g}/\text{m}^3$.

As NH_3 is emitted from the ground it is doubtful whether the concentration measurements at one site are representative for a large area. In Figure 4 the average monthly mean concentrations for one year are plotted versus the total net emission from animal manure for one year calculated by Buijsman et al. (1984) for the $5 \times 5 \text{ km}^2$ grids in which the sites are situated. The correlation is very good. For larger area's, however, it was estimated that the correlation is becoming worse. This relation can therefore only be used for small areas.

The average yearly $5 \times 5 \text{ km}^2$ emission for the Netherlands was calculated by Buijsman to be 120 tons/yr. From this relation the average NH_3 concentration over the land area of the Netherlands is $6 \mu\text{g NH}_3/\text{m}^3$.

HORIZONTAL CONCENTRATION GRADIENT MEASUREMENTS

The horizontal gradient measurements were, just like the vertical profile measurements, made with a more advanced sampling system with better materials and a lower detection limit (Figure 5). Air is sucked by a pump through a denuder coated with NaF, where gaseous HNO_3 and HCl were retained. The air stream passes the second denuder which is coated with H_3PO_4 on which free gaseous NH_3 is absorbed. Finally the air stream passes three filters, the first is a teflon filter (Mitex millipore LS $5 \mu\text{m}$, ϕ 47 mm) on which the aerosol particles (NH_4^+ , NO_3^- , SO_4^{2-} , Cl^- , Na^+) are retained. The second and third filter are paper filters (Whatman 41, ϕ 51 mm) impregnated with NaF and H_3PO_4 respectively. They are used to collect NH_3 and HNO_3 , generated by evaporation of NH_4NO_3 from the first filter. Samples were rinsed with water and analysed for the different components at

ECN. The accuracy for sampling air concentrations in this way is about 5 to 10%.

In order to be able to verify a dispersion model for NH_3 (after Horst, 1977), eleven horizontal concentration gradient measurements were carried out. Ten samplers were placed at several locations in an area with little or no NH_3 - emission (a piece of moorland), downwind of an area with very high NH_3 emissions (an area with intensive livestock breeding). Concentrations in the emission area were also measured. The sampling times were 5 hours and the winds were South-Westerly (4-5 m/s). In figures 6 and 7 the average horizontal concentration gradients are given for NH_3 and NH_4^+ . While NH_3 concentrations show a distinct decrease (concentrations are halved after 600 m), NH_4^+ concentrations remain almost constant over the moor.

VERTICAL PROFILE MEASUREMENTS

A total of 30-day and nighttime samples were obtained at the meteorological tower of the Royal Netherlands Meteorological Institute in the Central part of the Netherlands. The same sampling system was used as that for the horizontal gradient measurements. Sampling times were 12 hours. Meteorological data were available directly from the tower during most of the sampling periods. Samples were taken at heights of 2, 25, 100 and 200 m. The average concentrations are given in Figures 8 (daytime periods) and 9 (nighttime periods) (Erisman et al. 1986B). These averages are not yearly averages. Nevertheless, the measurements were carried out during different seasons, and meteorological conditions were such that these averages give a good picture of what the yearly averages could be. This was verified with the yearly average concentration - emission relation, shown in Figure 4.

For NH_3 a strong decrease with increasing height is observed. The decrease is much stronger during nighttime than during daytime. During nighttime ground temperature inversions were frequently observed. These inversions influence the profiles to a large extent, they are, together with the lower windspeed and increased stability, probably responsible for the relatively high NH_3 concentrations during nighttime.

For HNO_3 a strong increase with increasing height is observed. The increase can be explained by two processes: reaction and deposition. It was not

literature (see for a brief review Erisman et al. 1986B), the agreement between the theoretical predicted dissociation constants and the measured concentration products is very good for relative humidities below 80% (Figure 10). For relative humidities above 80%, however, our findings are not in agreement with the literature (Figure 11). From the literature it should be expected to find lesser NH_3 and HNO_3 gas concentrations in the air. The discrepancies could be the result of certain uncertainties in the measurements; such as low HNO_3 concentrations at very high NH_3 concentrations and the use of 12 hour average concentrations and meteorological data. Relative humidity data at temperatures below 0°C were not available. The concentration products at these conditions, however, are also plotted in Figure 11. The agreement between theory and measurements is far from reasonable. It can be concluded that the equilibrium calculations by Stelson and Seinfeld (1982) are valid at temperatures above 0°C and relative humidities below 80%.

Reactions 3) are radical reactions, which are very slow compared to the acid-base reactions, particularly in the lower atmosphere.

The overall reaction rate of NH_3 to NH_4^+ is a function of the amount of acid-gas or aerosol, temperature, relative humidity and radiation. Theoretically the reaction rate can be calculated from the difference of the sum of the NH_3 and NH_4^+ flux at height z , and the NH_3 flux at reference height assuming first-order kinetics. However, several assumptions should be made: a) steady state conditions; b) no horizontal diffusion; c) no deposition; d) homogeneous distribution of sources at the earth's surface. Because of the long sampling times these assumptions might not always be valid. The calculated reaction rate constants will therefore be rather uncertain. We calculated a pseudo first-order reaction rate constant of $6 \cdot 10^{-4} \text{ (s}^{-1}\text{)}$ for day time periods and $4 \cdot 10^{-4} \text{ (s}^{-1}\text{)}$ for nighttime periods, for the lower part of the atmosphere.

CONCLUSIONS

- A strong seasonal variation for ammonia concentrations, with a maximum in early spring;
- A very strong ammonia gradient over an area with very little

- ammonia emission;
- A strong decrease of ammonia concentrations with increasing height;
 - Equilibrium calculations for ammoniumnitrate were in good agreement with the concentration measurements at r.h. < 80% and $t > 0^{\circ}\text{C}$;
 - The overall pseudo-first order reaction rate constant was calculated to be $6 \times 10^{-4} \text{ (s}^{-1}\text{)}$ for daytime periods and $4 \times 10^{-4} \text{ (s}^{-1}\text{)}$ for nighttime periods.

AKNOWLEDGEMENT

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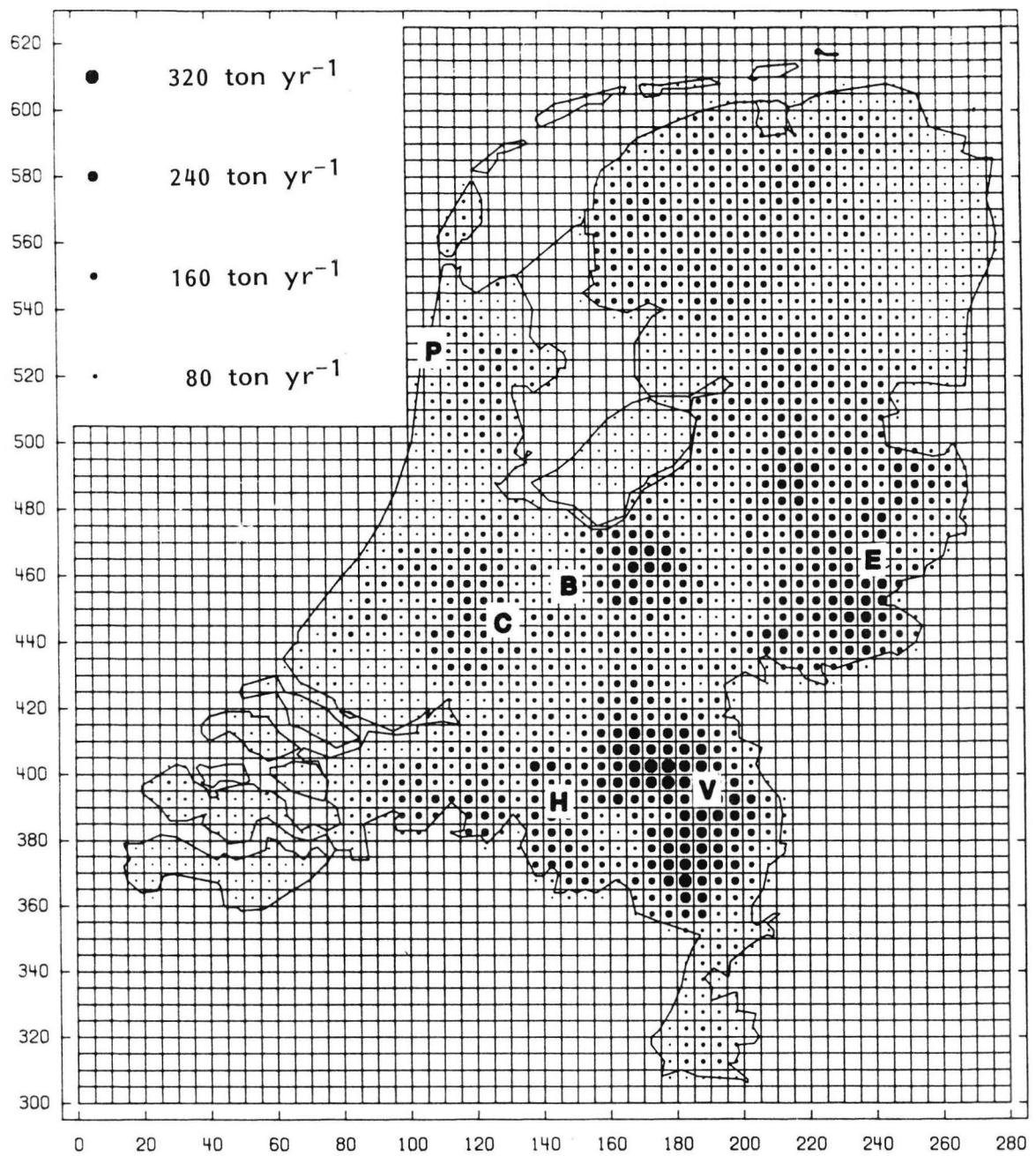


Figure 1. Total emission from animal manure on a 5x5 km² grid.

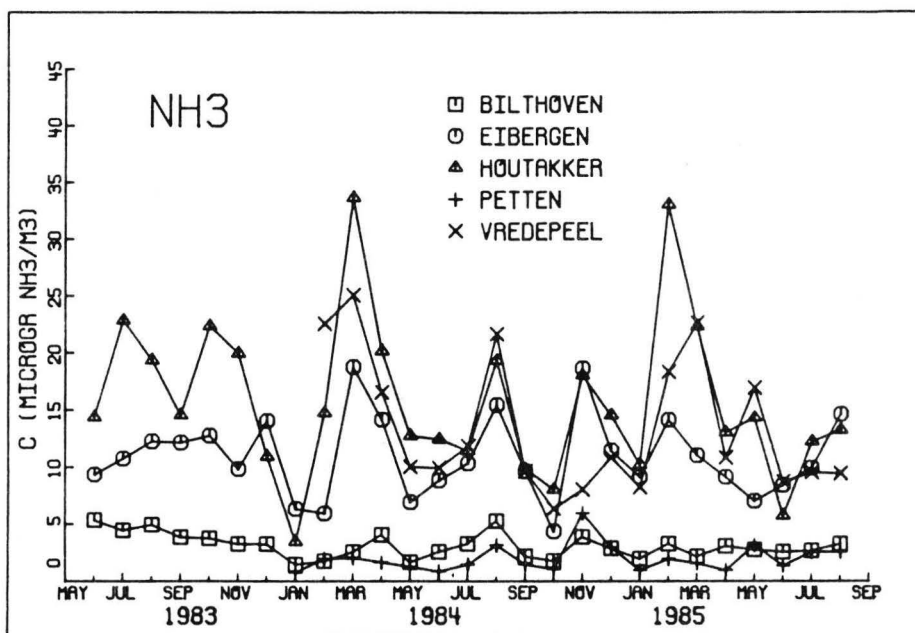


Figure 2. Monthly mean NH₃ concentrations.

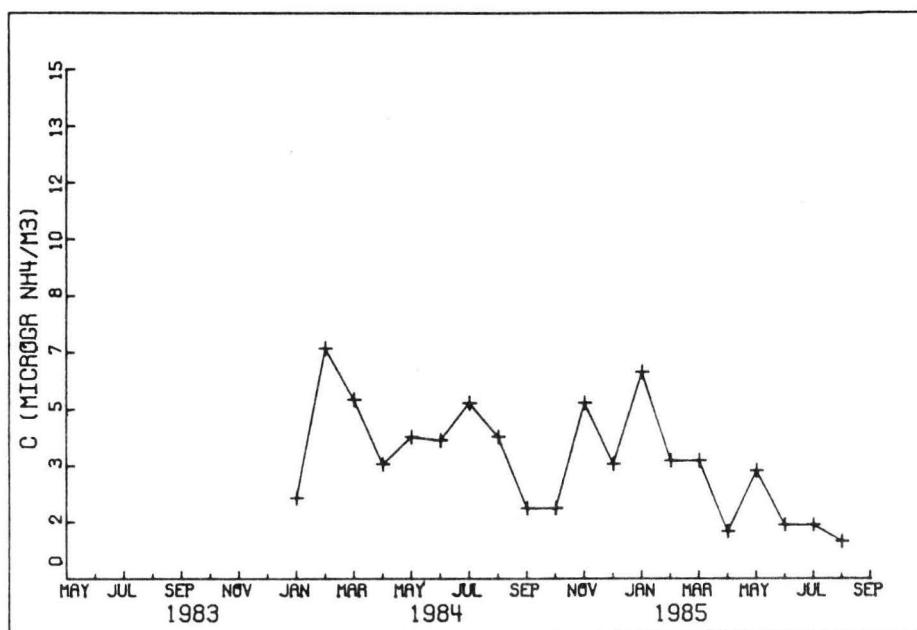


Figure 3. Monthly mean NH₄⁺ concentrations.

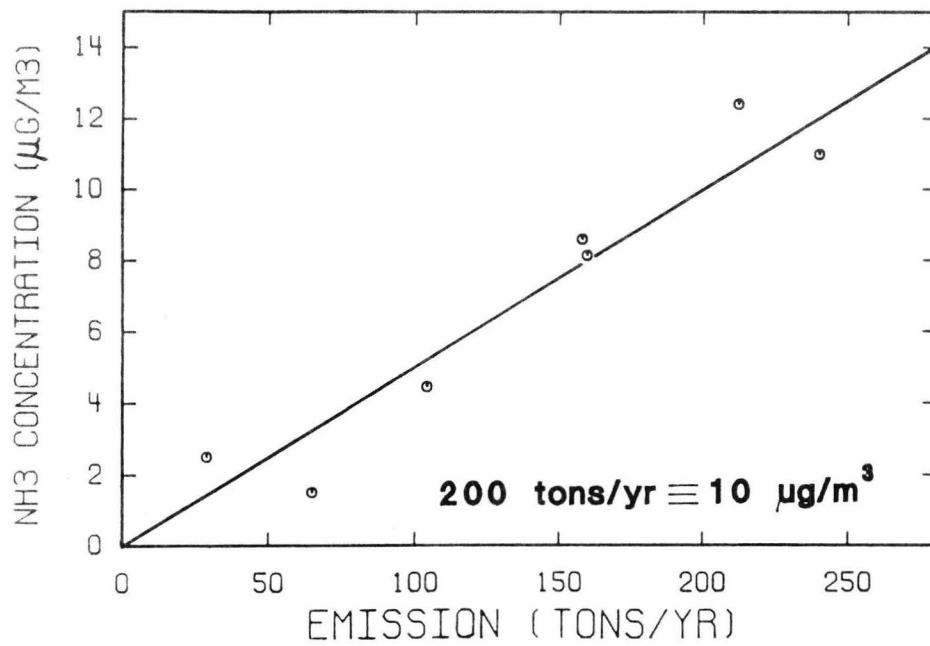


Figure 4. Measured NH₃ concentration vs. calculated NH₃ emission (5x5 km²) for the Netherlands (Erisman et al., 1986A).

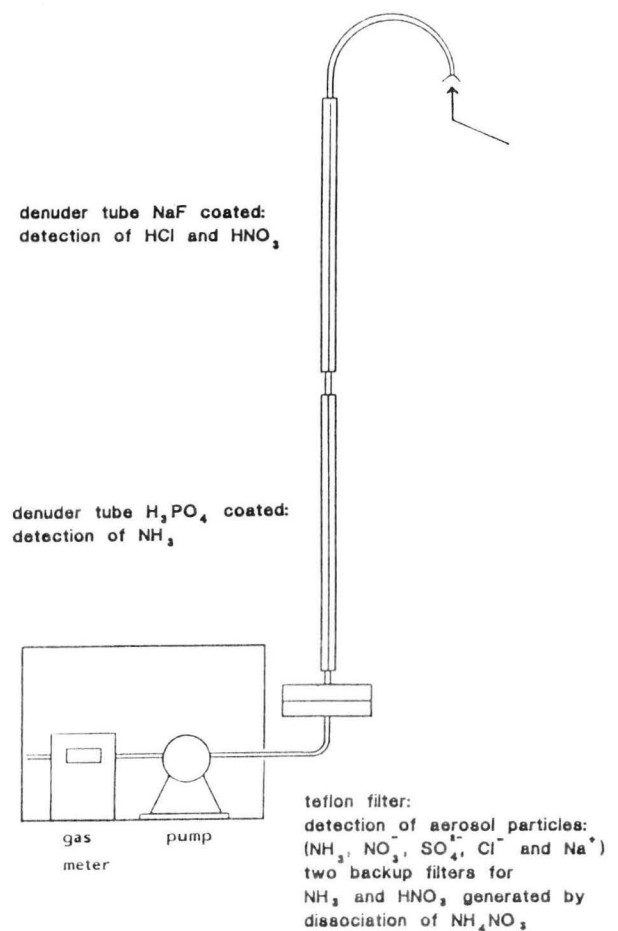


Figure 5. Sampling system.

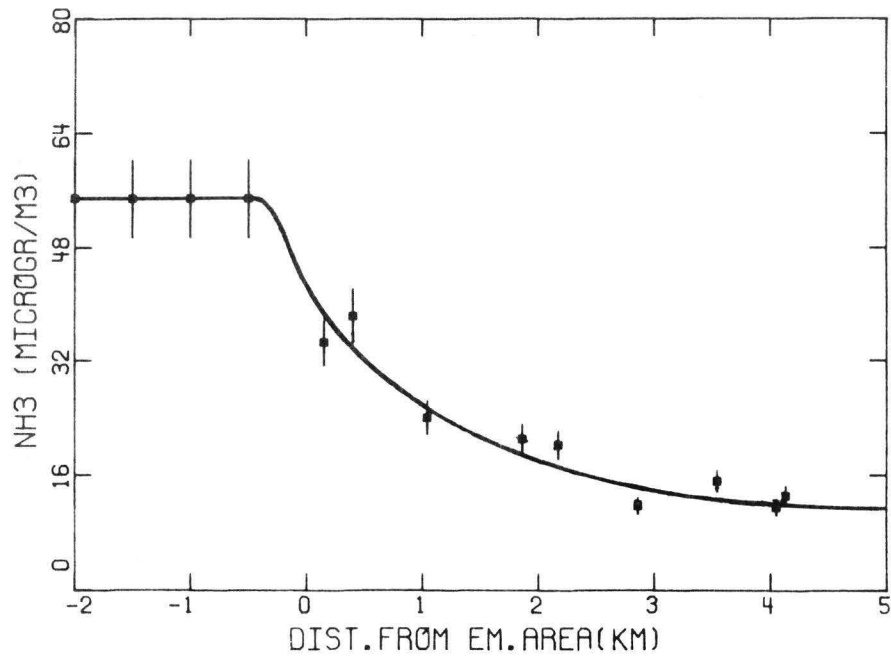


Figure 6. NH₃ concentration gradient over the moor.

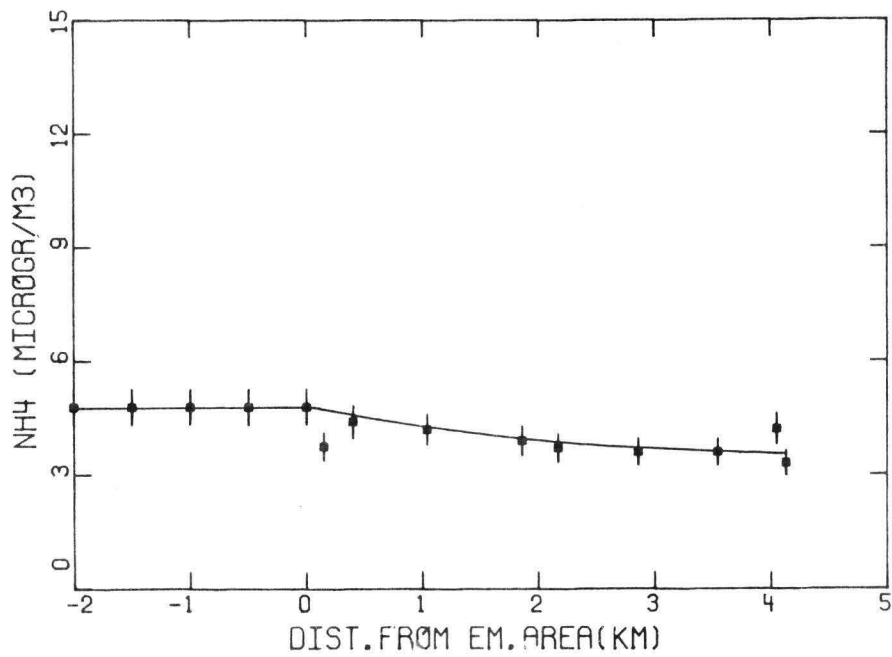


Figure 7. NH₄⁺ concentration gradient over the moor.

Height (m)

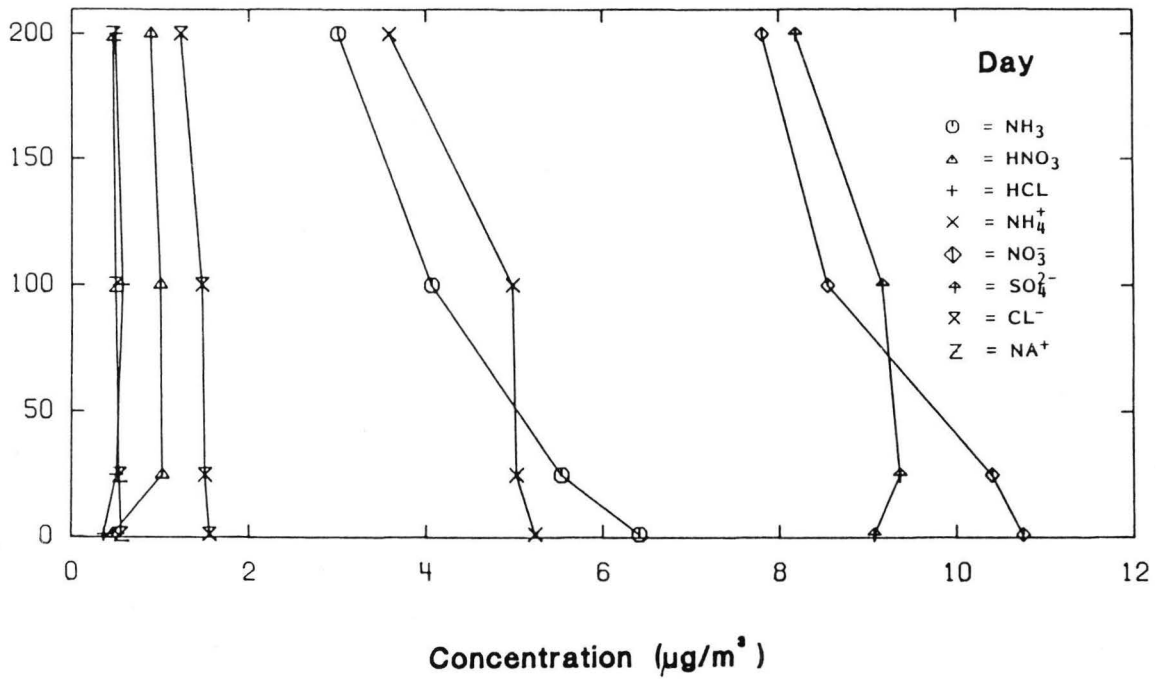


Figure 8. Average concentration profiles for daytime periods.

Height (m)

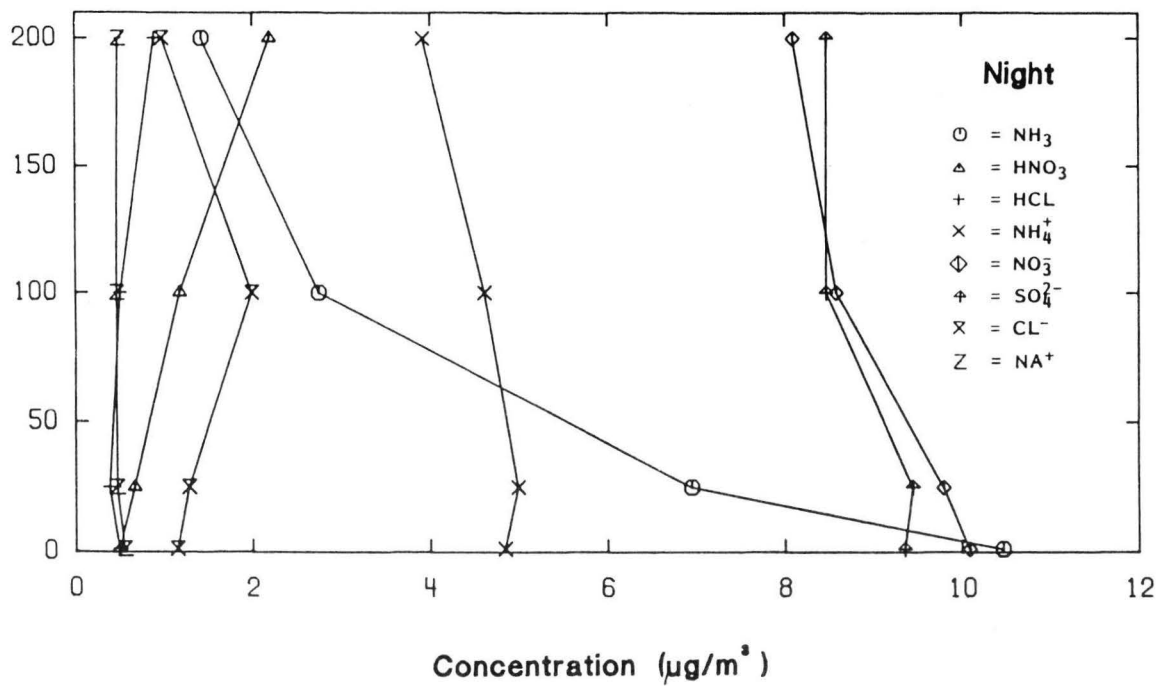


Figure 9. Average concentration profiles for nighttime periods.

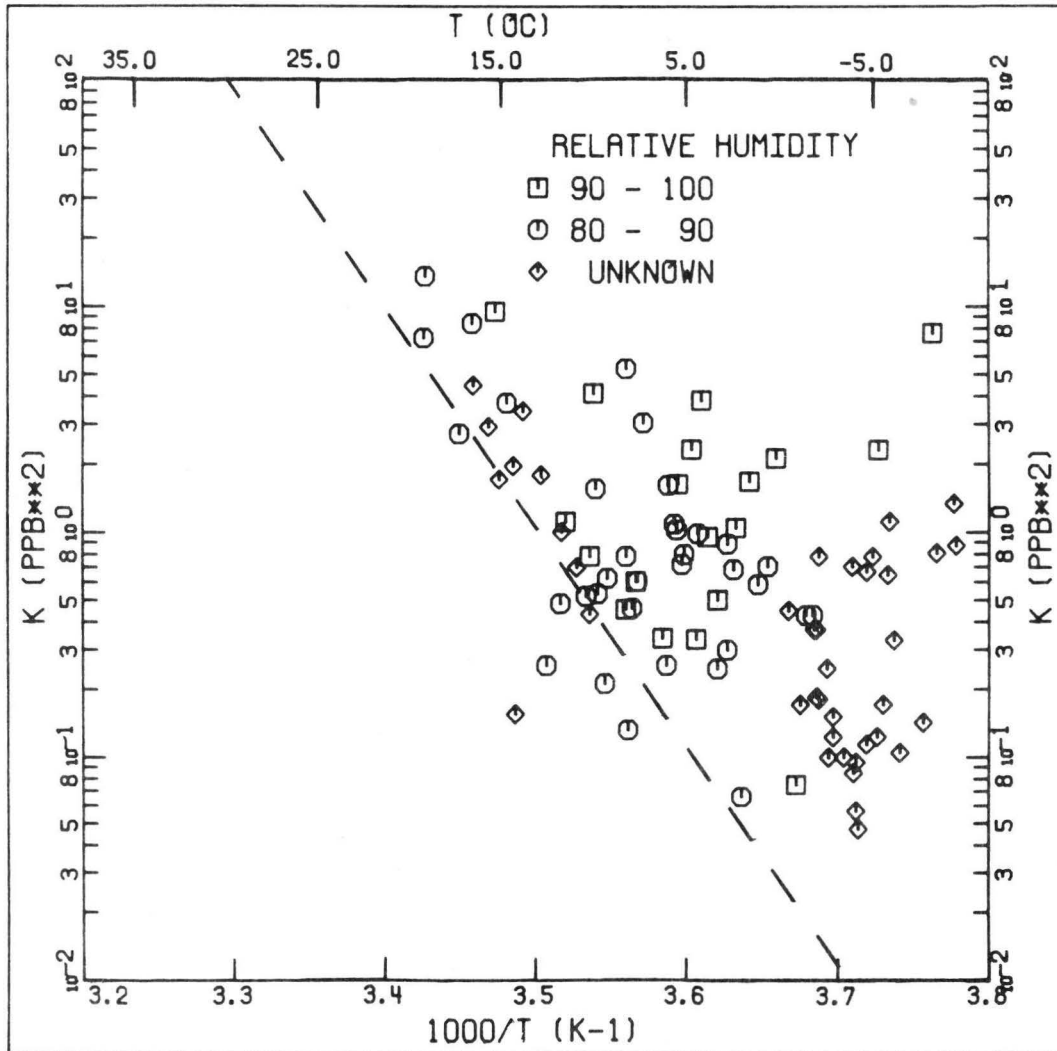


Figure 11. Comparison of the measured concentration product ($K_m = (\text{NH}_3)_x(\text{HNO}_3)_x$) with the calculated dissociation constant K_e as a function of temperature at relative humidities above 80%.

IONIC COMPOSITION OF AMMONIUM SALTS DURING AN ACIDIC WINTERTIME
EPISODE AT TWO SITES AT DIFFERENT ALTITUDE

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Introduction

The "Wienerwald" is a large forested sparsely populated hillside area extending westwards from the "Vienna basin". Within a framework of a group of projects dealing with the assessment on influencing factors for the forest damage observed in this region it is the task of our group to investigate the relative importance of different sulfur and nitrogen compounds for the dry deposition process. During February 1987 a widespread pollution episode occurred in the eastern part of Austria during persistent low temperatures (around - 5°C) and clear sky. While our sampling sites are situated 350 and 430 m above the ground level of the "Vienna basin" effects which we attribute to the mixing of oxidant rich air masses with air masses from the heavily polluted ground layer could be observed. In this paper we report about the accumulation of sulfur and nitrogen compounds and about concentration gradients observed in different layers approaching the measuring sites.

Instrumental

A diffusion denuder sampling train has been designed to collect organic and inorganic ionic species from the atmosphere. The basic arrangement of the diffusion tubes was chosen according to SLANINA et al. (1). However we extended the system with a tube for the collection of volatile organic acids and did not implement a second thermal diffusion unit. For the tubes an annular arrangement was used with the possibility of sampling

rates up to 12 l/min as proposed by POSSANZINI et al. (2). Coating materials were used as described by SLANINA et al. (1) with the exception of the organic acid tube which was coated with NaOH. The system was used in field studies in Linz, Vienna, Bologna and Ljubliana. A survey of the results was presented recently (3).

With the denuder system following components have been separated:
gas phase components: HCl

HNO₃

HCOOH

NH₃

particulate components:

a) thermally (140°C) volatile: Cl⁻ *)

NO₃⁻ *)

H₂SO₄

NH₄⁺ **)

b) thermally (140°C) stable: SO₄²⁻ ***)

NH₄⁺ ****)

*) from ammonium salts

**) from ammonium salts of Cl⁻, NO₃⁻ and partly from neutral sulfate

***) predominantly from ammonium sulfates (neutral and acidic sulfates)

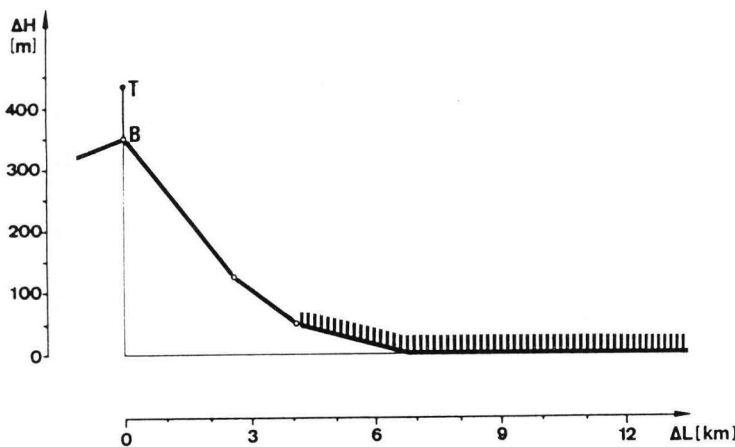
****) predominantly from acidic ammonium sulfate

The components SO₂, NO+NO₂, O₃, particulate matter and standard meteorological parameters are measured at a routine air quality station situated at the top of a telecommunication tower at the Exelberg. Additional information about the meteorological condition during the measuring period was obtained by the Central Institute for Meteorology and Geodynamics, Vienna.

Measuring conditions

The experimental site is situated 10 km NW of Vienna in a hillside area. The average height of the hills is around 300 m above the average level of the city. The denuder sampling was performed

at the "Exelberg" in two different height levels (Fig.1). The "lower" sampling site was situated at the edge of a forested area at the highest elevated summit of the Exelberg (site "B"), the "higher" sampling site (T) was placed at the upper platform of the tower 80 m above the ground level. As the upper sampling site exceeds the ground level of Vienna (170 m asl) of about 400 m the observation of the thermal stratification of the PBL becomes an important influencing factor for the observed composition of atmospheric trace constituents. Changes of pollutant concentration can be followed by the diurnal variation of atmospheric stability, namely of inversion layers. During 24 h we performed two sampling runs: a daytime run from 12:00 to 16:00 LST and a nighttime run from 0:00 to 4:00 LST. The samples were collected during the duration of the pollution episode for 5 days. The reason for taking two samples per day was limitations from the laboratory capabilities. The day/night sampling approach was chosen to obtain information about the air composition during wide and small extension of the mixed layer. Fig.1 illustrates the location of the monitoring sites.



a



b

Fig 1: (a) Cross sectional profile N-E of Vienna and experimental sites, (b) schematic presentation of the Vienna urban region

During the episode several meteorological parameters were relatively constant. During most of the sampling runs the air mass had passed the city of Vienna before arriving at the receptor point. The relative humidity ranged from 77 to 89%, cloud cover was neglectable and the temperature remained in the range of -2 to -10°C.

Description of the episode

During the winter season Central Europe may be affected by a permanent continental High coupled with low temperatures, mostly clear days, light winds and the development of a strong temperature inversion layer, which does not dissipate during the daylight hours. If these conditions occur for a few days the poor ventilation is responsible for a significant accumulation of pollutants.

Such an episode occurred in the first week of February 1987. In Vienna SO₂ began to increase on January 31, 1987 accompanied with an easterly synoptic flow. The measuring campaign started at February 2. At this time an adiabatic lapse rate had been established capped by an inversion layer above 600 m. Moderate to high wind was observed. On February 4 the velocity of the easterly flow diminished and dropped to total stagnation for a couple of hours as observed at several meteorological stations in the Vienna area. At night the upper layer inversion, which initially was at a height of about 600 m reached the ground level. The stagnating wind field together with a shallow PBL determined the air quality for at least two days. The advection of westerly winds at higher altitudes caused an amelioration on February 6.

Results and discussion

The beginning of the episode was dominated by high SO₂ concentrations (maximum 1 hourly mean value at Exelberg 318 ug/m³, 149 ppb NO_x on February 2) at typical advective conditions. Under stagnant conditions at the second half of the episode SO₂ concen-

tration did not exceed the value reported above. In contrast, ambient NO_x concentrations continued to rise and reached a maximum 1 hourly mean value of 251 ppb at February 5. The NO_x/SO₂ volume ratio exceeds a factor of 2, unlike concentration ratios typical for background air masses from eastern countries. We conclude that the dominating fraction of the observed NO_x concentrations can be attributed to local sources. The different behavior of SO₂ in the time series as compared to NO_x (Fig.2) indicates a significant background contribution from remote sources.

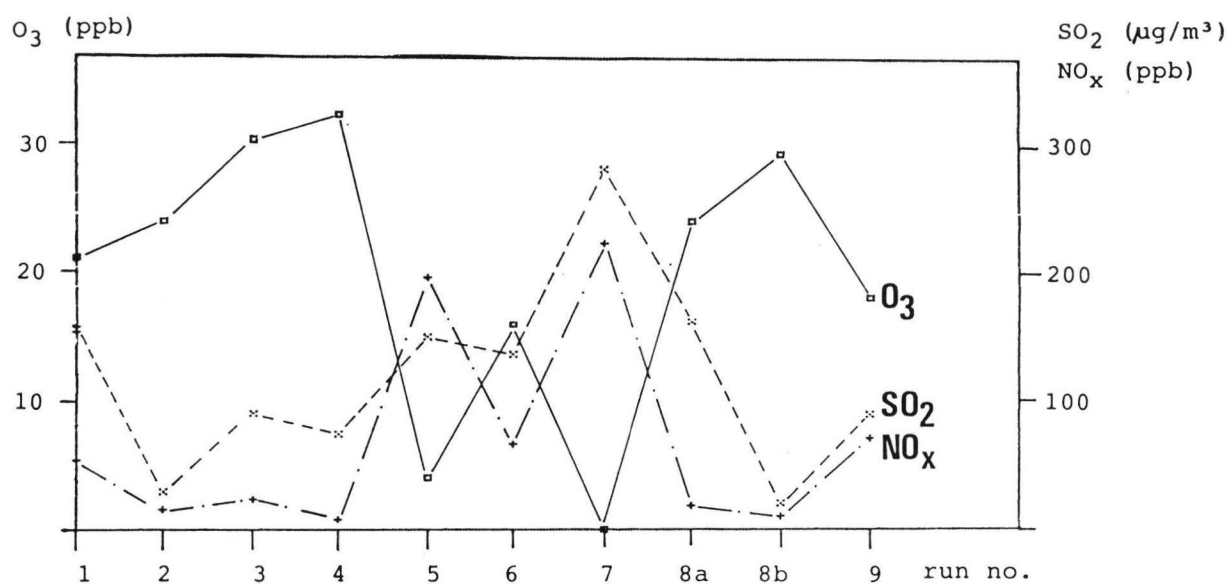


Fig. 2: O₃, SO₂ and NO_x concentrations for each sampling run (4-hourly mean values)

The results of the denuder sampling runs from the two sampling stations (T ... top of the tower, B ... base of the tower) as sums of total atmospheric Cl⁻, NO₃⁻, SO₄²⁻ and NH₄⁺ are given in Table 1. No free ammonia was detected during this period (d.l. 8 nmol/m³). The ratio of equivalents of anions (Cl⁻ + NO₃⁻ + SO₄²⁻) versus cations (NH₄⁺) is used as an indicator for changes in the potential acidity of the gas- and particulate aerosol components. Air masses from the urban area were generally enriched from chlorides and NH₄⁺.

Tab. 1: Results from the denuder samples. Sum of gaseous and particulate Cl^- , NO_3^- , SO_4^{2-} , NH_4^+ .

Ratio of Cl , NO_3 , SO_4 / NH_4 (equivalents)

Run no.	Date	Time	ΣCl^- (nmol/m ³)	ΣNO_3^- (nmol/m ³)	ΣSO_4^{2-} (nmol/m ³)	ΣNH_4^+ (nmol/m ³)	an^-/cat^+ (eq)
Site T (Top of the tower 600 m asl)							
1	2.2.	12:00-16:00	13	130	370	460	1.9
2	3.2.	0:00- 4:00	5	120	410	490	1.9
3	3.2.	12:00-16:00	5	100	420	560	1.7
4	4.2.	0:00- 4:00					
5	4.2.	12:00-16:00	33	310	1210	870	3.2
6	5.2.	0:00- 4:00	6	250	740	890	2.0
7	5.2.	12:00-16:00	35	250	1030	1110	2.1
8a	6.2.	0:00- 4:00	6	420	930	810	2.8
8b	6.2.	5:00- 8:00	13	690	360	710	2.0
9	6.2.	12:00-16:00	8	230	770	640	2.8
Site B (Base of the tower 520 m asl)							
1	2.2.	12:00-16:00	20	110	390	470	1.9
2	3.2.	0:00- 4:00	9	100	510	490	2.3
3	3.2.	12:00-16:00	14	120	530	490	2.4
4	4.2.	0:00- 4:00	9	120	700	400	3.9
5	4.2.	12:00-16:00	56	460	980	1440	1.7
6	5.2.	0:00- 4:00	7	260	920	970	2.2
7	5.2.	12:00-16:00	50	450	1170	1950	1.5
8a	6.2.	0:00- 4:00	14	420	1270	990	3.0
8b	6.2.	5:00- 8:00	9	370	480	1120	1.2
9	6.2.	12:00-16:00	13	360	690	1320	1.3

For the presentation of results the data were classified according to three different meteorological conditions. Concentration gradients between the bottom and the top of the tower are given in Figure 3.

Class I Beginning of the episode, moderate to high winds from easterly directions (cases no. 1 - 3)

Concentration profiles at advective conditions show almost no differences between the two sampling sites. A slight decrease of concentration of nitrate and ammonium species can be observed at the base of the tower and may be due to deposition processes.

Class II Stagnation; Sampling within the inversion layer (daytime cases no. 5, 7, 9)

A strong concentration gradient is observed for NH_4 , particulate nitrate and for thermally unstable sulfates. Thermally stable sulfate decreases with height, whereas free sulfuric acid increases. At the elevated point obviously less ammonia is available to neutralize the acidic compound H_2SO_4 . In contrast, the equivalence ratio for NO_3 , Cl and related NH_4 is found to be around 1. The thermal stratification suppresses the vertical motion, so that a preference of individual species in different height levels can be better observed as compared to the nearly uniformly mixed case I.

Class III Turbulences at the top of the mixing layer (nighttime cases no. 6, 8a, 8b)

During the nighttime cases of February 5 and 6 most components show a decrease of concentration at the elevated site with the exception of free nitric acid, which shows the opposite trend. This phenomenon has been examined in more detail. A further sampling run has been inserted between 5:00 and 8:00 LST when in this case the mixing layer reached the minimum height. 6 and 10 ppb of HNO_3 were detected during the 0:00-4:00 and 5:00 to 8:00

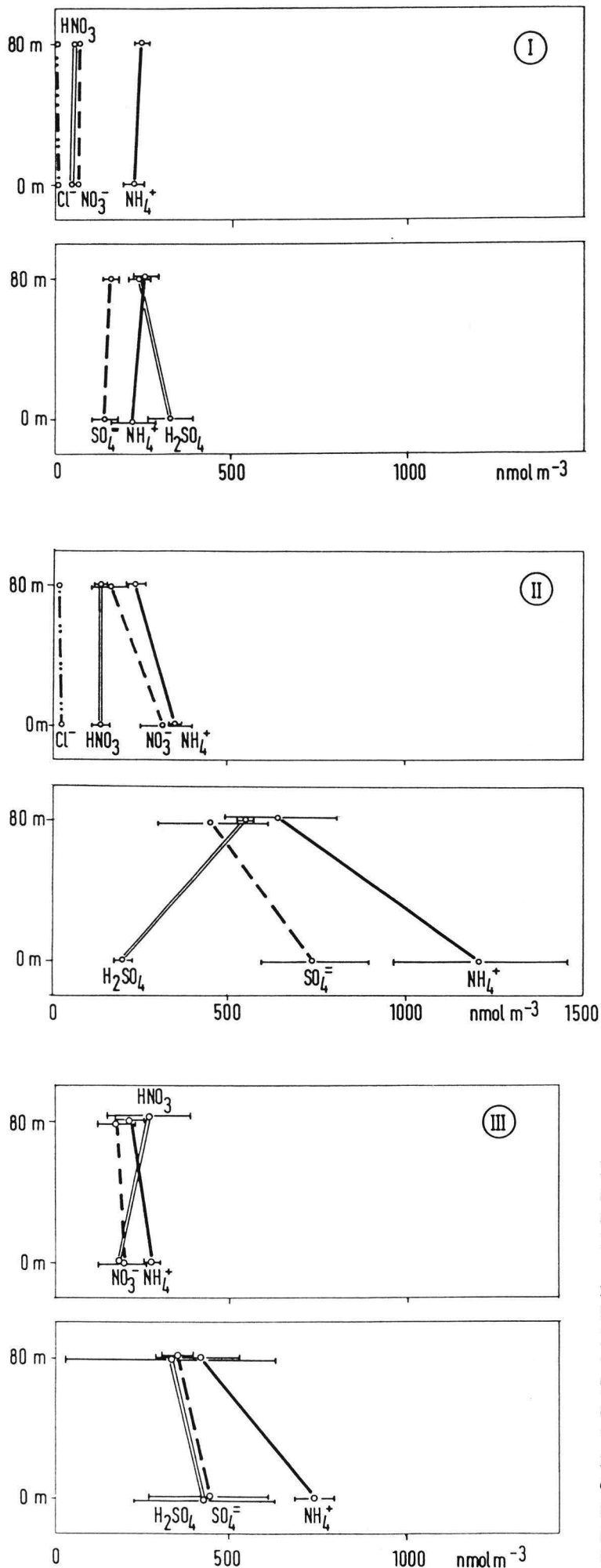


Fig.3: Concentrations of the analyzed components at the base and the top of the tower during 3 meteorological conditions (Class I: Beginning of episode, moderate to high wind, Class II: Stagnation; within the inversion layer, Class III: Turbulence at the top of the mixing layer). The upper graph of each class describes the concentration of the volatile ammonium and the related anions. The lower graph describes the concentration of sulfuric acid and thermally stable ammonium with related sulfates.

sampling run, respectively (Fig.4). The HNO_3 production appears to become important at the interface of the polluted mixed layer and the oxidant rich layer above. The parallel trend between HNO_3 and ozone confirms this view. The HNO_3 /ozone trend (Fig.4) appears only, if the NO_x as precursor was present from local emission (Fig.2).

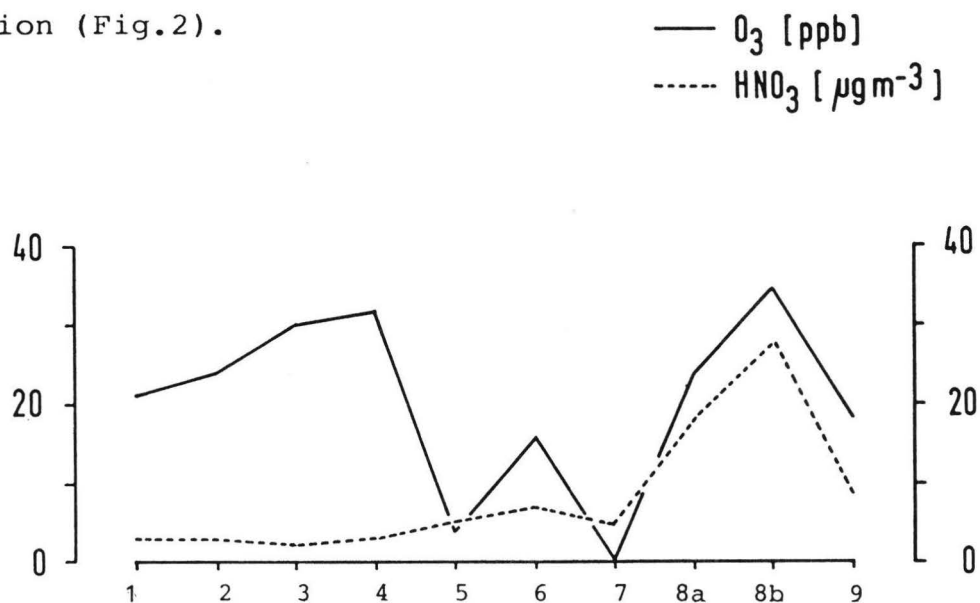


Fig.4: O_3 und HNO_3 concentrations for each sampling run

The precursors to the resulting nitrate and sulfate, namely SO_2 and NO_x , as well as the secondary anionic compounds, accumulated during the wintertime episode. Free ammonia was generally below the detection limit of 8 nmol/m^3 , which was in agreement with equilibrium conditions (4). While secondary pollutants extended to higher altitudes, it was apparent that neutralisation of acidic compounds takes place near ground level, whereas free acids were predominating in absence of neutralizing compounds at the top of the mixed layer.

From the observed data we can derive:

The mid-tropospheric oxidizing layer has a clear effect on the nitric acid production during the episode.

NO_x rich air masses from the urban area have a high particulate nitrate content clearly present as ammonium salt.

Sulfate accumulates during the episode. The raise of SO₄ is practically not affected by the presence of the NO_x rich and oxidant depleted urban air masses (Fig.3, Case II).

The particulate ammonium content in the advected air masses is rising in a similar way as the sulfate component. In the urban NO_x and nitrate rich air masses it appears additionally in phase with the particulate nitrate.

The air masses at the lower site are significantly less acidic as compared to the air masses at the higher elevated site due to neutralization of the acidic aerosol by NH₃ near ground level sources.

The work has been performed within the projects "Backgroundstation Exelberg" and "Occurrence and deposition of acidic components in a forest ecosystem" funded by the Austrian Ministry for Health and Environmental Protection. Data support was provided by the Central Institute for Meteorology and Geodynamics and the environmental departments of the state of Lower Austria and the municipality of Vienna (MA 22).

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DETECTION OF AMMONIUM COMPOUNDS AT THE SINGLE PARTICLE LEVEL.

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INTRODUCTION

The high reactivity of ambient aerosol particles makes it rather difficult to investigate the form as they occur in the atmosphere. Indeed, transformations of the aerosol can take place during sampling, storage and analysis. This is certainly the case for ammonium compounds in ambient aerosols.

For bulk analysis, different methods have been developed which allow speciation of gaseous NH_3 and particulate NH_4^+ (with distinction between the chloride, nitrate and sulfate salt) in aerosols. They are based on the separation of the gaseous and particulate phase by a combination of diffusion denuders and backup filters. (Niessner and Klockow, 1980).

Although several single particle methods are available, the analysis of ammonium compounds containing aerosol at the single particle level is not so straightforward. A number of relevant problems, will be discussed. Results of measurements on ambient aerosol particles will also be presented.

INSTRUMENTAL

Sampling is done with a low volume (1 l/min) cascade impactor with five stages (cut-off diameter of 4, 2, 1, 0.5 and 0.25 μm). The collection time is approximately 10 minutes. The impaction surfaces are equipped with Formvar coated electron microscope grids.

The impactor is preceded by an acid removing NaF coated denuder and an ammonia removing oxalic acid coated denuder. The removal of the reactive gaseous compounds is necessary in order to avoid any gas-particulate interactions on the impaction surfaces. The reactions merely amplify the existing atmospheric reactions (Otten et al., 1986). Particle-particle interactions are avoided by adjusting the sampling time so that the impaction surfaces are not overloaded.

The samples are analysed with a single particle technique, Laser Microprobe Mass Analysis or LAMMA (Verbueken et al., 1985). In the LAMMA-500 instrument, a particle on the Formvar coated electron microscope grid is first selected by means of a visible low power laser, that does not damage the particle. Then the particle is vaporised and ionised by a high power laser puls. The ions are analysed in a time of flight mass spectrometer. Both positive and negative mode spectra can be recorded. This technique allows analysis of thermally unstable compounds like ammonium containing aerosols. If not the only one, it is one of the rare techniques that can perform analysis of these particles directly after collection, without any further preparation. Electron microprobe analyses of these compounds can be performed indirectly with the aid of spotting techniques (Ferek et al., 1983).

EXPERIMENTAL

By separating the gaseous and the particulate phase, the equilibrium between particulate ammonium and gaseous ammonia is disturbed, and dissociation of the collected particles is due to occur. This process is temperature dependent and can be slowed down by keeping the samples at low temperature and by minimalising the time between sampling and analysis of the particles. The demand for a fast analysis technique is obvious.

Aerosols were collected near Antwerp, Belgium on several occasions during the winter of 1986/1987. Samples were taken during dry inversion periods with dominantly easterly winds. Under these atmospheric conditions the highest pollution occurs and then also the highest bulk particulate ammonium concentrations are observed.

RESULTS AND DISCUSSION

Standard aerosol particles were generated by means of a pneumatic nebuliser. Compounds like NH_4Cl , NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ could be identified unambiguously from their LAMMA spectra. Mixtures of these ammonium salts, with and without added Na^+ and K^+ , were also investigated. Comparison of mass spectrum pattern from standards and ambient aerosols is necessary because the limited resolution of the LAMMA-500 mass spectrometer (850 at $m/e=208$) does not allow differentiation between two different ions with the same nominal mass.

LAMMA results show clearly the presence of ammonium compounds in ambient aerosols. In the first place this is confirmed by the presence of a mass

peak at $m/e=18$ in the positive mode spectra. Since the relative sensitivity of LAMMA for the ammonium ion relative to other cations like sodium and potassium is rather low, the ammonium content of the analysed particles must be substantial and can be estimated by the use of relative sensitivity coefficients. One of the most striking features is the occurrence of Cl^- , NO_3^- and SO_4^{2-} in the same particles together with NH_4^+ . No pure ammonium salt particles were detected. The occurrence of ammonium nitrate and ammonium sulfate in the same particles was already postulated by other workers (Harrison and Sturges, 1984) and is now confirmed by the detection at the single particle level. The composition of the analysed particles is quite uniform in the collected size range (4 to $0.25 \mu\text{m}$) although in the smallest particles, the sulfate compound is predominant.

In an important number of particles, elements like Al, Fe and trace metals like Mn and V were also detected. This indicated the complexity of the aerosol at the single particle level. Most of the analysed particles consist of combinations of different compounds.

An interesting question is whether it is possible to discover if these combined particles have a certain morphological structure, like for instance a layer of ammonium salts around a soil dust or fly ash particle. The desorption capabilities of the LAMMA technique may offer some possibilities in this field, although careful analysis of laboratory prepared standards has to be performed first.

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INTERACTION OF GASEOUS AMMONIA WITH COATED SULFURIC ACID AEROSOL - LABORATORY RESULTS

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Abstract

Ultrafine monodisperse sulfuric acid droplets were coated with different organic substances under well controlled conditions. The rate of neutralization by ammonia was determined by chemical characterization of the particulate and gaseous phase before and after the mixing in a flow reactor. A remarkable decrease in reaction rate was observed, depending on molecular structure of the organic coating substance and the thickness of the coating.

The results obtained by chemical methods were independently supported and verified by employing a multistep condensation nuclei counter.

Introduction

The observed coexistence of acidic aerosols (H_2SO_4 , HSO_4^- containing particles) and ammonia in the atmosphere can be explained by NH_3 being present only in insufficient amounts or by rate limitations in the neutralization reaction between sulfuric acid and ammonia. As hypothetically assumed by Junge and Scheich in 1969, such limitations may be due to organic material coating the surface of sulfuric acid droplets. In polluted air organic compounds such as long chain alcohols or fatty acids are present. These are able to form surface films which may affect the behaviour of atmospheric particles or droplets (Gill et al., 1983), e. g. the transport of water molecules into or out of a droplet as shown by

Chang and Hill (1980).

The scope of the present work was to study the influence of well defined organic coatings on the rate of neutralization of sulfuric acid droplets by ammonia. Additionally the properties of these coated droplets to act as condensation nuclei were investigated by applying a multistep condensation nuclei counter.

Experimental

A. Kinetic measurements

The experimental set-up is given in Fig. 1. A modified La Mer generator was used to produce a submicron sulfuric acid aerosol (Niessner and Klockow, 1980). A monodisperse fraction was obtained by electrostatic classification (electrostatic classifier, model 3071, Thermo Systems Instruments Inc., St. Paul, MN). The encapsulation of the monodisperse droplets with the organic component was accomplished by a condensation technique (Niessner, 1984). Coating substances were n-hexadecanol, n-hexadecane and 1-(hydroxymethyl)-adamantane. The aerosol was mixed with the organic vapour in the heated ring-gap mixing nozzle shown in Fig. 1. Heterogeneous condensation of the vapour on the sulfuric acid droplet surface took place in the thermostated condensation section. The thickness of the coating was determined by measuring the penetration of the monodisperse particles before and after encapsulation through a calibrated screen-type diffusion battery (Niessner, 1986). The corresponding calibration curves are shown in Fig. 2. For particles < 40 nm diameter small size changes - due to the condensation of the coating substance - could be detected. The ammonia trace gas for reaction was produced by a refillable permeation tube (Teckentrup and Klockow, 1978).

After fast mixing of the aerosol with ammonia, the reaction was stopped after a certain reaction time. This was accomplished by depositing the unreacted NH_3 in a citric acid coated denuder tube

(Ferm, 1979, Bos, 1980). The remaining sulfuric acid aerosol was collected in a thermo-denuder coated with sodium fluoride (Niessner and Klockow, 1982). Reaction products - particulate NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ - were deposited on a back-up filter. The collected unreacted and reacted species were determined by suitable analytical techniques.

B. Measurements with a multistep condensation nuclei counter

To support and verify the results of the kinetic measurements, especially the dependence of the coating tightness on the molecular structure of the organic substance, a multistep condensation nuclei counter (CNC) was applied. The generation and layer thickness determination of the coated aerosols was similar to the procedure just described under kinetic measurements. The sulfuric acid droplets obtained by electrostatic classification and used for the investigation were ultrafine (10 nm diameter). The thickness of the layer of the different organic substances mentioned before was chosen to be $\Delta r = 5$ nm and the resulting particle size was controlled again by diffusion battery measurements. By this means all the investigated particles had the same diameter of about 20 nm. This diameter was compared with the Kelvin-equivalent diameter of the coated droplets as determined by a multistep CNC. The multistep CNC and its capabilities have been described by Niessner and Helsper (1985).

The experimental set-up is given in Fig. 3. After having evaluated the coating thickness with the diffusion battery, the particle number concentration (N_E) of the aerosol was determined by applying an aerosol electrometer (model 3068, Thermo Systems Instruments Inc., St. Paul, MN). The concentration was adjusted to a certain value by dilution with humidified particle-free nitrogen. After feeding the aerosol into the expansion chamber of the multistep CNC, a given supersaturation - according to an equivalent Kelvin diameter (Liu, 1984) - was generated by introduction of clean, particle-free nitrogen up to a certain pressure value,

humidification (20 sec residence time) and rapid adiabatic expansion. Measurement of the light extinction before and after expansion led to a CNC indicated droplet concentration (N_{CNC}). The system automatically was running through 16 increasing saturation ratios to determine the Kelvin-size spectrum.

Results

A. Kinetic measurements

The length of one n-hexadecanol or n-hexadecane molecule is ≈ 2 nm. This results in an increase in diameter of the primary droplet by 4 - 5 nm due to the condensation of one complete monolayer. A distinct growth of the coating layer was obtained by a slight increase of the coating substance vapour pressure.

In a first experiment the reaction time was kept constant at 10 seconds and the fraction of reacted H_2SO_4 -aerosol was measured as a function of the thickness of the n-hexadecanol layer for relative humidities of 20 % and 45 %, respectively (Fig. 4). For 20 % r. h. a strong decrease in the neutralization rate was observed for a coating thickness of more than one n-hexadecanol layer ($\Delta r = 2$ nm). Only 2 - 3 monolayers of n-hexadecanol led to a complete preservation of the acidity. For higher r. h. (45 %) the same effect was obtained for a coating layer thickness of 8 - 10 nm, corresponding to 4 - 5 monolayers. Fig. 5 shows the result of an analogous experiment with n-hexadecane as coating substance. In this case the effect of coating was less pronounced. A possible complete preservation of the acidity for coatings $\Delta r > 3$ nm could not be shown experimentally, because the supersaturation of n-hexadecane vapour required to coat the H_2SO_4 droplets could not be obtained without partial evaporation of the primary H_2SO_4 droplets in the heated ring-gap mixing nozzle. Fig. 6 shows results of reaction rate measurements at a n-hexadecanol coating of $\Delta r = 3$ nm thickness. The reaction observed at a relative humidity of 20 % was rather slow: Only about 80 % of the sulfuric acid

aerosol reacted with excess ammonia within 20 seconds. A higher relative humidity (45 %) led to a higher reaction rate (see Fig. 4). The reaction time necessary for a complete neutralization under these conditions was about 4 seconds. In comparison to uncoated sulfuric acid aerosol, however, the reaction rate is still low. Pure sulfuric acid droplets ($d_p \leq 200$ nm) are completely neutralized within one second even at a r. h. of 0 % (Robbins and Cadle, 1958). With n-hexadecane as a coating a decrease in reaction rate was also observed (Fig. 7).

From these results one can conclude that long, straight chain molecules are able to form compact films on H_2SO_4 droplet surfaces and to retard neutralization by ammonia. For comparison a 1-(hydroxymethyl)-adamantane coating was used as a model substance for a branched hydrocarbon. From Fig. 8 it can be seen, that a fast neutralization reaction took place and that the coating had no noticeable effect in decreasing the reaction rate.

B. Multistep CNC measurements

The results of the multistep CNC measurements are shown in Fig. 9. The normalized number concentration N_{CNC}/N_E was plotted as a function of the Kelvin diameter and the saturation ratio, respectively. As can be seen, uncoated H_2SO_4 droplets, according to their hygroscopicity, start to take up water vapour already at a very low supersaturation. A 5 nm thick coating with 1-(hydroxymethyl)-adamantane led to a small increase in supersaturation needed for activation as condensation nuclei. With a 5 nm thick n-hexadecane coating, the effect was more pronounced. For n-hexadecanol coated H_2SO_4 droplets a remarkably high saturation ratio was required for activation. This means, n-hexadecane and in particular n-hexadecanol molecules were able to form tight coatings on the H_2SO_4 droplet surfaces, while 1-(hydroxymethyl)-adamantane was a rather inefficient coating. These findings correspond very well to the results obtained by kinetic measurements.

Conclusions

Further investigations are needed to evaluate the consequences of the results obtained, e. g. for inhalation toxicology or cloud and fog chemistry. One question arising is whether there exists a connection between coated particles and the "interstitial aerosol" in cloud and fog systems. A further question is whether coated aerosol particles with a reactive core are present in the atmosphere and how they contribute to the long range transport of reactive material under atmospheric conditions.

Acknowledgement

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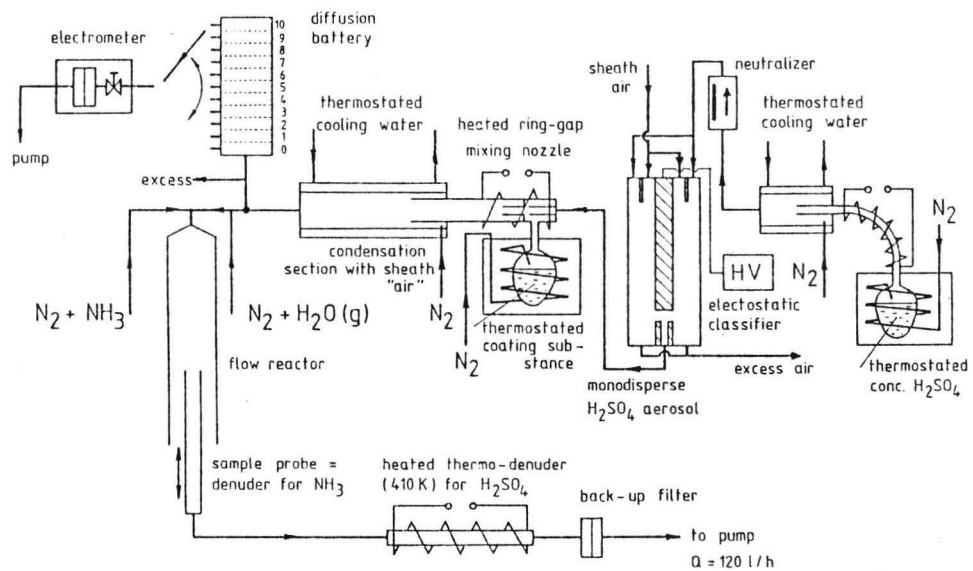


Fig. 1: Experimental set-up for kinetic measurements. The aerosol was either fed into the diffusion battery or into the flow reactor

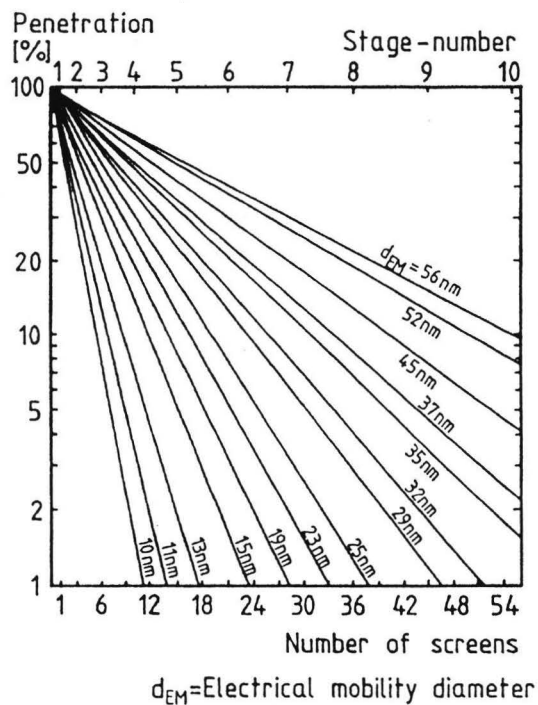


Fig. 2: Calibration of diffusion battery with monodisperse aerosol

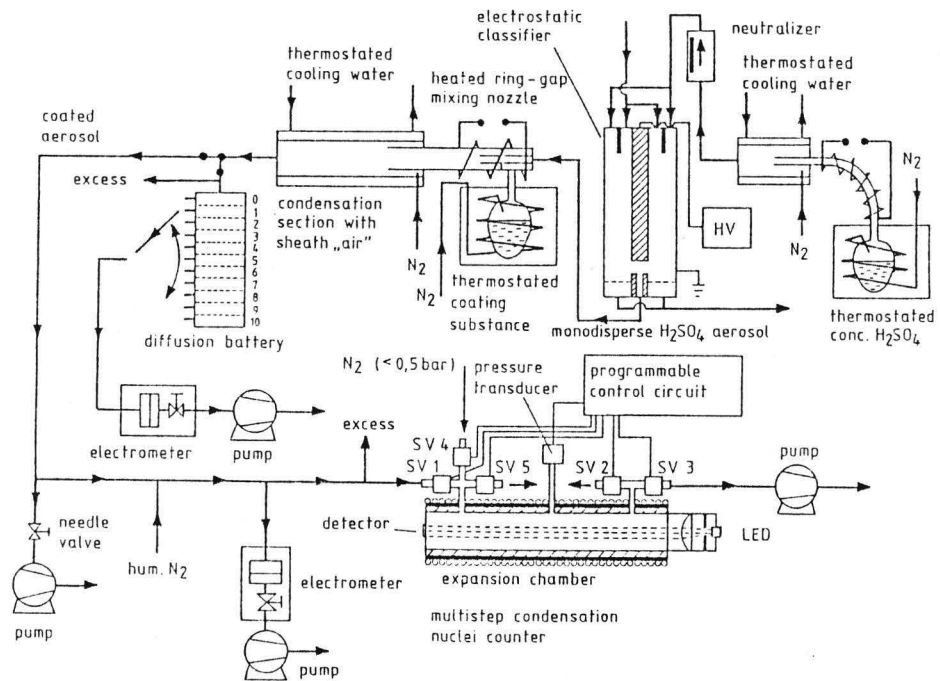


Fig. 3: Experimental set-up for measurements with a multistep condensation nuclei counter. The aerosol was either fed into the diffusion battery or into the CNC.

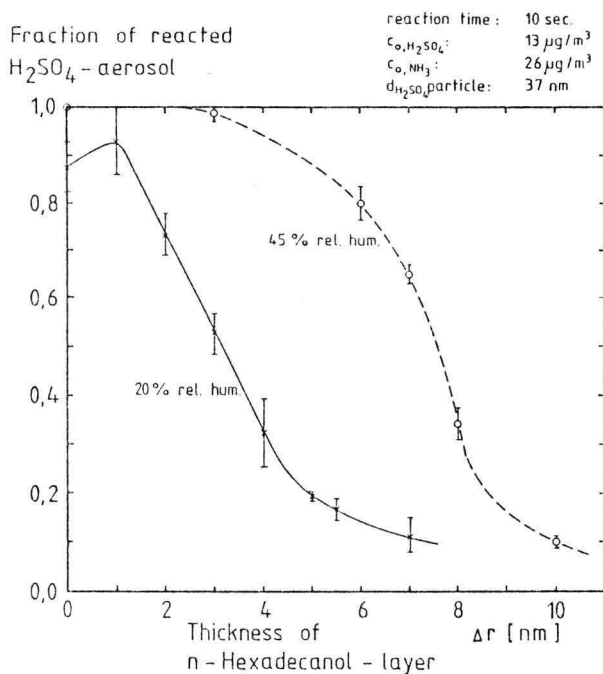


Fig. 4: Fraction of reacted H₂SO₄-aerosol vs. thickness of n-hexadecanol-layer for different r. h. and a reaction time of 10 seconds.

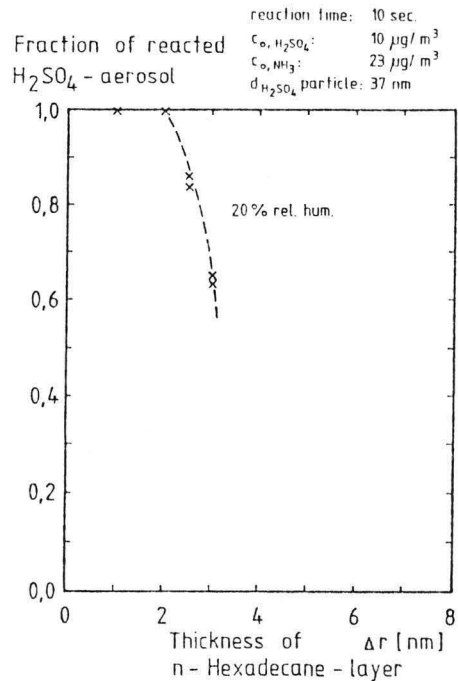


Fig. 5: Fraction of reacted H₂SO₄-aerosol vs. thickness of the n-hexadecane-layer for 20% r. h. and a reaction time of 10 seconds.

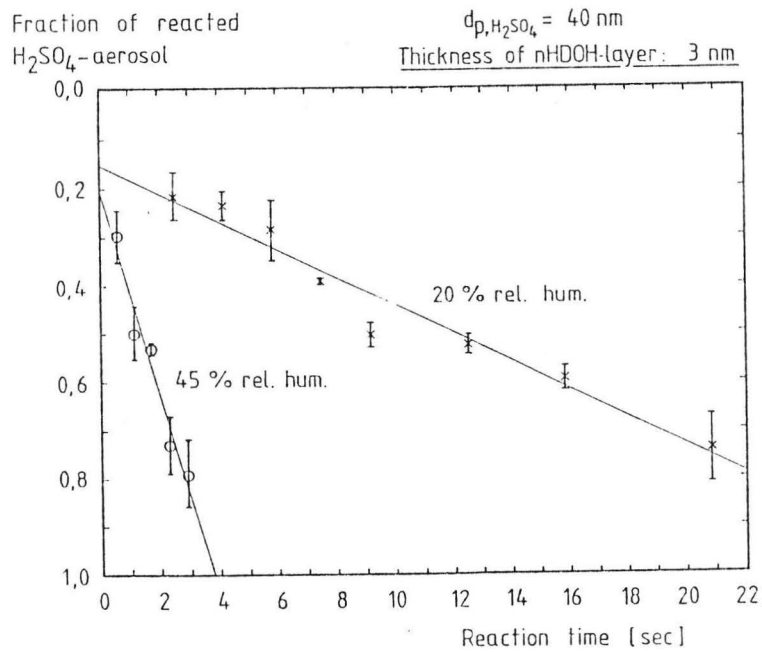


Fig. 6: Fraction of reacted H_2SO_4 -aerosol vs. reaction time at a coating thickness of 3 nm n-hexadecanol and 20% and 45% r. h., respectively.

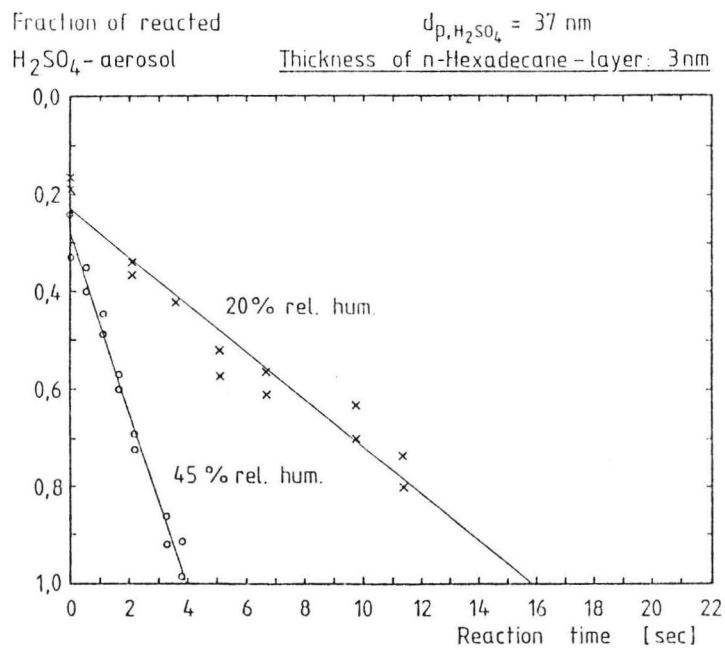


Fig. 7: Fraction of reacted H_2SO_4 -aerosol vs. reaction time at a coating thickness of 3 nm n-hexadecane and 20% and 45% r. h., respectively.

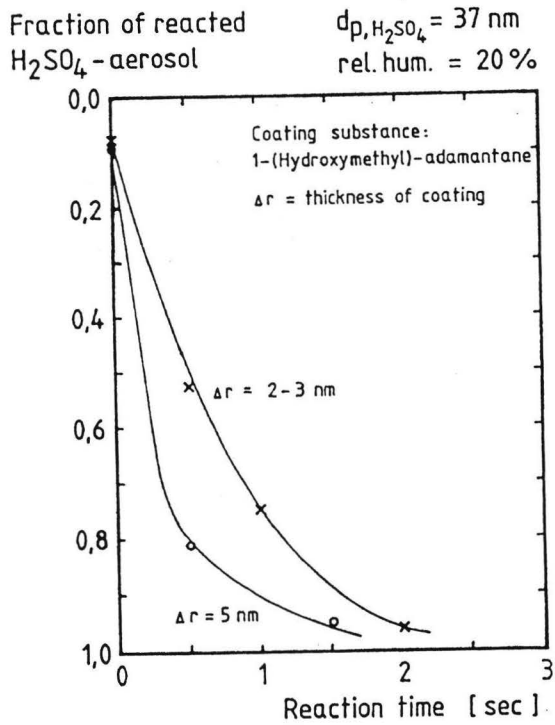


Fig. 8: Fraction of reacted H_2SO_4 -aerosol vs. reaction time at a coating thickness of 2 - 3 nm and 5 nm, respectively, of 1-(hydroxymethyl)-adamantane at 20% r. h.

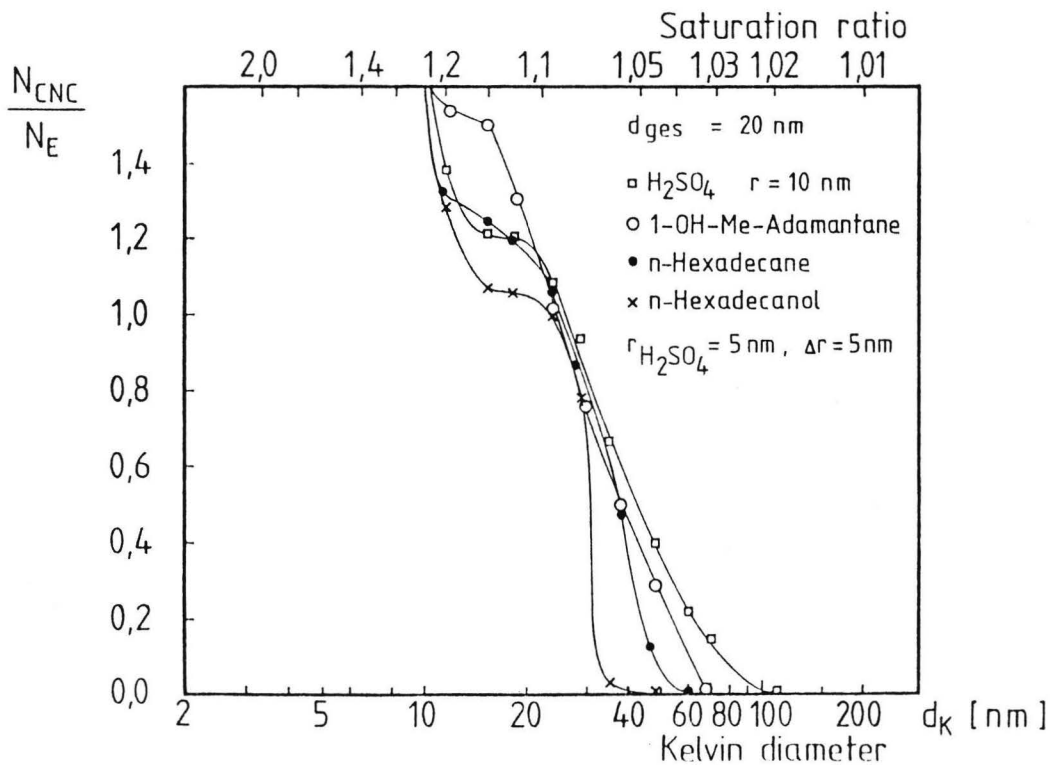


Fig. 9: Kelvin-spectra of different coated H_2SO_4 -droplets
 N_{E} = Particle concentration measured with an aerosol electrometer,
 N_{CNC} = Particle concentration indicated by the CNC.

ASSESSMENT OF DRY DEPOSITION FLUXES OF NH_3 AND NH_4^+ OVER NATURAL TERRAINS

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ABSTRACT

The dry deposition velocity of NH_3 and NH_4^+ ions in particles was determined using the micrometeorological gradient method. The vertical concentration gradient of NH_3 , necessary to calculate the flux, was measured using oxalic acid coated denuders. NH_4^+ ions were determined in the airstream leaving the denuders using impregnated filters. Measurements were performed in different seasons over mainly heather/purple moor grass vegetation and a pine plantation with 2.5 m high Corsican pine. NH_3 appears to deposit relatively fast an average deposition velocity over all location of 1.9 cm.s^{-1} was observed in approximately 100 hourly observations. The influence of surface wetness was clearly established. Wet vegetation acts as a perfect sink for NH_3 . For NH_4^+ present in particles a much slower deposition velocity of average 0.2 cm.s^{-1} was observed.

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INTRODUCTION

In 1984 a large research project (entitled: Amonia; from emission to deposition) was started under contract with the Commission of the European Community and the Dutch Ministry of Housing, Physical Planning and the Environment. This project was subdivided into several subprojects each dealing with separate processes determining the atmospheric fate of NH_3 . Participants in the project were the Dutch institutes: Netherlands Energy Research Center (ECN) (Petten), Institute for Meteorology and Oceanography of the State University Utrecht (IMOU) and TNO Division of Technology for Society (MT-TNO, Delft) and the Kernforschungs Anlage Jülich (FRG).

In this paper the MT-TNO contribution, about measurement of dry deposition fluxes, is described. The goal of this subproject was to determine dry deposition fluxes of NH_3 and NH_4^+ ions into sensitive natural ecosystems in Western Europe.

The dry deposition flux of NH_3 and NH_4^+ is an important parameter for model simulation of the atmospheric transport of these species. On the other hand this flux is relevant for studies into the effect of pollutants on sensitive terrestrial ecosystems.

The parameter relating the deposition flux (F) of a compound to the concentration (c) is the so-called deposition velocity (v_d) i.e. $F = -v_d \cdot c$.

In this paper the results of a large number of measurements of the dry deposition velocity of NH_3 and NH_4^+ are presented. Measurements were performed mainly over heather fields and forest.

The dry deposition velocity of a compound can be determined in several ways. In micrometeorological methods the vertical flux through a horizontal plane over the surface is measured. The assumption is that the flux through this plane is equal to the flux into the surface. This assumption will only hold under specific conditions, i.e. the measurement site must be relatively flat and must have a large uniform 'fetch' in the upwind area. Moreover the site must be sufficiently far away from sources to prevent the measurements are disturbed by advection fluxes.

The dry deposition velocity, v_d , of a certain compound over a certain ecosystem is a function of a large number of meteorological, chemical and biological parameters such as wind speed, atmospheric stability, surface roughness, specific compound vegetation interactions etc. Moreover v_d will probably show an extra diurnal and seasonal variability caused by biological factors.

To model the dry deposition process a surface layer (resistance) model is often used. The idea of the model is that a depositing gas molecule passes subsequently through a series of resistance layers before entering the vegetation. In analogy with Ohm's law the flux is equivalent to current and the potential difference is equivalent to the difference in gas concentration in the air and inside the plant. A simple form of the model is given by:

$$\frac{1}{v_d} = \frac{C_{\text{air}}}{-\text{Flux}} = R_{\text{tot}} = R_a + R_b + R_s$$

Here R_{tot} is the total resistance to the transport of gases or particles from the air into the plant. R_a is the aerodynamic resistance, i.e. the resistance to the transport through the layer of air over the surface. R_b is the resistance of the quasi-laminar boundary layer just over the vegetation elements. R_s is the so-called surface resistance.

In this model approach the aerodynamic part of the deposition process can be treated separately. Then it is possible to derive the surface resistance from measurements of v_d simply by subtracting the aerodynamic and boundary layer resistances from the total resistance. The surface resistance is specific for the compound vegetation combination and does not show the variability in the deposition velocity caused by meteorological factors such as the wind speed. On the other hand the surface resistance can be combined with meteorological information to derive local deposition velocities, for instance in model calculations. If some function is assumed for the variation of the surface resistance over the year the information of a relatively limited number of measurements can be used to estimate yearly averages of deposition fluxes.

Many micrometeorological methods can be used to measure dry deposition velocities. Since no fast response NH_3 analyser is available (suitable for the attractive eddy correlation method) the gradient technique was used. For the measurements over forest the modified Bowen-ratio method was also applied.

In the gradient method the dry deposition flux is determined from measurement of the vertical concentration gradient, dc/dz , and a measurement of the turbulent diffusion coefficient (k_z).

The flux is calculated from: $\text{flux} = -k_h \frac{dc}{dz}$. In this formula k_z is taken equal to the turbulent heat exchange coefficient, k_h .

EXPERIMENTAL PROCEDURE

Measurements were performed in campaigns during about one week. In each campaign a 10 m mast was erected on a suitable spot (depending on wind direction). Measurements normally took place during the day. In principle measurements were performed during dry periods. Occasionally short showers occurred during the measuring period. Sampling was stopped completely during heavy showers or long lasting rain periods.

Night-time measurements appeared to be troublesome for several reasons. During nights with occasional showers expected, measurements were not undertaken because work was not safe whereas during the typical dry nights owing to inversions windspeed dropped beneath the stalling speed of the cup-anemometers.

In the measurement described here k_z was determined by measurement of vertical windspeed and temperature profiles from 0.5 to 7 metre over the vegetation-canopy. The windspeeds were determined using cup-anemometers. Air temperature profiles were determined using ventilated and shielded platinum resistance thermometers. The concentration profile of NH_3 was determined after preconcentration on an oxalic acid coated denuder according to procedures described by Ferm [1].

At each level a set of three denuders was mounted. To measure NH_4^+ ion concentrations in particles filters (impregnated with oxalic acid) were mounted in the air stream leaving the denuders.

Normally a determination consisted of a one - or two - hour sampling period. After sampling the denuders and filters were stored and analysed within one week using a photometrical method. Special care was taken to avoid any contamination of the samples with NH_3 gases.

The average flux was calculated from

$$\text{Flux} = - \frac{k \cdot U_* z}{\phi_h} \frac{dc}{dz}$$

The friction velocity, U_* , and the dimensionless flux profile relation for heat, ϕ_h , were calculated from the profiles measured using procedures described by Berkowitz and Prahm [2] k is von Kármán's constant (0.4).

Typical standard errors in the concentration measurement of NH_3 at one level were $0.2 \mu\text{g} \cdot \text{m}^{-3}$ and $0.6 \mu\text{g} \cdot \text{m}^{-3}$ for NH_4^+ . Four levels of concentration, windspeed and temperature were used.

Since vertical concentration gradients are very small the error in the final flux estimate is dominated by the error in the concentration gradient. For NH_3 , errors in the flux estimates were typically in the range of 10-50%. Statistically, gradients are considered not significantly different from zero when the error is greater than 50% (95% confidence interval). Roughly 60% of the NH_3 measurements were considered significant. For NH_4^+ hardly any gradients were significantly different from zero. For measurements showing significant gradients the deposition velocity and the surface resistance were calculated. These results were used to calculate the averages. To calculate the average flux, however, all gradient results were used except, of course those of clear erroneous measurements. This is to prevent the average results from being biased towards high fluxes. If only the significant gradients were used the high fluxes (that are easier to measure) would dominate the average results.

In the calculations the following formulae were used:

$$R_a = \frac{U}{U_*^2} - \left(\frac{\Psi_h - \Psi_m}{kU_*} \right)$$

$$R_b = 2 \left(\frac{1}{kU_*} \right) \left(\frac{Sc}{Pr} \right)^{2/3}$$

Where, Ψ_h and Ψ_m are the integrated flux profile relations for heat and momentum, Sc and Pr are the Schmidt and Prandtl numbers, respectively.

RESULTS

Measurements were performed on several locations. The locations are indicated in Figure 1.



Figure 1. Measurement locations from NH_3 deposition measurements.

The location Fochteloerveen is a peat moor, relatively far from important source areas of NH_3 with a heather vegetation covered with purple moor grass. The other two heather locations (Strabrechtse heide and Terletse heide) are much closer to source areas. The location Koningsheide is a young pine plantation of mainly Corsican pine and some birch. The height of the trees during the campaigns ranged from 2 to 3 metre.

In Table 1 the averages for all locations based on approximately 100 hourly measurements are given for NH_3 and NH_4^+ . It is obvious that NH_3 deposits very fast, whereas NH_4^+ ions in particles deposit much slower.

In Figure 2 all measurements showing a significant gradient are presented as a function of daynumber. It is clear that no explicit difference between the locations or seasonal variation can be observed. A further analysis shows no significant influence of air temperature, time of the day on the deposition velocity. It is often suggested that there would be an air concentration (turnover point) below which NH_3 would be emitted from the plants and above which NH_3 would deposit. It is therefore interesting to note that no clear dependence on NH_3 air concentration was found.

Table 1 Averages and standard deviations (between brackets) for heather locations.

	NH_3	n	NH_4^+	n
v_d ($\text{cm}\cdot\text{s}^{-1}$)	1.92 (1.09)	51	0.18 (0.54)	71
R_s ($\text{s}\cdot\text{cm}^{-1}$)	0.38 (0.36)	51	-	
F ($\text{kg}\cdot\text{ha}\cdot\text{yr}^{-1}$)	14.5 (15.2)	73	3.8 (11)	71

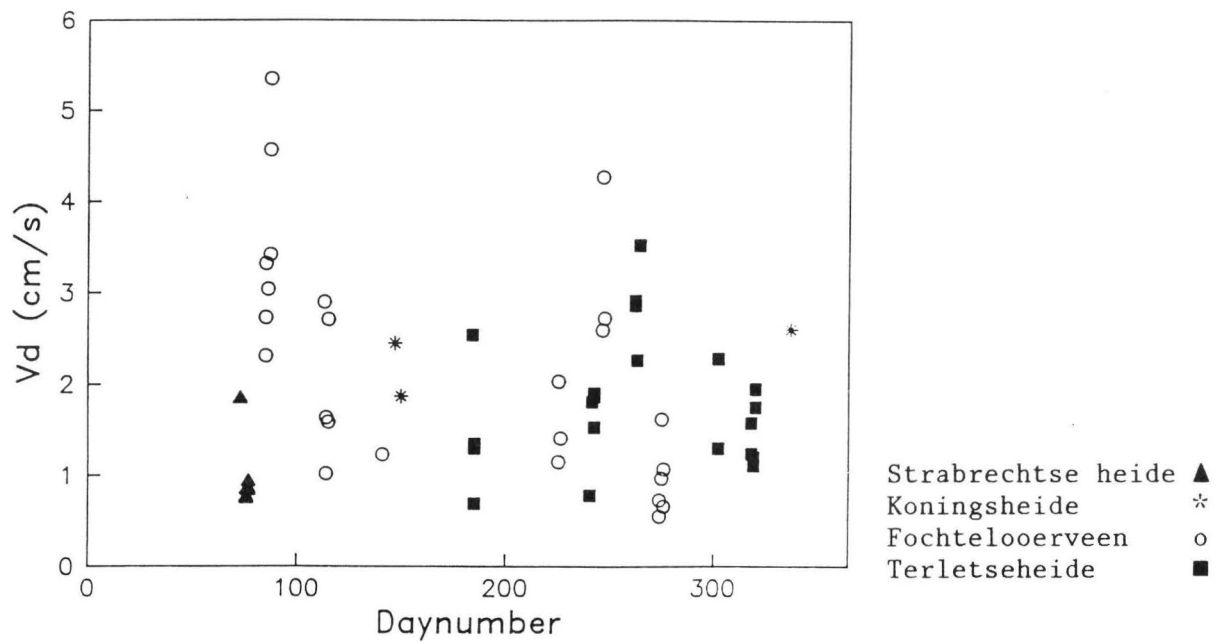


Figure 2. NH_3 dry deposition velocities (v_d) as a function of daynumber for different locations: Strabrechtse heide, Koningsheide, Fochteloerveen; Terletse heide.

However, all effects should show more clearly in the surface resistance, because variation in v_d caused by variation in meteorological parameters are filtered out of R_s . Indeed the total variation in the deposition velocity can be explained on the basis of variation in meteorological magnitudes (30%). The rest of the variation must be attributed to the variations in the surface resistance and scatter in the measurements due to random errors in the measurement procedures.

In Figure 3 the surface resistance is presented again as a function of daynumber. It is clear that there is a distinct influence of surface wetness on the surface resistance. For wet surfaces the average surface resistance

For "remote" areas with a typical air concentration of $4 \mu\text{g.m}^{-3}$ the total yearly NH_3 flux would be $18 \text{ kg.ha}^{-1}.\text{yr}^{-1}$. In areas with high concentrations of NH_3 ($12 \mu\text{g.m}^{-3}$) this leads to an average flux of $54 \text{ kg NH}_3 \text{ ha}^{-1}.\text{yr}^{-1}$.*).

Table 2 Frequency of occurrence of night time Pasquill classes and average windspeed at Cabauw (NL). Calculated aerodynamic resistance R_a and boundary layer resistance R_b **).

	Pasquill class				
	Dl	Dm	Dh	E	F
freq. (%)	26	26	14	8	18
U 1 m (m.s^{-1})	1.1	2.4	3.5	1.4	0.4
Ra 1 m (s.cm^{-1})	0.35	0.15	0.10	0.31	1.11
Rb 1 m (s.cm^{-1})	0.26	0.12	0.08	0.21	0.72

*) It is important to note that in an area where NH_3 is depositing, the concentration of NH_3 at the one metre level may be much lower during inversion periods because of dry deposition.

***) A relation between stability class and the Monin-Obukhov length given by van Aalst [3] was used to estimate R_a from the measured windspeed.

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CATCH OF ATMOSPHERIC DEPOSITION IN RELATION TO VEGETATION
STRUCTURES OF HEATHLAND

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Abstract

Deposition of air-pollution is not equally distributed not even on a fine scale, but depends on the structure of the intercepting surface. Vegetation has a strong filtering effect in which its canopy structure is a most important factor, also in low vegetation.

In this paper the importance of spatial and temporal differences in canopy structure of low vegetation for interception of air pollutants is shown. Analogous to measurements in forests throughfall measurements were carried out to determine the deposition of different ions. In a heathland two vegetation structure types were selected on the basis of dominance of one plant species, viz. heather (*Calluna vulgaris*) and purple moor-grass (*Molinia caerulea*), respectively. The results of measurements in these two different structure types show a clear correlation between changes in structure during the year and amount of deposition of sulphate relative to its bulk deposition. The throughfall deposition pattern of an ion less inert than sulphate, such as ammonium, differs significantly from that of sulphate as a result of ion exchange in the canopy.

Introduction

The impact of air-pollutants is increasingly felt especially in nature reserves. In the Netherlands, most of the nature reserves are located on weakly buffered, nutrient-poor sandy soils, which are vulnerable for disturbances in ionic-balances.

Semi-natural ecosystems are originally often characterised by their relative species richness. In general changes in species composition elapse gradually and go on for years before changes are distinguished (Diemont & Heil 1984).

Until recently, the impact of atmospheric deposition on the species composition of (semi-)natural vegetation was mainly considered to result from acidification. Nowadays eutrophication problems become more and more evident due to deposition of $\text{NH}_3/\text{NH}_4^+$. It has been established that eutrophication undesirably decreases the plant species diversity of semi-natural ecosystems (Heil & Diemont 1983; Vermeer & Berendse 1983; Roelofs 1984; Schuurkes et al. 1986).

Results of small scale windtunnel experiments showed the co-deposition of SO_2 and NH_3 (Adema et al. 1986). The opposite pH-dependent behaviour of these air-pollutants mutually stimulates their deposition on wet surfaces (Adema et al. 1986; Van Hove 1987). The sink capacity for co-deposition of SO_2 and NH_3 strongly depends on the amount of moisture on the vegetation canopy. To simplify deposition models it is often assumed that the canopy of vegetation, and with that the interceptive properties, are constant during a year. Low vegetation has a strong filtering effect on SO_2 and NH_3 in which a varying canopy structure is an important factor.

In this study the relations between the structure of a heathland vegetation and throughfall deposition of SO_4^{2-} and NH_4^+ , as estimation of the deposition of their main precursors SO_2 and NH_3 , are described.

Study area

The study has been carried out in the heathland "Uddelerbuurtveld" (Veluwe), The Netherlands. The vegetation can be classified as Genisto-Callunetum (De Smidt 1977). The heathland is surrounded by agricultural areas with episodic high emissions of NH_3 during a year.

In the heathland two vegetation 'types' were selected, based upon a number of equivalent structure parameters, viz. height and geometrical irregularity. At the beginning of the study the mean age of the vegetation was approximately 6 years, and the vegetation was 50cm tall on the average. The two vegetation 'types' are dominated by heather (*Calluna vulgaris* (L.) Hull) or purple moor-grass (*Molinia caerulea* (L.) Moench), respectively. Both study sites occupy an area of approximately one hectare each and are adjacent to each other.

Methods

To estimate total atmospheric deposition, the sum of throughfall and stemflow is frequently used. In low vegetation, however,

stemflow measurements can hardly be carried out under natural conditions. Therefore, a method for throughfall measurements has been employed, which produces total fluxes based upon throughfall concentrations and estimations of evaporation (Mulder 1986; Heil & van Dam 1986). For throughfall measurements half-open pipelines of PVC were used, which can be placed within the canopy without disturbing its structure (Fig. 1).

In both vegetation pipelines with a capturing surface of 165 cm^2 were installed halfway down the canopy. To prevent photochemical conversion of the precipitation, the collecting bottle was placed in hole in the soil, and covered with a black plastic sheet. Bulk deposition was measured above the vegetation. All series were replicated five times. Throughfall and bulk deposition were collected every fortnight during a period of one year (May 1985 - May 1986). The samples of throughfall and bulk deposition were colorimetrically analysed on SO_4^{2-} and NH_4^+ (SKALAR auto-analyser).

To determine structural characteristics, the *Calluna* and *Molinia* vegetation were sampled once a month from April to December 1985. The samples were replicated five times. The plants were clipped at soil surface and separated on green leaves and rest of above ground plant material (viz. standing dead, stems, inflorescences). The samples were used for measurements of 'Leaf' Area Index, being the total surface area of leaves and all other plant parts in this instance.

The results are statistically analysed using two-way ANOVA (Dixon et al. 1981; Sokal & Rohlf 1979). The calculations involved periods of 28 days.

Results

Figure 2 shows the amount of SO_4^{2-} and NH_4^+ deposition per period of 28 days. It is obvious that the SO_4^{2-} and NH_4^+ throughfall of Calluna as well as Molinia exceeds the bulk deposition in most periods during the year.

Contrary to SO_4^{2-} , however, NH_4^+ throughfall of both vegetation is less than the amount in bulk precipitation during some periods (Fig. 2).

The total amount of SO_4^{2-} and NH_4^+ throughfall in Molinia is significantly more than in Calluna, and both are significantly more than the bulk deposition (Table 1 and 2). The significant difference in amount per sampling date can be expected, because of differences in atmospheric conditions throughout a year (Table 2). Striking, however, is the significant interaction between amount of deposition per site and date (Fig. 3). This implies that the difference in total amount of deposition between the bulk, Calluna and Molinia is not the result of a constant factor, but changes during the measuring period of one year.

Figure 3 shows the relation between SO_4^{2-} and NH_4^+ in the bulk, in throughfall of Calluna and throughfall of Molinia, respectively. Obviously, there is a significant correlation between the amount of SO_4^{2-} and amount of NH_4^+ deposition in all three cases (Fig. 3).

Compared to the SO_4^{2-} bulk deposition, the SO_4^{2-} throughfall deposition of Molinia, and to some extent also of Calluna, shows a clear peak during the period September 1985 - January 1986 (Fig. 4). As SO_4^{2-} , the NH_4^+ throughfall deposition of Molinia

and Calluna shows an increase relative to the bulk during this period (Fig. 4). Contrary to SO_4^{2-} , however, NH_4^+ throughfall shows a negative deposition (viz. $< 100\%$) during some periods, which is most probably the result of canopy-exchange.

Figure 5 shows the LAI values of the different parts of Molinia and Calluna. Although all above ground parts (Molinia and Calluna total) considerably contribute to the 'LAI', merely a part of the total will substantially contribute to the interceptive structure (architecture) of the vegetation, because a considerable amount of the LAI of Molinia is located in tussocks at the bottom of the vegetation in the beginning of the growing season.

Especially the first year leaves of Molinia contribute to the structure, which is important for the increase of the deposition. The LAI values of the first year leaves of Molinia (Molinia green) are significantly correlated with the relative deposition of SO_4^{2-} of Molinia ($P < 0.05$) (Fig. 4 and 5). The structure of Calluna, as shrub, is hard to express in LAI, and no significant correlation has been found between LAI and amount of throughfall. However, other structure parameters, measured by a digital picture processing technique, show a significant correlation with SO_4^{2-} deposition for both plant species, Molinia as well as Calluna (Heil & Roebertsen in prep.).

Discussion

As a result of canopy-exchange several processes influence the ionic composition of throughfall deposition (Ulrich 1983). In general, however, assimilation of SO_2 by vegetation is limited, and a considerable amount of the SO_2 deposited will be converted

to SO_4^{2-} (Hoffland 1987). With respect to canopy-exchange, SO_4^{2-} can therefore be considered to be an inert ion (Ulrich 1983, Klaassen 1987). Thus, the SO_4^{2-} throughfall deposition of *Molinia* as well as of *Calluna* will give a good estimation of the increase in deposition relative to the bulk.

Assimilation of $\text{NH}_3/\text{NH}_4^+$ by grassland vegetation can be considerable (Heil et al. 1987). Assimilation of $\text{NH}_3/\text{NH}_4^+$ by *Molinia* is rather limited, however, because of a relatively short growing season of this grass species, viz. from the end of May to the beginning of September (Jefferies 1915, Heil 1984). *Molinia* completely dies off at the end of September, so that the structure is completely formed by standing dead after September. Thus, the negative throughfall deposition of NH_4^+ is distinctly to interpret for *Molinia* (Fig. 4). The growth of *Calluna*, as an evergreen, elapses irregularly during a year (Grace & Woolhouse 1970). The heathland "Uddelerbuurtveld", as most of the Dutch heathlands, was strongly affected as a result of severe frost periods during the winters of 1984/1985 and 1985/1986. As a consequence the growth of *Calluna* was limited in 1985. Canopy-exchange of $\text{NH}_3/\text{NH}_4^+$ by *Calluna*, however, has been significant on several occasions (Fig. 4).

The results of this study show a significant correlation between changes in LAI values of *Molinia* and amount of SO_4^{2-} deposition. Although, there is not such a significant correlation for *Calluna*, it is obvious that also the structure of *Calluna* plays an important role in the process of deposition. Our conclusions implicate that the available (wet) deposition surface, being a sink for SO_2 and NH_3 , will considerably increase as a result of the structure of low vegetation.

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Table 1. Total amount of deposition ($\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) during the period of May 1985 - May 1986.

	bulk	Calluna	Molinia
SO_4^{2-}	40.3	50.9	61.8
NH_4^+	17.3	19.7	24.5

Table 2. Significance levels of the two-way ANOVA of total amount of deposition per sampling site per year (amount), amount of deposition per sampling date (date), and interaction between amount of deposition per site per date (interaction).

		SO_4^{2-}	NH_4^+
bulk v.s. Calluna	amount	**	**
	date	***	***
	interaction	*	*
bulk v.s. Molinia	amount	***	**
	date	***	***
	interaction	**	*
Calluna v.s. Molinia	amount	*	*
	date	***	***
	interaction	*	*

* = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.001$

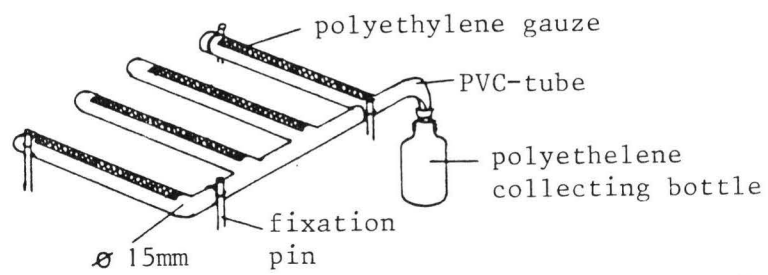
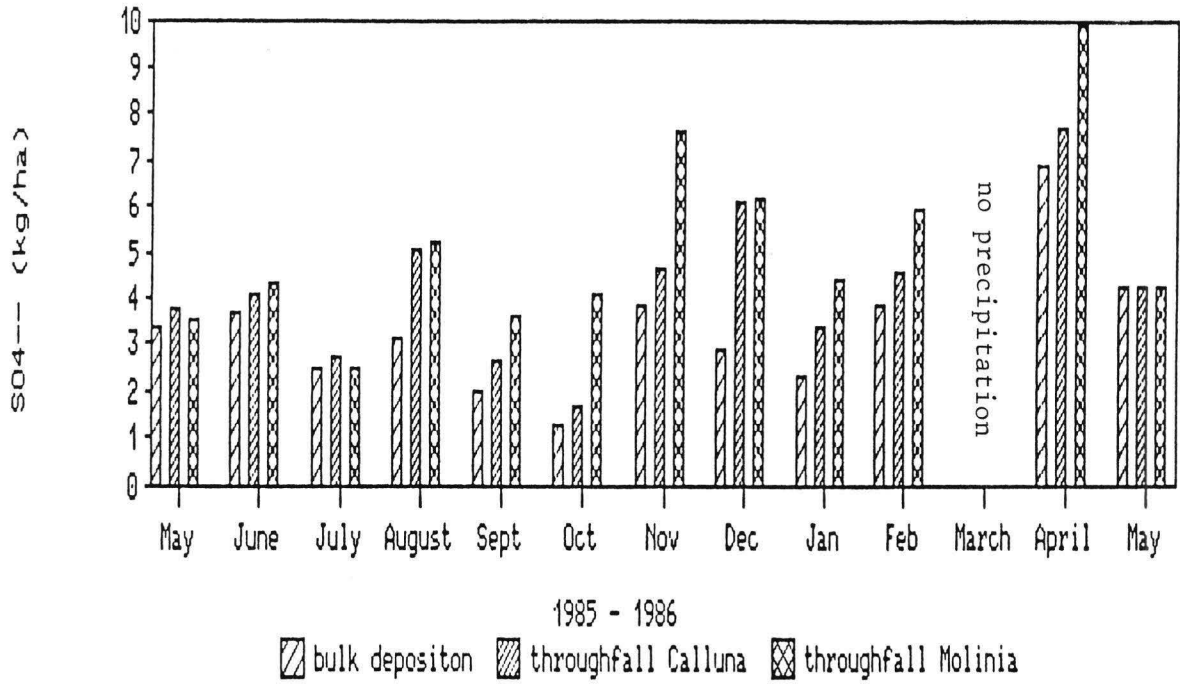


Figure 1. Troughfall measuring apparatus.

amount of SO₄²⁻ deposition (kg/ha)
heathland Uddelerbuurtveld



amount of NH₄⁺ deposition (kg/ha)
heathland Uddelerbuurtveld

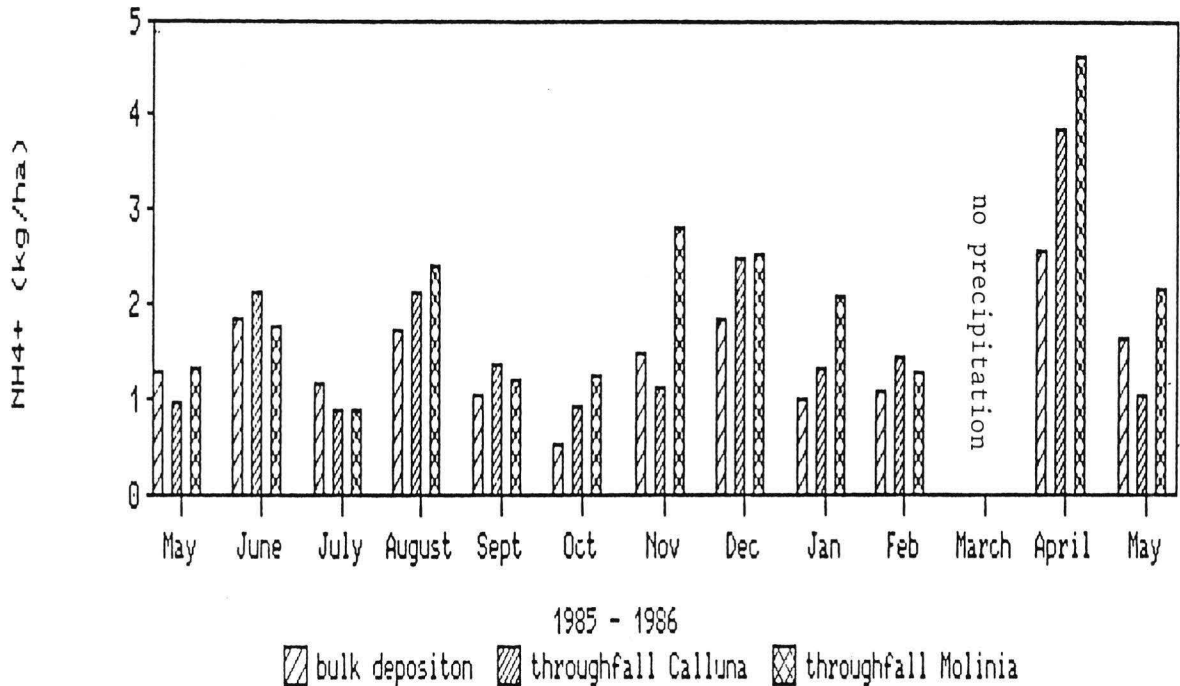


Figure 2. Amount of SO₄²⁻ and NH₄⁺ deposition during May 1985 - May 1986 at the heathland Uddelerbuurtveld.

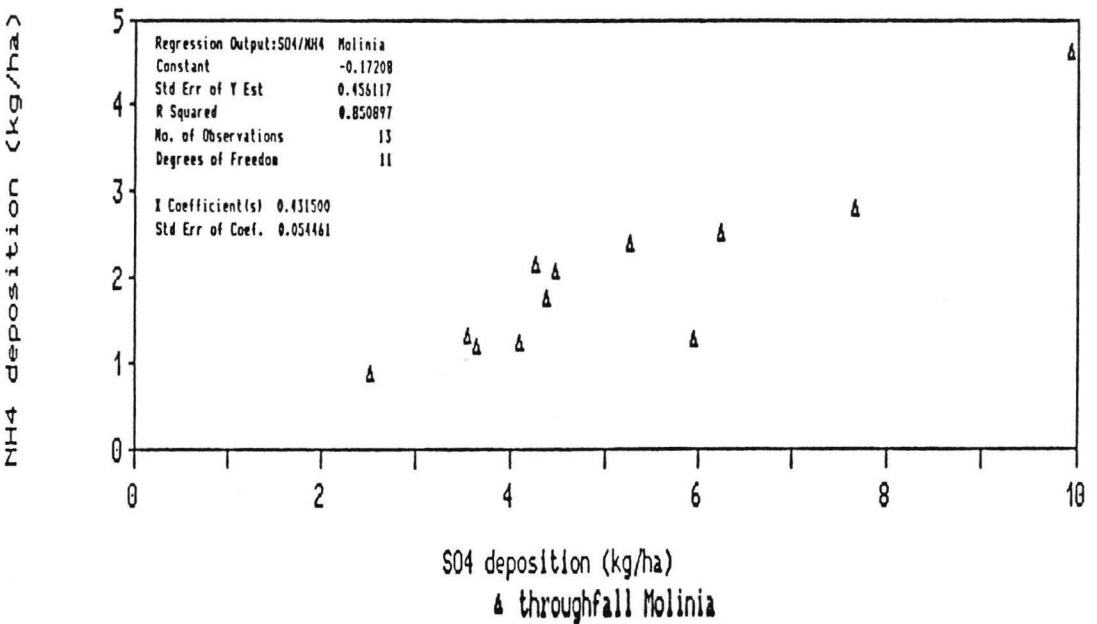
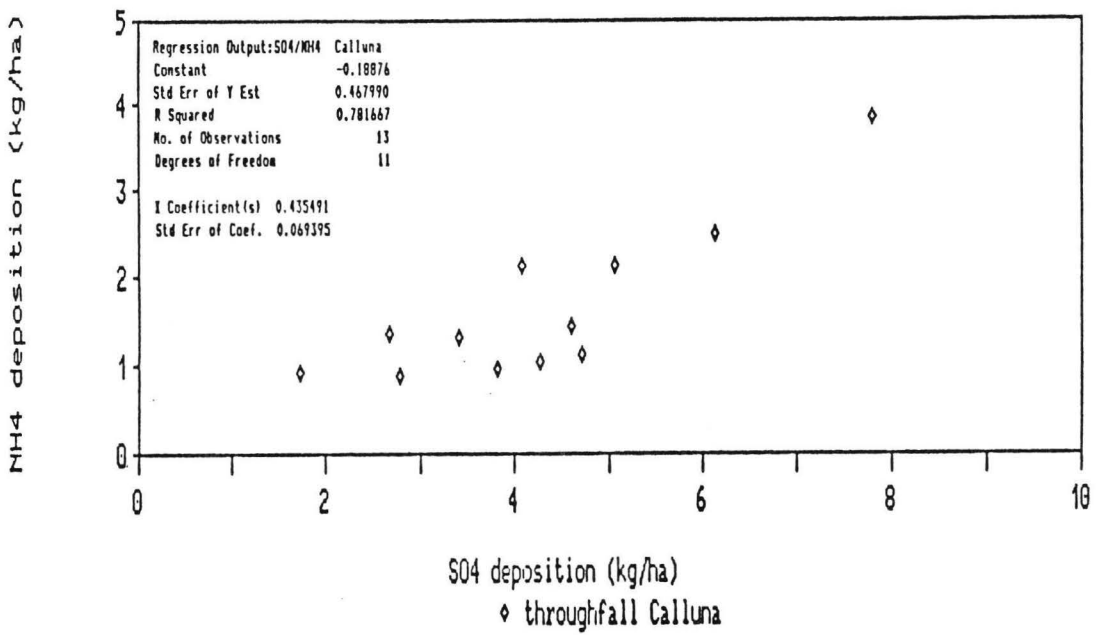
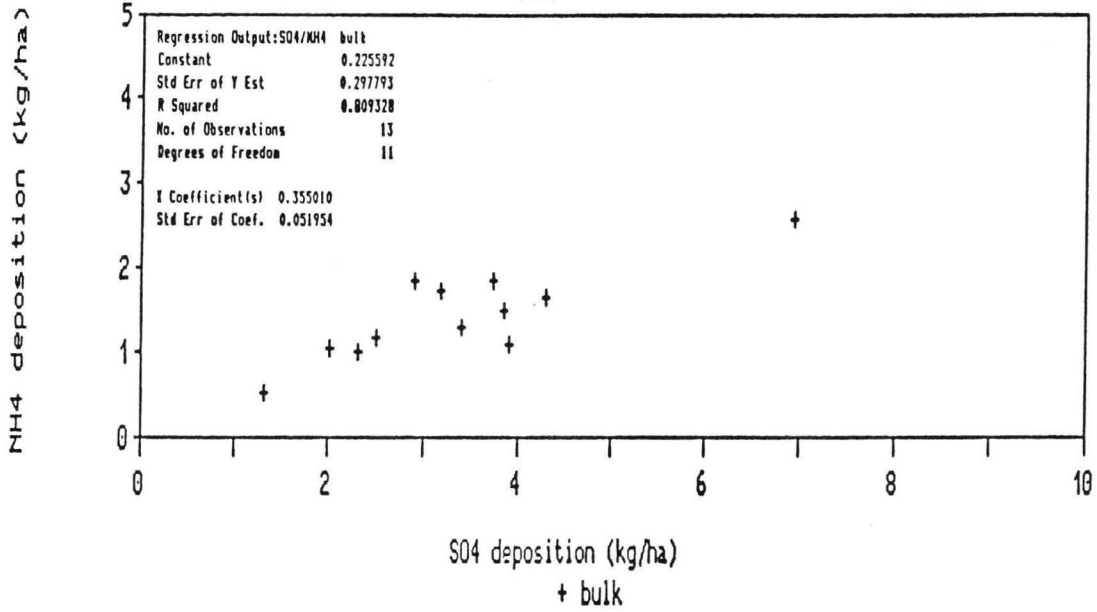
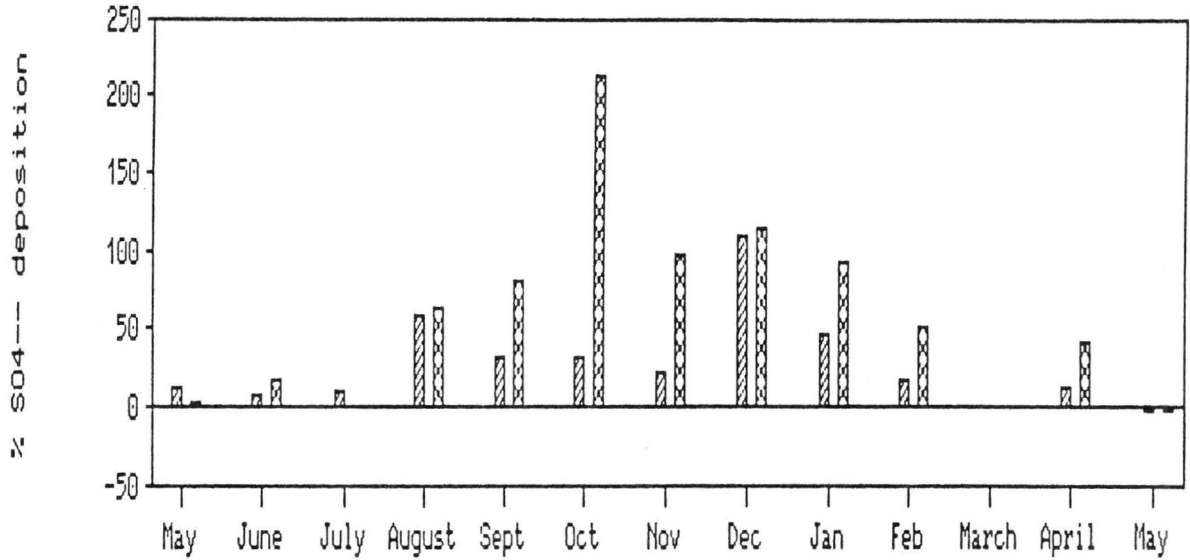


Figure 3. Relation between amount of SO_4^{2-} deposition and NH_4^+ deposition in bulk precipitation, throughfall of Calluna and throughfall of Molinia, resp.

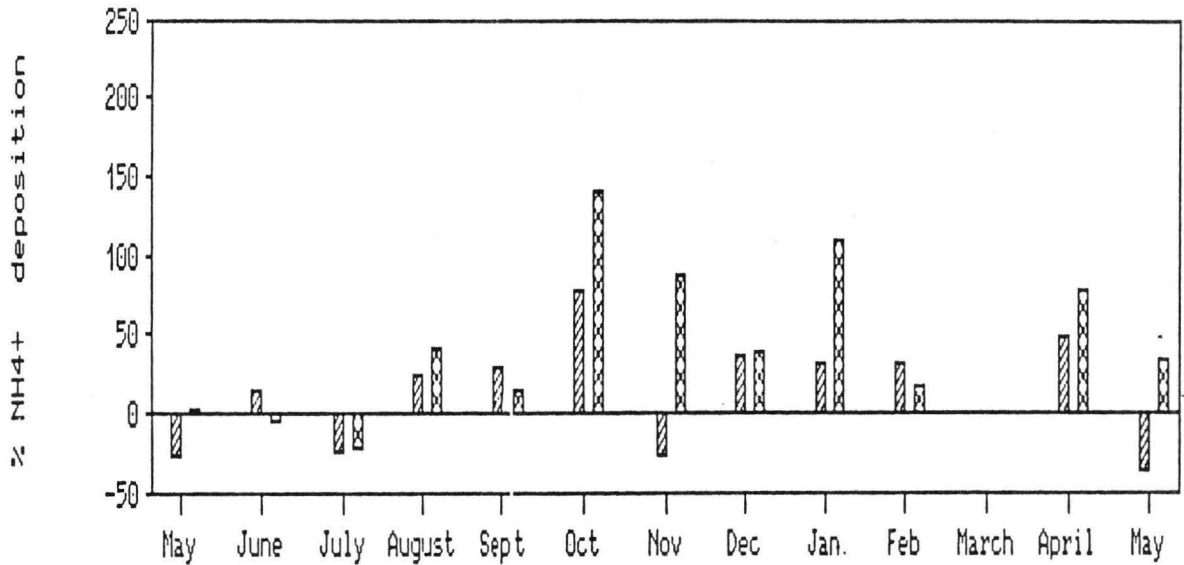
extra SO₄²⁻ deposition (%) relative to the bulk



1985 - 1986

throughfall Calluna throughfall Molinia

extra NH₄⁺ deposition (%) relative to the bulk



1985 - 1986

throughfall Calluna throughfall Molinia

Figure 4. Amount of extra SO₄²⁻ and NH₄⁺ deposition in percentage relative to the bulk.

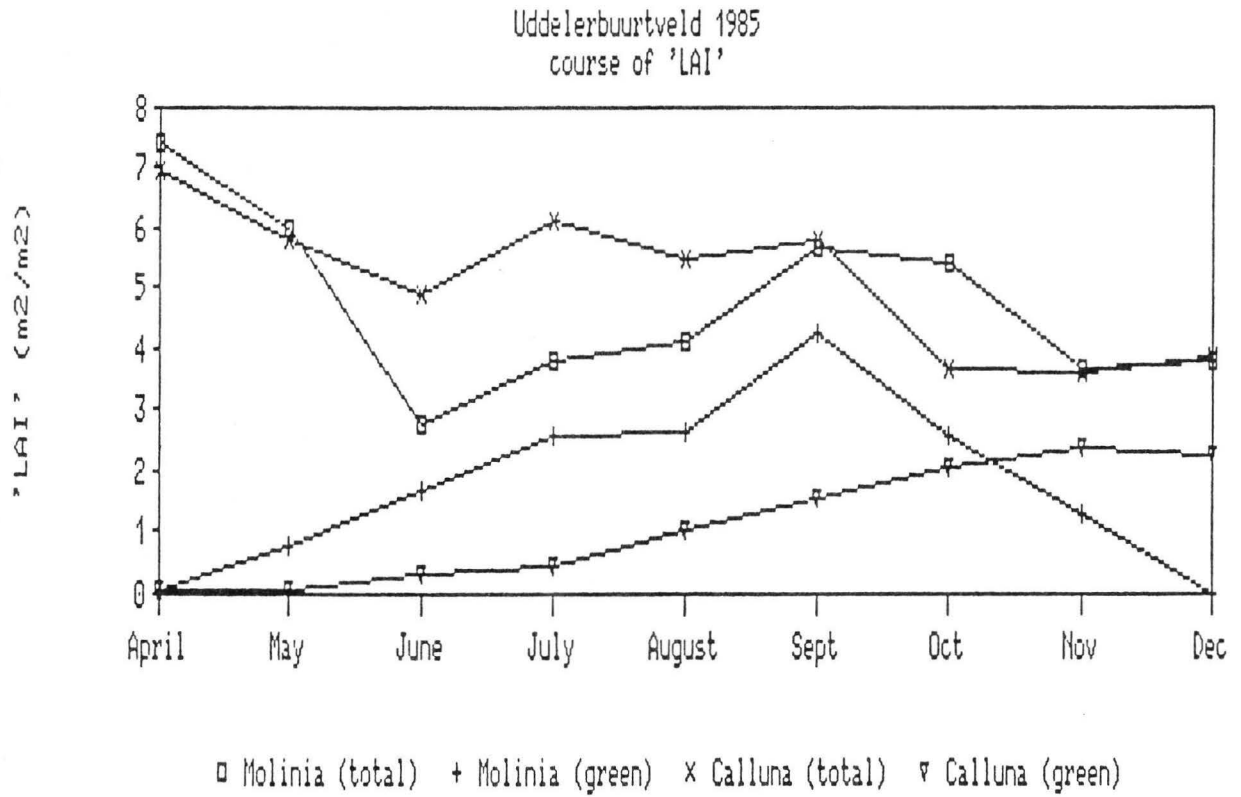


Figure 5. Course of LAI (Leaf Area Index) of Molinia first year leaves (green); Molinia standing dead, inflorescences, first year leaves (total); Calluna first year leaves (green); and Calluna stems, standing dead, inflorescences, green leaves (total) during April - December 1985. Mean age of the vegetation was 6 years at the beginning of the research.

THE DEPOSITION OF AMMONIUM AND NITRATE TO FOREST EDGES

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The deposition of air pollutants is in most cases considered as a vertical flow from the atmosphere boundary layer to the ground. This way of treating the deposition is very practical for modelling atmospheric source receptor relationships especially for grid elements normally used in mesoscale and regional models. However, for small scales or when the purpose is to quantify input for the assessment of effects, it may be necessary to consider inhomogenities in the nature where the horizontal flow may be important for the deposition.

There is a large variety of natural or manmade obstacles for the horizontal flow of the air, which due to impact or other mechanisms may give rise to increased deposition. Hillsides have been pointed out as areas which will receive substantially more pollutants compared to the flat land (Lovett et al., 1982; Scherbatskoy and Bliss, 1983). We have recently shown that forest edges are receptors for considerably larger quantities of pollutants compared to the closed forest (Hasselrot and Grennfelt, 1987). In a half-year study of an edge in a pine forest we showed that the sulphur flow by throughfall was 50% higher at the edge compared to the closed forest. Corresponding figures for nitrate was 190% (Figure 1).

The edge effect was further studied at 8 different forest edges (spruce and pine) in the south Sweden and in this paper we will present the results from an one-year period at three sites with a large variation with respect to pollution environment.

Experimental

The edge effect was studied by means of throughfall sampling. Open funnels were placed in parallel lines at the edge and within the forests. At one site funnels were placed at four parallel lines (10, 25, 50 and 100 m from the edge) in the forest, at the two other sites, funnels were only placed at one line (50 m from the edge). Open precipitation collectors were placed in front of the edges. The precipitation samples were collected twice a month and were mixed to monthly samples prior to analysis. Details on sampling and analysis are given elsewhere (Hasselrot and Grennfelt, 1987).

The three edges presented in this paper are Södra Vram, situated in the agricultural area in the very south of Sweden; Tönnersjö, situated in a forested area on the south-west border of the south Swedish highlands; and Ydrefors situated in the north of the same highlands (Figure 2). Södra Vram is exposed to local as well as to regional pollution, Tönnersjö mainly to regional while Ydrefors is much less exposed. The stands at Södra Vram and Tönnersjö are spruce stands (Picea abies) while that at Ydrefors is a stand with both spruce and pine (Pinus Sylvestris). Site characteristics are given in Table 1.

Sampling was performed from October 1, 1984 - September 30, 1985.

Results

The 1-year deposition of NH_4^+ and NO_3^- by precipitation and by throughfall at the edge and the different lines behind the edge are shown in Figure 3. The deposition at Tönnersjö, where samples were taken at five parallel lines, shows a continuous decrease in throughfall flow from the edge and further into the forest, showing that the edge effect was extended to at least 50 meters into the forest.

The deposition by precipitation varied at the three sites for NO_3^- from 3.4 kg ha^{-1} to 7.7 kg ha^{-1} and for NH_4^+ from 5.2 kg ha^{-1} to 10.0 kg ha^{-1} . At the edge the deposition with throughfall of NH_4^+ is at the agricultural site 3.6 times the deposition by precipitation or 36 kg ha^{-1} . At Tönnersjöheden it is 2.1 times the precipitation and at Ydrefors the throughfall flow at the edge is only 0.73 times the flow by precipitation. The results show at Ydrefors a net loss of NH_4^+ in the canopy. The throughfall flows are even smaller in the closed forest and at Ydrefors and Tönnersjö it is less than the deposition by precipitation (50% and 75% of the precipitation, respectively).

A similar but not so pronounced effect is also observed for nitrate. A smaller throughfall flow than the flow by precipitation is, however, only noticed for NO_3^- at the closed forest line at Ydrefors (79% of the deposition by precipitation).

The variation in canopy uptake is very large throughout the year. At Tönnersjö there is a smaller flow in NH_4^+ by throughfall at the 50 m line during the months February and April-October (Figure 4). At the edge the throughfall flow is smaller than the precipitation during the period May-September. The smallest ratio $\text{NH}_4^+ \text{ edge} / \text{NH}_4^+ \text{ precip}$ was observed in June (0.19) and the largest in March (5.0). The results show that during the summer a large portion of the deposition of NH_4^+ is absorbed in the canopy. The yearly variation in throughfall of nitrate is presented in Figure 5. From the results it is obvious that throughfall measurements is not at all an appropriate method for monitoring of the total deposition of NH_4^+ and NO_3^- .

At the most exposed edge (Södra Vram) where an 1-year throughfall of $36 \text{ kg NH}_4^+\text{-N ha}^{-1}$ was observed, the throughfall flow at the edge was smaller than the deposition by precipitation only in May. The largest ratio for NH_4^+ flow was observed in January when the flow at the edge was 10 times the deposition by precipitation.

The edge effect is a consequence of the horizontal flow of pollutants. It might be caused by precipitation at high wind speeds, the capture of mist and fog droplets containing high concentrations of pollutants or the dry deposition of gaseous and particulate pollutants.

The importance of the precipitation can to some extent be considered by studying the edge effect in precipitation. At Tönnersjö, where throughfall samples were taken at 5 lines, there was a continuous decrease in the flow of water from the edge and into the forest (Figure 6). At the edge, the canopy precipitation was 1090 mm and 100 m into the forest it was 648 mm. The precipitation collected over the open field was 1143 mm. If we assume that the edge behaves in the same way as the closed forest with respect to retention of precipitation in the canopy, precipitation at the edge will be 1585 mm, i.e. substantially more than the precipitation monitored by open funnels.

This edge effect in water inflow will contribute to the total edge effect for the deposition of NH_4^+ and NO_3^- . It will generate a deposition of ammonium with precipitation of 10.9 kg ha^{-1} compared to the monitored wet deposition of $7.9 \text{ kg ha}^{-1} \text{ yr}^{-1}$.

The results clearly show that it is impossible to use throughfall data for the estimate of deposition of nitrogen. But, if we assume that the winter throughfall represents the total deposition and assume that the ratio between deposition by precipitation and the total deposition to forests is the same summer and winter, we can calculate the total input of NH_4^+ and NO_3^- . Such a calculation leads to a total deposition of NH_4^+ -N of $28.0 \text{ kg ha}^{-1} \text{ yr}^{-1}$, compared to the monitored flow by throughfall of $16.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Corresponding figures for NO_3^- -N are $37.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$ and $23.9 \text{ kg ha}^{-1} \text{ yr}^{-1}$. The total nitrogen deposition will then be $66 \text{ kg ha}^{-1} \text{ yr}^{-1}$. This will probably represent a maximum load of nitrogen, since the dry deposition is expected to be less in the summer than the winter. This is due to lower concentrations and lower wind velocities. The air concentrations of $\text{NH}_3/\text{NH}_4^+$ and $\text{HNO}_3/\text{NO}_3^-$ was not monitored at any of the sites,

but at a site with an exposure situation similar to that of Tönersjöheden total ammonium (NH_3 + particle-borne NH_4^+) and total nitrate (HNO_3 + particle-borne NO_3^-) is monitored since March, 1986. Data from the period March - December 1986 indicate that the concentrations of total nitrate and total ammonium are slightly higher in the winter compared to the summer:

$$\frac{\text{NH}_4^+(\text{tot})_{\text{summer}}}{\text{NH}_4^+(\text{tot})_{\text{winter}}} = 0.94 \text{ and}$$

$$\frac{\text{NO}_3^-(\text{tot})_{\text{summer}}}{\text{NO}_3^-(\text{tot})_{\text{winter}}} = 0.57 \text{ (Figure 7).}$$

Of course, the way to estimate depositions by throughfall monitoring will involve a number of other uncertainties, such as deposition of NO_2 through stomata, emissions of NO_x and NH_3 from the plant etc. These uncertainties will, however, not change the overall picture of a substantial increase in deposition at forest edges.

Conclusions

The atmosphere - vegetation exchange of nitrogen compounds is a process involving different species and different mechanisms. The possibility to quantify these fluxes is today very limited. The problem is becoming even more complex if the very strong effects of inhomogenities in the form of hillsides, forest edges etc. should be included. If atmospheric transport deposition models should ever be used in order to estimate ecosystem effects, it is necessary to include the topography induced variations in deposition in the estimates of deposition. Over large forest areas in Europe, hillsides and inhomogenities in vegetation will be more common than homogenous forests in flat land.

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Scherbatskoy, T. and Bliss, M. (1983) Occurrence of acidic rain and cloud water in high elevation ecosystems in the green mountains of Vermont. Proc. of the APCA speciality meeting, "The Meteorology of Acidic Deposition", Hartford CT, Oct. 16-19, 1983.

Hasselrot, B. and Grennfelt, P. (1987) *Water, Air and Soil Pollution*. (In press).

Table 1. Characteristics of three edge sites in the deposition study
October 1984 - September 1985.

Location	Södra Vram	Tönnersjö	Ydrefors
	56°03'N, 13°06'E	56°42'N, 13°06'E	57°49'N, 15°33'E
Height a.s.l. (m)	55	90	200
Forest type	spruce	spruce	spruce and pine
Age (1985) (yrs)	40	87	60
Height (m)	10-15	25-30	12-15
Edge direction	WSW	SW	SSW
Surrounding area	agricult. area cattle farm 1.5 km west of the edge	coniferous forest	coniferous forest
Mean precip (mm)	865 (Bjuv)	1070 (Knäred)	680 (Svinhult)
Exposure charact.			
Regional poll.	high	high	moderate
Local and meso- scale pollution	high	moderate	low

CAPTIONS

- Figure 1. Sulphate and nitrate in throughfall at the edge of a pine forest and four different lines behind the edge (Hasselrot and Grennfelt, 1987a).
- Figure 2. Field sties for the edge studies presented in this paper.
- Figure 3. Throughfall and bulk precipitation of nitrate and ammonium at the field sites Ydrefors, Tönnersjöheden and Södra Vram from the period October 1984 - September 1985. Distances in m from the edge (-25 m is the bulk sampling in front of the edge). Deposition in $\text{kg N ha}^{-1}\text{yr}^{-1}$.
- Figure 4. Monthly variation in bulk precipitation and throughfall of NH_4^+ (g ha^{-1}) at Tönnersjöheden October 1984 - September 1985.
- Figure 5. Monthly variation in bulk precipitation and throughfall of NO_3^- (g ha^{-1}) at Tönnersjöheden October 1984-September 1985.
- Figure 6. The edge effect in precipitation at Tönnersjöheden.
- Figure 7. Air concentrations of total NH_4^+ and total NO_3^- at Vavihill, Skåne March - December 1986.

FIGURE 1.

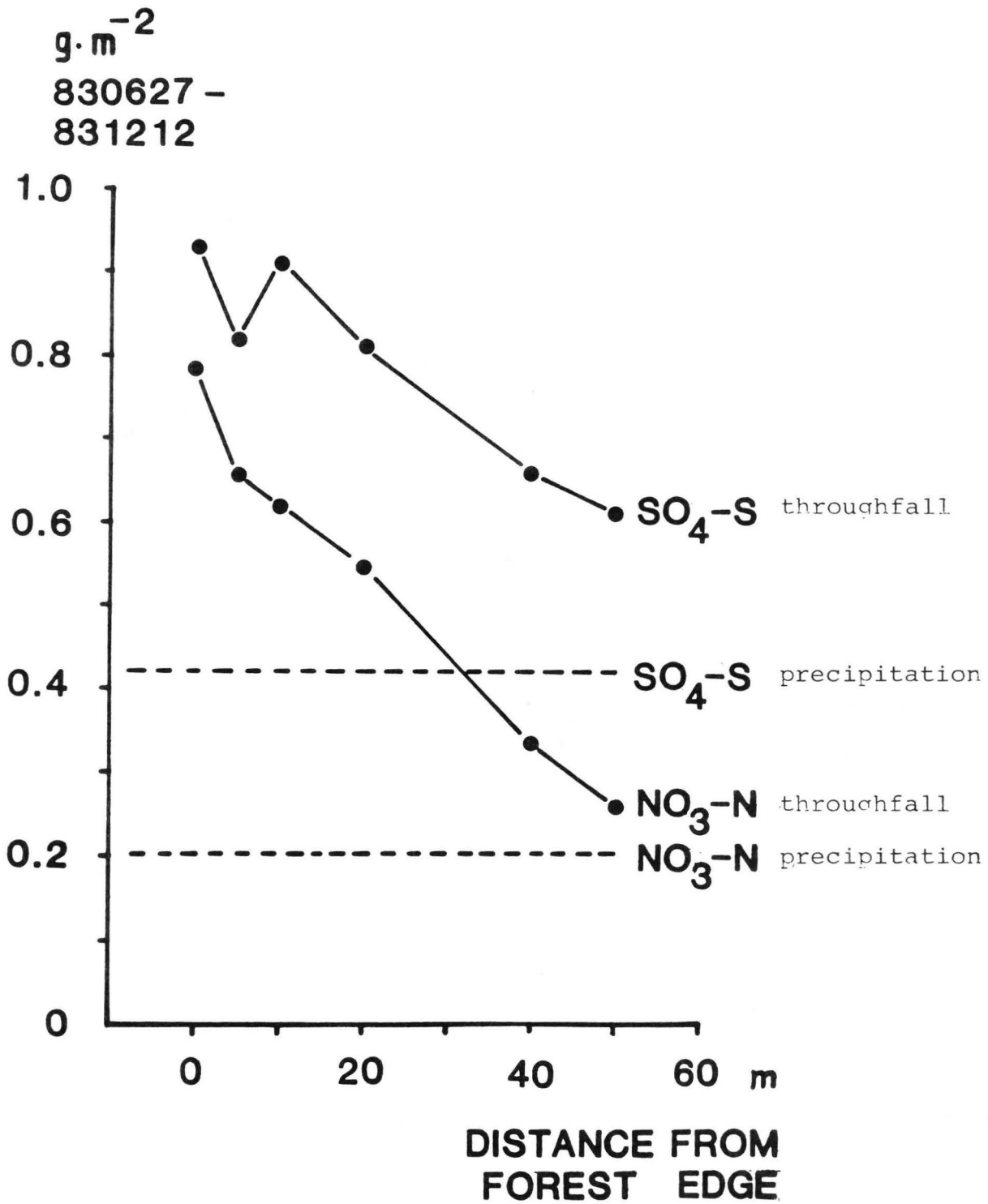
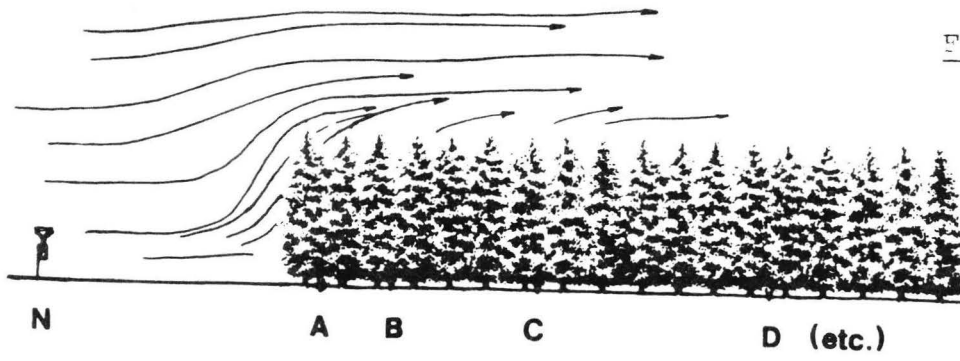
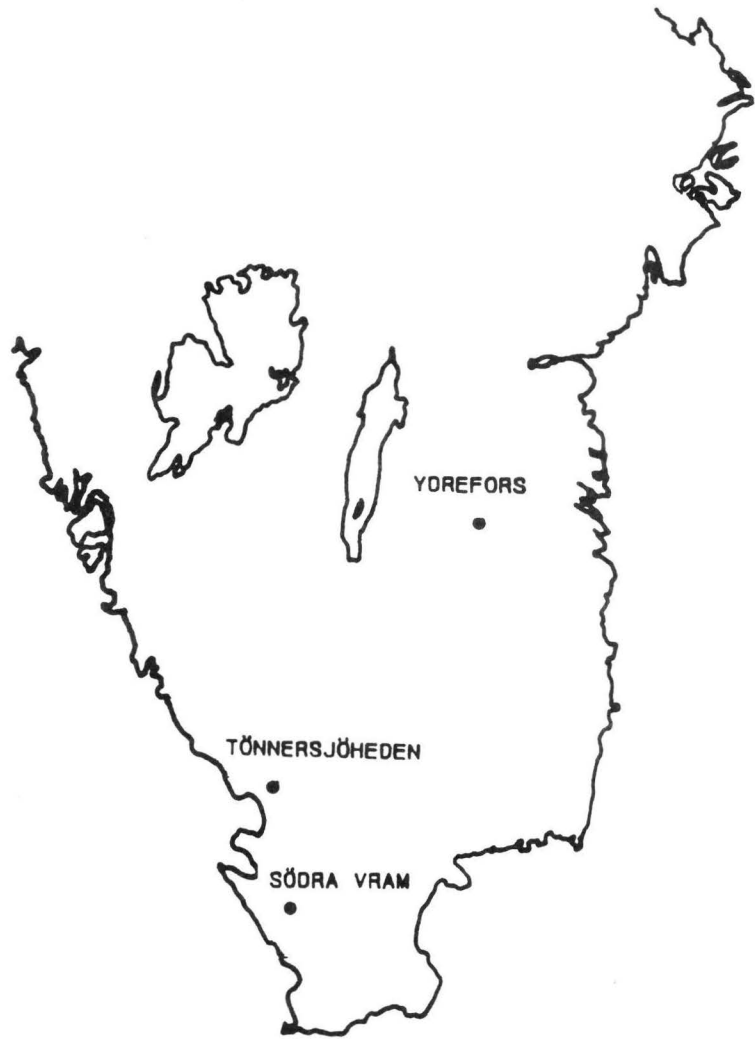
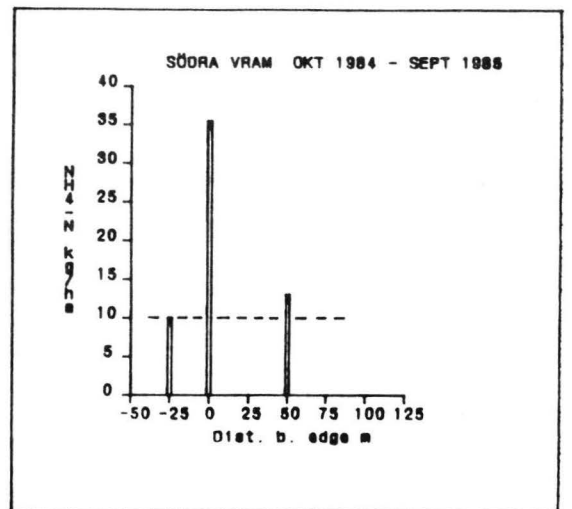
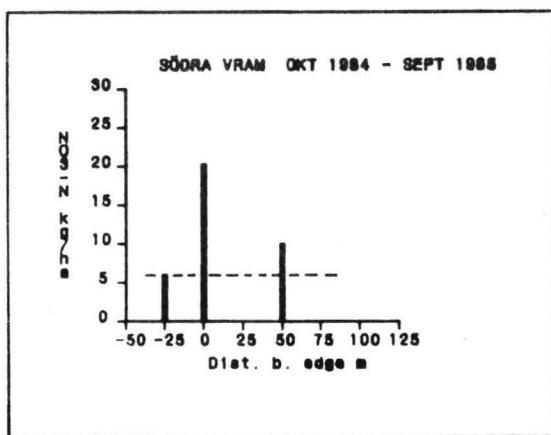
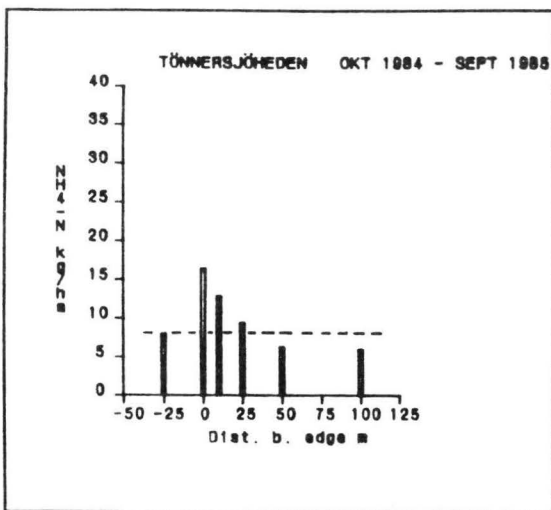
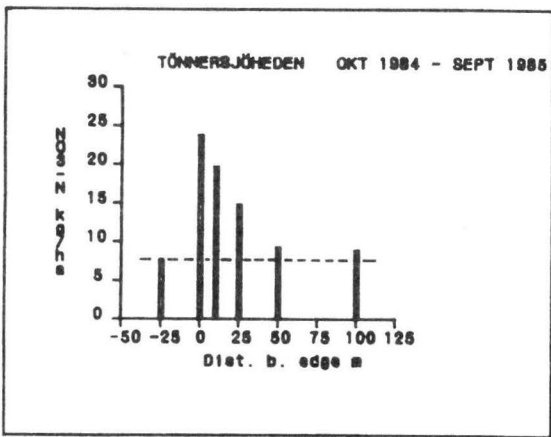
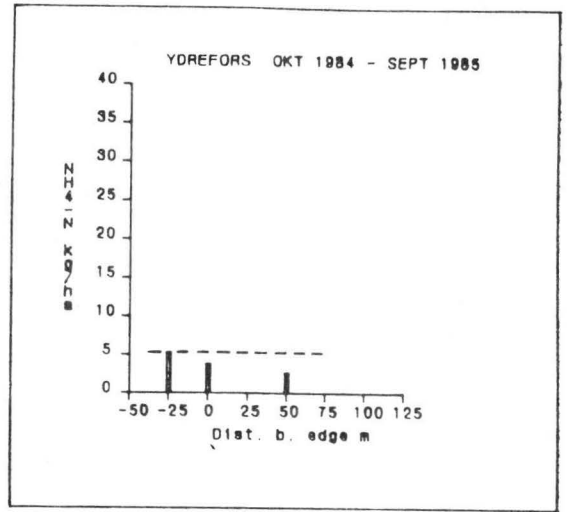
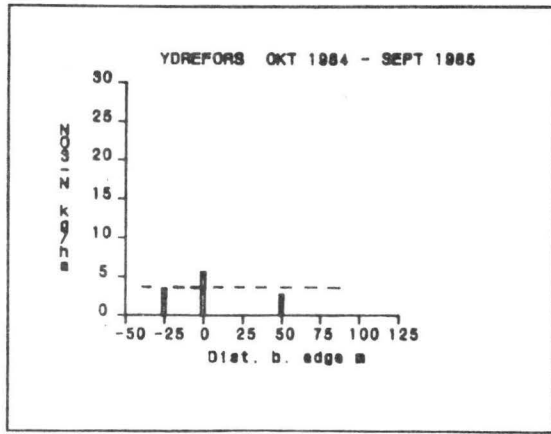
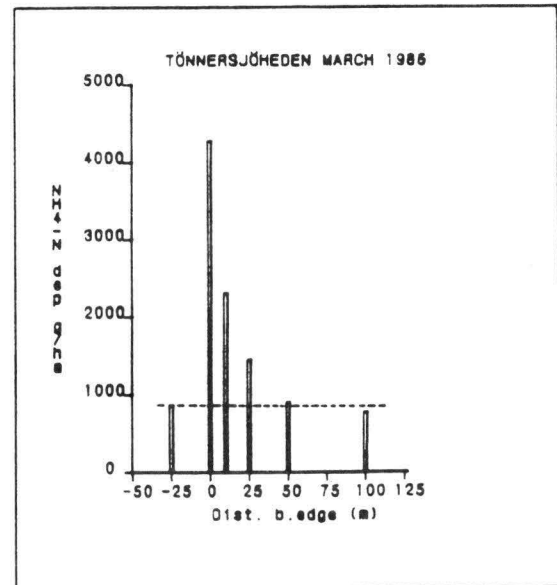
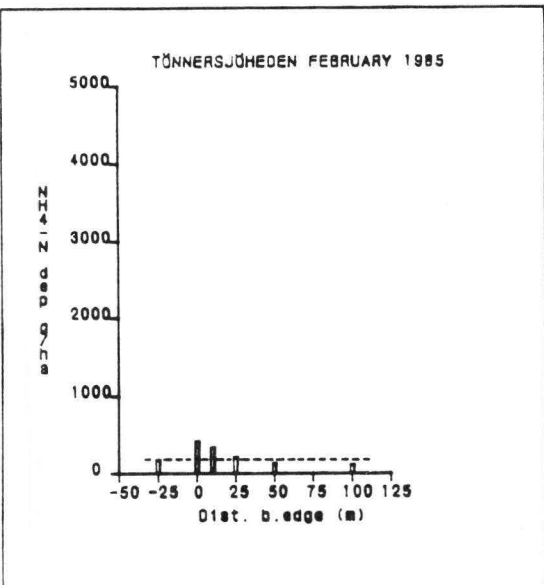
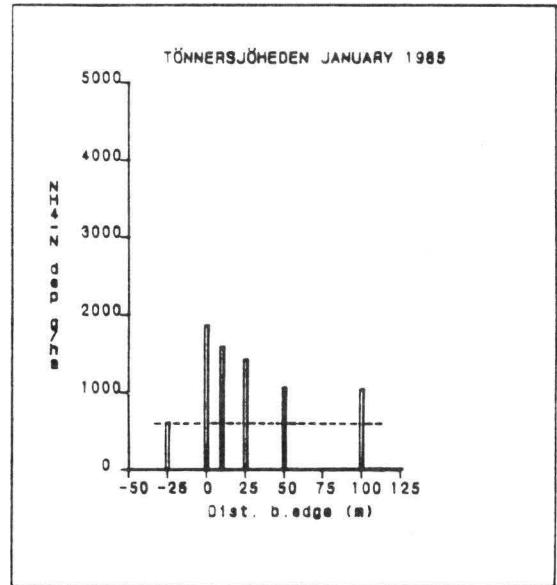
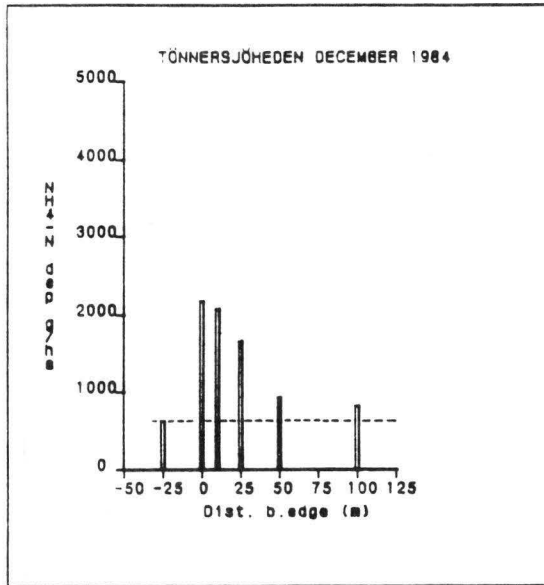
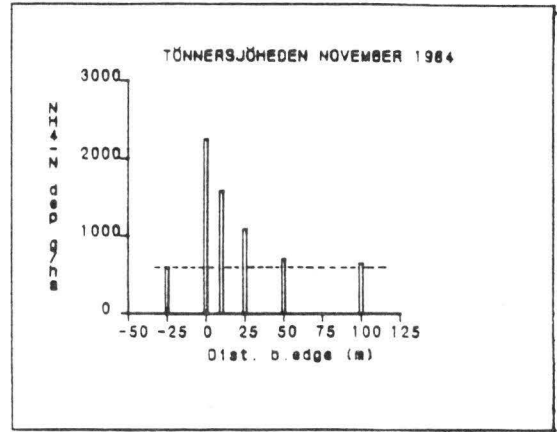
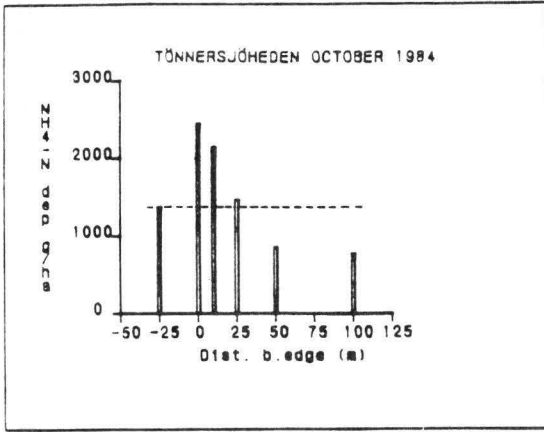
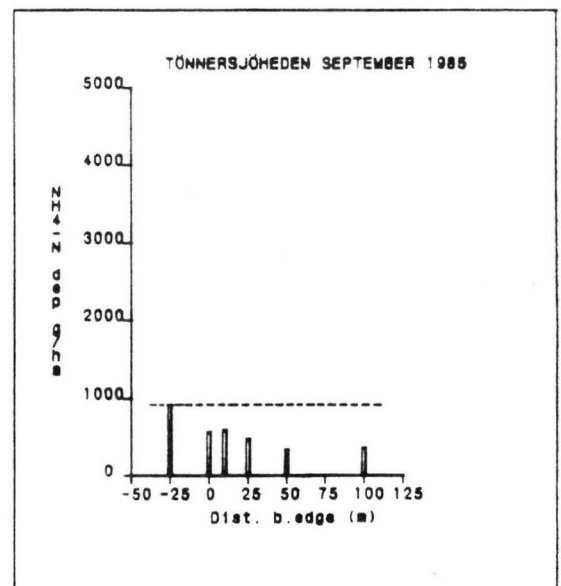
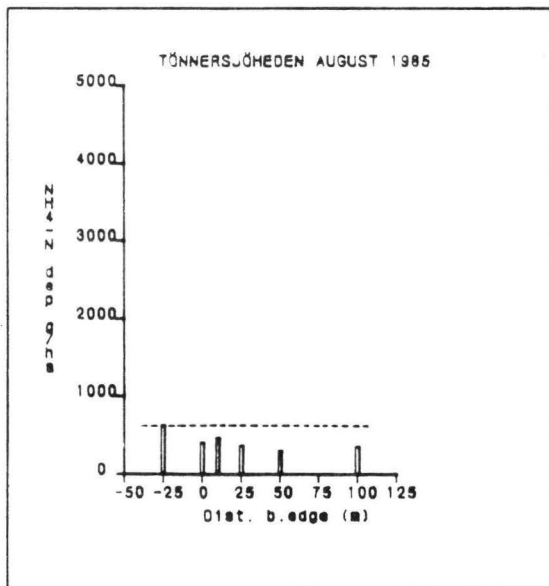
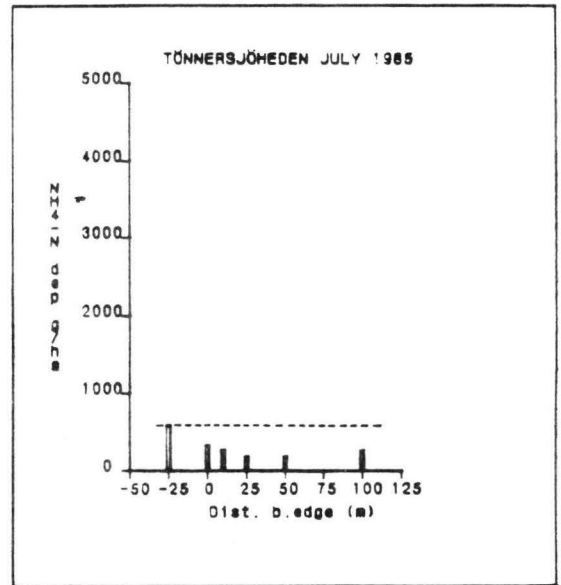
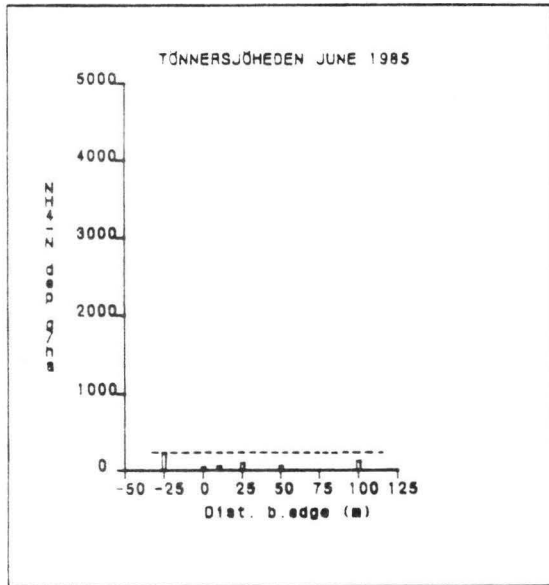
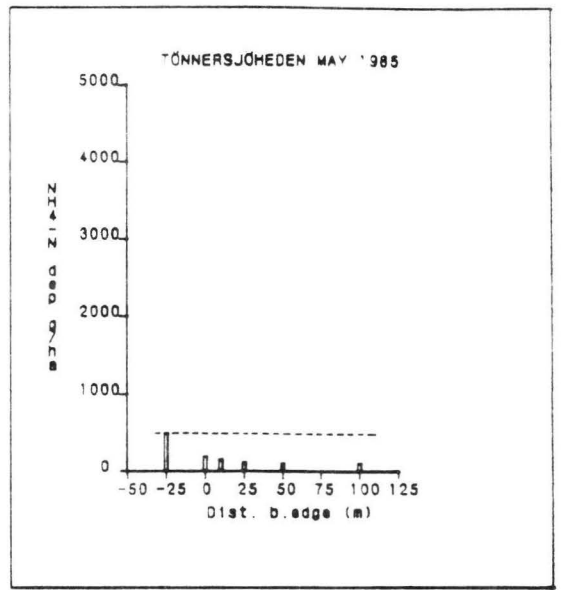
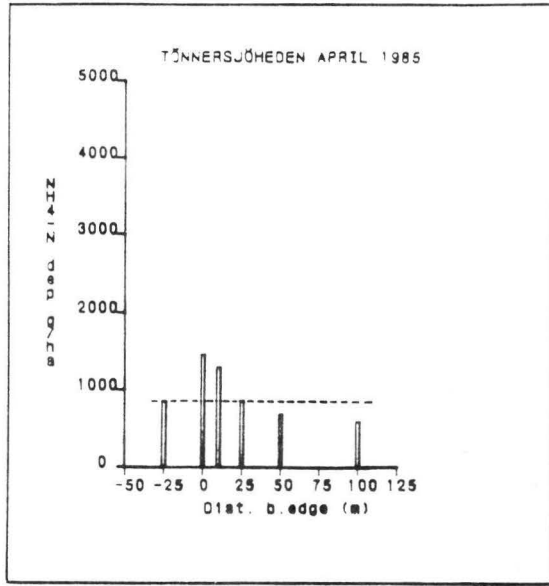


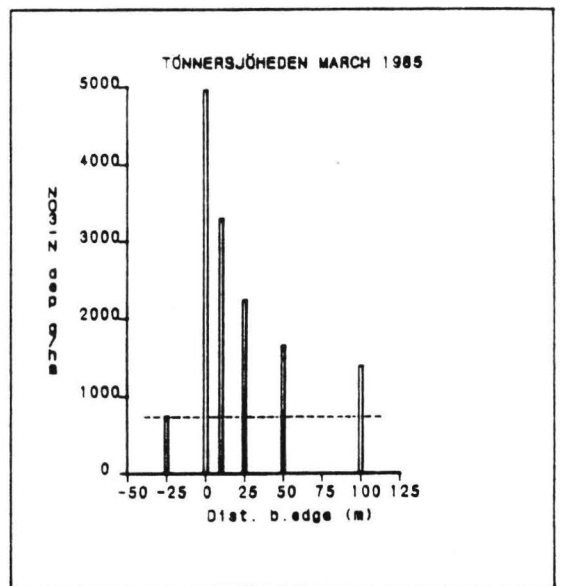
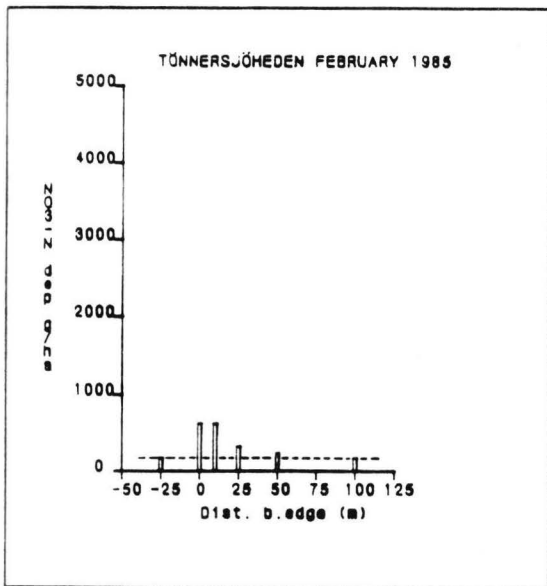
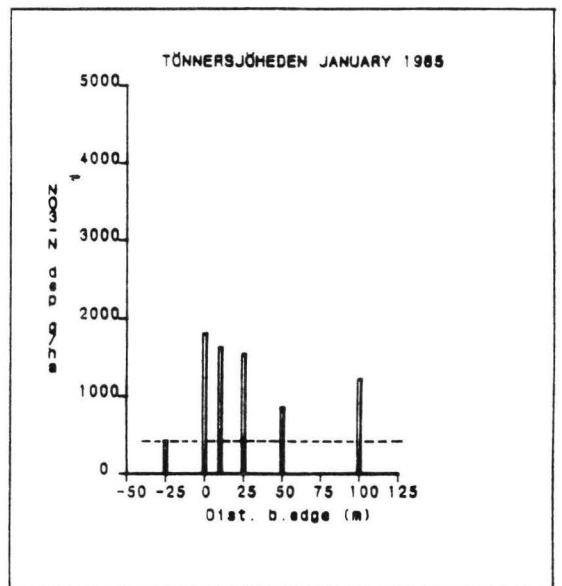
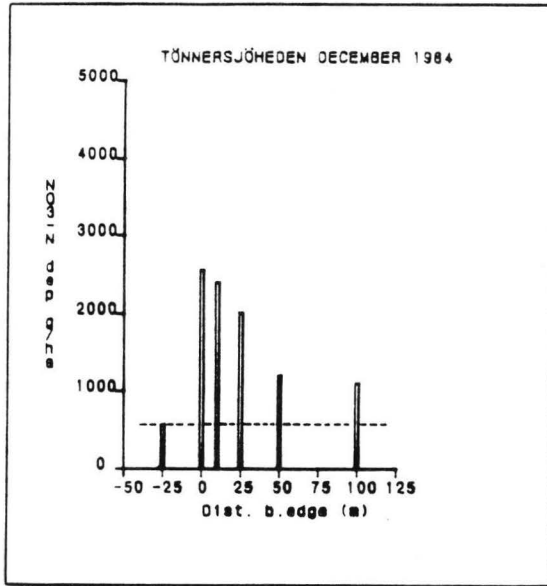
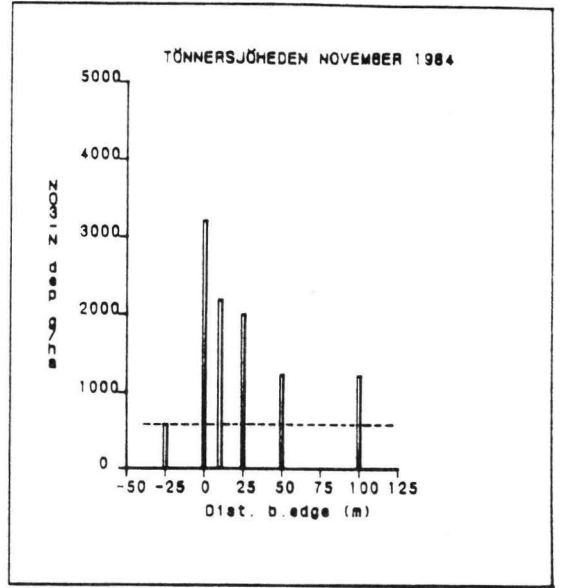
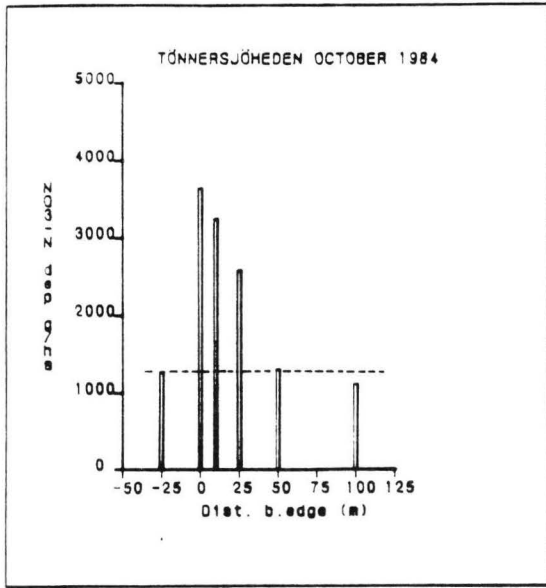
FIGURE 2.











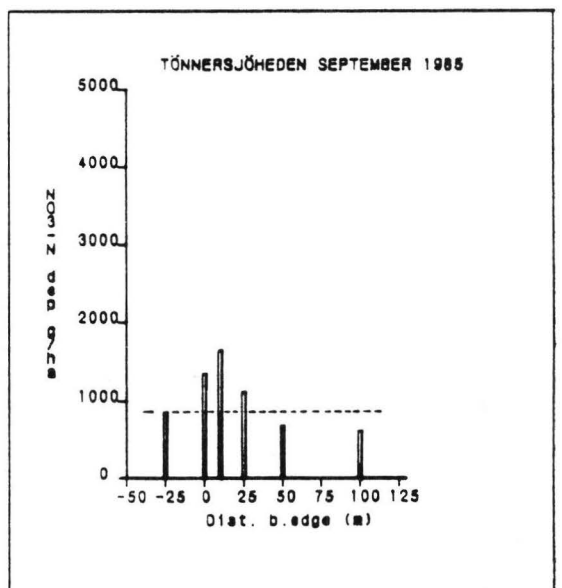
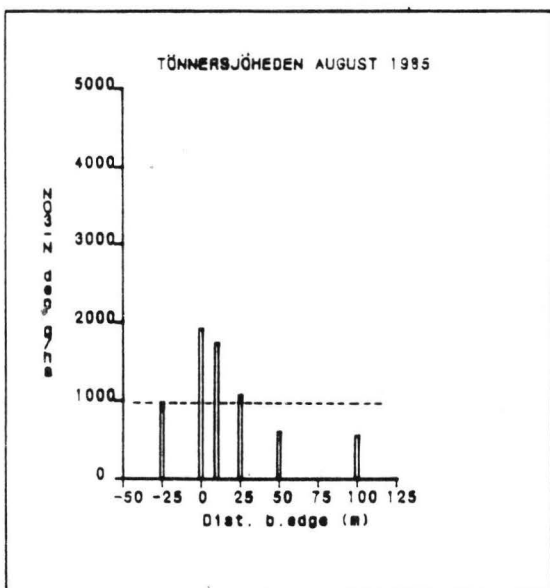
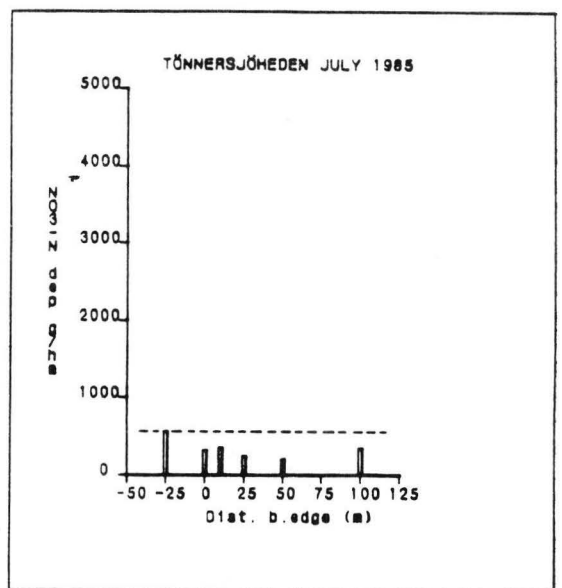
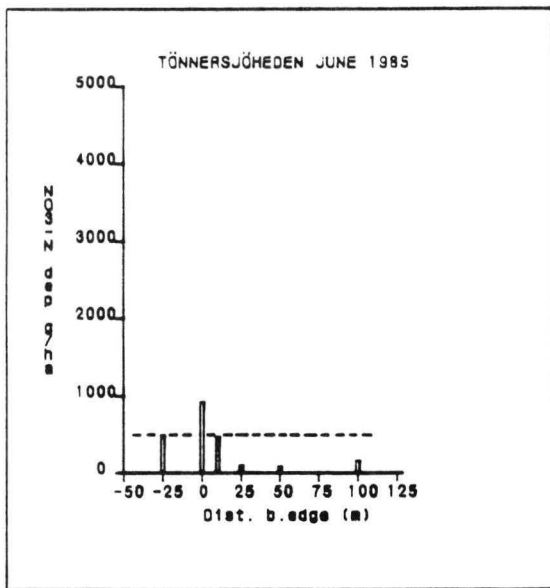
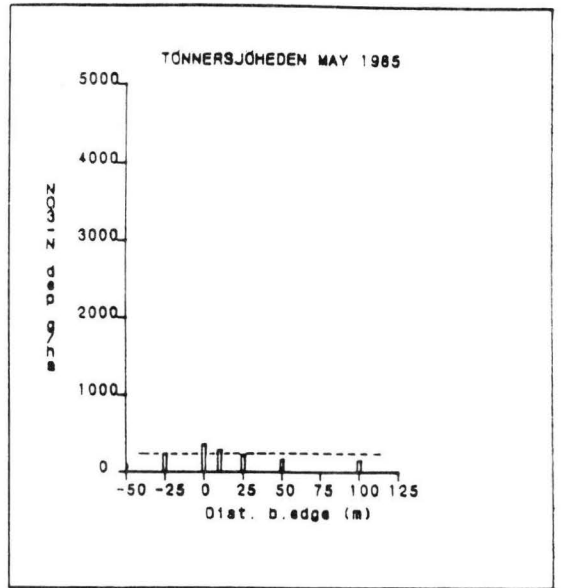
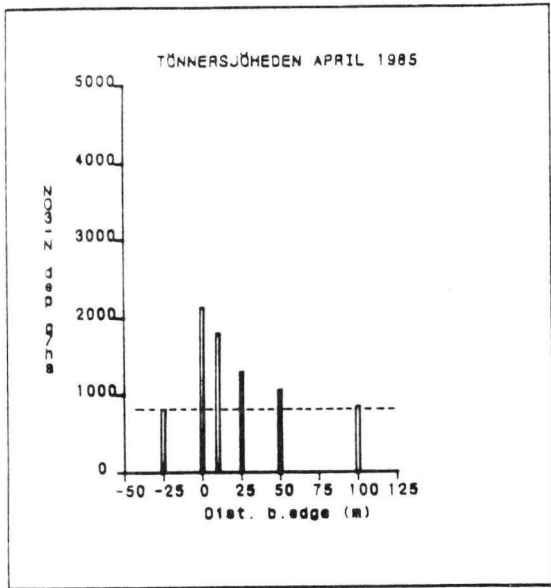
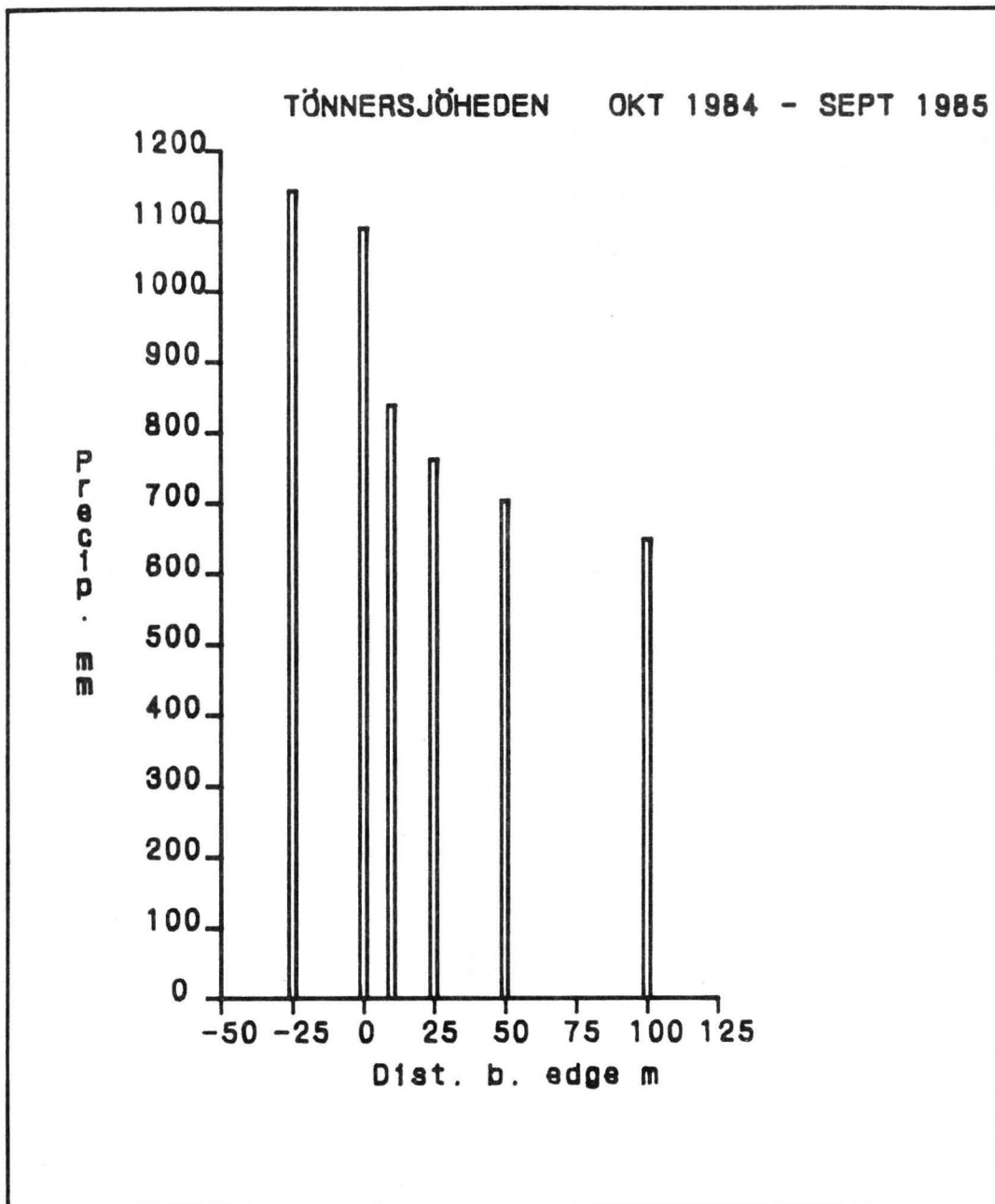
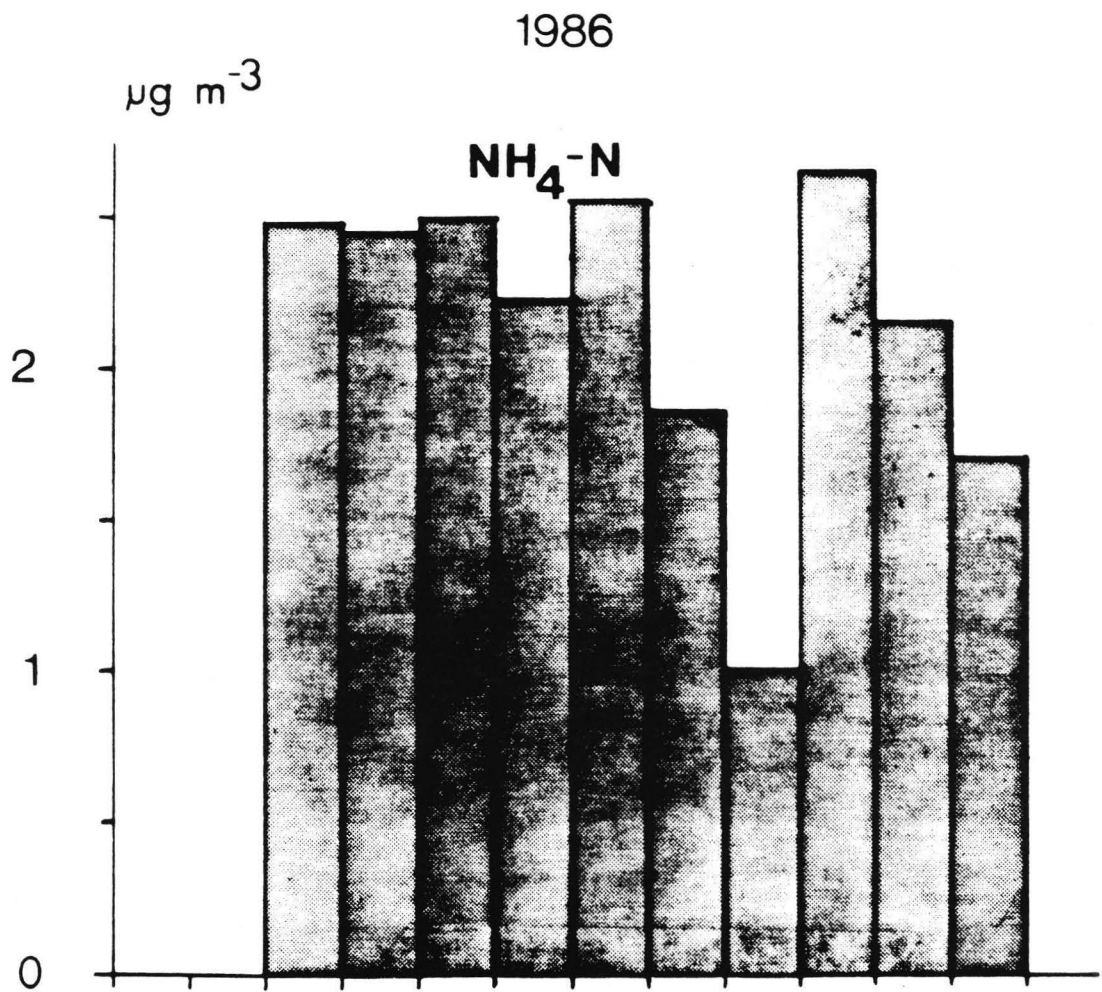
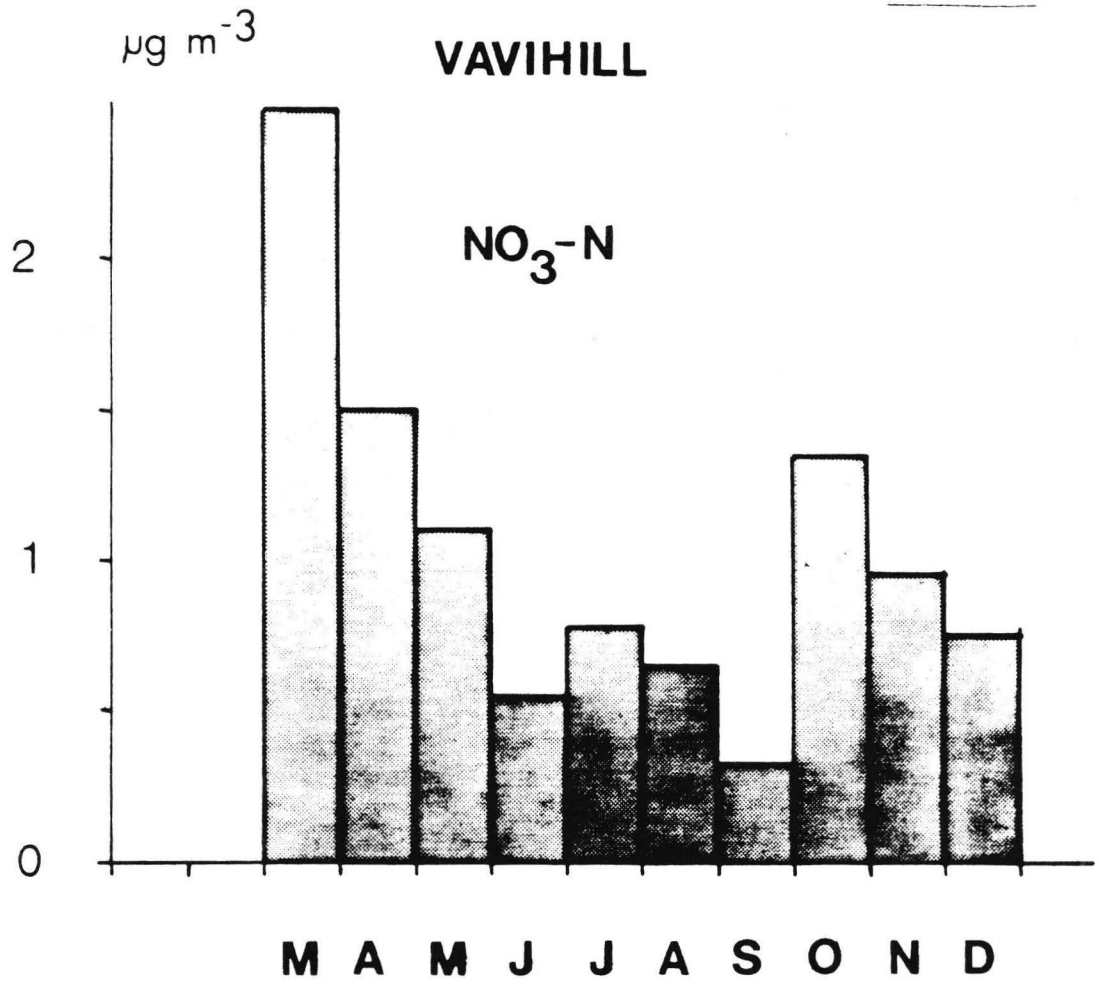


FIGURE 6.





THE INTERACTION OF NH₃ AND SO₂ IN THE PROCESS OF DRY DEPOSITION ON PLANT SURFACES

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SUMMARY.

Based on recent research an interaction between NH₃ and SO₂ in the process of dry deposition on plant surfaces is suggested. To study the importance of this possible interaction, the chemical composition of the dry deposition accumulated on tree-canopies is measured. The chemical composition of this dry deposition is reflected in the first water dripping from tree-canopies at the beginning of rainstorms (initial throughfall).

Although very large amounts of NH₄⁺ and SO₄²⁻ are deposited and a high correlation exists between the NH₄⁺ and SO₄²⁻ concentrations in initial throughfall, the amounts deposited in general and especially in summer are not equivalent. It is supposed that exchange-processes (for example the leaching of HCO₃⁻ in summer) may influence the process of dry deposition of NH₃ and SO₂ on plant surfaces.

1. INTRODUCTION.

An interaction between NH₃ and SO₂ in the process of dry deposition on plant surfaces is suggested because:

- in areas with high densities of manure production extremely high NH₄⁺ and SO₄²⁻ concentrations in throughfall were measured in equivalent quantities (van Breemen et al, 1982).
- small scale windtunnel experiments have shown that a wet surface strongly stimulates the dry deposition of NH₃ and SO₂. In this case NH₃ and SO₂ have a synergistic effect on each others solubility (due to their basic respectively acidic character) through which very large amounts can be deposited in equivalent quantities (Adema, 1986).
- plant surfaces are covered with a waterfilm during fog, dew or rainfall. Even without fog, dew or rainfall, a very thin waterfilm on plantsurfaces may occur (van Hove, 1987).

2. METHODS.

To study the importance of this possible interaction, the chemical composition of the dry deposition accumulated on tree-canopies was measured. Previous research has shown that the chemical composition of this dry deposition is reflected in the first water dripping from tree-canopies at the beginning of rainstorms. The concentrations in this initial throughfall

strongly depend on the duration of the dry period before the sampled rainstorm, which determine the amount of dry deposition accumulated on the tree-canopies (Ivens et al, 1987).

Samples from throughfall were collected from 9 Douglas fir trees near Kootwijk in the Netherlands (fig. 1). The first 275 ml. water dripping from the canopies was collected separately from the remainder. For this 275 ml. throughfall, a rainperiod was necessary with at least 5 mm. precipitation within a couple of hours. During 1 year (October 1985 until October 1986) 16 such rainperiods were sampled.

The sample sites were located close to an intensively used agricultural area with a high density of manure production ("Gelderse Vallei"). In this area high air-concentrations of NH_3 could be expected. Based on measurements done at other locations in the Netherlands (Erisman et al, 1986) the mean NH_3 air-concentrations at the study sites were estimated as 10-15 $\mu\text{g}/\text{m}^3$ in summer and 15-20 $\mu\text{g}/\text{m}^3$ in winter.



fig. 1 : location of the study sites.

RESULTS.

Although a high correlation exists between the NH_4^+ and SO_4^{2-} concentrations in initial throughfall ($r = 0.90$, $n = 122$), the equivalent-ratios of $\text{NH}_4^+/\text{SO}_4^{2-}$ appeared to range from 0,7 to 2,5 (table 1). In only 7 percent of the observations an $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio exactly equal 1,0 was measured. This contradicts the results from other research (van Breemen et al, 1982). It may be concluded that at our study sites the interaction between NH_3 and SO_2 is not the only important process for the dry deposition of these gases.

The $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios in initial throughfall vary with the season. In summer (from May until October) significantly higher ratios were measured. The mean $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio in this period was 1,84 (st.dev. 0,31) and in winter 1,04 (st.dev. 0,18).

	mean	stand. dev.	median	minimum	maximum
summer (n = 61)	1,84	0,31	1,80	1,30	2,50
winter (n = 61)	1,04	0,18	1,10	0,70	1,40

table 1 : $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios (eq./eq.) in initial throughfall.

The seasonal variation in $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios does not result from seasonal variations in air-concentrations of SO_2 (fig. 2). During both summer and winter no significant correlation exists with the mean SO_2 air-concentration in the dry period preceding the rainfall. With equal mean SO_2 air-concentrations in the preceding dry period, in summer significantly higher ratios were measured.

The SO_2 air-concentrations were provided from measurements done at two nearby locations, within the framework of the Dutch National Network for Air Pollution (R.I.V.M., 1985/1986). Unfortunately no NH_3 air-concentrations were available for the study sites.

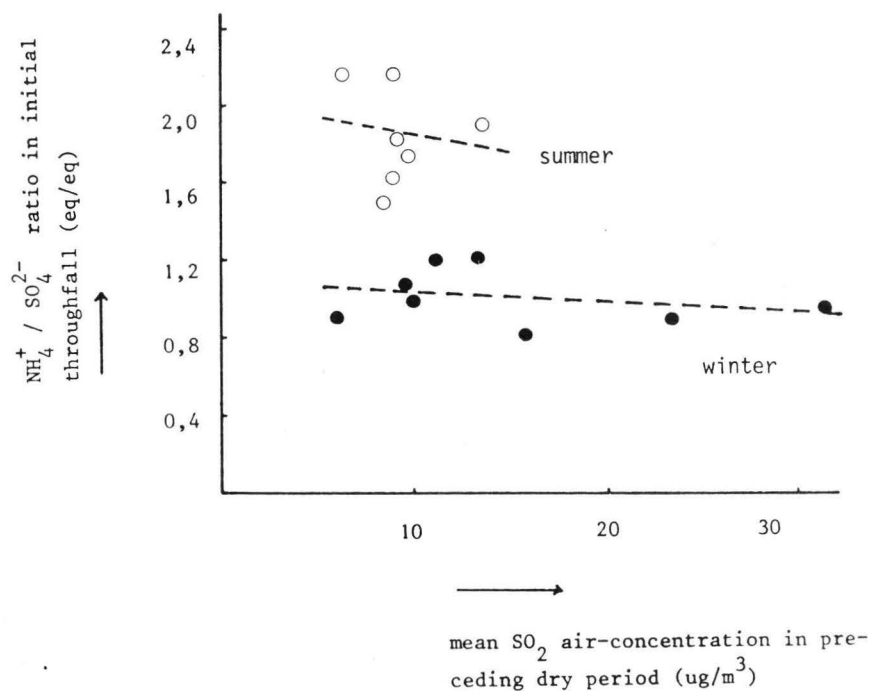


fig. 2 : relation between the mean $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio and the mean SO_2 air-concentrations in the dry period preceding the rainfall.

$$\text{summer : } y = -0,018 \cdot (x) + 2,01 \quad r = -0,15 \text{ (n.s.)}$$

$$\text{winter : } y = -0,005 \cdot (x) + 1,09 \quad r = -0,30 \text{ (n.s.)}$$

Because of the close relation between high $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios and the growing season, it may be assumed that exchange processes between the waterfilm covering the plant surface and the plant surface itself may cause the relative high $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios in summer. In this period the stomatal resistance of the plant surface is relatively low.

To illustrate this assumption the relation between the $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio and the concentration of HCO_3^- in initial throughfall is presented in fig. 3. HCO_3^- is expected to be leached from the canopy in summer (Ulrich, 1983; Draaijers et al, 1986). Significantly higher $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios were measured with higher concentrations of HCO_3^- in initial throughfall. With low HCO_3^- concentrations (occurring in winter), $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios were found to differ only slightly from 1,0.

A possible explanation for this phenomenon is that the leaching of HCO_3^- in summer causes changes in pH and thereby also changes in chemical equilibria in the waterfilm. These changes in chemical equilibria may influence the dry deposition of NH_3 and SO_2 in such a way that no longer equivalent quantities are deposited. In future, more research will be done on this phenomenon and the chemical reactions involved.

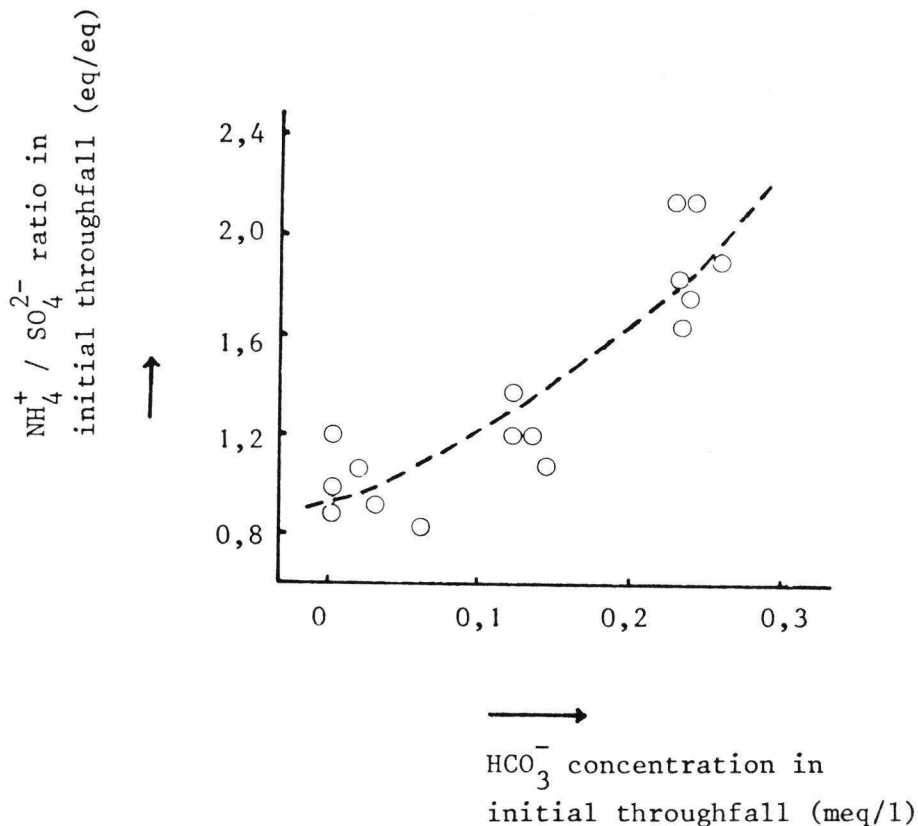


fig. 3 : relation between the mean $\text{NH}_4^+/\text{SO}_4^{2-}$ ratio and the mean HCO_3^- concentration in initial throughfall.

$$y = 0,92 e^{0,05 \cdot (x)} \quad r = 0,88 \quad (p < 0,001)$$

In figure 4 the relation between the NH_4^+ and SO_4^{2-} concentrations in initial throughfall and the duration of the preceding dry period is shown. Because after a rainperiod nearly always some dry deposition remains on the tree-canopy, only rainperiods with substantial amounts of rainfall in the preceding rainperiod were used. In this case it may be expected that relatively small quantities of dry deposition belonging to an earlier dry period were sampled.

A rapid increase of the concentrations occurred within the first 24 hours of the dry period, followed by a relatively slow increase here after. The rate of dry deposition on the canopy tends to decrease with the duration of the dry period. It may be possible that just after a rainperiod, when the dry deposition is washed off (and the vegetation surface is still wet), large amounts of NH_3 and SO_2 are deposited. Since this figure is based on relatively few observations, it must be interpreted with caution. Future research will provide more observations.

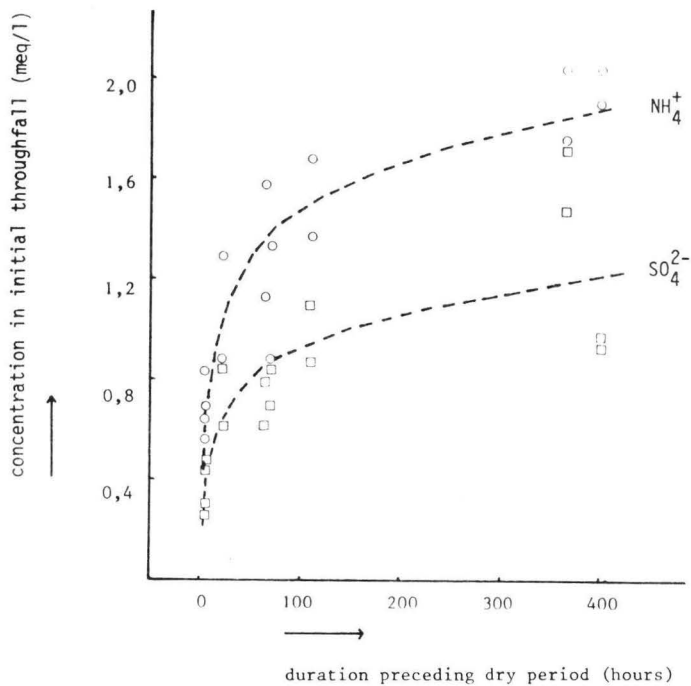


fig. 4 : relation between the NH_4^+ and SO_4^{2-} concentration in initial throughfall and the duration of the dry period preceding the rainfall (preceding rainperiod > 7 mm. rainfall; results from 2 trees from which rainperiods were sampled with very short (< 24 hours) preceding dry periods).

$$\text{NH}_4^+ : y = 0,28 \ln(x) + 0,21 \quad r = 0,91 \quad (p < 0,001)$$

$$\text{SO}_4^{2-} : y = 0,19 \ln(x) + 0,06 \quad r = 0,83 \quad (p < 0,001)$$

In table 2 the highest concentrations of NH_4^+ and SO_4^{2-} measured in initial throughfall are given. These concentrations were measured after a dry period of almost 4 weeks and are more than 31 respectively 39 times larger than the mean concentrations measured in rainwater.

These high concentrations are of the same magnitude as those concentrations used in experiments where Douglas fir trees were exposed to artificial rain and direct tree-damage occurred (van der Eerden et al, 1987). These experiments have shown that when needles are exposed to these concentrations the cuticula of the needles almost entirely vanish. As dilution with rainwater occurs during the washing-off process, it is likely that the concentrations to which needles are exposed (in the waterfilm covering the needle surface) are even higher than those measured in the initial throughfall.

	Highest concentration initial throughfall	Mean concentration rainwater
NH_4^+	5867 ueq/l	187 ueq/l
SO_4^{2-}	5269 ueq/l	134 ueq/l

table 2 : measured highest concentrations in initial throughfall and mean concentrations in rainwater.

Although the mean duration of the preceding dry period was longer in summer, the mean concentrations of NH_4^+ and SO_4^{2-} in initial throughfall were significantly higher in winter (table 3). This may be due to:

- the relatively high air-concentrations of NH_3 and SO_2 in winter
- the persistence for some days or even weeks together of a waterfilm on the vegetation surface during winter (due to a relatively low evaporation in this period)
- the relatively large influx of fogdroplets containing $(\text{NH}_4)_2\text{SO}_4$ aerosols during winter.

	summer	winter
NH_4^+	1960 ueq/l	2860 ueq/l
SO_4^{2-}	1030 ueq/l	2670 ueq/l
duration preceding dry period	202 hours	188 hours

table 3 : mean NH_4^+ and SO_4^{2-} concentrations in initial throughfall and mean duration of preceding dry period.

In table 4 the mean NH_4^+ and SO_4^{2-} throughfall fluxes measured directly under the canopy of the Douglas fir trees are presented. The throughfall fluxes are more than a factor 2 larger than mean values for several Dutch forests mentioned in literature (van Breemen et al, 1982; Verstraten et al, 1983).

This means that processes like soil-acidification and eutrophication at the study sites potentially will be even stronger than at other locations in the Netherlands. Indeed very low soil pH values were measured. The mean pH from the parent material at a depth of 60-100 cm. was 3,2 (minimum value measured was 2,9).

The wet deposition contributes only 10 percent of the total deposition on the forest floor.

	Throughfallfluxes beneath the canopy of Douglas fir trees	Wet depositionfluxes
NH_4^+	9520 eq/ha/year	1013 eq/ha/year
SO_4^{2-}	6520 eq/ha/year	754 eq/ha/year
N-(NH_4^+)	133,4 kg/ha/year	14,2 kg/ha/year
S-(SO_4^{2-})	104,7 kg/ha/year	12,1 kg/ha/year

table 4 : mean throughfall fluxes beneath the canopy of the 9 Douglas fir trees and the mean wet deposition fluxes.

CONCLUSIONS.

Although very large amounts are deposited and a high correlation exists between the NH_4^+ and SO_4^{2-} concentrations in initial throughfall, the amounts deposited in general and especially in summer are not equivalent. The interaction between NH_3 and SO_2 is not the only important process for the dry deposition of these gases on plant surfaces.

It may be expected that exchange-processes between the waterfilm covering the plant surface and the plant surface itself (for example the leaching of HCO_3^- in summer) may influence the pH of the waterfilm and so the dry deposition of NH_3 and SO_2 .

It will be necessary to do more research on the chemical equilibria in waterfilms covering plant surfaces, especially on how these equilibria are influenced by interactions with the plant surface.

The rate of dry deposition of NH_3 and SO_2 tends to decrease with the duration of the dry period. Just after a rainperiod, when the dry deposition is washed off (and the canopy is still wet), relatively large amounts are deposited. More research has to be done to confirm the first results.

The needles of the Douglas fir trees at the study sites are exposed to extremely high concentrations of NH_4^+ and SO_4^{2-} . This may result in an almost entirely vanishing of the cuticula.

The throughfall fluxes of NH_4^+ and SO_4^{2-} under the canopy of the Douglas fir trees at the study sites are extremely high. This may lead to extreme soil-acidification and eutrophication.

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MODEL INVESTIGATIONS OF ATMOSPHERIC AMMONIA SCAVENGING

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ABSTRACT

At ambient atmospheric conditions, ammonia is highly soluble in water and can strongly influence the solubility of other gases and the net acidity of precipitation. In this study, a one-dimensional reactive storm model was used to calculate vertical concentration profiles of atmospheric ammonia and to examine the behavior of these concentrations during precipitation events. The model was initially used to generate clear-air profiles that were found to be consistent with those reported in the literature. A simple, convective storm was then applied to these initial profiles to determine the response of the gaseous ammonia concentrations to the precipitation event. The vertical ammonia concentrations were found to be significantly depleted by the storm event, with the maximum depletion occurring in the cloud layer. This alteration of the ammonia concentration profiles during the storm event can have potentially significant effects in calculated reaction rates and in the upward flux of ammonia to the stratosphere. Several different storm conditions were tested, and all cases displayed the same characteristic depleted profiles. The chemistry was kept as simple as possible to ease interpretation of the results. The calculations were performed for gaseous and aqueous ammonia only to assess the usefulness of this method for determining the depletion of highly soluble atmospheric gases and to specify the minimum amount of gaseous ammonia depletion occurring during a precipitation event.

INTRODUCTION

Ammonia (NH_3) is emitted primarily from natural surface sources and is known to participate in a number of important tropospheric reactions. It is well-known, for example, that gaseous NH_3 interacts readily with atmospheric acids to form particulate salts such as ammonium sulfate and ammonium nitrate. Ammonia gas and ammonium ion are important determinants of cloud and rain chemistry as well. Ammonia is highly soluble in water and is readily scavenged by storms. Its neutralizing effect often has a strong influence on the solubility of other gases and on the net acidity of precipitation. Moreover, the alkaline nature of NH_3 can have a profound influence on the chemical reactivity of other chemical species.

In a recent paper [Luecken and Hales, 1986 (hereafter cited as "LH")], we investigated the effect of precipitation on the vertical profiles of atmospheric NH_3 with the use of the PLUVIUS reactive scavenging model (Hales, 1982). From this study we identified two major conclusions in the context of our understanding of atmospheric NH_3 and its interaction with precipitating systems. The first of these was the strong model-based evidence that vertical profiles of gaseous NH_3 are distorted radically by storms and that any scavenging analysis based on the presumption of uniform vertical distributions is likely to be in error. Depletion of atmospheric NH_3 by precipitation may have serious implications for the prediction of any atmospheric chemistry feature that is directly or indirectly affected by NH_3 concentrations, such as the pH of any cloud that forms in the depleted layer. In addition, upward fluxes of NH_3 to the stratosphere are impeded strongly by the scavenging action of the storm. The distortion of the NH_3 profiles also has strong implications in the context of sampling strategy. Surface NH_3 samplers, for example,

should be used only with extreme caution to estimate concentrations aloft, especially in air masses that have recently experienced precipitation events. The second important implication of these model simulations is the prediction that precipitation scavenging is extremely effective in removing atmospheric NH_3 and thus in limiting its upward transport to the stratosphere.

The LH study also provided a review of recent experimental and theoretical studies of atmospheric NH_3 concentrations, particularly the vertical profiles of these concentrations, as a basis for establishing reasonable initial conditions for the modeling simulations. The major conclusions of this review are briefly summarized here. Past NH_3 -concentration measurements, which have been obtained mainly under fair weather conditions, indicate relatively smooth horizontal distributions and vertical profiles that decrease with height, reaching relatively constant values at 1.5 to 3 km (Georgii and Muller, 1974; Georgii, 1978; Levine et al., 1980; Alkezweeny et al., 1986). A few of the vertical profiles measured in some recent investigations, however, show an increase in concentration above cloud base (Alkezweeny et al., 1986). Erisman et al. (1986) have reported NH_3 surface and profile measurements in the Netherlands. These results probably represent an upper limit, since the Netherlands has the highest emissions density of NH_3 in Europe.

The few available theoretically derived NH_3 profiles also show a decrease with increasing altitude (Stedman et al., 1975; McConnell, 1973). The profile derived by McConnell (1973) assumed a ground-level NH_3 mixing ratio of 6 ppbv and assumed that NH_3 exists in the gas phase under dry conditions and is destroyed in the atmosphere by OH radicals. In the LH study, the reactive storm model was applied under clear-air conditions to simulate a dry atmospheric NH_3 profile, using conditions similar to those applied by McConnell, but with

a smaller surface mixing ratio of 0.6 ppbv. The theoretical and experimental profiles from these earlier studies are summarized in Fig. 1.

As pointed out in LH, when the various profiles are compared, there are large differences in the magnitudes. These differences are not surprising since the experimental results were obtained at a number of geographic locations during different months of the year and the theoretical calculations ignore the effects of clouds and precipitation, variable surface emission densities, dry deposition, and reactions with acid aerosols.

On the experimental side, the data may be in error because NH_3 has a strong propensity to participate in aerosol-formation reactions and has a strong affinity for water. Some phase-equilibrium studies have been conducted regarding NH_3 's reactions with acids to form aerosol salts such as ammonium sulfate and ammonium nitrate (e.g., Tang, 1980; Bassett and Seinfeld, 1983; Hildemann et al., 1984). Although these theoretical analyses have indicated reasonable agreement with experimental measurements, aerosol formation and decay processes add significant complications to acquisition of routine field data because ancillary measurements of species other than NH_3 gas are necessary for strict interpretation of the results. During recent years a number of more comprehensive measurements, involving diffusional denuder systems and other devices, have provided valuable insights for improved measurement and interpretation (e.g., Ferm, 1979; Slanina et al., 1981). These composite measurements, however, have been mainly surface-based and, thus, have been of limited use in assessing vertical profile behavior. In addition to problems associated with aerosol formation, NH_3 high solubility in water leads directly to the question of partitioning between aqueous and gaseous phases under moist conditions, and it severely complicates associated air-sampling procedures. Thus,

accurately characterizing the behavior of the ambient aerosol under actual atmospheric conditions can be difficult because of uncertainties in both the experimental methods and the precise chemical make-up of the aerosol.

The sharp vertical gradients of the measured NH_3 concentrations, assuming that the measurements are correct, are quite different from the theoretical profiles. As suggested above, part of the difference may be the result of scavenging of NH_3 from the air by clouds and precipitation before its measurement. From the LH study, the effect of a storm on a McConnell-like profile is shown in Fig. 2. The modification of the profile, while in the right direction, still does not reproduce the observed vertical gradients and suggests that additional loss mechanisms, such as reactions with pre-existing acid aerosols in the lower atmosphere, are needed in the theoretical calculations, even in the clear-air case. The horizontal transport and dry deposition of NH_3 from areas of relatively high emission density to areas of relatively low emission density could also account for some of the differences between observed and calculated vertical profiles.

In this paper, we examine the sensitivity of the results given in LH with respect to storm intensity. At the conclusion, we suggest further numerical simulations that need to be performed to simulate more realistically the complex processes that involve NH_3 .

MODEL ASSUMPTIONS

The one-dimensional, time-variant PLUVIUS reactive storm simulation code has been applied for this investigation. The simulations described in this paper closely follow those given in LH; key features and assumptions are summarized here for clarity and completeness. The PLUVIUS code numerically ap-

proximates solutions to the conservation equations for energy, water species, and pollutant species (Hales, 1982; Easter and Hales, 1984). Thus, it models water condensation, pollutant transport, and associated phenomena as simultaneously occurring events. Interactions among only the water species, NH_3 , and ammonium (NH_4^+) species have been considered; the transfer of among NH_3 and NH_4^+ the various phases is shown in Figure 3. Equilibrium gas scavenging occurs in both the cloud and the rain phases.

The code's fundamental spatial domain can be envisioned as a vertical array of species concentrations, which extends upward from the surface to some predetermined height. Initial temperature and pollutant concentrations must be specified on this grid prior to numerical integration of the equations; boundary conditions must be supplied at each end. Storms are initiated within the model by stipulating an upward vertical velocity field, which leads to expansion, cooling, and condensation of water vapor.

Initial conditions for the storm simulation, corresponding to the time just prior to storm onset, are given in Table 1. In this table and throughout the paper the cloud phase is used to denote cloud liquid water and the term " NH_x " represents the sum of NH_3 and NH_4^+ concentrations in the aqueous media. Boundary conditions during the storm are specified as zero flux of all species at the grid top, zero flux at the grid bottom for the gaseous species, and outflow at the grid bottom for precipitation and the precipitation-borne pollutant species. The vertical grid for this case has been set to incorporate 0.2 km spacing over the first 4 km. Above this height, the vertical grid slowly expands until reaching a constant spacing of 1.2 km. The total grid height is 20.0 km.

The simple, isolated, convective storm simulated for this computation is shown schematically in Fig. 4. A parabolically distributed vertical updraft velocity was applied over the first 4 km to initiate the storm activity. The velocity was calculated from the following equation:

$$v = v_0 (P - 0.25P^2) \quad (1)$$

where v is the updraft velocity (cm s^{-1}), v_0 is the maximum updraft velocity, and P is the height (km). Above 4.0 km, the velocity is set equal to zero. The storm was simulated for 1.94 h of model time with this constant updraft. Subsequently, a smaller downward vertical velocity equal to 0.25 times the original updraft was applied for 1.56 h to simulate a decaying convective disturbance and to aid in evaporation of any remaining cloud water. These expressions were chosen because such velocity distributions are reasonable approximations to actual convective updraft behavior and because the magnitude and vertical extent used in this simulation are typical of mild convective storms. In this study, v_0 values of 20, 40, and 60 cm s^{-1} , respectively, were used in the simulations to examine the sensitivity of NH_3 scavenging and vertical profile distortion as a function of storm intensity. The reference case in the LH simulations, shown in Fig. 2, used a value $v_0 = 40 \text{ cm s}^{-1}$.

Because the vertically varying updraft requires horizontal inflows and outflows to maintain conservation of mass, horizontal winds were supplied as additional input. These winds were determined by superimposing a macroscopic volume element around the vertical grid, as shown in Fig. 4, and calculating the y -direction winds, as appropriate. Pollutant concentrations associated with y -direction inflow were set equal to concentrations of the external ambient

environment. This corresponds, essentially, to a storm ingesting ambient air and exhausting processed air. Fig. 4 is a schematic representation only; cloud characteristics varied substantially with time during the course of the simulations. Some indication of this behavior is given by Fig. 5, which is a plot of simulated cloud-water density profiles for $v_0 = 40 \text{ cm s}^{-1}$ as a function of time throughout the life of the storm. In performing the simulations for differing storm intensities, the storm depth was held constant at 4 km. This is perhaps not a very realistic assumption since storm depth and storm intensity are closely related. The sensitivity of the profile distortion to this parameter, however, was not large.

Ammonia solubility was computed in this investigation through formulation of a total ion balance for ammonium and carbonate species and any strong acids or bases that may be involved. Upon consideration of all pertinent dissociation equilibria, the appropriate solubility equation may be expressed as (Hales and Drewes, 1979):

$$\frac{[\text{NH}_3, \text{ gas}]}{[\text{NH}_x, \text{ aqueous}]} = \frac{[\text{OH}^-]}{\text{Ha} ([\text{OH}^-] + K1a)}, \quad (2)$$

where the OH^- concentration is obtained from the ion balance, and

where $[\text{NH}_x, \text{ aqueous}] = [\text{NH}_3, \text{ aqueous}] + [\text{NH}_4^+]$

$$\text{Ha} = \frac{[\text{NH}_3, \text{ aqueous}]}{[\text{NH}_3, \text{ gas}]}$$

$$K_{1a} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3, \text{aqueous}]}$$

Solubilities were computed assuming a constant CO_2 mixing ratio of 340 ppmv and constant background monobasic acid concentration of 10^{-4} m. This background concentration corresponds to the chemical content of water in the absence of NH_3 ; as the model simulates the absorption of this gas, the computed hydrogen-ion concentrations shift to reflect the associated dissociation equilibria.

These simulations are comparable to those of McConnell in the sense that they ignore the gas-aerosol partitioning of NH_3 . Throughout the calculations, it is assumed that both NH_3 gas and NH_4^+ have similar physicochemical characteristics and that the major tendencies of both can be represented by calculations involving NH_3 gas and NH_x aqueous. Although this assumption should not alter the characteristic depletion behavior of the profiles, it may slightly alter the quantitative values of the results in several ways. Precipitation scavenging efficiencies of the two species can be expected to differ, although at the onset of a storm event, the major fraction of both the aerosol and the gas in the cloud layer will be scavenged into the cloud very quickly. When the cloud evaporates, it is assumed that all of the NH_x is returned to the air as NH_3 gas. Thus, since some of the cloud water NH_x will transfer to the aerosol phase, the calculated NH_3 depletion will be a minimum estimate.

STORM SIMULATIONS

The initial gaseous NH_3 clear-air mixing-ratio profile was assumed to be similar to that calculated by McConnell, but with smaller atmospheric

concentrations. Initial dry atmosphere model simulations were executed to generate the pre-storm clean-air NH_3 profiles. In these simulations, the eddy diffusivities and chemical destruction parameters of McConnell were used. The temperature and pressure characteristics were set equal to those used later in the storm system. A zero vertical velocity was used to characterize the atmosphere prior to the storm, and the code was executed with a fixed surface mixing ratio of 0.6 ppbv until steady-state NH_3 profiles were approached. The concentration profile resulting from this analysis was used as the atmospheric NH_3 distribution before the onset of a storm and is shown as the initial curve (0 h) in Fig. 2.

The storm system, with the initial NH_3 profile determined from the dry computations, was initiated by setting the vertical velocity to the value specified in Equation (1) with three different values of v_0 and stipulating a zero flux boundary condition for NH_3 gas at the surface.

Examples of primary computed results of the storm simulation are shown in Figs. 2, 5, 6(a) and 6(b). Fig. 5 is simply a plot of the cloud-water profile for $v_0 = 40 \text{ cm s}^{-1}$ at various times throughout the storm's duration; it is useful for interpreting results shown in the remaining plots. As can be seen from Fig. 5, the extent and density of the cloud grow almost continually until the subsidence condition is applied (1.94 h), whereupon they recede to eventually attain a clear-air environment.

Figs. 2, 6(a) and 6(b) present more chemically oriented results of the simulation for different storm intensities, i.e., for the maximum updraft velocity $v_0 = 40, 20, \text{ and } 60 \text{ cm s}^{-1}$, respectively. Fig. 2 represents the reference case of a moderately intense convective system, while Figs. 6(a) and 6(b) represent weaker and stronger systems, respectively, than the reference

case. The curves in these figures represent the sum of gaseous and cloud-borne NH_3 as a function of height. The initial dry-air curve is included, with the remaining curves indicating profile evolution as the storm progresses. Gaseous plus cloud-borne NH_3 , as contrasted to gaseous NH_3 alone, is shown in these figures because of the solubility equilibrium between these two entities. Uptake of NH_3 gas is assumed by the model to result in an instantaneous adjustment of the cloud-borne material; thus the observation of the decay of this sum with time provides a more satisfactory index of total atmospheric NH_3 depletion. NH_3 gas alone exists at extremely low concentrations whenever condensed water is present. This is a consequence of the high water solubility of this material. The final curve ($t = 3.5$ h) corresponds to a post-storm profile where essentially all of the previously condensed water has been evaporated.

The results indicate a large degree of depletion in the total atmospheric NH_3 and NH_x concentrations in the area where cloud forms. The rates of transfer of NH_3 to the rain are dominated at most heights by the formation of precipitation via cloud-water accretion and autoconversion. These rates depend on the corresponding values of the rain and cloud concentrations and the NH_x content in the cloud. Thus, large amounts of NH_3 are quickly scavenged from the gas phase into the cloud phase, followed by removal from the atmosphere as rain. In the rain shaft below the cloud base, atmospheric NH_3 is depleted by simple rain scavenging, which is less efficient than in-cloud scavenging. During later stages of the storm, as the cloud water decreases, the gaseous NH_3 concentrations increase because of evaporation of the cloud.

The additional storm simulations, performed using the two different numerical values for the model storm-intensity parameter, show that NH_3 depletion

depends strongly on the characteristics of the storm system and that any variable which affects the simulated amounts of rain or cloud can also affect the atmospheric NH_3 profiles. In both cases, the same basic concavity of the profile in the lower atmosphere, where the NH_3 has been depleted, occurs. When the maximum vertical velocity during the storm is increased to 60 cm s^{-1} , both rain and cloud water form earlier and persist in greater concentrations until the end of the storm. This greater rain amount similarly causes a greater degree of depletion of the NH_3 gas [Fig. 6(b)]. In contrast, when v_0 is decreased to 20 cm s^{-1} , both rain and cloud water form later and persist in lesser concentrations, thus causing a lesser degree of depletion of NH_3 gas [Fig. 6(a)]. One sees in this latter case that up until around 1.5 h of simulation, no appreciable depletion of NH_3 has occurred.

Fig. 7 presents simulated species concentrations in surface rain, along with the corresponding precipitation rates. These variables compare well both in magnitude and temporal trends with previously measured sequential rainfall data (e.g., Chapman et al., 1987). NH_x concentrations in surface rain generally decrease as rain rate increases, as would be expected on the basis of aqueous dilution effects. Between about 1.6 and 2.0 h for the moderately intense storms (e.g., $v_0 \geq 40 \text{ cm s}^{-1}$), however, concentrations decrease despite a decrease in rain rate. In the case of a rather weak convective situation, the concentrations of NH_x in rain are large, because of the rather low precipitation rates. This is simply a consequence of the large solubility of NH_3 , which results in virtually complete extraction of the gaseous material in the presence of condensed water. From these results, we conclude that relative NH_x scavenging occurs as a complex of mechanisms and cannot be explained on the basis of simple dilution arguments alone.

DISCUSSION

In this article, the sensitivity of NH_3 scavenging-to-storm intensity has been examined. The calculations were compared with the results given in the LH study. For the cases examined, the important conclusions of the LH study were reconfirmed, namely 1) the vertical profiles of NH_3 are radically distorted by storms; and 2) precipitation scavenging is extremely effective in removing atmospheric NH_3 and, thus, limiting its upward transport to the stratosphere. These conclusions are valid even for rather weak storms. However, the simulations performed in this and the previous LH work, where the scavenging of NH_3 was calculated in isolation from other atmospheric species, are only indicative of the important and complex processes that involve this substance and other species in the atmosphere.

Also, as noted in the Introduction, the measured NH_3 vertical profiles are variable and quite different from the theoretical profiles. As suggested by our analysis, part of the difference may be the result of scavenging of NH_3 from the air by clouds and precipitation prior to its measurement. The modification of the profiles by scavenging, however, still does not seem to reproduce the observed vertical gradients. This may be a result of several factors. First, the initial vertical profiles used in the calculations were generated to agree with McConnell's published profiles. Second, the storm systems used in the simulations were rather simple and not very realistic; more complex representations of storm environments might be expected to produce substantially different profile modifications than those reported here. Third, additional gas-phase loss mechanisms, such as reactions with pre-existing acid aerosols in the lower atmosphere, have been ignored. Finally, the reaction products of NH_3 with strong acids [e.g., NH_4NO_3 , NH_4HSO_4 , and $(\text{NH}_4)_2\text{SO}_4$] are

also scavenged in storms and may further participate in aqueous phase reactions. Thus, further modeling studies need to be performed in order to simulate more realistically the complex processes that involve NH_3 . These include:

- Add gas-phase aerosol NH_4^+ (SO_4^{2-} , NO_3^-) profiles.
- Add gas-phase chemical loss of NH_3 by reaction with acids (H_2SO_4 , HNO_3).
- Improve storm environment simulation.
- Include storm scavenging of NH_3 and aerosol NH_4^+ .
- Simulate reactive scavenging of NH_3 , SO_2 , and aerosol.
- Study partitioning sensitivity of NH_3 and NH_4^+ in the presence of other species.

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Table 1. Summary of clear-air conditions prior to storm

Species	Variable Status	Initial Condition
Temp	computed	determined using moist adiabatic lapse rate
Vapor and Cloud	computed	set to values corresponding to 90% RH
Rain	computed	0.0
Snow	computed	0.0
Cloud	constrained by equilibrium	0.0
NH _x in gas and cloud	computed	steady-state profile obtained from dry-air simulation
NH _x in rain	computed	0.0
NH _x in snow	computed	0.0
NH _x in gas NH _x in cloud	both variables are constrained by gas-cloud partitioning of NH _x in gas and cloud	

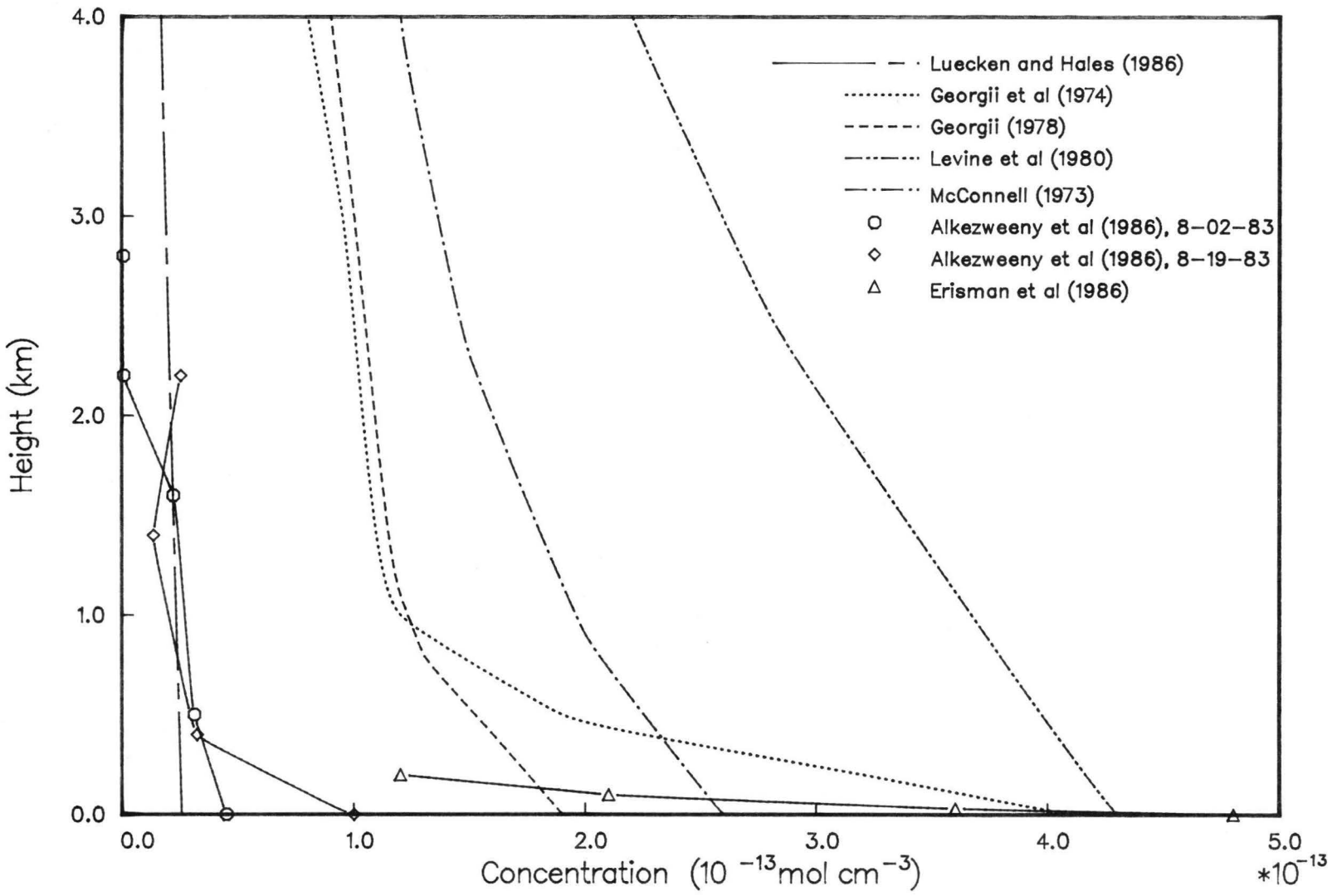


Fig. 1. Comparison of vertical concentrations of gaseous NH_3 that have been previously reported in the literature.

Fig. 2. Total NH_x concentration profiles in gas and cloud phases with time from beginning of the storm event, $v_0 = 40 \text{ cm s}^{-1}$.

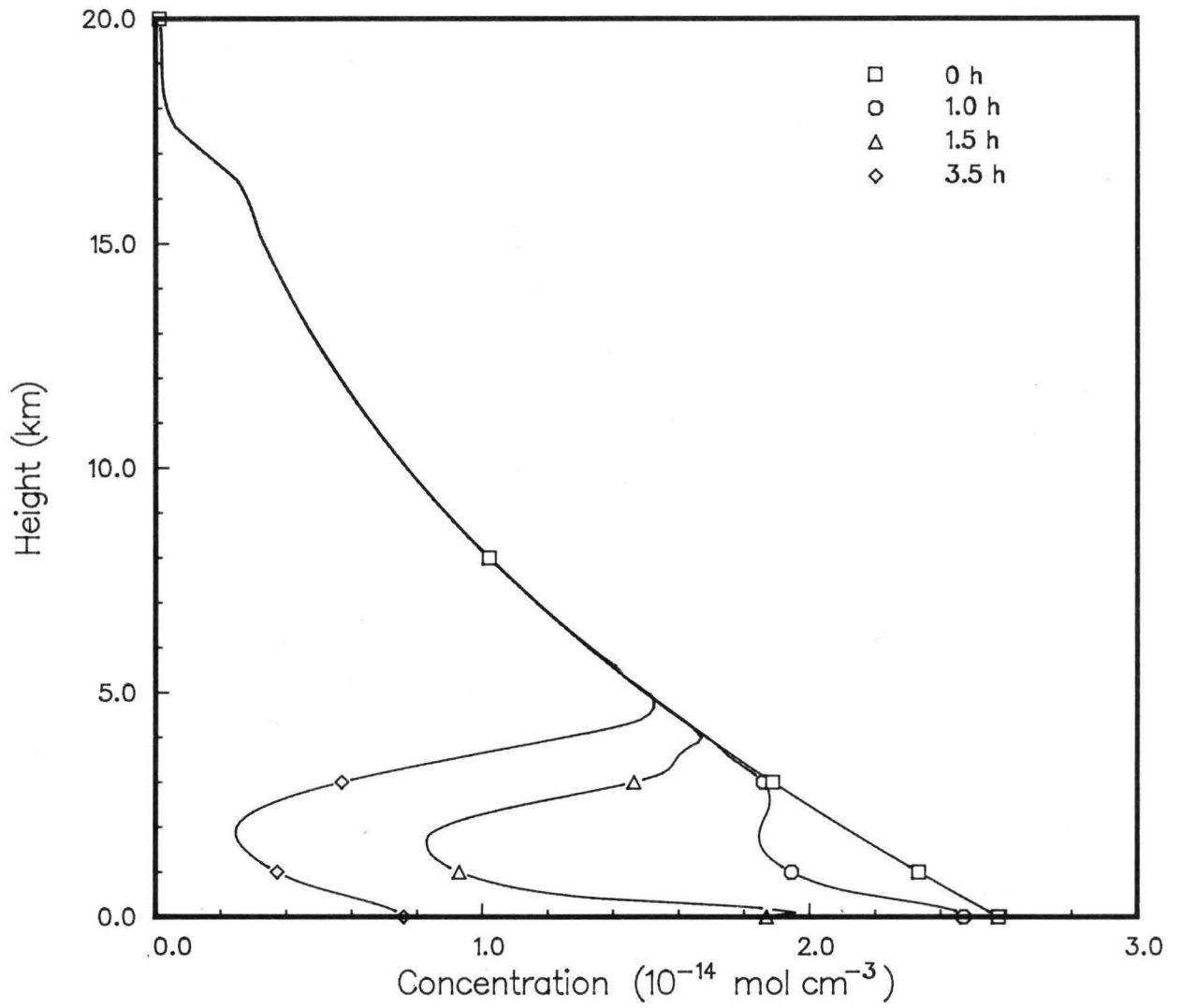


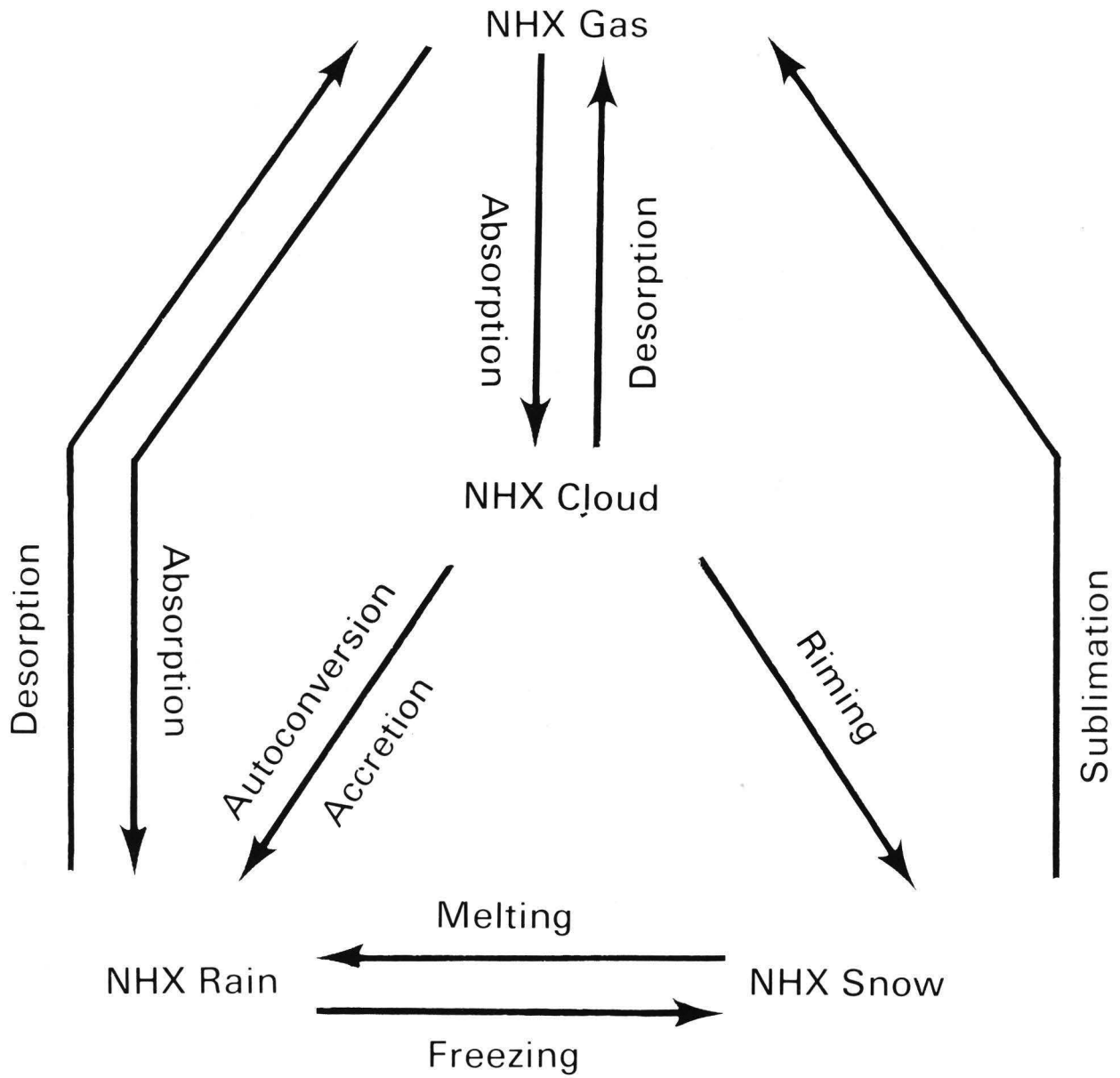
Fig. 3. Interaction of NH_3 and NH_x among the various phases.

Fig. 4. Simple idealization of modeled convective storm system.

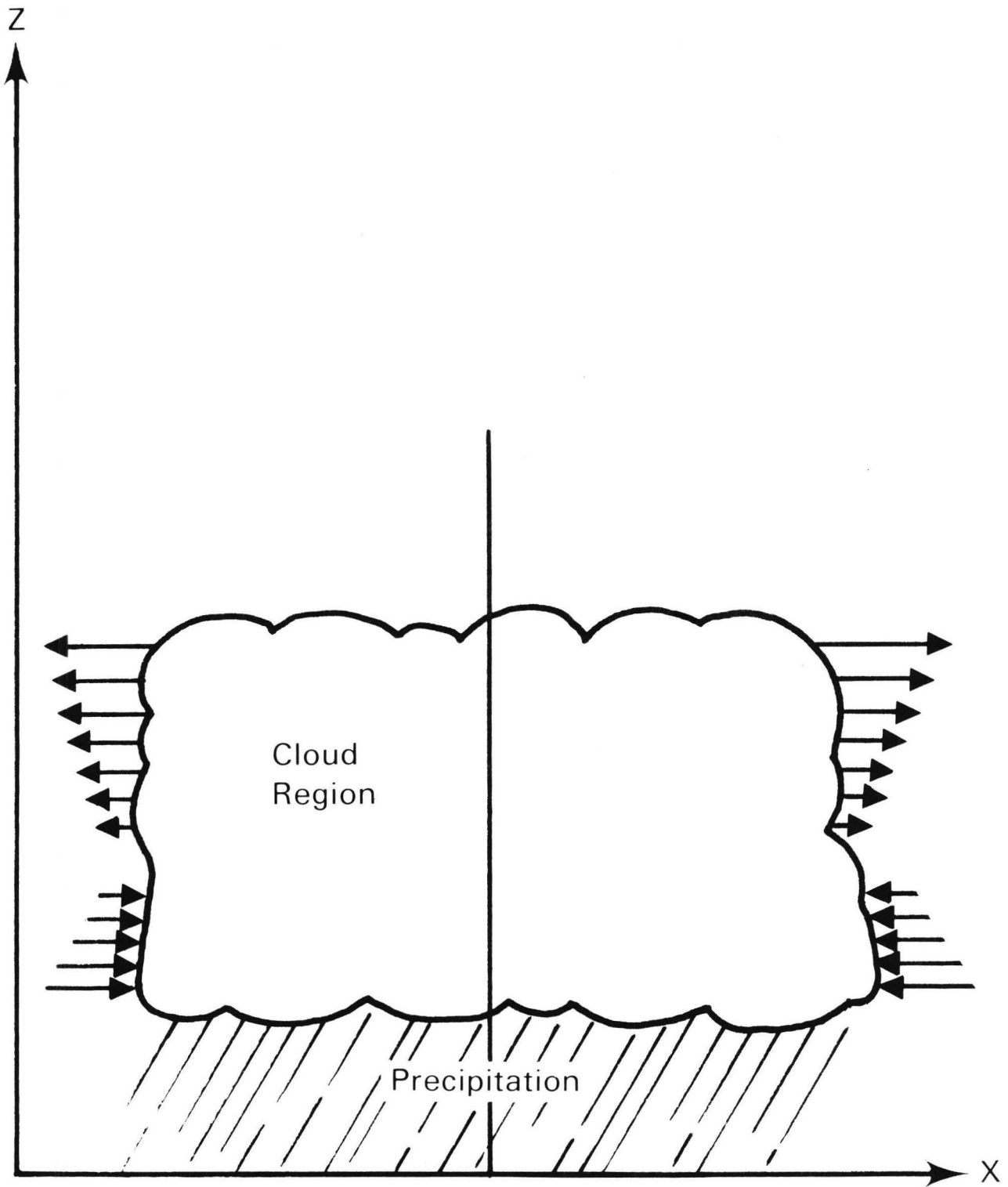


Fig. 5. Cloud water vertical concentration profiles with time from beginning of storm event, $v_0 = 40 \text{ cm s}^{-1}$.

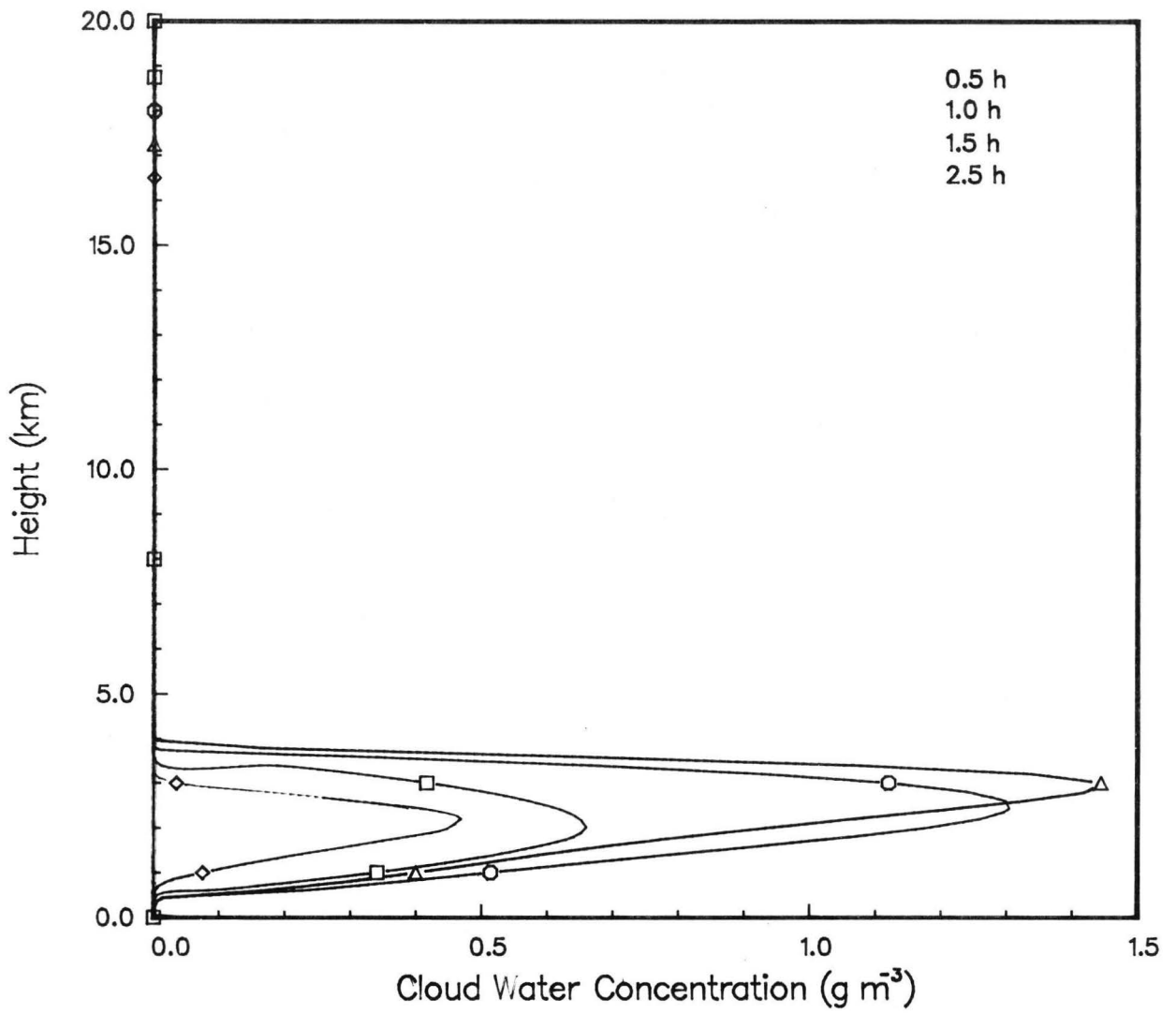


Fig. 6(a). Total NH_x concentration profiles in gas and cloud phases with time from beginning of the storm event, $v_0 = 40 \text{ cm s}^{-1}$.

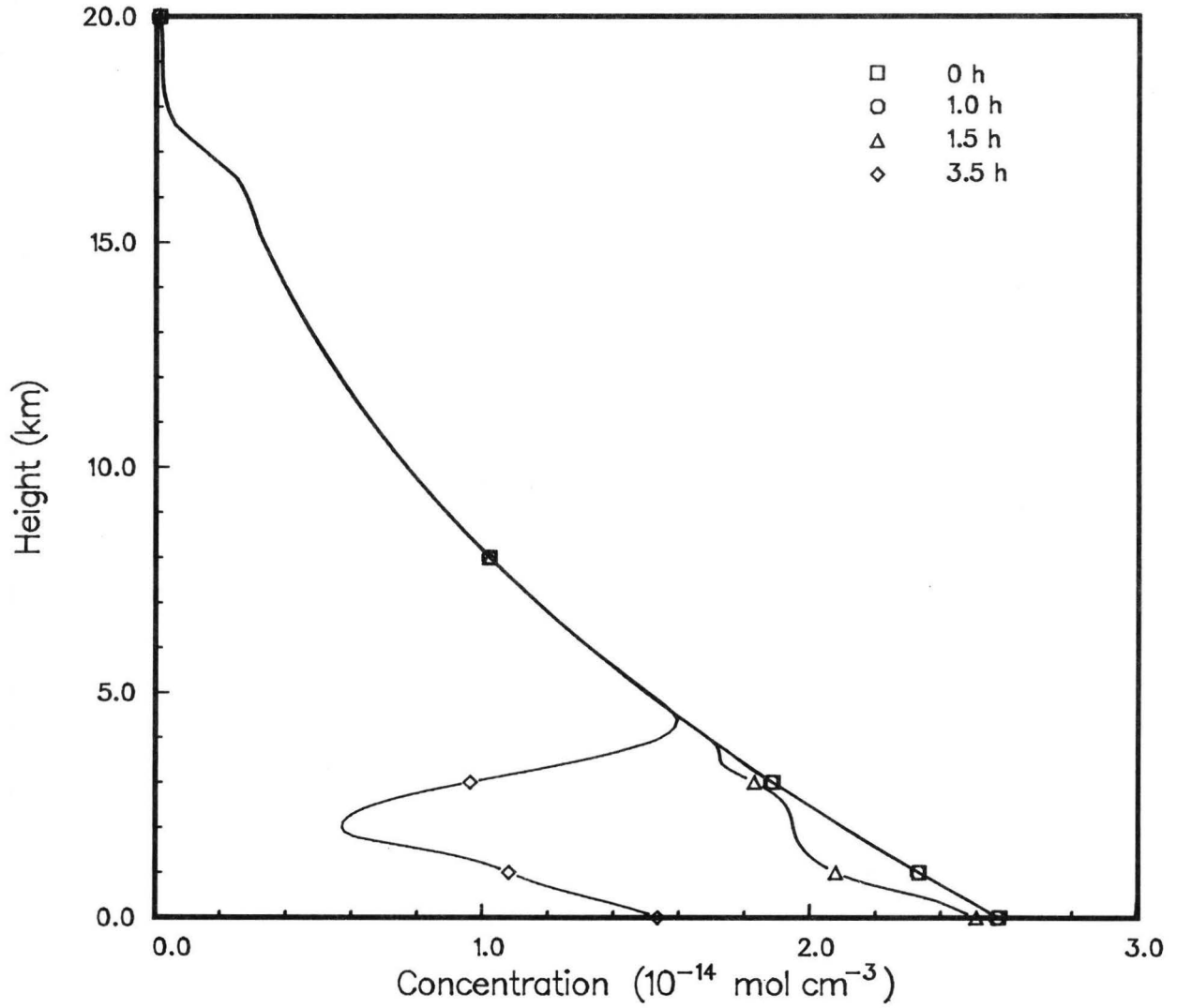


Fig. 6(b). Total NH_x concentration profiles in gas and cloud phases with time from beginning of the storm event, $v_0 = 60 \text{ cm s}^{-1}$.

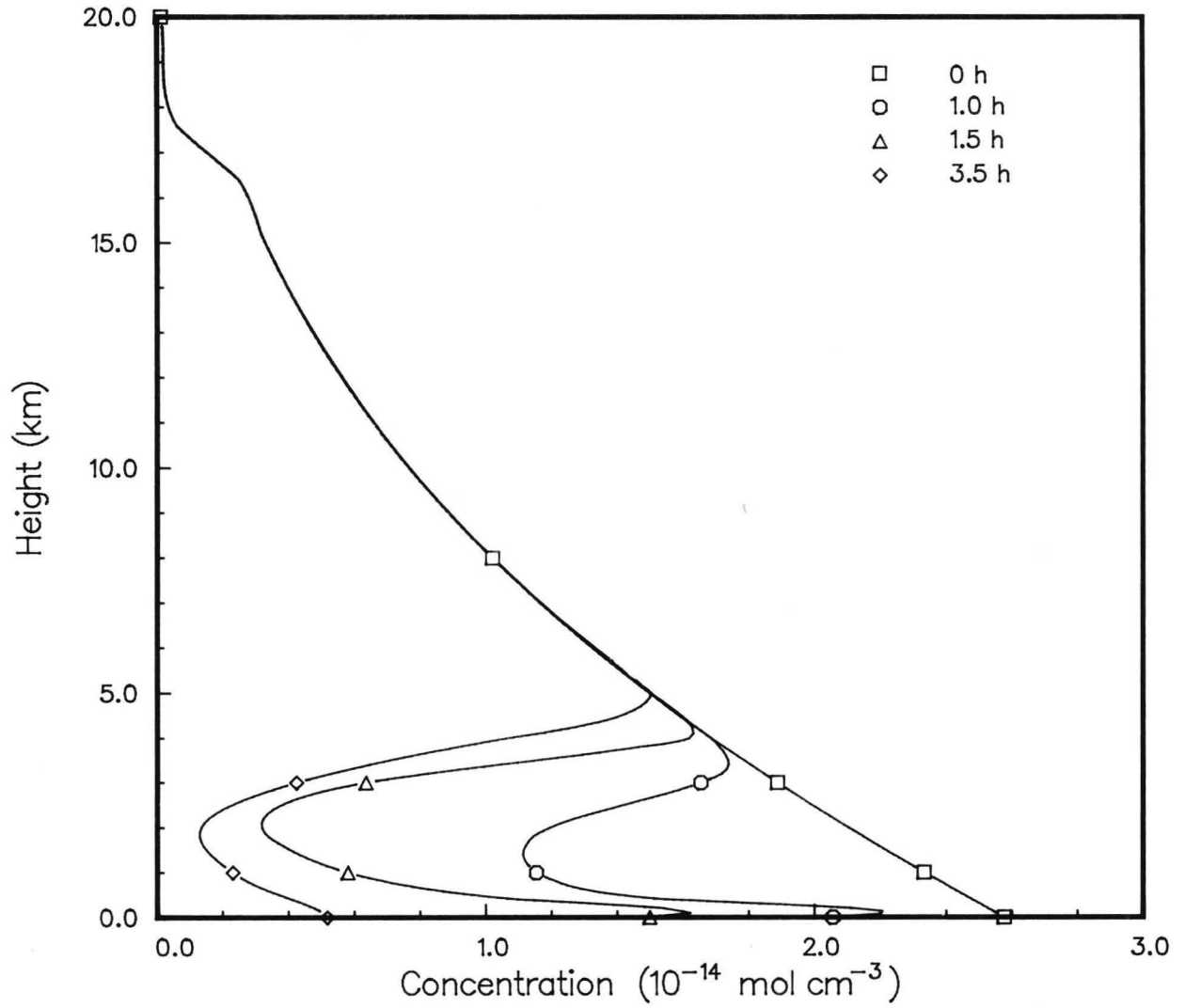
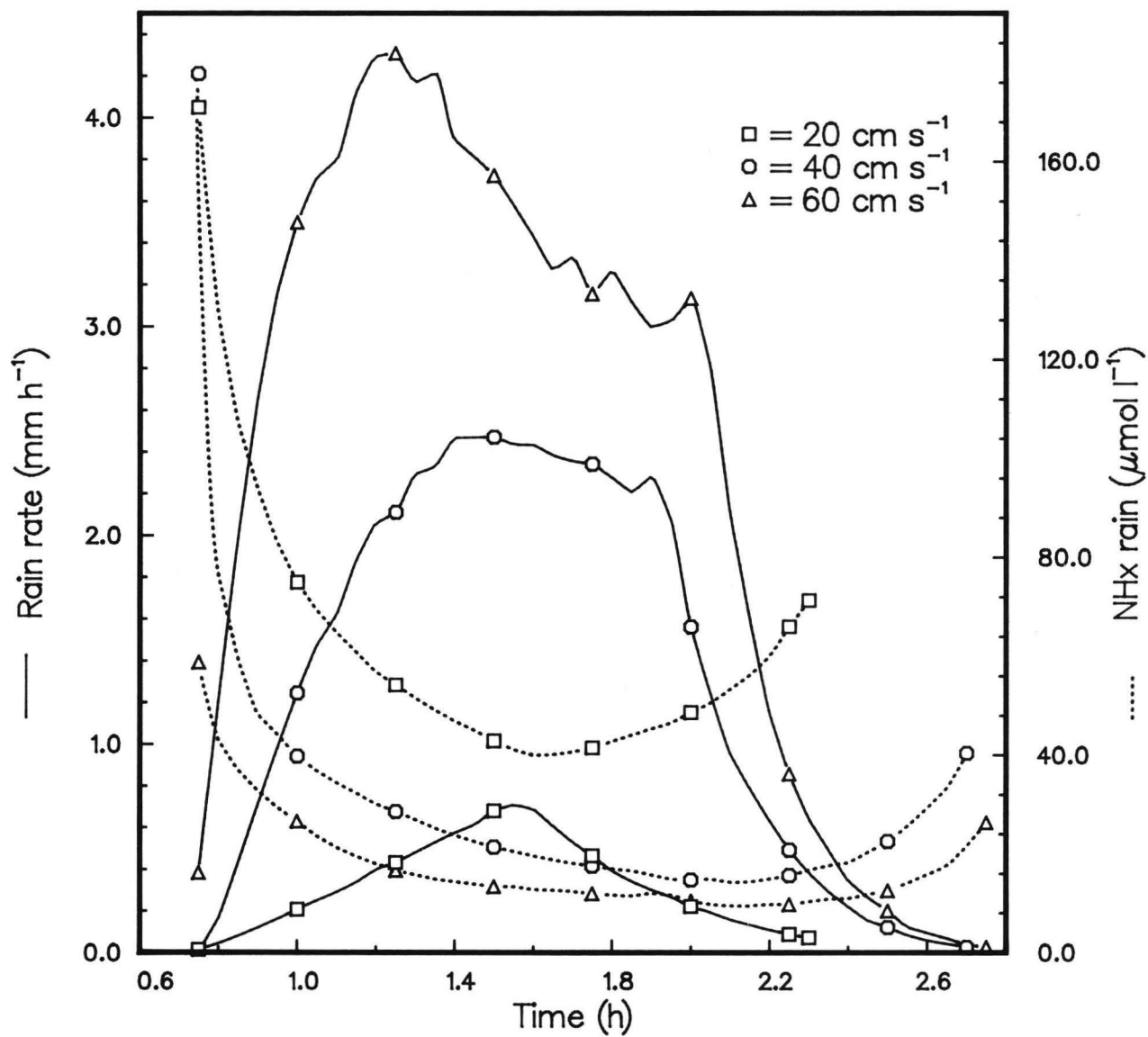


Fig. 7. Precipitation rate and surface rain NH_x concentration during the storm event for the three different storm intensities.



IDENTIFICATION OF AMMONIUM COMPOUNDS IN RIME AND AEROSOLS SAMPLES

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Abstract

Microscopic and diffraction methods (which are often inadequately appreciated in environmental science and technology) were used for the qualitative identification of atmospheric aerosol particles. Making use of these methods, ammonium sulphate was identified in particulate samples. The study also involved chemical analyses of airborne gaseous pollutants (NH_4^+ , SO_4^- , NO_x) and rime samples (NH_4^+ , SO_4^- , NO_3^-). Samples were collected in a mountainous area Karkonosze Range and in the vicinity of a large, lignite-fired power plant. The results obtained support the utility of microscopic and diffraction when used for identifying the source of origin of the pollutants and for investigating their long-range transport and transformations.

Introduction

In recent times, much attention has been given to the problem of aerosol formation in the vicinity of the emission source, to the identification of pollutants and their environmental impact (1,2,3). Aerosols have a particular contribution to such phenomena as visibility degradation, acid precipitation and long-range transport of air pollutants (4,5). Airborne particles are often vapour condensation nuclei and centres of gas adsorption in the atmosphere.

This paper presents the possible applications of microscopic and diffraction methods to identify ammonium sulphate in aerosol samples. Chemical analyses were carried out for NH_4^+ , $\text{SO}_4^{=}$ and NO_3^- in aerosol, and for NH_4^+ , $\text{SO}_4^{=}$, NO_3^- and pH in rime. It is a well-known fact that there is a continuous increase in the concentration of airborne sulphur dioxide. The interaction of ammonia and sulphur dioxide yields products which accounts for the occurrence of acid precipitation and acid soils. The presence of ammonium sulphate in aerosol samples indicates that, depending on the meteorological conditions, there is either catalytic or photochemical oxidation of pollutants in the atmosphere.

Methods

In this study the following procedures were involved:

(1) transmission electron microscopy (TEM), using selected area electron diffraction (SAED); (2) scanning electron microscopy (SEM) coupled with energy dispersion X-ray spectroscopy (EDXS), and (3) X-ray diffraction (XRD).

Aerosol samples were collected at two different sites. One of these was located 4 km from a lignite-fired power plant (plant T); the other one at the summit of Szrenica (1362 m a.s.l.), 40 km from plant T.

Aerosol samples for electron microscopic examinations were collected direct onto copper grids which were placed in a microvessel of special design. Chemical analyses involved colorimetric methods. The thoron method and the Salzman approach were used for determining the concentration of sulphate ions and nitrate ions, respectively. The concentration of airborne ammonium ions was determined, using a ion selective electrode.

Results

Microscopic examinations of aerosol samples collected 4 km from plant T (with prevailing west wind) have revealed light spots which have not been observed in fly ash samples taken in the immediate vicinity. These spots were rapidly disappearing in the course of the experiments. Electron diffraction tests have shown slight reflections exhibiting a crystalline structure. But there was no possibility to record the diffraction pattern on a photographic plate because of the very rapid disappearance of the spots. These spots were supposed to be ammonium sulphate particles (6,7). To support the hypothesis, a standard sample of ammonium sulphate was prepared. The microscopic image and behaviour of the standard sample were similar to those of the light spots. Hence, they were likely to be ammonium sulphate particles (Fig. 1a, 1b and 1c). Ammonium sulphate is a secondary air pollutant and its identification is helpful when analyzing the transformations of air pollutants.

The aerosol samples collected at the Szrenica measuring site (40 km from the emitter) showed ammonium sulphate particles in the form of small grains (Fig. 2a). Ammonium sulphate generally occurs in the presence of solid particles, e.g. aluminumsilicates (Figs. 2b and 2c). Figure 2d gives the elemental composition determined by EDXS of the surface layer deposited on the particle of Fig. 2c.

It has been anticipated that the polluted air masses moving from plant T towards the Szrenica site may have a significant contribution to the chemical composition of atmospheric aerosol and rime. To support the assumption, chemical analyses involving determinations of NH_4^+ , SO_4^- , NO_x , NO_3^- and pH were carried out. The results were surprising. Rime samples displayed an acidic pH which varied from 3.4 to 4.7. This is to be attributed to the occurrence of strong mineral acids. It should be remembered that air pollution coming from westerly directions creates greater environmental hazards than that from other directions. While the rime concentrations of nitrates and nitrites were found to be low: 0.5 mg N

dm^{-3} and $0.002 \text{ mg N dm}^{-3}$, respectively, those of sulphate ions and ammonium varied from 6.12 to $13.86 \text{ mg SO}_4^{=} \text{dm}^{-3}$ and from 1.04 to $3.51 \text{ mg NH}_4^+ \text{dm}^{-3}$, respectively. Rime may, therefore, be regarded as a good experimental material to represent the long-range transfer of air pollutants.

Atmospheric pollution over areas with no industrial sources (mountains forests, rural regions) owes its origin to gas and aerosol particles produced in, and coming from industrial and urban regions. Mountainous areas, and particularly mountain summits, create favourable conditions for investigating the transport of air pollutants over far distances. Chemical analyses of gaseous pollutants (sampled at both sites) give evidence of the transformation processes occurring in the atmosphere.

Statistical analysis of the data sets obtained has revealed significant correlations between (NH_4^+) and $(\text{SO}_4^{=})$ and between (NH_4^+) and $\text{H}(\text{NO}_x)$:

$$(\text{NH}_4^+) = 5.23 + 0.77 (\text{SO}_4^{=})$$

$$r = 0.52$$

$$(\text{NH}_4^+) = 2.055 + 1.48 (\text{NO}_x)$$

$$r = 0.88$$

The presence of ammonium ions and sulphuric acid vapours suggests and substantiates the formation of ammonium sulphate. The correlation coefficients obtained in this study ($r = 0.52$; $r = 0.88$) approach those reported for an urban region in France (8,9).

The mechanism governing the oxidation of SO_2 and the transformation of nitric oxides (NO , NO_2) in the atmosphere is significantly influenced by a number of analytical and meteorological factors (e.g., oxidative index;

concentrations of NH_3 , NO_x and free radicals; insolation; relative humidity). Thus, there is a high probability that in the winter season sulphur dioxide is oxidized in a catalytic process. The contribution of catalytic oxidation decreases in the summer season with prevailing photochemical reactions.

Conclusions

1. The identification of airborne ammonium sulphate by microscopic and diffraction methods has supported their utility when applied to source apportionment and to the study of long-range transport and transformations of air pollutants.
2. The amount of ammonium sulphate in the form of atmospheric aerosol measured at a farther distance (about 40 km) from SO_2 emission is greater than in the immediate vicinity of the source.
3. Rime may be regarded as a good material to represent long-range transport of air pollutants. Mountainous areas and particularly mountain summits, provide favourable conditions for investigating this problem.
4. The presence of ammonia nitrogen in the atmosphere and reaction with sulphur dioxide create serious environmental hazards from acid precipitation.

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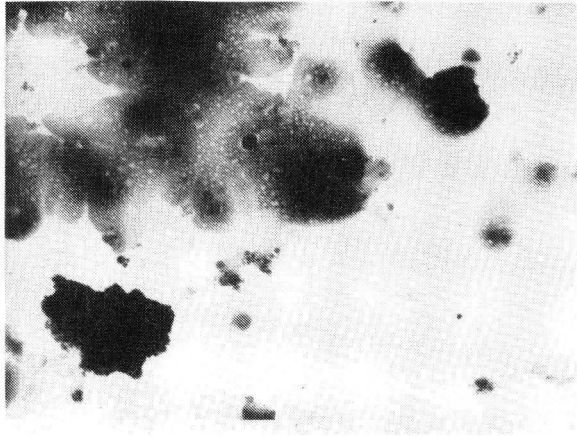


Fig. 1a.

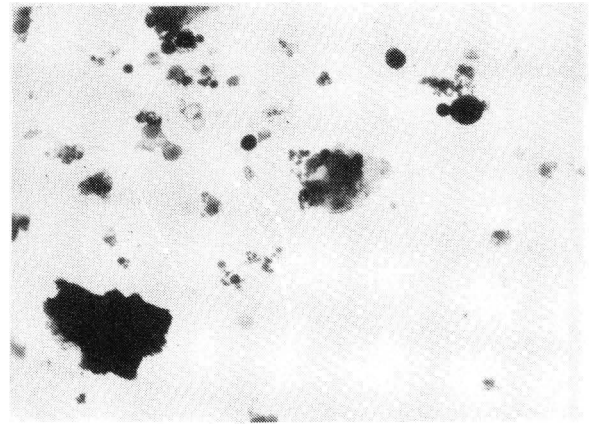


Fig. 1b.

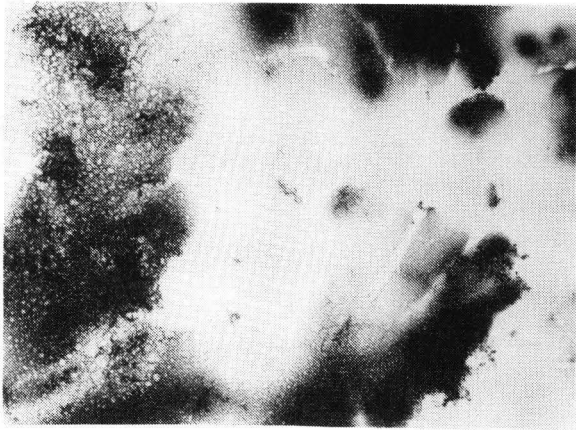


Fig. 1c.

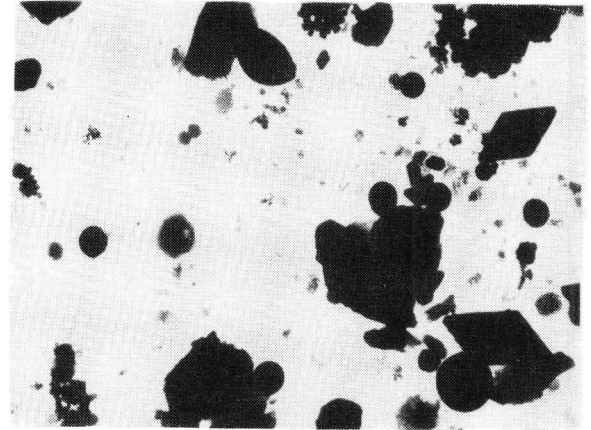


Fig. 2a.

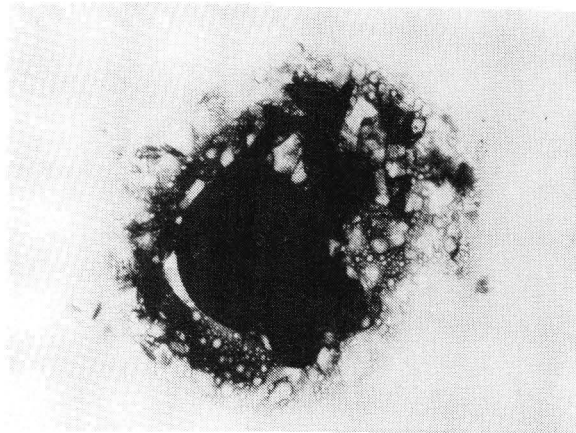


Fig. 2b.

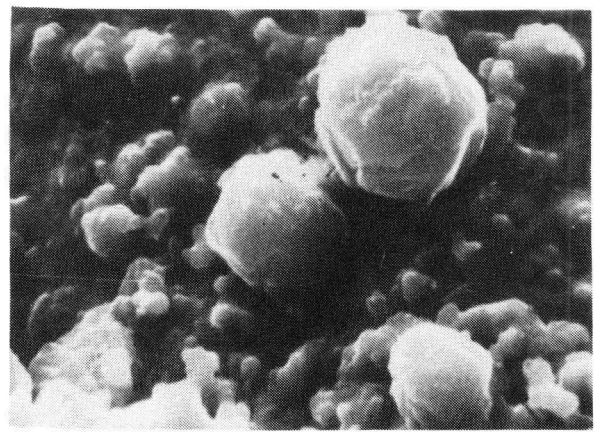


Fig. 2c.

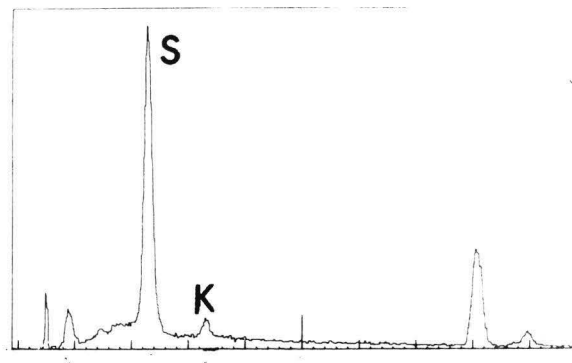


Fig. 2d.

ACIDITY OF RAINFALL IN HIGHLY INDUSTRIALIZED AND URBANIZED REGION

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One of the basic air self-purification processes is pollutants wash-out through precipitation e.g. rain, snow. Rainfall is one of the most important causes of pollutants removal from troposphere, which is the layer of atmosphere where water circulation occurs. Therefore, it is very important and useful to study rainfall chemistry also because it can be one of the possibilities of air chemical constitution assessment. Atmospheric precipitation (rain, snow) contains air components, both gaseous ones and those occurring in aerosol form. Alekin /1/ says that a raindrop weighting 50 mg, falling from the height of 1 km, washes-out 16.3 l of air. Assuming that distribution of raindrops size is consistent, the author has estimated that 1 l of water washes-out $3 \cdot 10^5$ l of air.

According to Mason /2/, the "wash-out" effect of substances from air consists of the following processes:

- vapour condensation on aerosol particles during clouds development process;
- collision of aerosol particles circulating according to Brownian movements with water droplets, which results in those particles absorption by water droplets;
- aerosol particles binding with cloud elements resulting from Facy's process /3/; i.e. small aerosol particles hit a water droplet as a result of forces operating in diffusion field around the suspended liquid drop, as a consequence of steam concentration gradient;
- aerosol particles accumulation on rainfall drops.

The effectiveness of the process depends upon rainfall drops size and aerosol particles size. Numerous examples from literature show that air cleaning effectiveness decreases with aerosol particles size.

Pollutants concentration in rainfall is usually proportional to pollutants concentration in air, however, the relation is different for every substance taking into account its properties, e.g. water solubility and

others. However, any substance concentration in rainfall is also dependant upon rainfall structure.

Taking all the above reasons into account it should be said that pollutants concentrations in rainfall are difficult to interpret and the problem has not been satisfactory solved so far. Despite interpretation difficulties, there is a growing interest in rainfall pollutants measurements because they are an important factor connected with pollutants removal from air. Analyzing air pollutants penetration into raindrops, one can notice that pollutants measured in rainfall come from the air mass within which a cloud has developed. Pollutants are then absorbed during the cloud movement and they also come from the air layer below the cloud within rainfall occurred. Thus, pollutants measured in rainfall come not only from local sources in the areas where rainfall occurred, but they also determine pollution of a larger area. The size of the area depends upon meteorological situation during a rain-cloud development process and during rainfall itself.

Rainfall studies carried out in the Institute of Environmental Protection in Katowice were aimed at collecting information on rainfall chemical constitution, amounts of dust pollutants washed-out by rainfall, as well as on rainfall pH. The term "acid rain" has already been very popular at that time. The present paper present results of studies on rainfall pH. In many papers published in Western Europe the term "acid rain" has been associated with rainfall pH and with air pollutants concentrations. For instance, Likens and Borman /4/, in their description of rainfall studies carried out in north-eastern regions of the USA, have related rainfall pH with air pollution, on the basis of two assumptions:

- 1 - Rainfall pH of clean air, without influence of any human activity, should be 5.7. The above statement is in agreement with Inge's theory /5/ where rainfall pH is associated with the impact of CO_2 contained in air. It is the pH of CO_2 dissolved in water with the consideration of CO_2 partial pressure in air, which, according to Erikson /6/ amounts to $3 \cdot 10^{-4}$ atm. According to this theory, rainfall pH should not be lower than 5.7.
- 2 - Rainfall with pH lower than 5.7 must contain strong acid resulting from human activity. This strong acid is related to H_2SO_4 originating SO_2 from oxidation. Rainfall is a highly dilute solution and it has a very

low buffer capacity. Thus, it is possible that small amounts of acid constituents in air can considerably decrease rainfall pH.

On the account of high sulphur dioxide concentrations in air around the Katowice District areas one should expect rainfall pH decrease, which is a typical example of acid rain effect. Studies on rainfall acidity were carried out in five measurements points situated in two towns of the Katowice District which is a highly industrialized and urbanized region. The following are some statistical data about the region:

The Katowice District covers the area of 6650 sq.km which makes 2.1% of overall Polish area. Simultaneously, in 1983 10.6% of total Polish population inhabits the district. In accordance with that, the average density of population, which amounts to 584.9 persons per km², is more than 4.9 times higher than all-Polish average.

The Katowice District has also a considerably high percentage of urban population, namely, about 86%, which can be compared to the average of 56% in other districts of Poland. On the account of the above numbers it should be stressed that the Katowice District belongs to the most highly urbanized regions in the world. The very high degree of urbanization results from considerable industry concentration in the area. Industry in the Katowice District is mainly situated in its central part called the Upper Silesian Industrial Region as well as in the coal region around the town of Rybnik. Many industrial plants are also situated along the District borders. Considering industry structure, one should stress serious environmental noxiousness of heavy industry and, to a smaller degree, of mineral and chemical industries.

Air pollutants emission from such an intensely industrialized and urbanized region is very high. Standard pollutants concentrations are often exceeded. For example, the average yearly SO₂ concentration in the Katowice District ranges from 41 to 107 ug/m³, whereas the standard for SO₂ is 64 ug/m³. SO₂ concentrations are especially high in the Upper Silesian Industrial Region. All the above considerations have been taken into account when we were beginning our studies aimed at determining acidity of rainfall in the Upper Silesian Industrial Region. Studies were carried out between February 1982 and February 1983 in five measurements points situated in the central part of the Upper Silesian Industrial Region, namely in the cities of Katowice

and Tychy. Rainfall was collected during 15 days. For rainfall samples collection, the sedimentation cone method was employed. In view of low sensitivity of chemical analysis methods, the necessity of collecting as large rainfall samples as possible was assumed. For that reason, the device proposed by prof. Juda was chosen. Figure 1 shows the sketch of the device where sedimentations cone is the basic element. In each individual measurements points the sedimentation cone was fixed in the metal stand, and the height of reception surface was 122 cm above the ground (following prof. Juda's recommendation). During our studies we were particularly anxious to sample pollutants washed-out from air through rainfall on rainy days. That is why the cone was replaced every day, always at the same time, which enabled us to minimize dry dust-fall impact upon rainfall sample composition. In each measurements point a dry dust-fall meter was installed separately for a monthly exposure. In winter-time, on days when it was snowing, after the cone replacement, the cone with snow sedimented on it, was transported into a warmed-up room where the snow was melting. Water from the melted snow was then collected in a separate container. Chemical determination was carried out separately for rain-water and for water from the melted snow. On the last day of the 15-day-long cycle, after measurements have been completed, rainfall samples were transported to the laboratory in order to carry out chemical analysis. Clean glass or pvc dishes were placed under the cones and measurements were continued. Rainfall pH, NH_4^+ , NO_3^- , SO_4^{2-} ions content, metals content and solid insoluble substances were determined in collected rainfall samples. Ionic content determination was carried out with the use of chemical methods commonly known as classical. Metals content was determined using atomic absorption method. Rainfall pH was determined with a pH-meter, type OP-211 produced by a Hungarian firm Radelkis. In measurements points, besides the use of sedimentation cones with the surface of 750 cm^2 , rainfall was also determined with Hellman's rain-gauge (surface - 200 cm^2). Total rainfall measured with cones was approximately 6% higher than total rainfall measured with Hellman's rain-gauge. Total rainfall for measurements points situated in Katowice ranged from 59.7 to 134.3 l/m^2 per month and for measurements points situated in Tychy it ranged from 85.3 to 217.0 l/m^2 per month.

All the obtained results of pH value and chosen ions concentrations, namely, NH_4^+ , NO_3^- , SO_4^{2-} , are shown in tables with reference to individual months. Summing up the data resulting from rainfall pH measurements, the following facts should be stressed:

- 125 elementary measurements of rain and snow pH value were performed;
- only 4 of 125 measurements, which makes 3.2% of all the measurements, resulted in pH value lower than 4.0;
- pH value ranging from 4.0 to 5.0 occurred in 28 cases (22,4%);
- pH lower than 5.7, which is the limiting value for rainfall without any influence of human activity emission sources, occurred in 49 cases (39,2%);
- in 76 cases (60,8%) rainfall pH was higher than 5,7 (snow, rain).

All the pH results were expressed here with reference to the number of cases in each scope, and not in average values, because calculations of pH average values make no sense from a chemical point-of-view.

The number of cases in individual scopes suggests that for measurements points situated in the Upper Silesian Industrial Region the reaction has shifted in alkaline direction. The generality of "acid rains" has not been recorded. Only 3,2% of total rainfall measured during one year demonstrated a typical acidity, in spite of the fact that in the studied area there were high concentrations of factors which could produce this phenomenon considerable intensity (e.g. high SO_2 concentrations in air).

The effect of extremely high rainfall pH values occurring in the Upper Silesian Industrial Region (above $\text{pH}=5.7$) in the presence of acid-forming factors, could be attributed to the prevailing impact of alkaline substances, mainly calcium and magnesium oxides, emitted to atmosphere in industrial regions with fly ash. We have not studied this phenomenon in detail so far. Probably such studies will be carried out in the future. One can only believe that, in the presence of atmospheric water, gases occurring in air, such as SO_2 , SO_3 , CO_2 , NO and NO_2 , join with alkaline components of industrial emission, namely, with metallic oxides and gaseous ammonia, producing aerosol from respective water-soluble salts. Rainfall pH in such a highly industrialized and urbanized area as the Upper Silesian Industrial Region does not produce a high risk of "acid rains" because of

alkaline components prevalence in dust from exhaust gases combustion processes (which is the basic part of emission).

We hope that at the present symposium some new and interesting information will be presented, especially on ammonia impact upon rainfall acidity.

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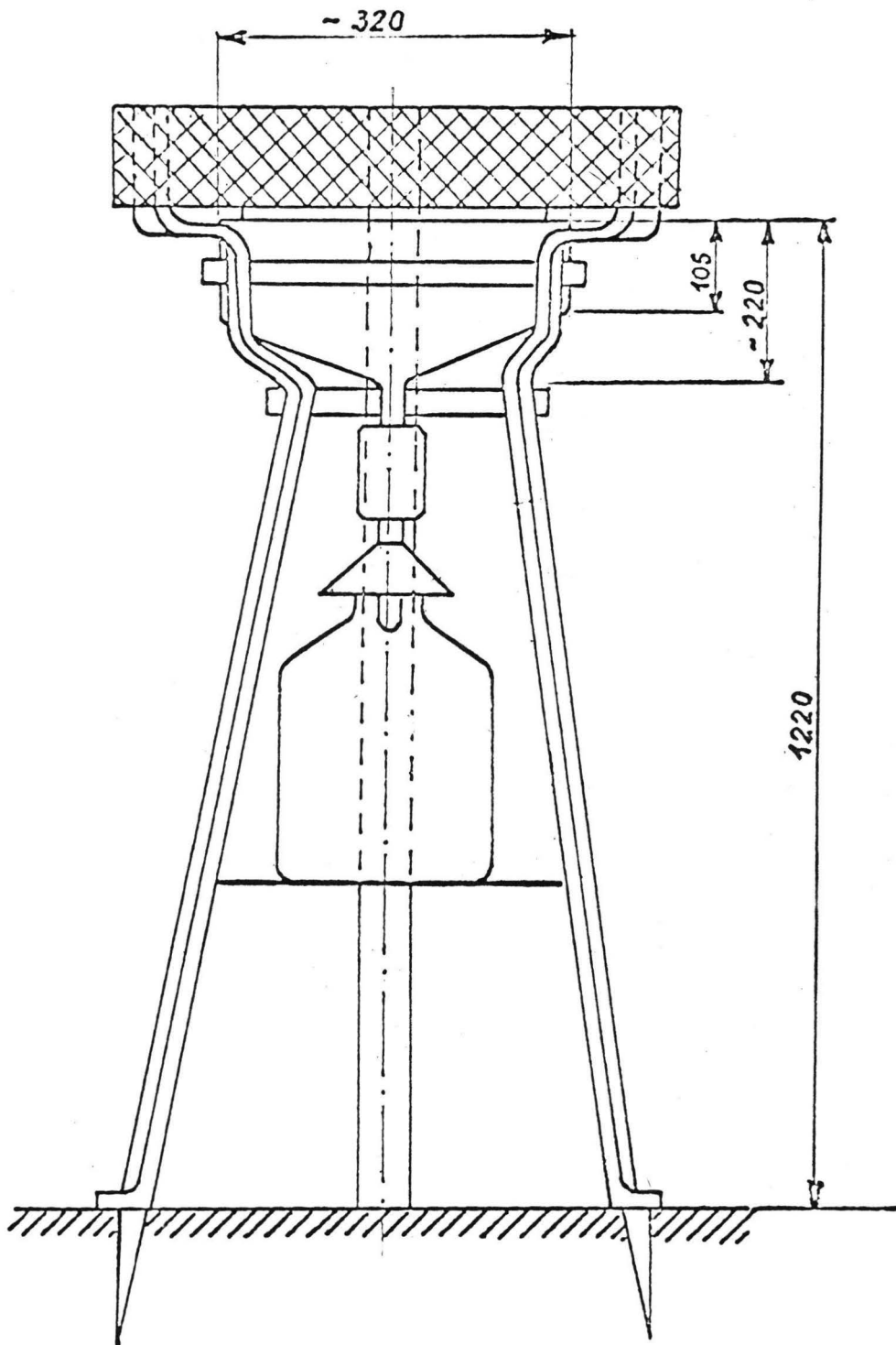


Figure 1. Rain collector

Rainfall Determination Results

Stand	measurments period deys, month, year	pH	Rainfall chemical Constitution, ionic content mg/l		
			NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻
1	1-15.02.82 rain	6,1	1,84	4,56	8,23
	snow	5,6	2,15	5,23	47,31
	16-28.02.82 rain	7,3	1,97	20,74	38,00
	snow	5,6	20,09	42,24	242,01
2	1-15.02.82 rain	6,9	1,23	3,19	21,26
	snow				
	16-28.02.82 rain	7,3	4,82	12,60	54,67
	snow	6,1	14,41	8,20	119,34
3	1-28.02.82 -	-	-	-	-
4	1-15.02.82 rain	7,2	1,23	5,78	32,23
	snow				
	16-28.02.82 rain	6,96	5,65	11,44	116,01
	snow				
5	1-15.02.82 rain	7,7	1,08	2,64	23,31
	snow	7,4	7,53	28,60	
	16-28.02.82 rain	7,8	2,43	17,55	95,34
	snow	7,4	7,07	11,99	73,34

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical Constitution, ionic content mg/l		
			NH_4^+	NO_3^-	SO_4^{2-}
1	1-15.03.82	6,7	4,30	7,32	30,88
	16-31.03.82	7,9	1,84	6,60	23,22
2	1-15.03.82	7,2	3,38	5,23	33,23
	16-31.03.82	7,8	2,86	5,50	18,36
3	1-15.03.82	6,2	3,62	5,36	19,47
	16-31.03.82	7,2	2,12	5,70	14,58
4	1-15.03.82	7,7	2,55	7,70	25,92
	16-31.03.82				
5	1-15.03.82	7,2	2,76	7,15	35,58
	16-31.03.82	7,6	2,52	5,70	19,44

Rainfall Determination Results

Stand	measurments period dey, month, year	pH	Rainfall chemical Constitution, inonic content mg/l		
			NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻
1	1-15.04.82	8,4	2,00	3,025	20,71
	16-30.04.82	7,8	4,15	6,05	36,65
2	1-15.04.82	8,1	1,14	2,255	14,79
	16-30.04.82	6,95	4,36	5,61	25,90
3	1-15.04.82	5,1	1,66	2,09	15,78
	16-30.04.82	5,7	3,47	5,34	20,10
4	1-30.04.82	6,9	3,84	5,50	31,10
5	1-15.04.82	7,3	1,26	2,145	19,40
	16-30.04.82	7,2	3,69	9,08	46,10

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical Constitution ionic content mg/l		
			NH_4^+	NO_3^-	SO_4^{2-}
1	1-15.05.82	5,7	3,26	4,84	19,73
	16-31.05.82	7,7	2,00	2,92	15,55
2	1-15.05.82	7,2	2,30	3,58	11,11
	16-31.05.82	7,5	0,92	2,42	
3	1-15.05.82	5,4	2,79	2,64	10,76
	16-31.05.82	7,3	1,90	3,52	17,78
4	1-31.05.82	6,9			
5	1-15.05.82	6,8	2,64	3,46	21,97
	16-31.05.82	7,1	2,09	4,35	27,33

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical Constitution ionic content mg/l		
			NH_4^+	NO_3^-	SO_4^{2-}
1	1-15.06.82	7,7	5,68	9,19	11,11
	16-30.06.82	5,8	3,90	6,32	15,02
2	1-15.06.82	-	-	-	-
	16-30.06.82	5,2	3,75	5,34	11,36
3	1-15.06.82	7,6	4,76	9,02	13,78
	16-30.06.82	5,9	3,44	4,40	10,26
4	1-15.06.82				
	16-30.06.82	6,8	2,67	0,94	16,85
5	1-15.06.82	7,6	7,83	10,74	39,55
	16-30.06.82	6,8	4,61	8,91	23,45

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical Constitution ionic content mg/l		
			NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻
1	1-15.07.82	7,12	1,38	2,97	5,33
	16-31.07.82	8,30	2,80	6,05	23,81
2	1-15.07.82	6,6	2,05	3,08	14,22
	16-31.07.82	8,2	1,90	5,78	11,90
3	1-15.07.82	4,6	2,30	2,92	15,11
	16-31.07.82	4,8	2,58	7,15	19,58
4	1-15.07.82	7,1	1,04	3,69	10,37
	16-31.07.82				
5	1-15.07.82	7,3	3,38	3,19	21,33
	16-31.07.82	7,2	6,27	11,39	48,00

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical Constitution, ionic content mg/l		
			NH_4^+	NO_3^-	SO_4^{2-}
1	1-15.08.82	7,2	4,58	1,38	12,75
	16-31.08.82	6,1	1,75	3,41	9,92
2	1-15.08.82	6,4	2,46	3,30	11,25
	16-31.08.82	4,8	1,63	3,30	9,12
3	1-15.08.82	5,9	3,44	2,20	10,50
	16-31.08.82	4,1	1,84	2,86	6,35
4	1-15.08.82	6,1	0,83	2,26	10,31
	16-31.08.82				
5	1-15.08.82	6,4	4,30	1,82	12,38
	16-31,08.82	6,4	2,52	4,07	20,43

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical Constitution, ionic content mg/l		
			NH_4^+	NO_3^-	SO_4^{2-}
1	1-15.09.82	4,7	2,15	4,84	11,02
	16-30.09.82	4,4	4,90	7,43	18,83
2	1-15.09.82	4,1	1,54	3,36	6,29
	16-30.09.82	5,3	2,70	7,59	10,34
3	1-15.09.82	3,5	1,44,	3,46	8,46
	16-30.09.82	4,2	3,44	4,51	11,08
4	1-30.09.82	4,7	3,29	4,40	14,03
5	1-15.09.82	5,2	0,86	1,82	9,84
	16-30.09.82	5,9	2,76	5,23	20,31

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical Constitution, ionic content mg/l		
			NH_4^+	NO_3^-	SO_4^{2-}
1	1-15.10.82	5,02	3,13	4,24	23,57
	15-31.10.82	4,26	3,16	6,82	18,61
2	1-15.10.82	5,58	2,67	3,30	17,60
	15-31.10.82	5,28	3,16	4,29	6,21
3	1-15.10.82	5,18	2,40	2,20	13,93
	15-31.10.82	4,18	2,55	3,91	19,44
4	1-15.10.82	-	-	-	-
	15-31.10.82	4,41	2,09	2,64	14,07
5	1-15.10.82	5,98	3,13	1,95	26,57
	15-31.10.82	-	-	-	-

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical Constitution, innic content mg/l		
			NH_4^+	NO_3^-	SO_4^{2-}
1	1-15.11.82	-	-	-	-
	15-31.11.82	4,80	4,12	2,48	40,49
2	1-15.11.82	-	-	-	-
	15-30.11.82 rain snow	5,73 5,95	7,10 2,64	3,85 1,38	44,66 7,51
3	1-15.11.82	-	--	-	-
	15-30.11.82 rain snow	4,95	1,57	0,28	20,04
4	1-15.11.82	-	-	-	-
	15-30.11.82 rain snow	4,80	7,40	7,98	151,10
5	1-15.11.82	-	-	-	-
	15-30.11.82 snow	6,01	3,47	3,41	57,60

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical constitution, ionic content mg/l		
			NH_4^+	NO_3^-	SO_4^{2-}
1	1-15.12.82 rain	4,8	2,00	3,46	27,57
	16-31.12.82 snow				
	1-15.12.82 rain	4,8	2,00	3,46	27,57
	16-31.12.82 snow	3,9	1,14	3,91	33,90
2	1-15.12.82 rain	4,2	2,61	3,35	40,86
	16-31.12.82 snow				
	1-15.12.82 rain	4,2	2,61	3,35	40,86
	16-31.12.82 snow	4,9	3,29	3,08	8,41
	1-15.12.82 rain	4,9	3,29	3,08	8,41
	16-31.12.82 snow	5,9	4,06	2,70	11,38
3	1-15.12.82 rain	3,8	5,38	4,12	24,99
	16-31.12.82 snow				
	1-15.12.82 rain	3,8	5,38	4,12	24,99
	16-31.12.82 snow	6,2	2,00	1,15	17,45
	1-15.12.82 rain	6,2	2,00	1,15	17,45
	16-31.12.82 snow	4,1	1,44	3,08	14,33
	1-15.12.82 rain	4,1	1,44	3,08	14,33
	16-31.12.82 snow	5,8	3,59	3,63	14,33
4	1-31.12.82 rain	4,8	0,92	5,50	28,21
	1-31.12.82 snow				
5	1-15.12.82 rain	6,1	4,30	3,52	52,36
	16-31.12.82 snow				
	1-15.12.82 rain	6,1	4,30	3,52	52,36
	16-31.12.82 snow	5,4	3,13	3,63	34,58
	1-15.12.82 rain	5,4	3,13	3,63	34,58
	16-31.12.82 snow				

Rainfall Determination Results

Stand	measurments period day, month, year	pH	Rainfall chemical constitution, ionic content mg/l		
			NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻
1	1-15.01.83 snow	7,3	3,04	3,03	14,0
	16-31.01.83 rain	4,5	3,23	4,02	26,95
	snow snow	5,5	1,75	3,19	17,05
2	1-15.01.83 snow	5,1	4,61	2,64	16,80
	16-31.01.83 rain	4,1	2,15	2,92	14,32
	snow snow	5,7	0,77	3,03	3,37
3	1-15.01.83 snow	6,6	4,67	0,99	6,40
	16-31.01.83 rain	3,7	1,47	2,26	7,37
	snow snow	5,5	1,84	1,65	10,02
4	-	-	-	-	-
5	1-15.01.83 snow	6,9	5,65	1,93	24,00
	16-31.01.83 rain	4,3	1,94	2,53	19,16
	snow snow	7,0	2,30	3,74	19,58

Rainfall Determination, Results

Stand	measurments period day, month, year	pH	Rainfall chemical constitution , ionic content mg/l		
			NH ₄ ⁺	NO ₃ ⁻	SO ₄ ²⁻
1	1-15.02.83 rain	4,4	5,38	6,33	25,86
	snow				
	snow	5,4	3,38	3,19	13,05
	16-28.02.83 snow	5,0	11,06	15,68	104,43
2	1-15.02.83 rain	4,7	3,84	6,05	20,98
	snow				
	snow	5,8	2,61	3,58	11,18
	16-28,02.83 snow	7,2	4,36	8,80	34,53
3	1-15.02.83 rain	4,5	5,06	5,28	24,70
	snow				
	snow	6,9	3,60	1,93	9,26
	16-28.02.83 snow	-	-	-	-
4	1-28.02.83 snow	5,4	2,61	5,78	35,37
5	1-15.02.83 rain	4,8	3,38	5,23	43,80
	snow				
	snow	7,2	3,38	4,40	40,54
	16-28.02.83 snow	7,1	11,06	21,50	134,33

WET DEPOSITION OF AMMONIUM IN EUROPE

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Abstract

Ammonium concentration data in precipitation throughout Europe have been gathered to derive a concentration and a deposition field for ammonium in Europe. A total number of 218 measuring sites were considered. In view of the changes of the ammonium concentrations in precipitation once sampled, a correction procedure has been proposed. Thus making allowance for the type of sampler used, the length of the sampling period and the use of light protected or non light protected sampling bottles. The total wet deposition flux of ammonium in Europe amounts to $2.6 \text{ Mt NH}_4 \text{ y}^{-1}$. In several parts of Europe the flux cannot be estimated very reliably, because of the lack of measuring sites. This holds especially for the southern and eastern parts of Europe as well as maritime areas, i.e. the North Sea.

Introduction

Nowadays there exist many precipitation networks in Europe operating with the primary goal to monitor concentrations of components in precipitation. Our main interest concerns data from these networks referring to the period 1975-1985, because our objective is to get an impression of the average wet deposition of ammonium in Europe about 1980.

Data from chemical precipitation networks were accepted for a first consideration, if the following conditions were fulfilled:

- measurements at a measuring site have been performed at least during a complete period of 12 months.
- in view of the correction procedure information about sampling details (type of equipment, length of sampling period) should be available.

By doing so we compiled information from 2 European, 5 national and 12 local networks, all together representing a total number of 218 measuring sites throughout Europe (Figure 1).

Correction procedure

Our main assumption underlying our calculations is that the ammonium concentration in precipitation sampled with a wet-only sampler with light protected sample bottles during a short sampling period, is most in agreement with reality.

If precipitation is sampled with a bulk sampler also a part of the dry deposition is monitored.

If sample bottles are not protected against light the light induced action of micro-organisms causes the ammonium concentration in precipitation already sampled to be lowered. Mainly based on the results published by Ridder et al. (1984) we propose a correction procedure as shown in Table 1.

The wet deposition of ammonium in Europe

From the results reported for each measuring site a volume-weighted average value for a period of a year (or longer) has been calculated, regardless of the year(s) for which results were reported. Next the appropriate correction factor was applied. Calculations which give the final deposition field were based on the IE grid system. This is a grid system with an approximate grid size of $75 \times 75 \text{ km}^2$ at 60°N .

If more measuring sites appeared to be located within the same grid element, first a volume-weighted average concentration was calculated for that specific grid element. Depositions in grid elements were calculated on the basis of the average ammonium concentration and amount of precipitation from meteorological observations in grid elements.

The deposition field (Figure 2) has been derived by an interpolation procedure.

Countrywise depositions, derived from the deposition field, are given in Table 2.

The total wet deposition in Europe, excluding the Soviet Union, amounts to $2.6 \text{ Mt NH}_4 \text{ y}^{-1}$.

Discussion

We have the impression that the use of correction factors, although one might discuss the absolute value of the correction factors, leads to a better estimate of the wet deposition flux of ammonium in Europe. Nevertheless there are several areas in Europe for which the wet deposition flux is not estimated very well or affected with a high uncertainty. The latter holds for southern and eastern European countries, primarily because of the small number of measuring sites. Furthermore the deposition field shows that areas where high ammonia emission occur, receive a high wet deposition flux of ammonium; this holds for the Netherlands and the western part of the Federal Republic of Germany. High ammonia emissions occur also in Denmark and in the north-western part of France (Figure 3).

The deposition field shows no enhanced values for these areas, which is likely to be caused by the lack of measuring sites in these areas.

In literature no estimates have been presented for the wet deposition flux of ammonium in Europe for around the year 1980. However, Bonis et al. (1980) give an estimate of the wet deposition flux of ammonium in Europe in 1960. After correcting their estimate (data obtained with bulk samplers, 1 month sampling period) a flux of 1.9 Mt NH_4 results. The conclusion could be that the wet deposition flux has increased by 35% in a 20-year period.

Reference

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Table 1: Sampling details in relation to correction factors

Sampling detail	correction factor
-bulk sampler	0.80
-wet-only sampler	1.00
-sampling period (no protection against light)	
day	1.09
week	1.15
month	1.21
-sampling period (light protected)	1.00*

* regardless of the length of the sampling period

Table 2: Wet deposition of ammonium in
European countries

country	number of measuring sites	wet deposition (kt NH ₄ y ⁻¹)
Austria	10	56
Belgium	1	34
Bulgaria	0	88
Czechoslovakia	8	86
Denmark	3	29
Finland	9	129
France	9	241
FRG	46	196
GDR	1	91
Greece	0	44
Hungary	1	73
Ireland	9	20
Italy	13	154
Luxemburg	0	2
Netherlands	22	57
Norway	9	106
Poland	1	336
Romania	6	214
Spain	0	112
Sweden	21	190
Portugal	2	21
Switzerland	1	28
U.K.	33	121
Yugoslavia	4	170

Figure 1. Centrepoinets of grid elements (IE grid) for which chemical precipitation data are available.

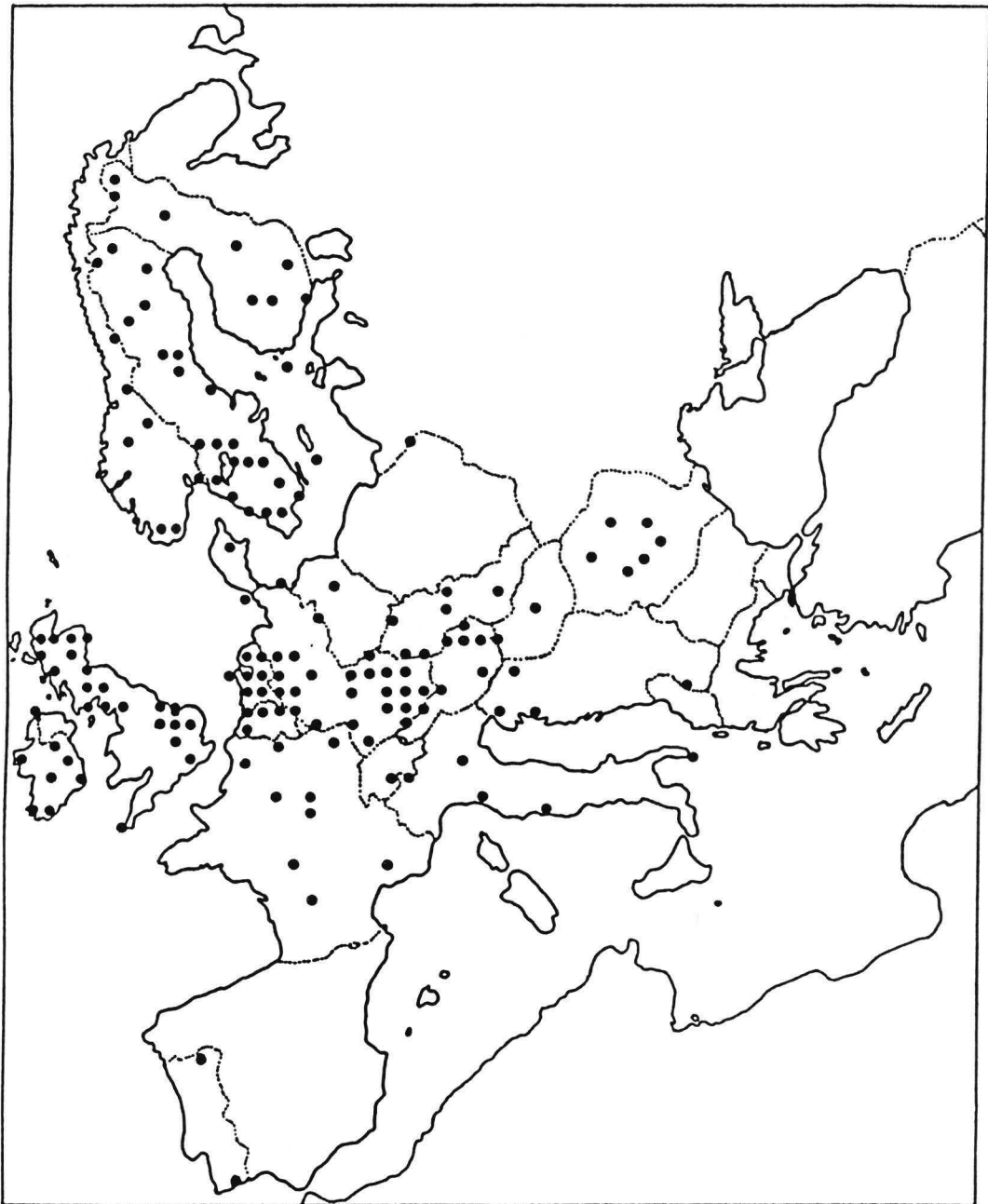
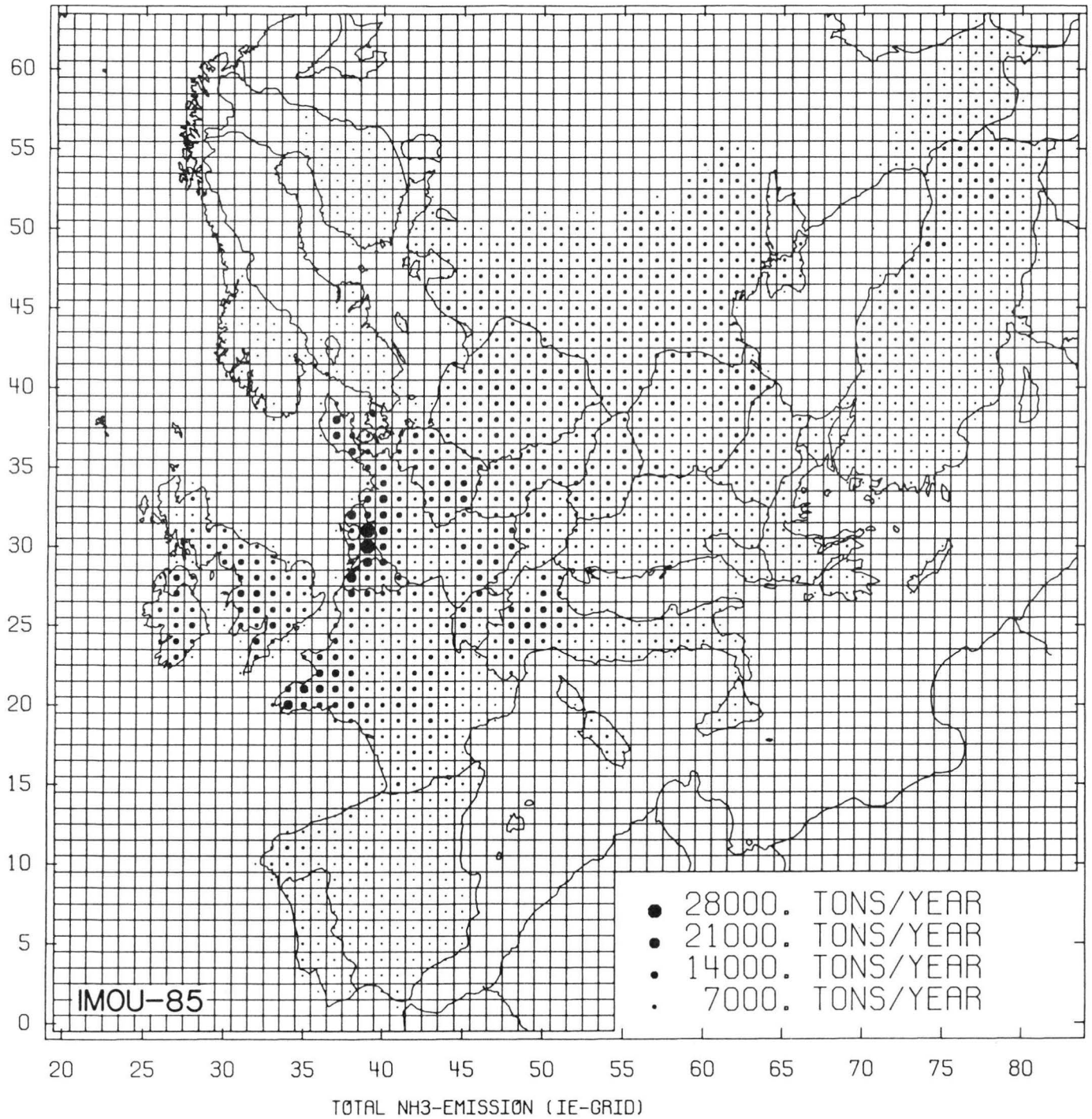


Figure 2. Wet deposition field for ammonium
(data in $\text{mmol m}^{-2} \text{y}^{-1}$).



Figure 3. Anthropogenic ammonia emissions in Europe
(~1982).

EMISSIONS < 488.082 NOT PLOTTED.



A LONG-RANGE TRANSPORT MODEL FOR AMMONIA AND AMMONIUM FOR EUROPE

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A Lagrangian long-range receptor oriented transport model was developed for ammonia and ammonium for Europe (Asman and Janssen, 1986). Many aspects of the behaviour of ammonia are different from the behaviour of, for example, sulphur dioxide. As a consequence not only parameter values for ammonia are different from those for sulphur dioxide, but also the model is different. This is necessary because ammonia has a relatively high dry deposition velocity and a relatively high reaction rate and because most of the ammonia is emitted from sources at or near ground-level. As a result the ammonia concentrations at ground-level can be influenced to a considerable extent by nearby emissions and by the adopted values of the dry deposition velocity and the reaction rate. To get reasonable model results the behaviour of ammonia near the earth's surface should be treated with more care than would be necessary for sulphur dioxide. In the following sections information concerning the parameters in the model is presented.

1. Emission data used

The gridded (net) NH_3 emission data used in the model are based upon the work of Buijsman et al. (1986). To take account of sources which could not be included in their gridded emission survey the emission is raised by 20%. Moreover, emissions for Iceland, Morocco, Algeria, Tunisia, Libya and an extended part of the USSR were added. No important sources for NH_4^+ are known, which means that all NH_4^+ found in the atmosphere originates from the conversion of emitted NH_3 . To compute historical concentration and deposition patterns (1870-1980) historical emissions of NH_3 were estimated from historical animal and fertilizer statistics (Asman et al., 1987). The same emission factors were used for 1870 and 1980, although the emission factors are likely to be lower in 1870.

2. Dry deposition of ammonia and ammonium

An upward flux of NH_3 will exist when the partial pressure of NH_3 (P_{NH_3}) of the earth's surface (e.g. manure etc.) is larger than the P_{NH_3} of the ambient air. A downward flux of NH_3 will exist in the opposite case. The flux can be modelled if at least P_{NH_3} of the earth's surface would be known as a function of time (e.g. season or time after spreading of manure), temperature and humidity (occurrence of precipitation) in connection with other meteorological circumstances (eddy diffusivity). But these parameters are mostly not known. Furthermore the fluxes should be overall fluxes representative of large areas ($150 \times 150 \text{ km}^2$). Within such areas different forms of land-use can exist with different P_{NH_3} , which even depend on the season. This makes it nearly impossible to model a flux. Only a rough estimate of the yearly averaged net emission of NH_3 from agricultural areas exists. The only way a flux can be estimated is then by using this emission and a somewhat reduced dry deposition velocity to account for the time that no net dry deposition exists because of emission. This approach was used in our model. The measured dry deposition velocity over natural terrains during daytime (moorland, heather) can be as high as $1.9 \times 10^{-2} \text{ m.s}^{-1}$ (Duyzer et al., 1987). We adopted a value of $8 \times 10^{-3} \text{ m.s}^{-1}$ for the overall dry deposition velocity of NH_3 in our model. For NH_4^+ a dry

deposition velocity of $1 \times 10^{-3} \text{ m.s}^{-1}$ was adopted.

3. Wet deposition of ammonia and ammonium

It should be pointed out here that for NH_3 no equilibrium exists between the air concentration at ground level and the concentration in raindrops, like that usually assumed for SO_2 . Moreover, the solubility of NH_3 is much larger than for SO_2 (Dasgupta and Dong, 1986). The solubility of NH_3 is enhanced by the reaction with H^+ in the drop. In the cloud most of the NH_3 will be transferred to cloud drops and because of the relatively long lifetime of the drops equilibrium will exist between the very low NH_3 concentration in air and the concentration in the drops.

The mass transfer rate through the drop-air interface is not high enough for raindrops of most sizes to reach saturation during their fall from the cloud base to the earth's surface. As the NH_3 concentration in the cloud is much lower than at ground-level, no equilibrium will exist between the air concentration at ground level and the NH_4^+ concentration in precipitation.

The wet deposition of NH_3 and NH_4^+ is computed by using a precipitation rate dependent scavenging ratio (Table 1).

4. Reaction of ammonia and ammonium

In Europe most ammonia will react with acid aerosol (e.g. containing H_2SO_4). A minor part will react with gaseous HNO_3 :
 $\text{NH}_3 + \text{HNO}_3 \leftrightarrow \text{NH}_4\text{NO}_3$. Reaction with OH , O and $\text{O}(^1\text{D})$ seems to be unimportant. We adopted a value of $8 \times 10^{-5} \text{ s}^{-1}$ for the pseudo-first order reaction rate constant of NH_3 to NH_4^+ . It is based on the results of sensitivity studies. This value is rather uncertain as it is difficult to measure a reaction rate (Erisman et al., 1987).

5. Parameter values used in the model

In the Lagrangian model used in our transport calculations instantaneous homogeneous mixing of emitted and produced components over the mixing layer is assumed, although it takes some time for the mixing to take place. Long-range transport and deposition processes can be described adequately with this simple model, provided two types of corrections are applied:

- a. Near the source, at or near the earth's surface, ground level concentration will be higher than computed if instantaneous mixing is assumed. This results in a relatively faster depletion near the source due to enhanced dry deposition. To correct for this effect the source strength Q (mole. s^{-1}) used in the model is reduced to a certain fraction of Q : γQ . However, if this reduced source strength is used right from the point of emission, not only will the rate of dry deposition near the source be underestimated but also the rate of production of reaction products. This is corrected for in the model by the introduction of an apparent direct local deposition αQ at the source and an apparent direct emission αQ of the reaction product (where $\alpha + \beta + \gamma = 1$; Janssen and Asman, 1986).
- b. At longer distances from the source when the components can be expected to be fully mixed, a vertical concentration gradient will still be present. The ground level concentration is lower than the concentration aloft, because depletion due to dry deposition occurs near the earth's surface. The dry deposition flux would therefore be overestimated if it were computed from the height-averaged concentrations (\bar{c}) computed in the model and the dry deposition velocity at reference height. This can be avoided by the introduction of effective dry deposition velocities (v_e) to be used in the model for both the precursor and the product. The dry deposition flux is then $\bar{c} \cdot v_e$.

Close to the source the deposition rate of NH_3 is relatively high. A good parametrization of this phenomenon is important as α not only determines the amount of NH_3 that is available for long-range transport, but also determines the calculated ground level concentration to a large

extent. Numerical values of α , β and v_e for NH_3 and NH_4^+ have been derived with a detailed numerical reactive diffusion model using K-theory (Janssen and Asman, 1986).

In our model the following equations are used for the height-averaged airborne concentrations of NH_3 and NH_4^+ . (The subscript 1 refers to NH_3 ; the subscript 2 refers to NH_4^+ aerosol).

$$\frac{D\bar{c}_1}{Dt} = - \left(\frac{v_{1e}}{H} + \frac{S_1 \cdot I}{H} + k \right) \cdot \bar{c}_1 + (1 - \alpha_1 - \beta) \cdot \frac{E}{H} \quad (1)$$

$$\frac{D\bar{c}_2}{Dt} = - \left(\frac{v_{2e}}{H} + \frac{S_2 \cdot I}{H} \right) \cdot \bar{c}_2 + k \cdot \bar{c}_1 + (\beta - \alpha_2) \cdot \frac{E}{H} \quad (2)$$

The operator D/Dt is the total time derivative, I is the precipitation rate (m.s.^{-1}) and E is the ammonia emission rate in the grid element ($\text{moles .m}^{-2} \cdot \text{s}^{-1}$). The remaining parameters are presented in Table 1 together with their values. The same parameter values were used to calculate historical concentration and deposition patterns.

6. Results and discussion

The results of the model calculations are shown in Figures 1-4. For NH_3 no measurements can be used to check model results directly because measured concentrations are not representative of the $150 \times 150 \text{ km}^2$ area for which the concentrations are calculated. Moreover almost no measurements of NH_3 exist. For NH_4^+ in aerosols a significant correlation exists between computed and measured concentrations ($r=0.71$, $n=16$). For NH_4^+ in precipitation the agreement between model results and measurements is good ($r=0.73$, $n=90$).

Although the model calculations give satisfactory results, this does not mean that our present knowledge of the atmospheric behaviour of ammonia and ammonium is in fact sufficient. One of the basic problems is that the emissions of ammonia are more uncertain than the emissions of sulphur dioxide. Adopting certain emission factors for ammonia has some influence on other model parameters (like the dry deposition velocity and the reaction rate) if the calculated concentrations should remain in agreement with measured data.

(A more detailed description of the model will appear in Atmospheric Environment).

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Table 1. Parameter values used in the model.

symbol	explanation	parameter value
v_1	Dry deposition velocity for NH_3	$8.0 \times 10^{-3} \text{ m s}^{-1}$
v_{1e}	Effective dry deposition velocity for NH_3	$5.6 \times 10^{-3} \text{ m s}^{-1}$
v_2	Dry deposition velocity for NH_4^+	$1.0 \times 10^{-3} \text{ m s}^{-1}$
v_{2e}	Effective dry deposition velocity for NH_4^+	$1.0 \times 10^{-3} \text{ m s}^{-1}$
S_1	Scavenging ratio for NH_3	$5000 \cdot I^{-0.36} (\text{mole m}^{-3} \text{ prec}) / (\text{mole m}^{-3} \text{ air})^a$
S_2	Scavenging ratio for NH_4^+	$5000 \cdot I^{-0.36} (\text{mole m}^{-3} \text{ prec}) / (\text{mole m}^{-3} \text{ air})^a$
k	Pseudo first order reaction rate NH_3 to NH_4^+	$8.0 \times 10^{-5} \text{ s}^{-1}$
α_1	Apparent direct local dry deposition of NH_3	2.4×10^{-1}
α_2	Apparent direct local dry deposition of NH_4^+	8.6×10^{-3}
β	Apparent fraction of the emission emitted as NH_4^+	9.2×10^{-2}
H	Mixing height	800 m

a) I = precipitation rate (m s^{-1})

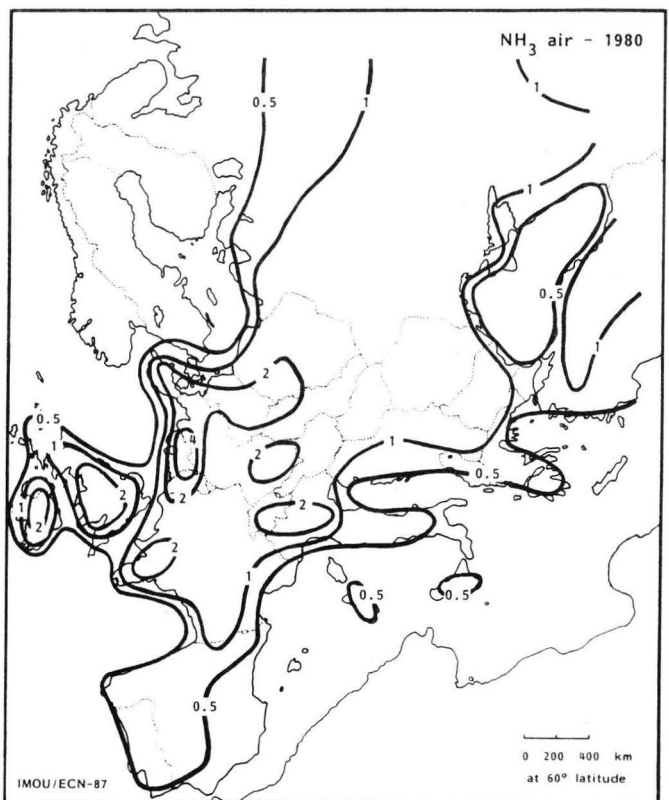
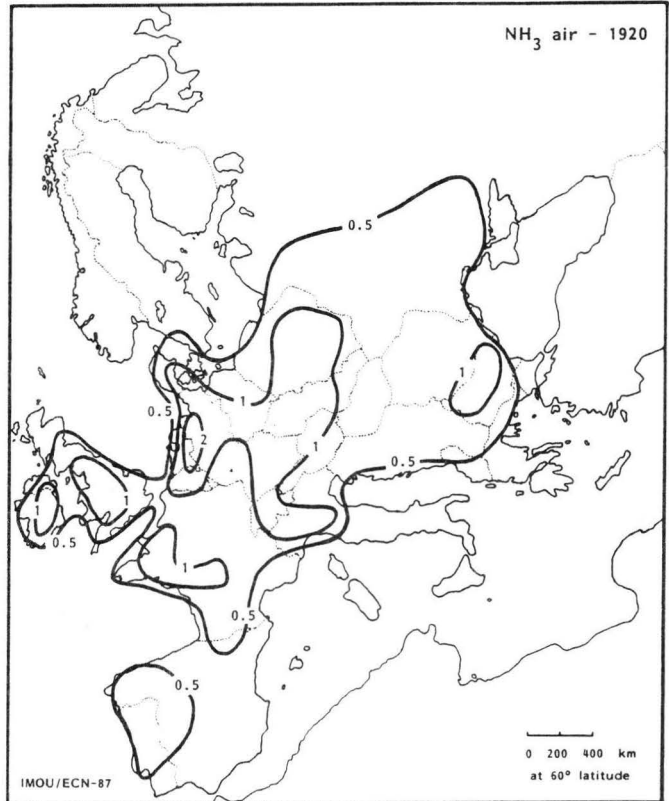
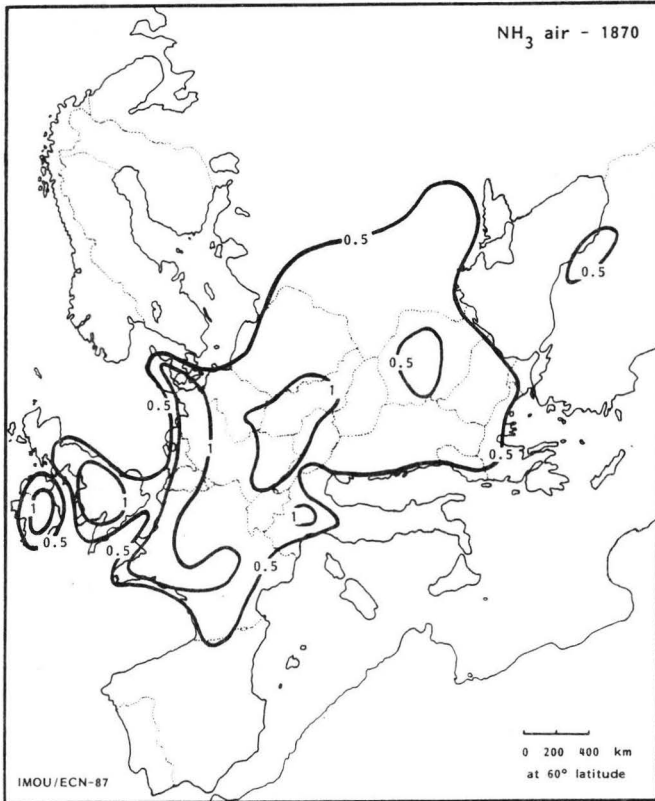
Figure 1. NH_3 concentration in air (10^{-6} g.m^{-3})

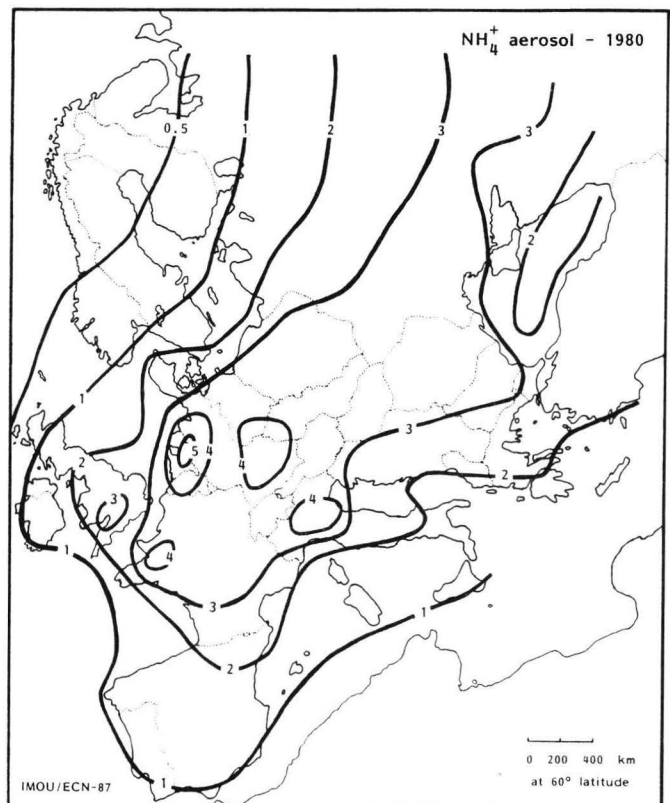
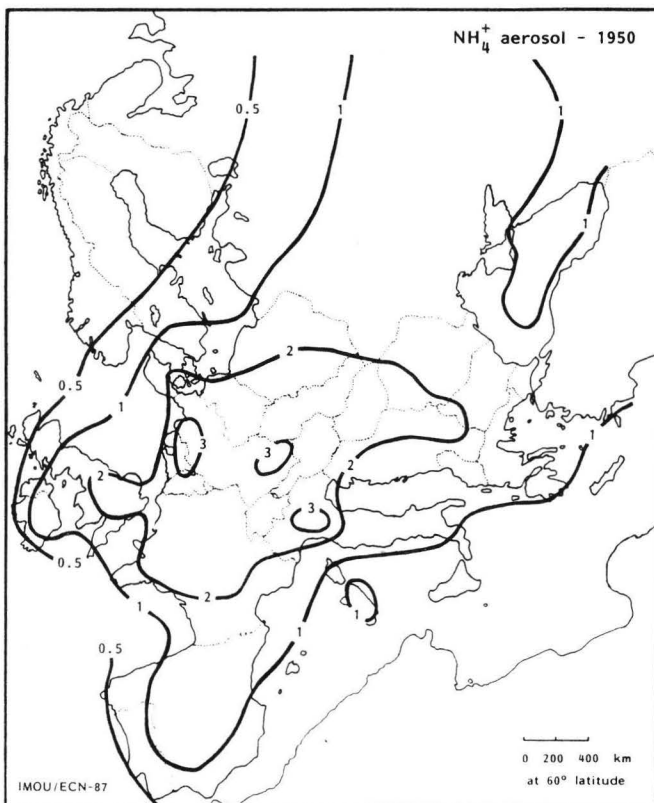
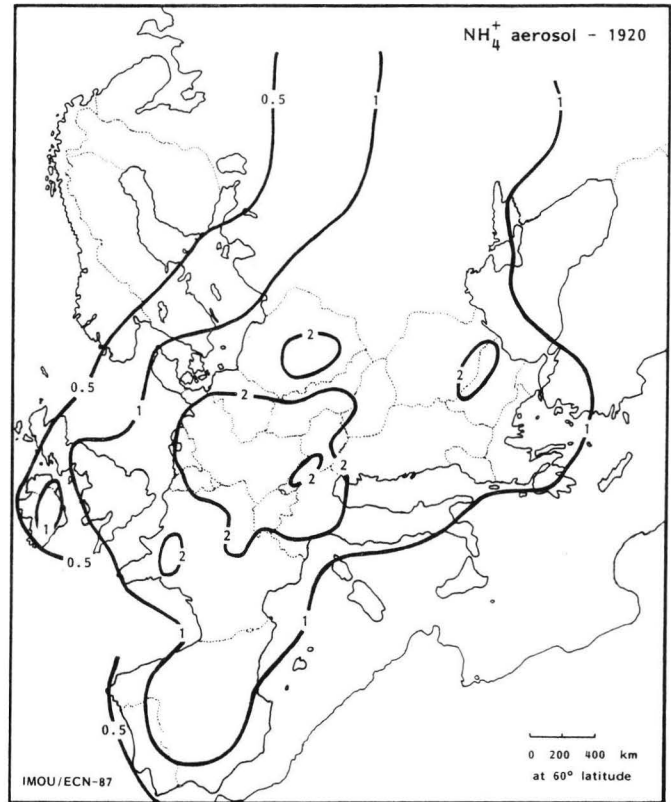
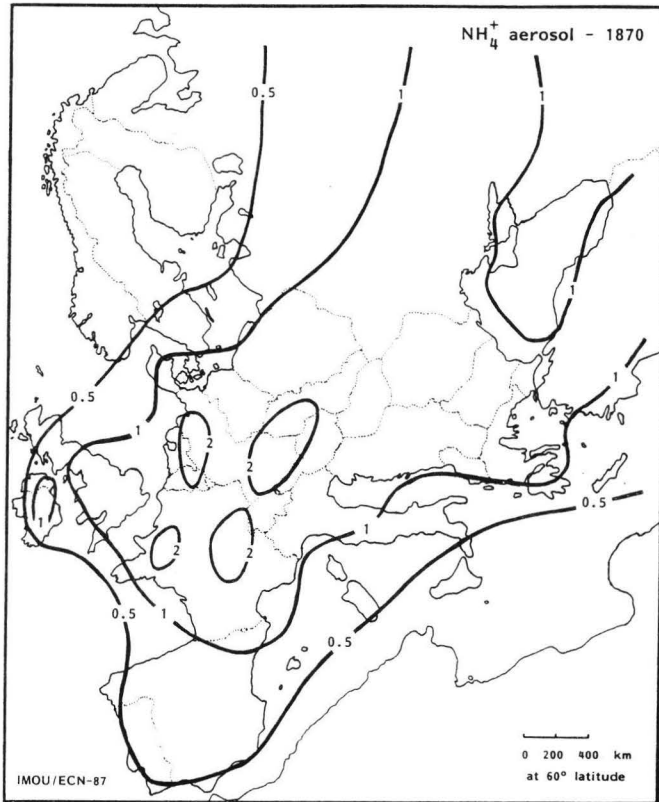
Figure 2 . NH_4^+ aerosol concentration (10^{-6} g.m^{-3})

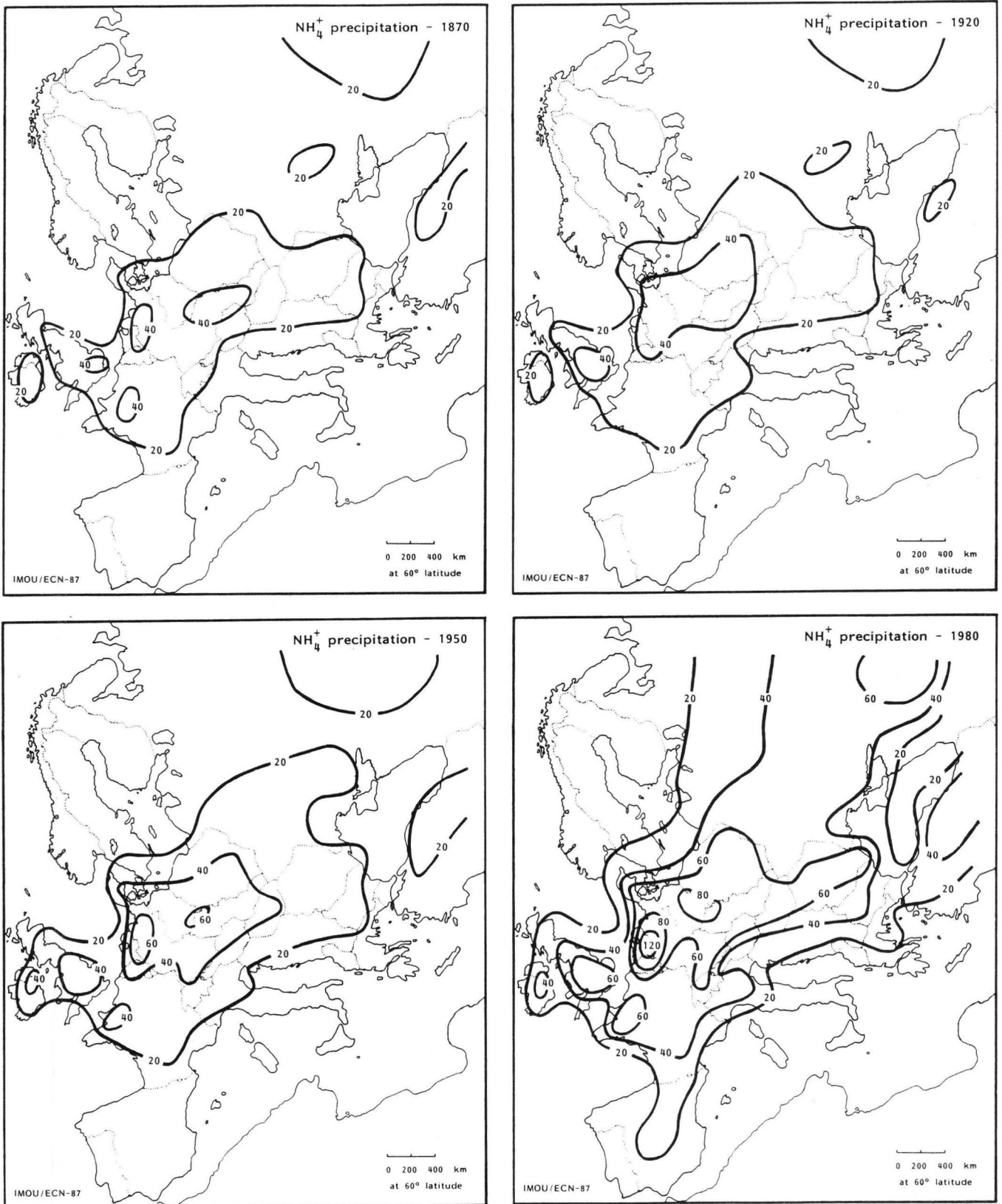
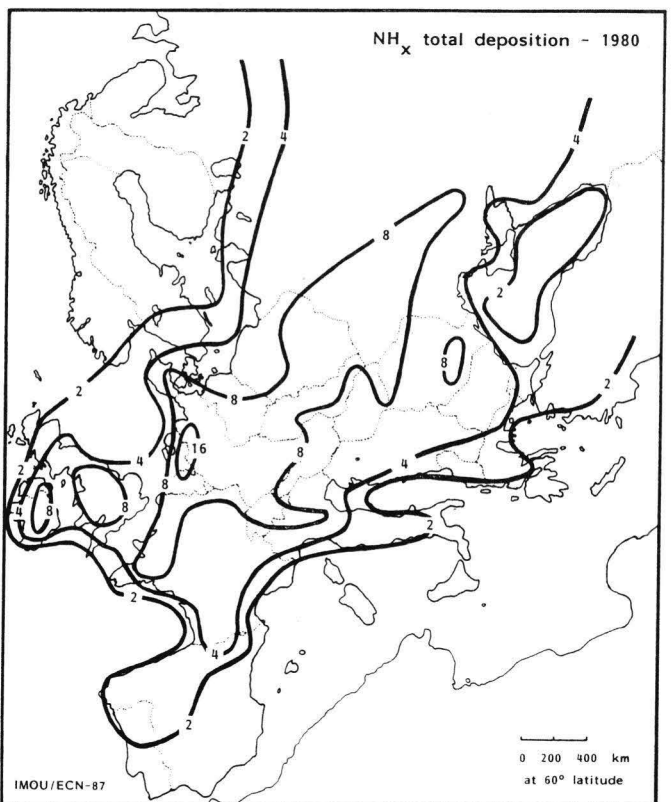
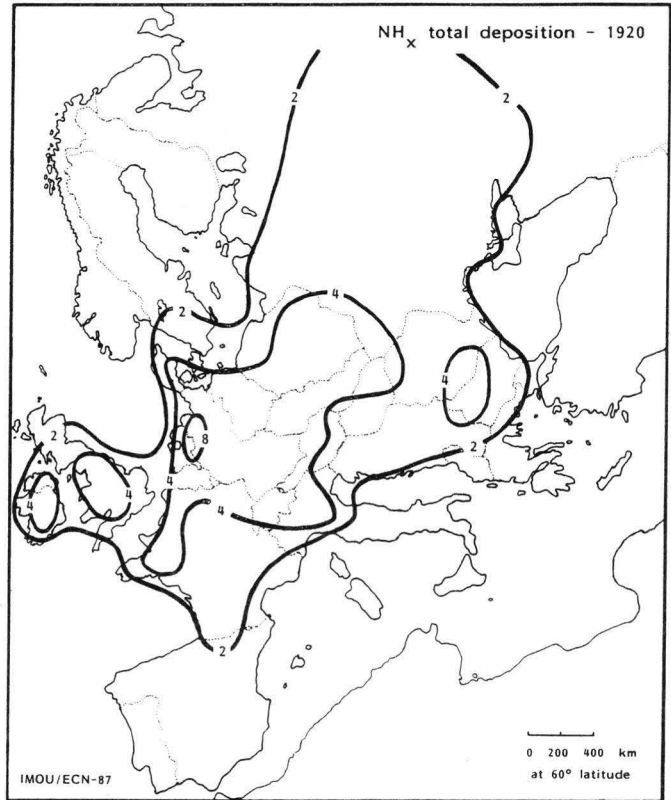
Figure 3 . NH_4^+ concentration in precipitation ($10^{-6} \text{ mole.l}^{-1}$)

Figure 4. Total NH_x deposition ($10^2 \text{ mole} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$)

Modelling the Long Range Transport of Ammonia and Ammonium Compounds

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1. INTRODUCTION

Interest in the ammonium ion content of precipitation dates from 1749, but it was the agricultural chemists who started many of the early investigations of ammonium compounds in rain water during the later part of the 19th Century. Some of the early observations have been reviewed by Erikssen, (1952) and his review shows ammonium concentrations in the range 0.04 - 1 mg N-NH₄ l⁻¹. The impression formed in these early studies was that natural sources were the most significant.

The recent interest in the acidification of the environment has largely addressed the long range transport and deposition of acidic sulphur species. Oxidized nitrogen species have been considered in this context but the role of ammonia and its compounds has yet to be assessed quantitatively. Ammonia has long been suspected to play a role in the acidification of remote environments through a number of possible mechanisms. These may involve:

- (i) the participation of ammonia in the cloud droplet phase reactions of sulphur dioxide,
- (ii) the influence of ammonia on the dry deposition removal of sulphur dioxide,
- (iii) the partial neutralisation of strong acids in precipitation,
- (iv) the formation of ammonium aerosols and their potential long range transport.

In this study, a simple trajectory model approach is employed to study the emission, transport, transformation and deposition of ammonia and its compounds over north west Europe. The aim is to evaluate the relative importance of the different elementary processes in the ammonia life cycle and to investigate where significant gaps in present understanding remain. Attention is directed to the formation of ammonium aerosols and the potential impact that this process may have on the deposition of acidity in remote environments.

2. THE TRAJECTORY MODEL

The behaviour of ammonia and its compounds over north west Europe has been studied using a simple trajectory model approach. The initial results obtained with this model have been presented elsewhere (Derwent and Nodop, 1987; Derwent, Dollard and Metcalfe, 1987), where the model philosophy and its origins in the pioneering work of Eliassen, (1978) have been pointed out.

The present computer modelling study has adopted a simple representation of the life cycle of ammonia and its compounds in the atmosphere. Ammonia is emitted into the atmosphere from intensive livestock farming, from other agricultural processes, from fertilizer manufacture and from coal combustion (Bottger, Ehhalt and Gravenhorst, 1978). Ammonia is readily removed from the atmosphere by dry deposition to the earth's surface. This process is not the only removal process operating since the ammonium ion is present in significant concentrations in both the atmospheric aerosol and in precipitation. Washout and rainout of ammonia could account for some of the ammonium ion in precipitation. However, chemical reactions to form ammonium sulphate, nitrate and chloride aerosols would explain the presence of ammonium ions in both aerosol and precipitation, the latter through the rain-out of cloud condensation nuclei.

A trajectory model approach has been used to provide a long-term description of the behaviour at each one of 36 receptor sites in north west Europe. The receptor sites were selected monitoring sites within the United Nations Economic Commission for Europe (UN ECE), European Monitoring and Evaluation Programme (EMEP), chosen to give an even coverage of about 1 site per $5 \times 10^4 \text{ km}^2$ over the land area of Belgium, Denmark, France, Netherlands, Norway, Federal Republic of Germany, Republic of Ireland, Sweden and the United Kingdom. The behaviour at each receptor point was obtained by averaging over the results for 24 separate trajectories arriving at that point, suitably weighted by the frequencies of the winds in each 15° sector. The complex interplay between the individual elementary processes was described by considering a column of air of arbitrary cross-section, extending from the earth's surface to the top of the boundary layer. Within this 'air parcel', mixing was assumed to be instantaneous so that vertical and horizontal gradients could be neglected. The 'air parcel' moved over the emission grid following a single trajectory for the whole boundary layer depth, that is vertical wind shear was neglected.

Furthermore, the trajectories were assumed to be straight lines over a travel period of between 48 and 96 hours. This is clearly a gross approximation.

The basic assumptions and model input parameters adopted in the model are detailed in Table 1. The wind roses for the 36 receptor points have been taken from the daily sector allocations carried out by the Meteorological Synthesing Centre-W (MSC-W) for the 636 day period from 1 February 1981 to 29 October 1982 (Lemhaus, Saltbones and Eliassen, 1985). This analysis provides wind roses with a resolution of 45° and provides an additional category where no wind sector allocation has been possible. Three trajectories 15° apart have been taken within each 45° sector.

Figure 1 illustrates the chemical mechanism which has been assumed in this study and Table 2 contains the detailed assumptions made concerning the rate coefficients of the elementary processes. The differential equations representing the concentrations, c , of the model species, i , had the general form:

$$\frac{dc_i}{dt} = \frac{E_i}{A} + P_i - Q_i \cdot c_i - \frac{V_i}{h} \cdot c_i - L_i \cdot c_i$$

where E_i is the annual pollutant emission rate in mass units on the EMEP grid,
 A is the conversion factor between mass units and ppb s^{-1} ,
 P_i is the total production rate of the species by chemical conversion processes,
 $Q_i \cdot c_i$ is the total rate of removal by chemical conversion processes,
 V_i is the dry deposition velocity of the species at some standard reference height, typically 1 metre above the surface, (see Table 3),
 h is the boundary layer depth,
 and $L_i c_i$ is the total wet removal rate by wet processes.

Differential equations of the above form were set up for nitric oxide, nitrogen dioxide, ozone, nitric acid, ammonia, ammonium aerosol, nitrate aerosol, sulphur dioxide, sulphuric acid and sulphate aerosol and were integrated numerically using a variable-order Gear's method program FACSIMILE (Curtis and Sweetenham, 1985) on the Harwell CRAY XMP 24 computer.

The emissions of nitric oxide, sulphur dioxide and ammonia on the 150 km x 150 km EMEP grid were taken from Eliassen, (1987), Dovland and Saltbones, (1986) and Buijsman et al., (1985). The precipitation scavenging, through the $L.c_i$ terms in the above differential equations, employed a 'constant drizzle' approximation and has the advantage of being simple, yet mass conserving. The first order wet removal coefficients are tabulated in Table 1 and were obtained from a statistical model using a random distribution of wet and dry periods.

3. RESULTS WITH THE TRAJECTORY MODEL FOR AMMONIA AND ITS COMPOUNDS

The spatial pattern of gaseous ammonia concentrations is illustrated in figure 2. The calculated concentrations show a broad maximum of 1 ppb which covers much of the south west areas of England, northern France and Belgium. Much of continental Europe is found within the 0.5 ppb contour with concentrations falling off rapidly northwards across Scandinavia.

There are few concentration measurements against which these results can be compared. The calculated spatial pattern for ammonia over the United Kingdom does not appear to agree well with the available observations (Derwent, Dollard and Metcalfe, 1987). Depletion of gaseous ammonia by reaction with acidic species such as sulphuric and nitric acids forming aerosols appears to have dramatically reduced the ammonia concentrations. Either these chemical conversion steps have been overestimated or emissions underestimated, particularly over the intensily managed arable and pasture areas of central England.

The resulting calculated spatial pattern of ammonia dry deposition is given in figure 3. This results from the superposition of two separate patterns; the first representing dry deposition and reflecting the shapes in figure 2, the second representing immediate dry deposition within the grid square where the ammonia is emitted and reflecting the spatial pattern of the emissions. The dry deposition pattern therefore shows two maxima; one over the United Kingdom and a second over Denmark, the Netherlands and the Federal Republic of Germany.

The spatial pattern calculated for ammonium in precipitation shown in figure 4 reveals much less structure than the corresponding pattern for ammonia, reflecting the much longer residence time for ammonium aerosol in the model. Ammonium in precipitation shows a maximum of $0.8 \text{ mg N-NH}_4 \text{ l}^{-1}$ over the Federal

Republic of Germany with concentrations falling off northerly over Scandinavia and westerly over the United Kingdom to background levels of about 0.2 mg N-NH₄ l⁻¹.

Maps of the observed spatial patterns of ammonium in precipitation (Asman and Janssen, 1986; Nodop, Skjelmoen and Schaug, 1985) reveal the presence of a broad maximum covering much of the Federal Republic of Germany, Belgium and the Netherlands of over 1.1 mg N-NH₄ l⁻¹. The maximum appears to be significantly higher in concentration in the observations compared with the model and to encompass a wider geographical region. This points to the ammonia emissions being significantly underestimated despite the assumption of a substantial background contribution of 0.2 mg N-NH₄ l⁻¹ in the model calculations.

4. DISCUSSION OF THE RESULTS

The comparison of the model calculations with the available observations of ammonia and its compounds points to a significant underestimation in the emissions of ammonia to the atmosphere. It would be a straightforward matter to scale the available emission inventory to reduce the magnitude of the discrepancies, particularly with the ammonium concentrations in precipitation. This would, however, leave the difficult questions of what the additional ammonia source might be and why would its spatial distribution be the same as that for intensive livestock farming.

In figure 5, an alternative approach is proposed. The basic formulation described above considers ammonia as an input-output model with emissions in balance with dry deposition and chemical removal. The alternative formulation decouples the dry deposition from the chemical removal and strongly couples it with the emission process. The overall behaviour of ammonia is seen as an equilibrium. If ammonia concentrations are locally higher than a compensation point then dry deposition occurs. If ammonia concentrations are locally lower than a compensation point then net emission occurs.

The resulting pattern of ammonium concentrations in precipitation are shown in figure 6. This pattern assumes a compensation point concentration of 2 ppb for ammonia, a background ammonium concentration in precipitation of 0.2 mg N-NH₄ l⁻¹ and the NH₃ emissions from intensive livestock farming. In this calculation, the extra emission source is driven by the local rate of sulphuric

and nitric acid generation. The greater the rate of ammonia depletion in the atmosphere above the soil, the greater the loss of ammonia from the soil.

Enhanced ammonium concentrations in precipitation result when the additional ammonia source is included, removing some of the discrepancies between model and observations. To maintain a steady state concentration of 2 ppb ammonia over Belgium, the Netherlands and the Federal Republic of Germany in Figure 6 an additional NH_3 source is required whose emission strength is about one quarter of the gridded emissions given by Buijsman et al., (1985), and is in turn, slightly higher than emission estimates used by Asman and Janssen, (1986).

Clearly, it is not the purpose of this study to speculate what this additional source may be. It may reflect the uncertainties present in the simple trajectory model approach adopted or the emissions from intensive livestock farming or the emissions from intensively-managed arable or pasture lands.

5. ACKNOWLEDGEMENTS

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Table 1

Input parameters adopted in the simple trajectory model calculations
taken from Derwent, Dollard and Metcalfe (1987)

Input Parameter	Adopted Value
windspeed, u	7.5 m s ⁻¹
boundary layer depth, h	800 m
tropospheric baseline ozone concentrations, O ₃	30 ppb
hydroxyl radical concentration	0.8 x 10 ⁶ molecule cm ⁻³
'constant drizzle' wet removal rate coefficients, HNO ₃ , NH ₃ nitrate and sulphate aerosol	9 x 10 ⁻⁶ s ⁻¹ 1.3 x 10 ⁻⁵ s ⁻¹
sulphur dioxide oxidation rate	1.0 x 10 ⁻² h ⁻¹

Table 2

Chemical kinetic data employed in the trajectory model calculations
taken from Derwent, Dollard and Metcalfe (1987)

Reaction	Rate Coefficient	Units	Notes
$\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2$	$1.8 \times 10^{-12} \exp(-1370/T)$	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
$\text{NO}_2 + \text{h}\nu = \text{NO} + \text{O}$	$1.45 \times 10^{-2} \exp(-0.4 \text{ sec } \theta)$	s^{-1}	
$\text{O} + \text{O}_2 + \text{M} = \text{O}_3 + \text{M}$	$5.8 \times 10^{-34} (T/300)^{-2.6}$	$\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	
$\text{OH} + \text{NO}_2 + \text{M} = \text{HNO}_3 + \text{M}$	1.5×10^{-11}	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
$\text{O}_3 + \text{NO}_2 + \text{M} = \text{NO}_3 + \text{M}$	$1.2 \times 10^{-13} \exp(-2450/T)$	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
$\text{NO}_3 + \text{h}\nu = \text{NO}_2 + \text{O}$	$8.94 \times 10^{-2} \exp(-0.06 \text{ sec } \theta)$	s^{-1}	
$\text{NH}_3 + \text{HNO}_3 = \text{NH}_4\text{NO}_3$	1.0×10^{-14}	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	a
$\text{HNO}_3 = \text{Nitrate Aerosol}$	3.0×10^{-5}	s^{-1}	b
$\text{NO}_3 + \text{NO}_2 + \text{M} = \text{N}_2\text{O}_5$	$2.3 \times 10^{-13} \exp(-1000/T)$	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
$\text{N}_2\text{O}_5 = \text{Nitrate Aerosol}$	3.0×10^{-5}	s^{-1}	b
$\text{NH}_3 + \text{H}_2\text{SO}_4 = \text{Sulphate Aerosol}$	1.0×10^{-14}	$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	a

Notes:

T 288 K

Table 3

Parameters employed to represent dry deposition removal in the trajectory model calculations taken from Derwent, Dollard and Metcalfe (1987)

Pollutant	Parameter value, V_i , cm s^{-1}
nitric oxide (NO)	0
nitrogen dioxide (NO ₂)	0.15
gaseous nitric acid (HNO ₃)	4.0
ammonia (NH ₃)	1.0
sulphur dioxide	0.5
nitrate and sulphate aerosol	0.1

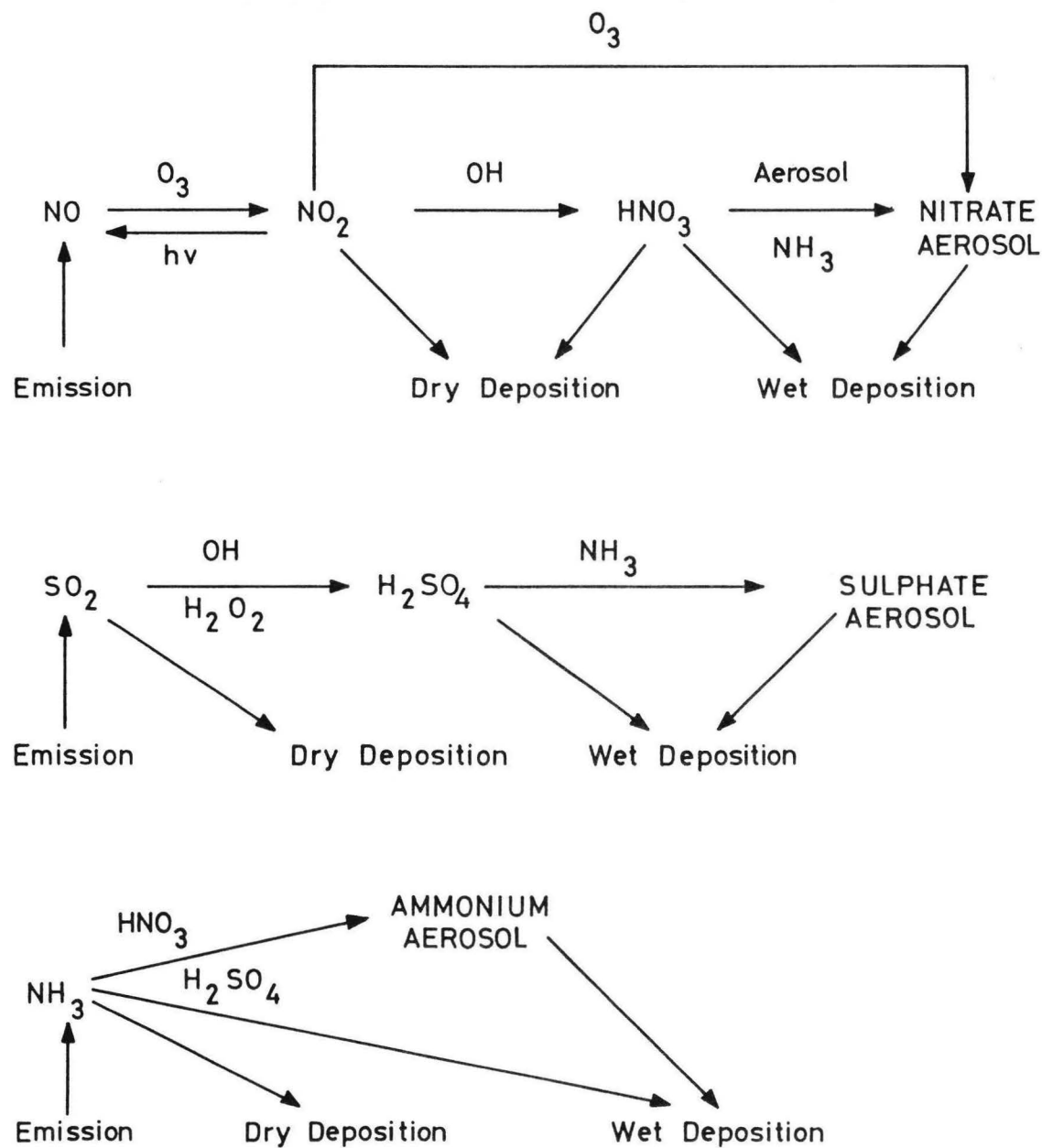


FIGURE 1. The chemical mechanism employed in the Harwell trajectory model.

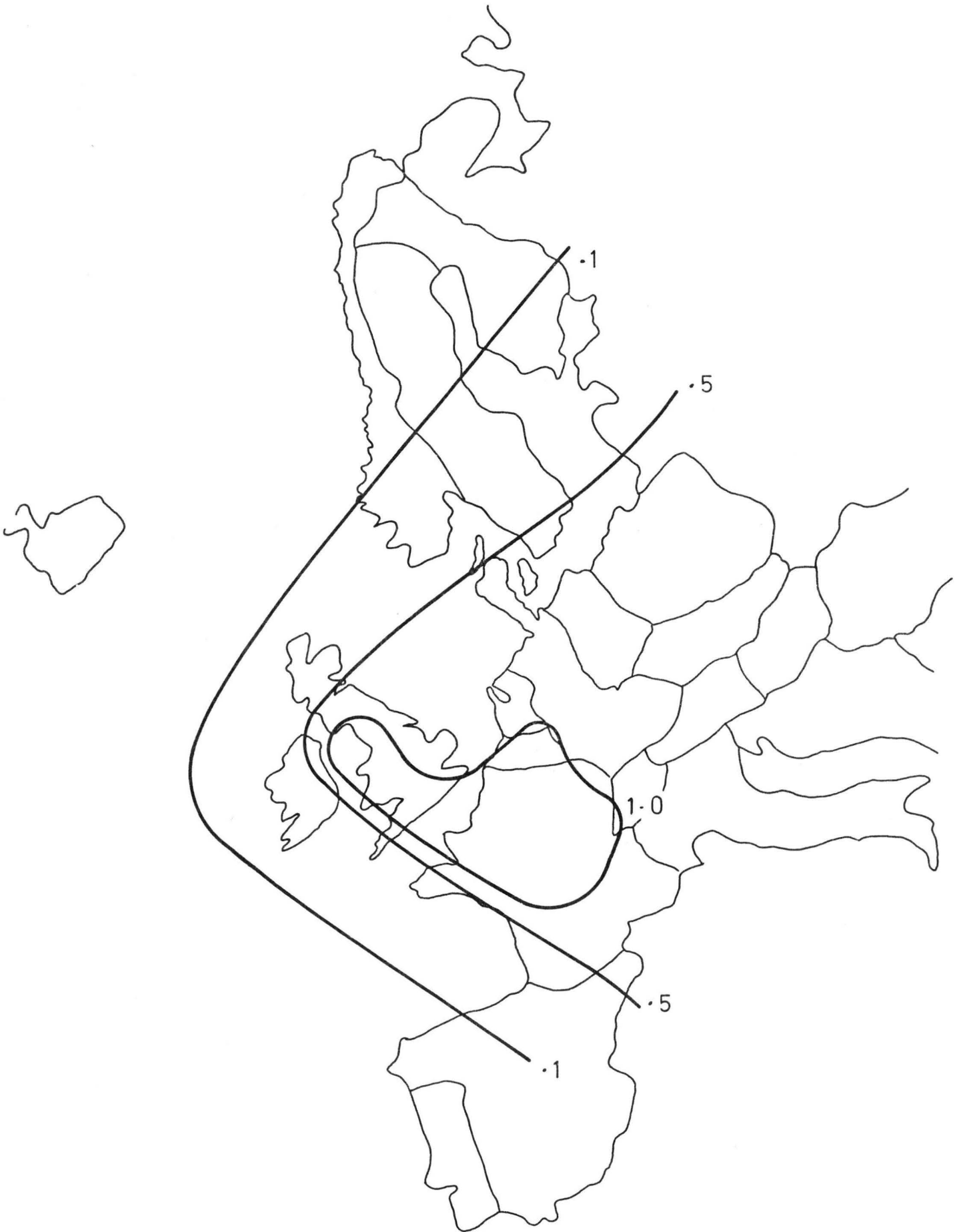


FIGURE 2. The spatial pattern of the ammonia concentrations in ppb calculated with the Harwell trajectory model.



FIGURE 3. The spatial pattern of the dry deposition of ammonia and its compounds in $\text{kg N ha}^{-1} \text{ yr}^{-1}$ calculated with the Harwell trajectory model.



FIGURE 4. The spatial pattern of the ammonium concentration in precipitation in $\text{mg N-NH}_4 \text{ l}^{-1}$ calculated with the Harwell trajectory model. A background precipitation concentration of $0.2 \text{ mg N-NH}_4 \text{ l}^{-1}$ has been assumed.

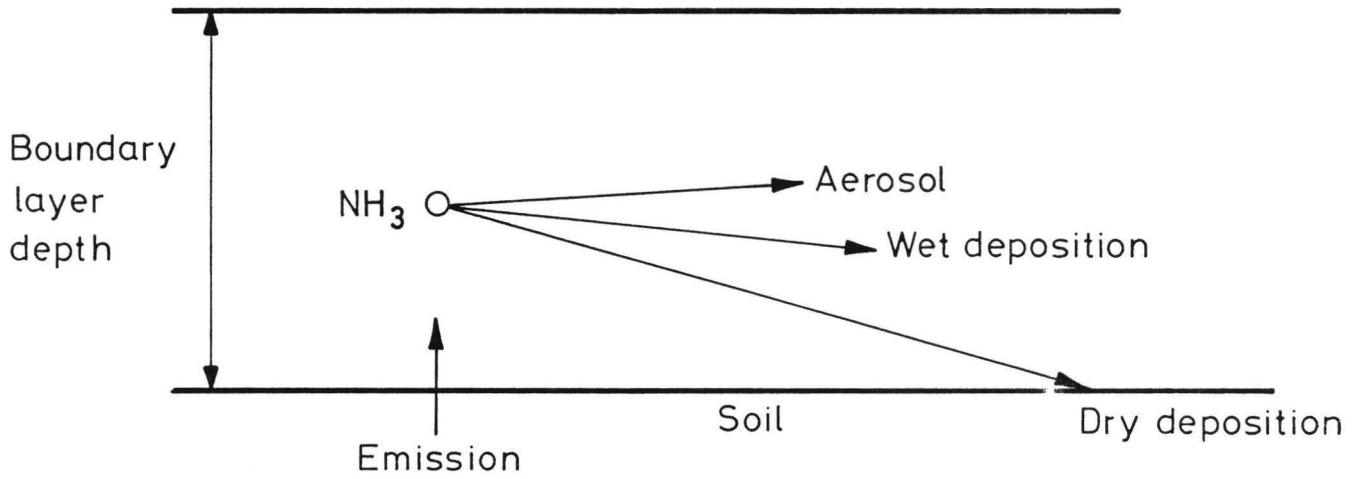
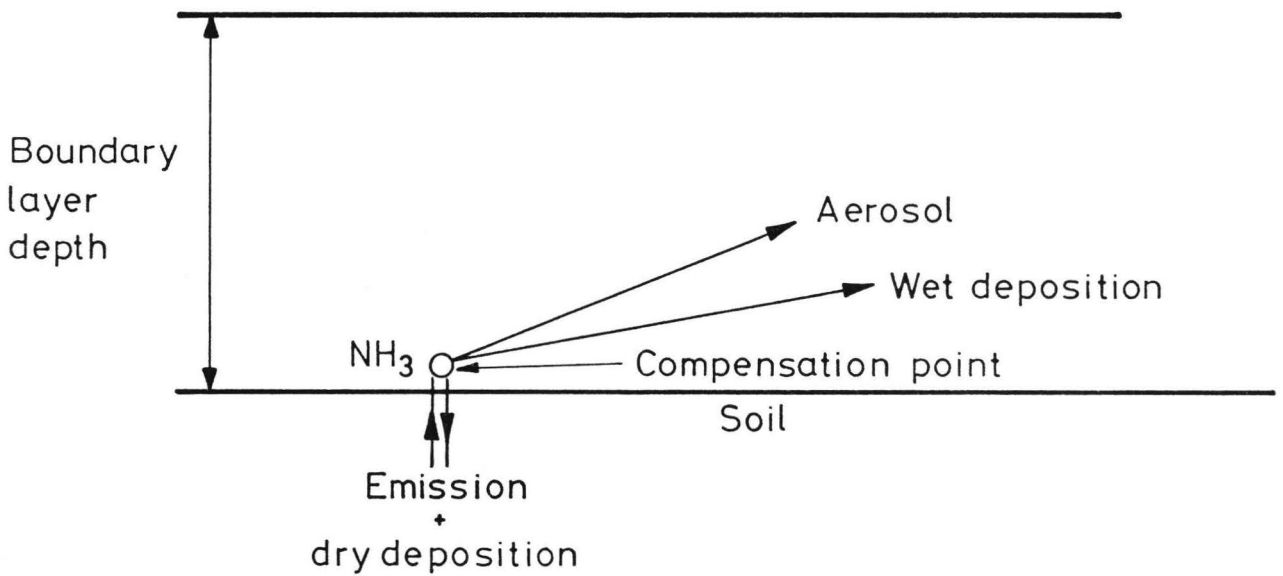
INPUT - OUTPUT MODELCOMPENSATION POINT METHOD

FIGURE 5. The different representations of the ammonia life cycles in long-range transport models.

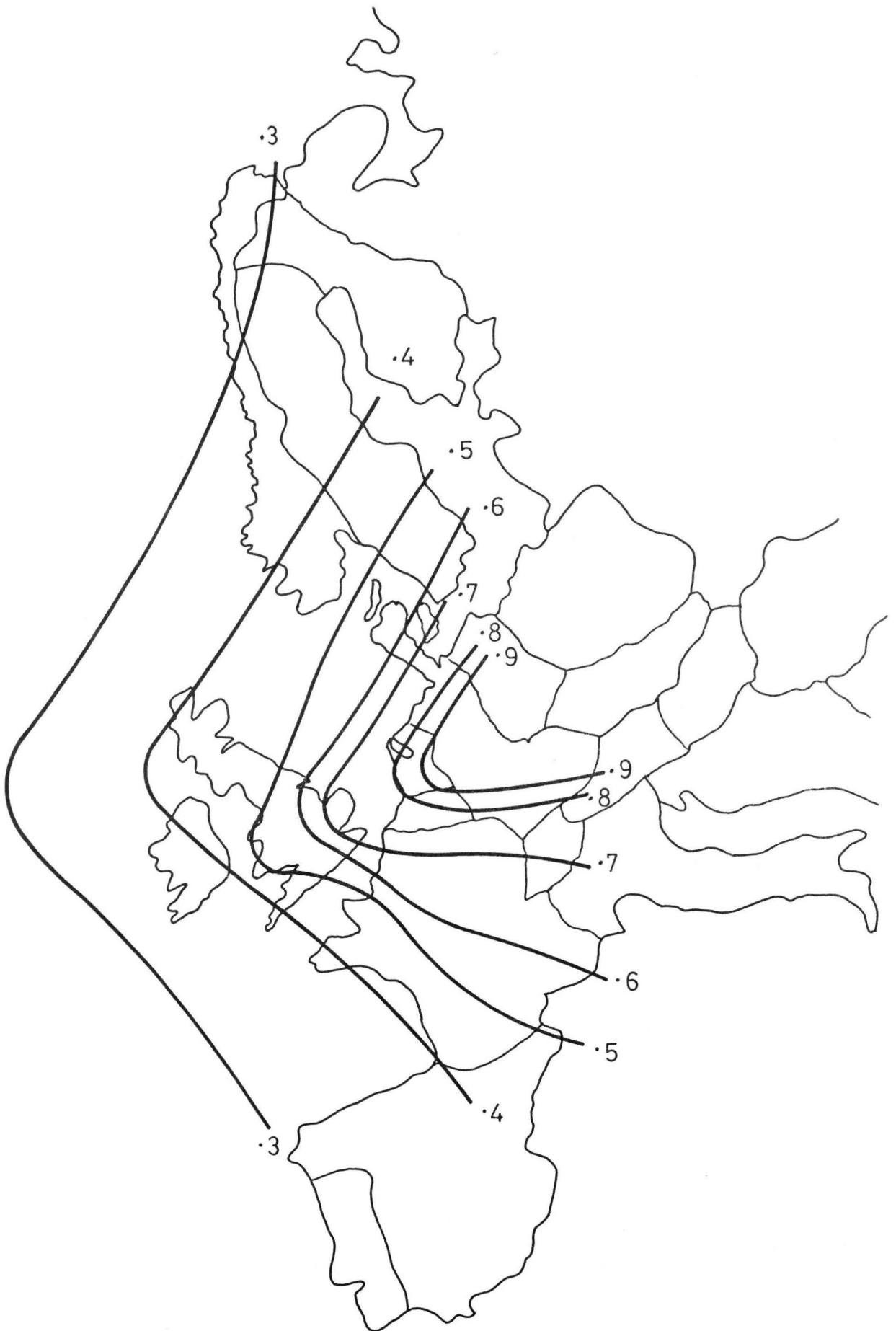


FIGURE 6. The spatial pattern of the ammonium concentration in precipitation in $\text{mg N-NH}_4 \text{ l}^{-1}$ calculated using a compensation point ammonia concentration of 2 ppb and a background precipitation concentration of $0.2 \text{ mg N-NH}_4 \text{ l}^{-1}$.

ASSESSING RECENT AMMONIA INVENTORIES USING A STATISTICAL LONG-RANGE
TRANSPORT MODEL

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SUMMARY

Ammonia plays an important role in acid deposition either directly as an acidifying component when it is deposited on the ground, or indirectly in promoting oxidation in cloud or rain droplets. It is therefore important to know where the considerable amounts of ammonium found in rain come from. A recent emission inventory has provided detailed information, but is based on various assumptions concerning emission factors associated with agricultural activities.

The purpose of this paper is to assess the ammonium inventory by using a statistical long-range transport model. The model has been previously used successfully to describe sulphur transport and deposition in the atmosphere. For the present application in which parameter values appropriate to a reactive gas are assumed, the model is used to relate ammonia emissions with measurements of ammonium in precipitation.

Though not a complete test (because airborne measurements are absent) it is difficult to explain observations solely in terms of this emission inventory, which suggests that either the inventory is an underestimate or certain aspects of the atmospheric cycle of ammonia differ in a fairly fundamental way from the behaviour expected from a reactive atmospheric gas.

1. INTRODUCTION

Interest in ammonia in the atmosphere arises for several reasons. As ammonium it is present in relatively large concentrations in precipitation being of roughly equal magnitude (when expressed in equivalents) with nitrate and equal to about half the concentration of sulphate, the predominant ion. In the atmosphere its presence will promote various liquid phase reactions, which lead to the oxidation of sulphur dioxide, by lowering acidity and thereby enabling more sulphur dioxide to go into cloud droplets.

After deposition to the ground it can enter into a number of exchange processes in the soil, which make the forms in which the nitrogen is held less clear. In simple terms ammonium may be increased in the soil by deposition and decomposition of dead biomass and lost by assimilation into live biomass and nitrification (conversion to nitrate). There may also be a small loss to the atmosphere from the soil (Dawson, 1977). Nitrate in the soil is involved in further exchange cycles, but is more readily leached to deeper soil layers than ammonium. The large capacity of soils to absorb ammonium in exchange for say, calcium, the nitrification reaction which produces acidity, as well as the difference in leaching rates, means that the potential for acidification of soils by ammonia becomes comparable or even greater than that of sulphur and nitrogen oxides.

This thinking has prompted several programmes of research, which started by assessing ammonia emissions in the UK and Europe (ApSimon, Kruse and Bell, 1986; Buijsman, Maas and Asman, 1985). The major sources of ammonia are livestock manure and to a much lesser extent fertilizer application. It is thought that most of the ammonia lost from a nitrogen source is volatilized over a relatively short period of time (less than one

week), after the source appears. It may therefore be very seasonally dependent. For the Netherlands it is estimated that about one third of the ammonia emission from manure comes from stables and cattle sheds, one third from cattle in the fields and one third from manure that has been spread.

The production of ammonia source inventories is largely a paper exercise and needs to be related to observed levels of ammonia compounds in air and rain. This can only be done with models of the atmospheric ammonia cycle. Earlier modelling work suggested that it was not easy to explain the long-term pattern of ammonium in precipitation across Europe (Fisher, 1984), nor ammonium in clouds measured on some specific occasions (Fisher and Callander, 1984).

More recent work (Asman and Janssen, 1986a), has shown more encouraging agreement between modelled ammonia emissions and observations. This work was based on a trajectory model and a new, refined ammonia inventory. It therefore seemed sensible to repeat earlier calculations using our statistical model and the new inventory. The results and conclusions of new calculations are reported here.

Emissions of ammonia are expressed in terms of total annual emissions per unit area. Since ammonia emissions represent a true ground level source some ambiguity may exist in the way they are treated in calculations. At any instant fresh sources of nitrogen are likely to be confined to concentrated patches, which will emit ammonia irrespective of ambient atmospheric levels. At the same time a source region, on a wider scale, is an absorber of ammonia, expressed in terms of a deposition velocity. Whether such a region as a whole is a nett emitter or absorber of ammonia depends on the source strength and ambient air concentration. One expects the deposition velocity of ammonia to be largely determined by the atmospheric resistance. The surface resistance should be low, because

most of the ammonia is readily absorbed in the presence of liquid water for pH's < 8.

The airborne concentrations of ammonia are difficult to measure and ground level concentrations are likely to be strongly influenced by local sources. Hence it is not possible to determine regionally representative concentrations which are needed by long-range transport models. Airborne ammonium and ammonium in precipitation are less influenced by local factors.

2. DESCRIPTION OF STATISTICAL LONG-RANGE TRANSPORT MODEL

The model used to describe the ammonia cycle is the same statistical long-range transport model used to describe the transport of sulphur oxides (Fisher, 1978). The ammonia concentration at a receptor point, a distance, x , downwind of a source, is given in terms of the solutions of the coupled diffusion equations:

$$\frac{\partial g_o}{\partial t} = \left[\frac{\partial}{\partial z} K \frac{\partial}{\partial z} - \lambda_o - \frac{1}{t_o} \right] g_o + g_1/t_1 \quad \dots (1a)$$

$$\frac{\partial g_1}{\partial t} = g_o/t_o + \left[\frac{\partial}{\partial z} K \frac{\partial}{\partial z} - \lambda_1 - \Lambda - \frac{1}{t_1} \right] g_1 \quad \dots (1b)$$

where $g_{o,1}(z,t)$ is the probability density of a unit emission in a constant wind u surviving to reach a height z in a dry (wet) period after a travel time $t (=x/u)$, $t_{o,1}$ are the mean durations of dry and wet periods, the onset of which are treated as stochastic processes. K is the (constant) vertical eddy diffusivity. $\lambda_{o,1}$ are the rates of conversion of ammonia to airborne ammonium during dry and wet periods respectively, and Λ is the rate of removal of ammonia by precipitation during wet periods.

$g_{o,1}$ are subject to the boundary conditions

$$K \frac{\partial g_{o,1}}{\partial z} = 0 \text{ at } z = a, \quad \dots (2a)$$

where $z = a$ is the top of the boundary layer, and

$$K \frac{\partial g_{o,1}}{\partial z} = v_g g_{o,1} \text{ at } z = z_s \quad \dots (2b)$$

where $z = z_s$ is an imaginary plane drawn some few metres above the ground surface and its associated roughness elements. The initial conditions on $g_{o,1}$ are

$$\lim_{t \rightarrow 0} g_{o,1} = \delta(z - z_s) \quad \dots (3)$$

Emission and deposition are therefore defined with reference to this notional plane $z = z_s$. The annual average concentration of ammonia from a source of strength Q is given by

$$C = fQ(g_o + g_1)/(2\pi ux) \quad \dots (4)$$

in which a weighting over a range of boundary layer conditions (specified by u , a and K) and a directional weighting factor, is implied by the factor f . The annual dry deposition rate of ammonia is $v_g C$ at $z = z_s$ and the annual wet deposition rate is:

$$D = \Lambda f Q \bar{g}_1 / (2\pi ux) \quad \dots (5)$$

where \bar{g}_1 is the vertical average of g_1 (with \bar{g}_0 defined similarly). The ammonium concentrations are determined by the probability density functions $G_{0,1}$, which satisfy

$$\frac{\partial G_0}{\partial t} = \lambda_0 \bar{g}_0 - (v_{g4}/a + 1/t_0)G_0 + G_1/t_1 \quad \dots (6a)$$

$$\frac{\partial G_1}{\partial t} = \lambda_1 \bar{g}_1 - (v_{g4}/a + \Lambda_4 + 1/t_1)G_1 + G_0/t_0 \quad \dots (6b)$$

where v_{g4} is the deposition velocity of ammonia and Λ_4 is the removal rate of ammonium in rain during wet periods. The ground level concentration of ammonium is given by

$$C_4 = fQ(G_0 + G_1)/(2\pi ux) \quad \dots (7)$$

with the same implied weighting over meteorological conditions. The dry deposition rate of ammonium is $v_{g4}C_4$ and the wet deposition rate is

$$D_4 = \Lambda_4 afQG_1/(2\pi ux) \quad \dots (8)$$

The weightings to obtain annual averages are chosen to be representative of central Europe and take the same value throughout the area of study. This is clearly unrealistic if one were seeking predictions with a high degree of accuracy. However the intention in our case is to see whether estimated emissions are consistent with such observations as are currently available. For this purpose the major uncertainties in the model depend on values of the removal parameters v_g , v_{g4} , $\lambda_{0,1}$, Λ and Λ_4 . The meteorological parameters used are the same as those used in long-range sulphur modelling (Fisher and Clark, 1985), where they have proved an acceptable representation of annual average behaviour.

3. APPLICATION OF THE MODEL AND COMPARISON WITH IMO RESULTS

The emission inventory reported by Buijsman, Maas and Asman (1985) was modified by the authors when undertaking calculations using their trajectory model (Asman and Janssen, 1986a). All source strengths in the original inventory were increased by a factor 1.2 and additional sources were included in the model area to cover regions, such as the eastern USSR and North Africa for which emissions had not been previously estimated. This inventory was used in our calculations. For some calculations it was also assumed that a "background" concentration existed in precipitation from sources outside the study area, or from aged material from sources inside the study area which left the area and returned later. A value of $0.1 \text{ mg l}^{-1} \text{ N}$ was assumed which is slightly greater than the mean value in precipitation collected on a weather ship in the North Atlantic (Buijsman, Asman, Ridder, Frantzen and Adolphs, 1985). The background deposition is obtained by multiplying this concentration by the rainfall amount allowing for its variation over Europe. The remaining parameter values chosen are summarised in Table 1.

Since ammonia and ammonium are readily removed by precipitation, the annual wet removal rate is largely determined by the incidence of precipitation. Conversion of ammonia to airborne ammonium is expected to be fairly rapid after emission, so that dry deposition of ammonia is only significant within the grid square of emission. The dry deposition of airborne ammonium is low as ammonium is attached to fine particles which are thought to have a low deposition velocity. The "own-square" deposition is rather sensitive to assumptions regarding how it is modelled, since emissions of ammonia take place at ground level and are therefore subject to high deposition rates locally.

The method of calculating local deposition adopted in the statistical model is first to calculate the fraction of the emissions which leave the grid square containing the emissions. This gives an estimate of the amount of material dry and wet deposited over the square. The fraction wet deposited is then set equal to the average probability of rain ($=t_1/(t_0 + t_1)$) and the remainder is assumed to be dry deposited ammonia. The separate contributions of dry and wet deposited ammonia are assumed to make a small contribution to the "own-square" deposition and are neglected.

The results of the model calculations are compared with observations of ammonia in air and of wet deposition collected within the EMEP network (EMEP, 1984) over the period 1978 to 1982. Additional ammonia measurements from other networks have been compiled by Buijsman and Erisman (1986) to produce the interpolated map of ammonia wet deposition shown in Fig. 1. The calculations from our statistical long-range transport model, using parameter values specified above but neglecting any ammonia background, substantially underpredict wet deposition over central Europe (see Fig. 2). Even allowing for some outliers in the measurements at many sites there is underprediction by a factor of two. In contrast the IMOU trajectory model calculations (Asman and Janssen, 1986a) are in good agreement with observations, in some regions overestimating ammonia concentrations in rain. These results are slightly disturbing, since the two models, though different in structure, are run using similar parameter values. In fact it would be difficult to increase the calculated wet deposition in the statistical model by changing parameter values alone, since the initial choice weights wet deposition

much more heavily than dry deposition. Alterations in parameter values to reduce dry deposition further would not enhance wet deposition sufficiently to explain the observations.

4. TREATMENT OF LOCAL DEPOSITION

There are two areas where the models are not strictly comparable and where differences in treatment may have caused differences in predictions. Firstly in the treatment of local deposition the IMO model leads to a greater "own-square" deposition than our model. The contribution of Dutch sources to deposition over Holland appears to be largely dominated by the dry deposition of ammonia (Asman and Janssen, 1986b). From our model the contribution to the total deposition over the Netherlands from Dutch sources is estimated to be 52% (neglecting background), while it is 72% in the IMO model. In the IMO model about one quarter of the emitted ammonia is assumed to be dry deposited locally. In the CERL model this is an implicit part of the calculation, but its influence may be estimated by recalling the basic equations. For a ground level source the fraction remaining airborne after travel time, x , is given approximately by (Fisher, 1978)

$$F = \frac{2(1+0.4\beta)}{1 + (1+\beta)(1+0.4\beta)} \exp - \frac{v_g x}{ua(1+0.4\beta)}$$

where $\beta = av_g/K$. If we let $a = 800$ m, $K = 6$ m² s⁻¹, $u = 8$ m s⁻¹ (the harmonic mean of the values proposed in Table 1) and $x = 150$ km/ $\sqrt{\pi}$ then the fraction remaining airborne is about 70%, or the amount of ammonia or ammonium dry deposited locally is of order 30%. Thus the treatment of local dry deposition is quite similar in the two models. Adjustments to the treatment of local deposition remain theoretical, since the observations currently available of wet deposition are not sensitive to the way in which it is dealt with.

The second difference arises from the treatment of precipitation. Precipitation fields over Europe are only available with a time resolution of 6 hours, which means that a grid element is either wet or dry during a 6 hour period. In reality the probability of encountering rain in a wet grid square is only about 33% (Eliassen and Saltbones, 1983). There is a danger of overestimating wet removal by overestimating the fraction of time the ammonia species encounter rain. In the statistical model the fraction of time that rain is experienced is introduced explicitly into the model, albeit that the treatment does not allow for variability across the region. The duration of wet periods depends on the definition of rain. Rainfall rates below 0.1 mm h^{-1} are normally classified as dry periods.

A reduction in the average duration of dry periods may make the two methods more consistent. Hence a reduction in the mean duration of dry weather by a factor of two was introduced ($t_0 = 35 \text{ h}$) and the results are shown in Table 2. The incidence of precipitation is now about 20%, twice what it was before and a background concentration of ammonium in precipitation has been included. It is seen that agreement between observations and predictions is much improved, compared with calculations based on our initial choice of parameter values. Agreement between calculated and measured ammonium concentrations in air is not improved (Table 3).

The rate of wet deposition at long distances from a source is rather insensitive to assumptions about the duration of dry weather. The revised values are similar to those adopted by Smith (1981). Only the amount of near-field wet deposition is very sensitive to the fraction of time it rains. Differences in the models may therefore be associated with the way in which local wet deposition is handled. It is plausible to

assume a shorter duration of dry weather for ammonia, than for sulphur dioxide, on the grounds that because of its high solubility the fraction of airborne ammonia influenced by rain is higher.

These points are demonstrated by the ammonia budget for the whole of the grid area presented in Table 4. Assumptions about the duration of wet periods make little difference to the overall budget. The presence of a background concentration of ammonium in precipitation results in the total deposition being greater than the emissions. The introduction of this extra term improves agreement with measurements, but the origin of this extra material must remain speculative at present.

The source-receptor relationships presented in Table 5 are calculated assuming the mean duration of dry periods is 70 hours. The table shows the importance of local deposition to the national budgets. Great uncertainty must still be attached to such estimates, but they do indicate how local deposition may have a greater effect on ammonia source-receptor relationships than on sulphur source-receptor relationships.

5. CONCLUSIONS

Results from the use of a statistical long-range transport model of ammonia do not appear to yield as good agreement with observations of ammonium wet deposition as a trajectory model. The differences may lie in the way in which local wet deposition is treated. Improved methods of dealing with local (wet and dry) deposition are required. The pattern of wet deposition is made up from a mixture of local and long-range influences, with the local component of greater importance at rural monitoring sites than the local component in the sulphur cycle. It is

rather difficult to confirm estimates of ammonia emissions using models because of the need to treat processes accurately over two widely differing time scales. The general level of emissions appear plausible and the coincidence in Europe of high ammonia emission areas with regions of high sulphur oxide emissions is probably the explanation for the similarities in the wet deposition patterns of sulphate and ammonium.

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Table 1: Parameter Values used in Statistical Model

ammonia deposition velocity, v_g	.008 m s ⁻¹
ammonium deposition velocity, v_{g4}	.001 m s ⁻¹
ammonium background in precipitation	0.1 mg l ⁻¹ N
ammonium background deposition	0.1 × annual rainfall (m) gN m ⁻² a ⁻¹
ammonia wet removal rate, Λ	4.10 ⁻⁴ s ⁻¹
ammonia wet removal rate, Λ_4	4.10 ⁻⁴ s ⁻¹
ammonia oxidation rate in dry periods, λ_0	8.10 ⁻⁵ s ⁻¹
ammonia oxidation rate in wet periods, λ_1	8.10 ⁻⁵ s ⁻¹
mean duration of dry periods, t_0	70 h
mean duration of wet periods, t_1	7 h

Probability of occurrence	Type of boundary layer	Mixing depth, a (m)	Windspeed, u (m s ⁻¹)	Diffusivity, K (m ² s ⁻¹)
.18	Mechanical	450	4	2
.10	Convective	1500	4	30
.30	Mechanical	600	10	6
.10	Convective	1500	10	30
.32	Mechanical	960	16	15

Probability of occurrence	Wind direction sector, θ
0.1	0 to 45
0.08	45 to 90
0.08	90 to 135
0.1	135 to 180
0.17	180 to 225
0.21	225 to 270
0.15	270 to 315
0.11	315 to 360

Table 2: Comparison of Observed and Predicted Annual Ammonium

Wet Deposition (g N m^{-2})

Name	Location (Lat. Long.)		Actual Value	Predicted Value ($t_o = 70$ h)	Predicted Value ($t_o = 35$ h)
Illmitz	47.8	16.8	.57	.41	.58
Neuglobsow	53.2	13.0	.38	.44	.64
Tange	56.4	9.6	.62	.43	.64
Keldsnor	54.7	10.7	.45	.39	.58
Faroerne-Akraberg	61.4	-6.4	.28	.14	.14
Vert-le-Petit	48.5	2.4	1.25	.34	.49
La Crouzille	46.0	1.4	.24	.39	.56
Valduc	47.6	4.9	.89	.39	.56
K-pusztá	47.0	19.6	.68	.41	.59
Birkenes	58.4	8.3	.87	.27	.31
Skreadalen	58.8	6.7	.63	.33	.36
Tustervatn	65.8	13.9	.12	.17	.17
Jergul	69.4	24.6	.04	.08	.07
Narbuvoll	62.4	11.5	.10	.13	.15
Bjornoya	74.5	19.0	.09	.04	.04
Karvatn	62.8	8.9	.12	.20	.21
Witteveen	52.8	6.7	.73	.55	.84
Rekken	52.1	6.7	1.02	.63	1.00
Braganca	41.8	-6.8	.10	.15	.20
Faro	37.0	-8.0	.05	.07	.08
Suwalki	54.1	23.0	.76	.39	.55
Paring	45.4	23.5	.66	.37	.51
Ekerod	55.9	13.7	.66	.32	.41
Rorvik	57.4	11.9	.45	.27	.34
Velen	58.8	14.3	.28	.22	.26
Bredkalen	63.9	15.3	.18	.12	.13
Hoburg	56.9	18.2	.43	.22	.26
Ahtari	62.6	24.2	.19	.18	.21
Virolahti	60.5	27.7	.61	.21	.25
Uto	59.8	21.4	.40	.18	.21
Eskdalemuir	55.3	-3.2	.38	.40	.54
Goonhilly	50.1	-5.2	.39	.26	.33
Stoke Ferry	52.6	.5	.46	.34	.49
Masun	45.7	14.4	.94	.47	.59
Puntijarka	45.9	16.0	.87	.40	.52
Zavizan	44.8	15.0	1.02	.45	.54
Ivan Sedio	43.9	18.0	2.96	.50	.59
Lazaropole	41.5	20.7	.49	.32	.40
Mean value (gN m^{-2})			.56	.30	.40

Measurements are from EMEP averaged over the period 1978-82. A background concentration of ammonium in precipitation has been included in the calculations.

Table 3: Comparison of Observed and Predicted Concentrations of
Airborne Ammonium ($\mu\text{g m}^{-3} \text{ N}$)

Name	Location (Lat. Long.)		Actual Value	Predicted Value ($t_o = 70 \text{ h}$)	Predicted Value ($t_o = 35 \text{ h}$)
Tange	56.4	9.6	2.97	2.02	1.34
Keldsnor	54.7	10.7	3.37	2.54	1.75
Faroerne-Akraberg	61.4	-6.4	.27	.51	.26
K-puszta	47.0	19.6	2.08	2.74	1.84
Witteveen	52.8	6.7	4.00	2.78	1.97
Rekken	52.1	6.7	4.00	2.99	2.15
Braganca	41.8	-6.8	2.12	.83	.53
Mean value ($\mu\text{g m}^{-3} \text{ N}$)			2.69	2.06	1.41

Table 4: Ammonia Budget for Grid Area

Total source strength 9200 kt N/year

Duration of dry period	$t_o = 70$ h	$t_o = 35$ h
NH ₃ dry deposition/source strength	22%	22%
NH ₄ dry deposition/source strength	12%	7%
NH ₃ wet deposition/source strength	10%	18%
NH ₄ wet deposition/source strength	61%	69%
Total wet deposition/source strength	71%	87%
Total deposition/source strength	105%	114%
Background wet deposition/source strength	29%	29%

Table 5: Source-Receptor Relationships for Ammonia
Percentage Contributions to Receptor Regions

Source area	Holland	Scotland	S. Norway	S. Sweden	S. Germany
DDR 200 kt N/a	1.2	.6	1.9	3.9	2.5
Czechoslovakia 170 kt N/a	.4	.3	.7	1.2	4.7
Belgium 80 kt N/a	8.2	.5	.9	.9	.9
FRG 370 kt N/a	17.3	1.3	3.3	5.9	49.1
Poland 400 kt N/a	.8	.6	1.9	4.6	1.8
Netherlands 140 kt N/a	47.8	.8	2.1	2.2	1.3
UK 400 kt N/a	4.3	55.4	6.1	4.3	1.4
France 890 kt N/a	6.9	3.6	4.8	4.8	8.5
USSR 3900 kt N/a	1.5	1.8	5.2	10.0	2.5
Sweden 50 kt N/a	.2	.1	1.0	23.5	.1
Norway 30 kt N/a	.1	.2	10.2	1.3	.1
Rest 2700 kt N/a	4.1	7.3	9.1	14.2	18.1
Background	7.4	27.6	52.7	23.2	9.1
Total deposition $\text{gN m}^{-2} \text{a}^{-1}$	1.1	0.6	0.4	0.3	0.9

Fig 1 Pattern of Ammonium Wet Deposition over Europe ($\text{g N m}^{-2} \text{y}^{-1}$) based on Observations (Buijsman and Ericman, 1986)



Fig 2 Calculated Ammonium Wet Deposition over Europe ($\text{g N m}^{-2} \text{y}^{-1}$)
from Statistical Model using Parameter Values in Table 1 (excluding background)



MODELLING THE INTERACTION OF NH_3
WITH OTHER ATMOSPHERIC SPECIES

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Abstract

The basis for a simple model of the behaviour of ammonia in the atmosphere and its interaction with S and N species will be described. This is a Lagrangian trajectory model with simplified representation of the chemistry. It is a 2-layer model with a well mixed dry layer below a cloud layer. The dispersal of NH_3 upwards, after emission, and its interaction with acidic species are treated separately below and within cloud. Deposition due to uptake in cloud droplets and rain processes as well as washout are represented.

It is intended eventually to apply this model to selected episodes using the MESOS meteorological databases at Imperial College.

Introduction

It is very much in the spirit of meetings of the European Association for the Science of Air Pollution that work in progress should be described, as well as more polished papers on work completed. This paper is very much a preliminary report on a new project.

Our interest in ammonia was increased when deriving an emissions inventory for England and Wales (Fig.1). The results obtained, although deduced independently of Asman and Buijsman (1), over a wider area of Europe are in good overall agreement and based on a finer grid resolution of 10 x 10 km. However it appeared that these emissions were likely to have doubled since 1950 as a result of intensified agriculture, and an examination of agricultural statistics for other countries implied a similar trend elsewhere in Europe and worldwide (2).

The questions then arose as to how this is likely to have affected the sulphur and nitrogen cycles and what are the implications for acidification. For example with respect to sulphur, the presence of ammonia has a well known effect in cloud where it is readily taken up by the cloud droplets, raising the pH and increasing the potential for uptake of SO_2 . Also the acidifying effect of wet deposition is not determined by the pH or merely the sulphur content but depends on the chemical composition. Thus $(\text{NH}_4)_2\text{SO}_4$ is able to liberate more protons to the soil than H_2SO_4 if the nitrogen is assimilated by plant uptake, and hence is potentially more acidifying. Such matters warrant more detailed examination as to their overall significance in the geographical distribution of acidification in soils.

To this end we have initiated development of a medium to long-range transport model to study the interaction of ammonia with sulphur and nitrogen species. So far we have concentrated more on the former, and this will be described in this paper. The model is composed of a number of modules as indicated in Fig.2. At present very simple component modules have been incorporated, which can be replaced as more sophisticated components are designed. The model is essentially Lagrangian and will make use of the extensive meteorological databases and trajectory techniques

assembled for the MESOS model (3) whose most recent application has been the Chernobyl release (4, 5).

The Emissions Module

For applications so far this has been based on the emissions inventory of Fig.1 for England and Wales, with a multiplying time-dependent factor applied to adjust for temporal changes relative to annual average values. This factor reflects seasonal and diurnal fluctuations and meteorological conditions. Emissions of SO_2 and other species also have to be specified.

The overlying atmosphere is represented by two compartments, one representing unsaturated air, and the other saturated air in cloud.

Within the dry air compartment ammonia entering the box readily reacts with H_2SO_4 , HNO_3 and HCl . At present the very simple picture is adopted of a well mixed box with these reaction rates primarily determined by the rate of turbulent mixing. Thus vertical profiles of pollutants in this compartment are currently ignored - a factor which may be an important refinement using a diffusion model. Oxidation of SO_2 to SO_4 is likewise simplified at present to a constant oxidation rate specified as input data. Dry deposition velocities are used to determine dry deposition, again with no correction for stability, vertical profiles or surface characteristics at present. Values currently adopted are given in Table 1.

Air is exchanged between the dry air and cloud compartment according to the scenario being considered. Thus with stratus cloud this corresponds to exchange of air across the condensation level. Air transferred downwards from the cloud into the dry compartment is assumed to evaporate with resuspension of material in the associated cloud droplets. Evaporation of raindrops is ignored so far.

Air transferred from the dry air into the cloud compartment supplies new pollutants to the interstitial air. Particulate sulphate and ammonia are assumed to be rapidly taken up into new or existing cloud droplets. Mass balances are maintained as though pollutants are uniformly distributed over the cloud water content. Uptake of SO_2 and oxidation within cloud droplets

are then calculated with a simple chemical model in much the same way as described by (6) describing the pH and equilibrium balance of the various ions in solution. When more species are introduced this may require a more complex chemical model.

If and when rain occurs a corresponding proportion of the cloud water is assumed to be removed as rain and its contents deposited unmodified on the ground beneath. However additional material may be scavenged from the dry air below as washout.

A parameter may also be specified to represent a leakage rate from the cloud compartment whereby material in updraughts in precipitation systems re-evaporates in the free troposphere above. Although such parameters may be difficult to specify ancillary storm modelling work may help to define ranges of values, and such treatment does allow the importance for such processes to be investigated.

In the event of cloud penetrating to ground level the dry air compartment shrinks to zero, and an enhanced deposition velocity is applied to estimate deposition of cloud droplet contents - so called occult deposition. At present the effective velocity is specified as data input.

The model, now named MARTA (Modelling Atmospheric Reactions and Transport of Ammonia), is being applied in its present simple state to the interesting experimental results obtained by the CEEB monitoring transport of SO_2 in an Easterly airflow from the industrial Midland regions of the U.K. across Wales (7). Fluxes of SO_2 , SO_4 and NH_4 were monitored by aircraft flying upwind and downwind of Wales where conditions were misty over the Welsh hills. A large proportion of the sulphur appears to have been deposited over Wales. Our ammonia inventory shows high emissions of ammonia along the Welsh borders in the intensive cattle farming areas plus moderate emissions from Wales itself. This situation thus provides an interesting case study with which to evaluate the model and determine whether the ammonia emissions can have stimulated sufficient increased take up of sulphur in the mist droplets and consequent enhanced deposition over the Welsh hills to explain the results obtained by CEEB.

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FIGURE 1. : AMMONIA EMISSIONS IN ENGLAND AND WALES
(TOTALS)



KEY (kg N as NH_3 emitted per 100 km²)

white	-	0% - 25%	(0	-	88 t N)
light grey	-	25% - 50%	(88	-	160 t N)
dark grey	-	50% - 75%	(160	-	255 t N)
black	-	75% - 100%	(255	-	1451 t N)

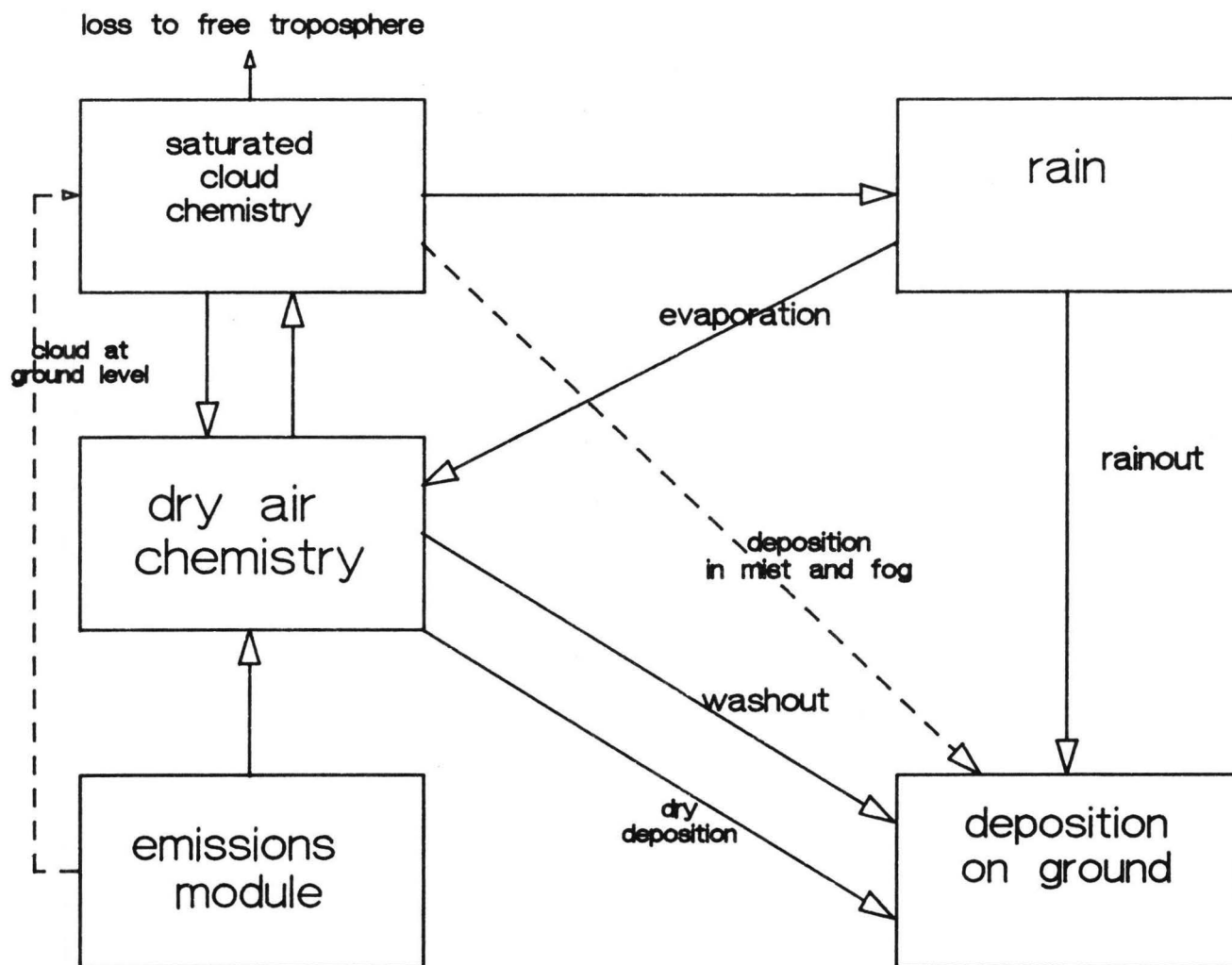


Figure 2. The MARTA model

EFFECTS OF AIRBORNE AMMONIUM ON NATURAL VEGETATION AND FORESTS

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Summary

In weakly buffered ecosystems a high deposition of ammonium leads to acidification and nitrogen enrichment of the soil. As a consequence many plant species characteristic of poorly buffered environments disappear. Among the acid tolerant species there will be a competition between slow growing plant species and fast growing nitrophilous grass or grass like species. This process contributes to the often observed change from heath- and peatlands into grasslands.

In forest ecosystems a high input of ammonium leads to leaching of K^+ , Mg^{2+} and Ca^{2+} from the soil, often resulting in increased ratios of NH_4^+ to K^+ and Mg^{2+} and/or Al^{3+} to Ca^{2+} in the soil solution. Field investigations show a clear correlation between these increased ratios and the condition of *Pinus nigra* var. *maritima* (Ait.) Melville, *Pseudotsuga menziesii* (Mirb.) Franco and *Quercus robur* L.. Ecophysiological experiments proved that increased ratios of NH_4^+ to K^+ inhibit the growth of symbiotic fungi and the uptake of potassium and magnesium by the root system. At high NH_4^+/K^+ and Al^{3+}/Ca^{2+} ratios there is a net flux of Mg^{2+} and Ca^{2+} from the root system to the soil solution.

Other experiments proved that coniferous trees take up NH_4^+ by the needles and compensate for this by excreting K^+ and Mg^{2+} .

This combination of effects often results in potassium and/or magnesium deficiencies, severe nitrogen stress, and as a consequence premature shedding of leaves or needles.

Furthermore the trees become more susceptible to other stress factors such as ozone, drought, frost and fungal diseases.

The change of heathlands into grasslands

The most obvious phenomenon in many heathlands during the last decades is the changing from heathland into grassland (Heil, 1984; Heil and Diemont, 1983; Roelofs et al., 1984; Roelofs, 1986). Particularly *Molinia caerulea* (L.) Moench and *Deschampsia flexuosa* (L.) Trin. expand strongly, at the expense of *Calluna vulgaris* (L.) Hull and other heathland species.

In order to estimate whether this phenomenon is related to changes in the physical-chemical environment, 70 grass-dominated and heather-dominated heathlands have been investigated (Roelofs, 1986). Many parameters such as the pH, showed hardly any differences. However, the nitrogen levels in grass-dominated heathlands appeared to be much higher (Table 1).

Table 1. The pH (H₂O) and average nutriënt concentrations in the soil-solution of 70 investigated heathlands.

Species	Coverage	pH (H ₂ O)	NH ₄ ⁺ μmoles kg ⁻¹	NO ₃ ⁻	PO ₄ ⁻	K ⁺
<i>Erica tetralix</i> L.	>60%	4.1	55	0.0	4.0	37
<i>Calluna vulgaris</i> (L.) Hull	>60%	4.1	84	1.4	4.4	46
<i>Molinia caerulea</i> (L.) Moench	>60%	4.2	248	17.2	4.7	88
<i>Deschampsia flexuosa</i> (L.) Trin.	>60%	4.1	429	29.0	6.0	182

Both in grass-dominated and heather-dominated heathlands the ammonium levels were 10 - 20 times higher than the nitrate levels. Investigations clearly show that a major part of the nitrogen originates from atmospheric deposition. Under natural conditions this atmospheric nitrogen deposition is only a few kg.ha⁻¹yr⁻¹. At the present time in The Netherlands the deposition on heathlands often varies between 20 and 60 kg.ha⁻¹yr⁻¹; 60 - 90% as ammoniumsulphate.

Impact of ammonium on heathland vegetations.Soil acidification

Although heathland soils are often acidic by nature, there are often certain spots or areas where, due to natural causes (loamy places, a calcareous underground, upwelling deeper groundwater) or to human activities (digging, cattle drinking-places) the soil has become slightly buffered and thus less acidic (Roelofs et al., 1984). Here plant species occur which are restricted to these slightly buffered, less acidic sediments (Table 2).

Table 2. The distribution of some plant species from heathlands in relation to the soil pH.

Species	n	mean	pH(H ₂ O)	
			min.	max.
<i>Erica tetralix</i> L.	>10	4.1		
<i>Calluna vulgaris</i> (L.) Hull	>10	4.1	4.0	4.3
<i>Molinia caerulea</i> (L.) Moench	>10	4.2	3.8	4.7
<i>Polygala serpyllifolia</i> Hose	>10	4.5	4.1	5.7
<i>Lycopodium inundatum</i> L.	>10	4.6	4.4	4.9
<i>Pedicularis sylvatica</i> L.	>10	4.7	4.2	5.9
<i>Thymus serpyllum</i> L.	>10	5.1	4.7	5.6

These plant species like *Thymus serpyllum* L. and *Pedicularis sylvatica* L. never occur on sediments with a pH value as low as 4.1. The deposited ammonium at these slightly buffered locations is transformed into nitrate very quickly by nitrification, which causes acidification of the soil (Van Breemen et al., 1983; Roelofs et al., 1984).

Laboratory experiments with artificially buffered heathland soils show that nitrification stops or is strongly inhibited in this type of soil at pH 4.1 (Roelofs et al., 1985). This appeared also to be the case for the average pH-value in both grass-dominated and heather-dominated

heathlands, which indicates that the pH in heathlands is probably determined by the nitrification limit. The final result of high NH_4^+ deposition levels is that the differences in pH disappear and thus also the plant species of slightly buffered locations. A poor plant community remains, consisting of only a few acid resistant species.

Nitrogen enrichment

If the soil on which ammonium is deposited acidic, a strong accumulation of nitrogen occurs in the upper soil layer, because ammonium is bound much more strongly to the soil absorption complex than nitrate. When there is competition between heather species such as *Erica tetralix* L. and *Calluna vulgaris* (L.) Hull and grasses such as *Molinia caerulea* (L.) Moench the grasses profit from these higher nitrogen levels (Scheikh, 1969; Heil and Diemont, 1983; Berendse and Aerts, 1984; Heil, 1984; Roelofs et al., 1984; Roelofs, 1986). Field fertilisation experiments have shown that nitrogen enrichment indeed stimulates the development of grasses in heathlands (Heil and Diemont, 1983).

However, the problem with these field fertilisation experiments is that the high atmospheric nitrogen deposition was not taken into account. For this reason, experiments were carried out in a greenhouse. A number of small heathlands were created, using undisturbed, natural heathland soils. Precipitation experiments during one year showed that the biomass development of the grasses *Agrostis canina* L. and *Molinia caerulea* is not influenced by the acidity of the precipitation (Fig. 1). If the precipitation contained ammonium sulphate, a strong increase in biomass with increasing NH_4^+ deposition was observed. The chosen annual ammonium deposition was comparable with the real field deposition. The increase in biomass of *Molinia* was the strongest between 1.4 and 2.8 $\text{kmol}\cdot\text{ha}^{-1}\text{yr}^{-1}$ (= 20 and 40 $\text{kg}\cdot\text{ha}^{-1}\text{yr}^{-1}$).

The results of these experiments show that the NH_4^+ deposition level in The Netherlands (20 - 60 $\text{kg}\cdot\text{ha}^{-1}\text{yr}^{-1}$) cause a marked increase in biomass of the two investigated grass species. For this reason it can be concluded that the high atmospheric nitrogen enrichment is a main cause for changes from heather-dominated into grass-dominated heathlands.

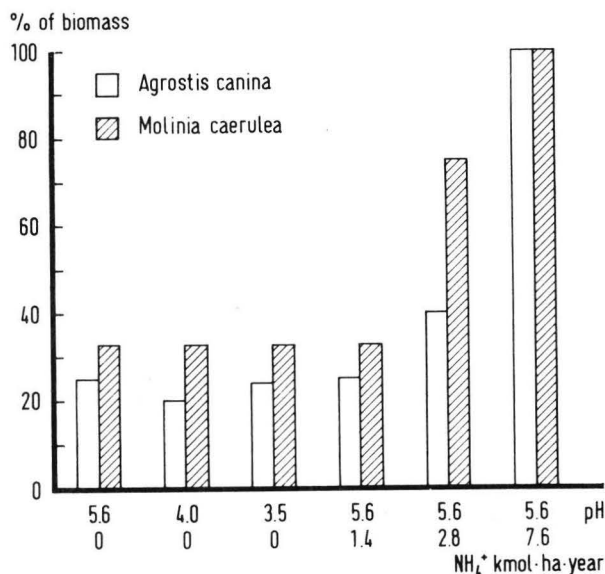


Fig. 1. The relative biomass development of *Agrostis canina* and *Molinia caerulea* on natural heathland soil during a one year treatment with precipitation with different pH and ammonium concentrations in a greenhouse.

Ammonium deposition and the condition of forests

The condition of the Dutch forests is alarming. A recent investigation by the Dutch State Forest Service reveals that 50.1% of the forest stands show a decreased vitality (Anonymus, 1985). The geographical pattern of the damage does not fit in very well with the occurrence of well-known pollutants as SO_2 , NO_x and O_3 (den Boer, 1986). The situation is most critical in the southeastern part of the country. Here nitrogen deposition in forest stands is very high and about 10 - 20 times the natural supply of $5 - 10 \text{ kg}\cdot\text{N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$. Due to the filtering action of the tree canopies deposition of gaseous ammonia, sulphur dioxide and ammonium sulphate is considerable higher in the forests than in the surrounding meadows (van Breemen et al., 1982; Nihlgård, 1985; Roelofs et al., 1985; see also Table 3).

Several authors mention a relation between agricultural activities and the condition of Pine trees (Hunger, 1978; Janssen, 1982; Roelofs et al., 1985). Mainly four types of damage can be observed:

- a. red or brown colouring of the needles of all year classes.
- b. yellowing of the needles; the older needles more frequently.
- c. yellowing of the youngest needles which is most pronounced at the base of the needles.
- d. the occurrence of fungal or insect diseases.

All these damages can be related to high or disturbed nitrogen budgets (Roelofs et al., 1985; Roelofs, 1986; van Dijk and Roelofs, 1986). The first type of damage mainly occurs in the neighbourhood of ammonia

sources like farms or fields dressed with animal slurry (Janssen, 1982).

Table 3. The average chemical composition of precipitation in open plots and throughfall in *P. nigra* forests in three different regions of the Netherlands during 1984 ($\mu\text{M/l}$).

	H^+	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	NO_3^-	Cl^-	SO_4^{2-}
North-West (Terschelling)									
open	100	65	25	308	47	62	48	370	72
throughfall	400	59	345	6700	460	1120	110	8000	860
South (Heeze)									
open	45	130	19	60	43	17	54	73	70
throughfall	6	1060	170	310	200	113	216	350	760
South-east (Venray)									
open	2	200	20	40	30	15	49	50	90
throughfall	1	2421	216	175	278	100	147	462	1400

It is caused by a combination of low temperature (frost) and high ammonia concentration in the air, probably as a result of a too low ammonia detoxifying capacity of the trees at low temperature (van der Eerden, 1982). The second type of damage, the yellowing of the needles, is related to potassium and/or magnesium deficiencies in the needles. These deficiencies are very significantly correlated with disturbed nitrogen budgets in both air and forest soil (Roelofs et al., 1985; Roelofs, 1986). The third type of damage, the yellowing of the youngest needles is strongly correlated with extremely high arginin levels in the needles, high ammonium concentrations in the precipitation and disturbed nitrogen budgets in the soil solution (van Dijk and Roelofs, 1987).

The last mentioned type of damage, the fungal and insect diseases, may be related to the disturbed nutrient balance in the plant tissue. Investigations in *P. nigra* forests have shown that all trees infected with the fungus *Sphaeropsis sapinea* (Fr.) Dyko and Sutton had significantly higher nitrogen levels in the needles compared to non-infected healthy trees (Roelofs et al., 1985).

Ammonia and the disturbed nutrient balance in the trees

In fact there are two ways in which ammonia can contribute to the observed nutrient disbalance in trees. At first by ammonia/ammonium uptake by the leaves and secondly while a high deposition of $\text{NH}_3/\text{NH}_4^+$ can cause a disturbed nutrient balance in the soil.

The role of ammonium in relation to the canopy-ion exchange

On locations with relatively low ammonium deposition levels, the ammonium concentration in the throughfall is even lower compared to the open-air bulk precipitation (Table 3). Persson and Broberg (1985) found the same in Pine forests in the lake Gårdsjön area (Sweden). On the locations with very high ammonium deposition levels sulphate is completely compensated by ammonium in the bulk precipitation, but only for 75 - 85% in the throughfall. All these observations may indicate that the needles take up ammonium, which also has been observed by Lovett and Lindberg (1984) for mixed Oak forests. This implicates that, when total nitrogen-deposition in forests is calculated from throughfall analysis, there might be a strong underestimation. Cation exchange experiments with needles of Corsican Pine (*Pinus nigra* var. *maritima* (Ait.) Melville) and Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) in artificial ammonium sulphate containing rain proved that the needles take up large amounts of ammonia and compensate by excreting equivalent quantities of potassium, magnesium and calcium (Tabel 4).

Table 4. Cation exchange of needles in acidic ($\text{pH} = 4.8 \pm 0.4$) artificial rainwater containing 100 μM sodium chloride (blanc) or 100 μM sodium chloride + 250 μM ammonium sulphate ($\mu\text{mol}\cdot\text{g}^{-1}$ DW 24h^{-1}).

Cation	NH_4^+		K^+		Mg^{2+}		Ca^{2+}	
	blanc	$+\text{NH}_4^+$	blanc	$+\text{NH}_4^+$	blanc	$+\text{NH}_4^+$	blanc	$+\text{NH}_4^+$
<i>Pinus nigra</i>	0.0	3.5	-1.0	-2.0	-0.1	-1.1	0.0	-0.8
<i>Pseudotsuga menziesii</i>	0.0	2.7	-0.3	-0.8	-0.1	-0.3	-0.2	-0.6

This process proceeds continuously in the course of time (Roelofs et al., 1985). Already at moderate ammonium concentration the leaching of Mg^{2+} by the needles can be more than ten times higher compared to acid artificial rain without ammonium.

Ammonium deposition and a disturbed nutriënt balance in the soil

Most of the Dutch forest stands are planted on acidic, nutriënt poor heathland soils. It is well known that nitrification, and thus acidification is possible in acidic forest soils (van Breemen et al., 1982; Klein et al., 1983; Kriebitzsch, 1978). Whether deposition of ammonium sulphate on acidic forest soils will result in strong acidification depends on the type of the forest soil. Kriebitzsch (1978) who conducted nitrification experiments in many types of acidic forest soils, divided them into groups: A, B, C and D. In the soils belonging to group A there was no nitrification. In the soils belonging to groups B and C there was partial nitrification and in those belonging to group D there was total nitrification. The investigations in this study showed that heathlands and *Pinus* soils mainly belong to group A. Field studies in the Netherlands in *Pinus nigra* and *Pseudotsuga menziesii* forests on former heathland soils showed indeed only partial or no nitrification. The nitrate levels were low, whereas the ammonium levels were high (Roelofs et al., 1985; Roelofs, 1986; Tabel 5).

Table 5. pH and chemical composition of soil-distilled water extracts (1:3) of A) healthy, B) moderately damaged and C) severely damaged *Pinus nigra* and *Pseudotsuga menziesii* forests ($\mu\text{moles kg}^{-1}$ dry soil).

	n	pH (H ₂ O)		NH ₄ ⁺	NH ₄ ⁺ (KCl)*	NO ₃ ⁻	K ⁺	Mg ²⁺	Ca ²⁺	Al ³⁺	
		mean	min.	max.	mean	mean	mean	mean	mean	mean	
<i>Pinus nigra</i>											
A)	20	4.1	3.5	4.6	334	687	271	137	77	153	191
B)	16	4.0	3.4	4.9	384	751	130	47	45	128	158
C)	20	4.1	3.7	4.4	509	1346	117	60	26	43	183
<i>Pseudotsuga menziesii</i>											
A)	10	4.1	3.9	4.4	245	499	164	89	60	106	214
B)	10	4.1	3.8	4.3	562	733	153	67	48	69	211
C)	11	4.3	4.0	4.6	692	1240	157	67	22	36	211

*0.5 M KCl extract.

The soils of healthy, moderately damaged and severely damaged forests had on an average a pH (H₂O) of 4.1, which indicates that also in this type of forest soil the pH is determined by the nitrification limit. In this type of soil a high ammonium deposition level leads to accumulation of NH₄ and leaching of K, Mg and Ca from the soil. As a result the NH₄/K, NH₄/Mg and the Al/Ca ratio increase. It is well-known that increased NH₄ to K and Mg ratios inhibit K and Mg uptake (Jacobs, 1958; Mulder, 1956). In both *Pseudotsuga menziesii* and *Pinus nigra* forests the NH₄/K and NH₄/Mg ratios are relatively low in healthy forests and significantly higher in damaged forests, while the average Al/Ca ratio is significantly higher in severely damaged forests and particularly in *Pseudotsuga* forests, far above the critical value for root damage (Ulrich, 1983).

Apart from premature shedding of needles as a result of nutriënt deficiencies and severe nitrogen stress, the forests become more susceptible to other stress factors such as O₃, drought, frost and fungal diseases.

Table 6. The ratios of some nutriënts in soil extracts of A) healthy, B) moderately damaged and C) severely damaged *Pinus nigra* and *Pseudotsuga menziesii* forests (mol/mol).

	n	NH ₄ ⁺ /K ⁺			NH ₄ ⁺ /Mg ²⁺			Al ³⁺ /Ca ²⁺		
		mean	min.	max.	mean	min.	max.	mean	min.	max.
<i>Pinus nigra</i>										
A)	21	4.7	0.5	14.0	6.4	1.1	24.3	2.0	0.4	5.6
B)	17	9.2	0.8	36.8	10.0	1.8	26.3	1.3	0.2	2.8
C)	21	11.3	1.9	51.8	22.1	1.6	57.2	5.5	1.7	16.7
<i>Pseudotsuga menziesii</i>										
A)	10	3.8	0.5	11.8	4.5	0.6	10.0	6.6	0.8	40.9
B)	10	8.7	1.5	31.2	19.3	2.0	51.1	8.9	0.7	46.7
C)	11	18.2	3.8	64.5	47.6	7.9	118.0	15.6	1.4	54.0

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1 9 8 6 N A T I O N A L F O R E S T H E A L T H S U R V E Y

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S U M M A R Y

Estimated on the basis of needle/leaves loss percentages and yellowing data the health status of the Dutch forest has declined, compared with 1985. The percentage of vital forest has fallen from 49.9% to 46.9%, whereas the combined percentage of hardly vital and non-vital forest has increased from 13% and 2.1% respectively to 16% and 5.1% respectively.

Over the past three years the combined percentage of hardly vital and non-vital forest has increased from 9.5% to 21.1%.

As concerns forest health per province, forests in the provinces of Groningen, North and South Holland, Zeeland and Flevoland are generally vital. In Friesland and the woody provinces of Drenthe, Overijssel, North Brabant and the northern part of Limburg major parts of the forest are hardly vital or non-vital. Notably the percentage and proportion of the categories "hardly vital" and "non-vital" forest have increased greatly in the past three years. The situation in the Peel-region gives most cause to concern.

In the 1983 and 1984 health survey reports the causes of the assessed vitality of Dutch forests have been discussed in depth. It has then been determined that the factors usually affecting forest health should include air pollution. Vital forest may be expected to recover from the effects of weather conditions, insect and fungal damages and the like. The effects of these factors may be directly or indirectly intensified by air pollution, which may be considered a major determinant of Dutch forest health.

In the framework of the National Health Survey it has not been possible to investigate air pollution, except its effect on the nutrient balance. In particular research within the framework of the Additional Programme on Acidification Research. Concerning the other determinants of forest health the following can be said in relation to tree species.

The decline in tree health in 1986 can mainly be attributed to the general decline in vitality of native oak, Douglas fir, and Corsican and Austrian pine. The health status of native oak seems also affected by insect damage which has been recorded for several years now. Insect damage, in combination with weather conditions of which the damage may be a result, is now causing

the dieback of stands.

The decline in Douglas vitality apparently has to be attributed to the results of heavy needle fall, which has occurred for several subsequent winters after a cold and sunny winter spell.

We are happy to note that the recovery of Scots pine recorded in 1985 has continued.

As concerns insect damages it has been observed that these remain at a high level, notably in deciduous trees.

Damage caused by *Tomicus piniperta* has been observed on 7% of the Scots pine surveyed, and on 1% of the Corsican and Austrian pine surveyed. The former is considered a high percentage.

Fungal damage in Austrian and Corsican pine is very extensive. Branch death by *Sphaeropsis* and *Brunchorstia* is common in a major part of the stands.

Throughout the Netherlands branch death has been recorded in Scots pine to a slight extent. This may well have been caused by the fungus *Sphaeropsis*.

Needle and leaf discolorations considered typical of deficiency symptoms as a result of disturbance of the nutrient balance, such as may be highly determinant as an effect of air pollution, are most pronounced in Corsican and Austrian pine, Scots pine, Douglas and native oak.

REPORT ON THE 1986 NATIONAL FOREST HEALTH SURVEY

1. GENERAL OBSERVATIONS

In 1983 the National Forest Service conducted its first tree health survey, with the purpose of gaining an insight into the health state of Dutch forests and to gain experience in surveying the situation in the Netherlands.

In the framework of the Additional Programme on Acidification Research, research was started in 1985 into the effects of air pollution on (forest) ecosystems. It will give us some insight into the extent to which and the way in which air pollution affects forest health in the Netherlands. This knowledge is very important for interpretation of health data that are gathered in the framework of the national forest health survey. Within a few years, the results of the afore-mentioned research will be available. At present, air pollution is considered a major determinant of the health of Dutch forests.

Under the Indicative Multi-Year Programme on Environmental Management, one of the objectives of environmental policy is to curb emissions by means of pollution controls at the source. On the forest health surveys conducted since 1983 the following can be said.

The 1984 forest health survey covered a representative sample of the Dutch forests. In addition, it was determined which factors should be considered determinants of health.

A similar survey was conducted in 1985, and special attention was paid to weather conditions, insect plagues, branch and twig diseases and the mineral status.

Like its predecessor, the 1986 report gives a survey of the weather conditions, insect plagues, branch and twig diseases and degree of discolouration. In general, the structure of the survey on which this report has been based was similar to that of the 1984 and 1985 surveys, so that they can be compared.

The objectives of forest health surveys are:

- describing the health of Dutch forests on the basis of a representative sample;
- describing forest health at the national, provincial and regional level, in general as well as per tree species;
- indicating changes in forest health in comparison with previous years;
- if possible, indicating causes that are thought to be determinants.

The report describes the national health situation, the situation per tree species and the situation per province. Now that the available data cover three years, the data of previous years are given as well. The report ends with a chapter on factors that are regarded as determinants of forest health.

2. SURVEYING METHOD

Forest health or the health state of individual trees is described mainly on the basis of leaf and needle loss and degree of yellowing. Other symptoms of decreased forest health merely support or reinforce these symptoms.

On the basis of characteristic leaf/needle loss and degree of yellowing, a tree's health is determined as follows.

Table 1: Health classification on the basis of leaf/needle loss and yellowing.

	yellowing			
	no	1-25%	26-60%	>60%
needle/leaf				
loss				
0-10%	1	1	2	3
11-25%	2	2	3	3
26-60%	3	3	4	4
> 60%	4	4	4	4

This classification is in line with the ECE-classification, as it has been laid down at Geneva by the Working Group on the Effects of Air Pollution on Forests. It is a relative classification in which the quantitative occurrence of tree yellowing is expressed in per cent. There is an ECE standard for needle and leaf loss, which may be adjusted to the national conditions. A direct comparison on the basis of needle year classes etc. is impossible, because the needle density of a species may vary from growing area to growing area. Relative categories are used because they can be compared. By now this method has been applied in many European countries, and at the Working Group's meeting in October 1985 it was accepted as a uniform type of presentation. The survey per health category is composed by classifying all individual trees that have been incorporated in the survey into a certain health category. Then this health classification is totalled for all sampled plots. Because the province and tree species of each sampled plot have been specified, it is possible to make a break-down per province and per tree species.

The classification is based on the following standards:

- to coniferous trees applies the potential needle density that is considered normal.

Scots pine	all branches in the canopy, where observation takes place, should be covered fully with at least two-year-old needles;
Douglas fir	all branches in the crown, where observation takes place, should be covered fully with five-year-old needles;
Pinus nigra	all branches in the crown, where observation takes place, should be covered fully with four-year old needles.
Picea and Abies	all branches in the crown, where observations are made should be covered fully with six year-old needles.

- in deciduous trees, the leaf density on the branch is estimated.

The rates are based on the distribution of frequency of surveyed trees over the health categories. The deviation from the percentages (with 95% reliability) is ca. 4%.

The meaning of the various health categories is as follows:

Category 1, healthy forest

The "healthy forest" category has characteristics that are normal for its species and age, so that there is no doubt about its life expectancy.

Category 2, less healthy forest

The "less healthy forest" category shows characteristics that indicate that it will realize its life expectancy, but there are also indications that this situation may change.

Category 3, forest in poor health

On the basis of its forest health characteristics, the "forest in poor health" category has no future. Although forests of this category may recover, the seriousness of their decline makes us fear that forests of this category run a high risk of being lost, if the frequency of the factors that determine loss of health remains the constant.

Category 4, unhealthy forest

On the basis of its health characteristics, the "unhealthy forest" category shows characteristics of being either doomed or already dead.

This is the first year that data on three successive sample years have been compiled, which allows comparison. A difference between two successive years is statistically significant if it exceeds a specific critical value. This critical value varies from case to case and depends on, inter alia, the number of sampled plots on which the estimated difference is based. Generally speaking, the differences are statistically significant if they are more than 10-20%.

3. RESULTS OF THE 1986 FOREST HEALTH SURVEY

3.1. National forest health

Table 2 Survey of forest health in the Netherlands. The forest area in the sample covers 281,000 ha of high forest.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	50.8	39.9	8	1.5
1985	49.9	35.0	13	2.1
1986	46.9	32.0	16	5.1

It may be concluded that the area of healthy and less-healthy forest declined by 3% in 1986, while the area of forest in poor health and unhealthy forest increased compared with the previous year.

Over the three years that samples have been taken, the area of healthy forest has declined by 4%, the area of forest in poor health has grown by 8% and that of unhealthy forest has grown by 3.6%. The area of forest in poor health has doubled, and the area of unhealthy forest has trebled since 1984.

3.2 Health per tree speciesScots pine

Table 3 National health survey of Scots pine. The forest area in the sample covers 113,400 ha, which is ca. 40% of the surveyed forest area.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	34	51	12	2
1985	48	36	14	2
1986	50.2	32.8	13.5	3.5

It may be concluded that the improvement of forest health that was found in 1985 continued in 1986. Over the three years that samples have been taken, the areas of forest in poor health and unhealthy forest have increased slightly (by 1.5%). For the unhealthy forest category this rise is statistically significant.

Austrian/Corsican pine

Table 4 National health survey of Austrian/Corsican pine. The forest area in the sample covers 15,860 ha, that is ca. 6% of the surveyed forest area.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	57	34	8	1
1985	40	42	15	3
1986	19.3	28.5	40	12.2

From the table it may be concluded that the decline in health of Austrian and

Corsican pine has continued. The growth in the "forest in poor health" and "unhealthy forest" categories is very striking.

Over the three years that samples have been taken, the area of healthy forest has declined from 57% to 19% of the total forest area, while the area of forest in poor health has risen from 8 % to 40% and that of unhealthy forest has grown from 1 to 12.2%.

Douglas fir

Table 5 National health survey of Douglas fir. The forest area in the sample covered 15,530 ha, which is ca. 6% of the surveyed forest area.

survey	healthy (%)	less healthy (%)	in poor health (%)	unhealthy (%)
1984	50	39	9	2
1985	33	43	22	2
1986	16.7	26.8	45.2	11.3

For Douglas fir, too, the deterioration that was found in 1985 continued in 1986. The area of healthy forest fell to 16.7%, while the categories of Douglas forest in poor health and unhealthy douglas forest now cover more than half (=56.5%) of the total area under Douglas firs.

Over the three years that samples have been taken, the area of healthy forest has declined from 50% to 16.7%, whereas the area of forest in poor health has increased from 9% to 45.2%, and the area of unhealthy forest has increased from 2% to 11.3% since 1984.

Norway spruce

Table 6 National health survey of Norway spruce. The sampled forest area covers 13,120 ha, which is ca. 5% of the surveyed forest area.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	62.5	28	7	2.5
1985	48	41	9	2
1986	49.4	34.4	12.4	3.8

The table shows that the area of healthy forest under Norway spruce has remained the same as in in 1985.

Over the three years that samples have been taken, the area under Norway spruce has declined from 62.5% to 49.4%, while the "forest in poor health" and "unhealthy forest" categories have increased from 9.5% to 16.2%.

Other coniferous species

Table 7 National health survey of the other coniferous species. The forest area in the sample covers 24.030 ha, that is ca. 9% of the surveyed forest area.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	62	32	4	1
1985	63	28	8	1
1986	63.1	24.3	8.6	4

It may be concluded that in other coniferous trees there has been a shift from the "less healthy" category to the "poor health" and "unhealthy" categories. In three years this has led to an increase in the "poor health" category from 4%

to 8.6% and an increase in the "unhealthy" category from 1% to 4%.

Oak

Table 8 National health survey of native oak. The forest area in the sample covered 43,850 ha, that is ca. 16% of the surveyed forest area.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	57	38	4.5	1
1985	40	39	19	2
1986	29.5	41.5	20.2	8.8

The table shows that the deterioration in the health of native oak has continued in 1986.

There has been a striking decline in the area of "healthy forest" and a very sharp rise in the area of "unhealthy forest" from 2% in 1985 to 8.8% in 1986. Over the three years that samples have been taken, the area of "healthy forest" has declined from 57% to 29.5%, while the area of "forest in poor health" and "unhealthy forest" has grown from 5.5% to 29% of the total area under oak.

Beech

Table 9 National health survey of beech. The forest area in the sample covered 8.550 ha, which is ca. 3% of the surveyed forest area.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	71	24	4	1
1985	72	21	6	1
1986	68	26	4.5	1.5

Over the three years that surveys have been conducted, the health of beech has remained fairly stable.

Other deciduous trees

Table 10 National survey of the forest health of the other deciduous tree species. The forest area in the sample covers 47,010 ha, that is ca. 17% of the surveyed forest area.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	74	23	2.5	0.5
1985	64	28	7	1
1986	63.2	27.2	7.3	2.2

The table shows that the situation has stabilized compared with 1985, except for the "unhealthy" forest, which has increased to 2.2%. Over the three years that samples have been taken, the area of "healthy forest" has declined from 74% to 63.2%, and the area of "forest in poor health" has increased from 2.5% to 7.3 % while the area of "unhealthy" forest has increased from 0.5% to 2.2%.

3.3 Forest health per province

The distribution of the sampled plots over the Netherlands is linked with the forest area in the various provinces. As a result of this method, there are insufficient data about Groningen, Friesland, South-Holland, North-Holland, Zeeland and Flevoland to make statistically justified calculations for these provinces. With the exception of Friesland, the forests in these provinces are healthy. The deterioration of the forest health in Friesland that we saw in 1985 intensified in 1986. It appears chiefly in Douglas fir, Corsican and Austrian pine and in oak. The forest health surveys in the other provinces have produced sufficient data to present them per province in a table.

Table 11 Survey of forest health in Drenthe. The forest are in the sample covered 25,220 ha.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	65	31	4	1
1985	50	42	7	1
1986	51.5	33.1	12.6	2.8

The percentage of healthy forest in Drenthe has increased slightly compared with 1985. The "less healthy" category has fallen substantially, so that the "forest in poor health" and "unhealthy forest" categories have grown sharply. Analysis of the basic material shows that this increase is due in particular to the decline in the health of Douglas fir and oak.

Table 12 Survey of forest health in Overijssel. The forest area in the sample covered 32,040 ha.

survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	25	62	12	1
1985	39	41	18	2
1986	44.7	33.1	17.3	5

In the province of Overijssel the area of healthy forest has increased by more than 5% to 44.7%. In the three years that surveys have been conducted the area of healthy forest has grown from 25% to nearly 45%. In addition, the trend is towards an increase in the area of unhealthy forest.

From basic data it appears that in Overijssel Scots pine has recovered substantially in the past two years. The increase in the "in poor health" and "unhealthy" categories is mainly due to Douglas fir and oak.

Table 13 Survey of forest forest health in Gelderland. The forest area in the sample covered 85,410 ha.

survey	Healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	49	40	10	2
1985	56	31	12	1
1986	45.7	34.6	15.6	4.1

The table shows that the healthy forest area in Gelderland has declined compared with 1986. The average increase in the other forest health categories has been 3%. This increase is due to Corsican and Austrian pine, Scots pine, Douglas fir and oak. On the other hand, the health of Scots pine has improved substantially since 1984.

Table 14 Survey of forest forest health in the province of Utrecht. The forest area in the sample covered 15,890 ha.

Survey	healthy (%)	less healthy (%)	in poor forest (%)	un-healthy (%)
1984	40	44	14	2
1985	55	34	10	1
1986	52.1	30.2	14	3.7

Except for the percentage of unhealthy forest, there has been no marked shift in Utrecht's forest area. The basic data show that this increase is largely due to oak. The health of Scots pine has improved sharply since 1984.

In the three years that surveys have been taken, the area of healthy forest in Utrecht has grown from 40% to 52.1%, while the percentage of healthy forest has remained the same. The area of unhealthy forest has increased from 2% to 3.7%.

Table 15 Survey of forest health in North-Brabant. The forest area in the sample covered 64,170 ha.

Survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	48	44	6	2
1985	37	40	19	4
1986	38	34.4	20.1	7.5

in 1986 the area of healthy forest in North-Brabant remained the same, while that of unhealthy forest almost doubled. The basic data show that the deterioration is particularly due to the decline in the health of oak, Douglas fir, Corsican pine and Austrian pine. Over the three years that samples have been taken, the area of healthy forest in North-Brabant have declined from 48% to 38%. The area of forest in poor health and unhealthy forest has risen from 6% to 20.1%, and the area of unhealthy forest has increased from 2% to 7.5%.

Table 16 Survey of forest health in Limburg. The forest area in the sample covered 28,610 ha.

Survey	healthy (%)	less healthy (%)	in poor health (%)	un-healthy (%)
1984	61	32	7	1
1985	59	32	8	1
1986	60.6	23.2	13.2	3

These figures show that the area of healthy forest in Limburg has remained constant. Compared with 1985, the area of low-forest health forest has increased from 8% to 13.2%, while the area of unhealthy forest increased from 1% to 3%. This increase is particularly due to the deteriorated health of Corsican and Austrian pine.

4. DETERMINANT FACTORS

The causes of the recorded decline in vitality of the Dutch forest have already been extensively discussed in the 1983 and 1984 health surveys. It has then been assessed that the factors usually affecting forest health should include air pollution. In the past few years various hypotheses have been developed to explain the present health status of European forests. A differentiation can be made between traditional and non-traditional determinants. Traditional factors include drought, frost, pests and diseases, whereas air pollution is considered a non-traditional factor. It has been recognized that a complex of both traditional and non-traditional factors - which has to be examined in depth - is responsible for the decline in forest health in Europe. These factors manifest themselves differently throughout Europe, thus justifying the variety in hypotheses. Since 1985 the study of causes and effects has been continued independently of the health study.

Within the framework of the "Additional Programme on Acidification Research" a study is being made of the causes and effects of forest health decline. This study includes the monitoring of various stress factors in Douglas fir and the effects of acid deposition and air pollution on the relationship between forests and soils. Further a study is made of the rhizosphere and of the effect of ammonium deposition on forest and moorland vegetations. The final report will be published in 1988.

Characteristics of damage caused by air pollution, with exception of the characteristics of disturbance of the nutrient balance system, cannot be distinguished during field studies, on which a health survey is based. It is therefore not possible to discuss air pollution as a determinant of vitality in the National Health Survey.

The study has to be restricted to indices which can be observed, i.e. traditional factors such as weather conditions, insects, fungi and the like. The effect of these factors may be intensified to a greater or lesser extent by air pollution. This has been extensively discussed in the 1985 National Health Survey. In the summary the following statement was made: "It has been observed that the severe winter, certain damage by insects and the *Sphaeropsis*-fungus have also affected the vitality assessed, the extent to

which may be directly or indirectly determined by air pollution." As concerns 1986, the following can be said about traditional factors and disturbance of the mineral status.

4.1 Weather conditions

On the basis of monthly reports issued by the national meteorological office (K.N.M.I.) the weather course which has affected the vitality assessed since August 1985 may be described as follows:

After a rather cool and wet August autumn began with a dry and sunny period. In November winter set in with rather wet, dull weather and cold spells. This weather lasted all through April, with the exception of February. This month was remarkably cold, very sunny and extremely dry. It is considered the coldest month of this century and one of the sunniest winter months. Spring ended with a rather warm and sunny spell. It should be mentioned that on May 30 and May 31 night frost was recorded. The month of June was relatively cold.

Summer was warm, dry and sunny with a dry spell in July and August, precipitation being markedly lower than usual (40 mm instead of 80 mm). The last two weeks of August, however, were cool, wet and dull, after which a dry, sunny and extremely cold September set in. As in the preceding years, survey period ran from July 14 to September 12.

Particular effects on forest health may be expected as a result of:

- a. the very cold, sunny and extremely dry month of February 1986.
- b. the late night frost in the month of May 1986.
- c. the dry summer months of July and the first two weeks of August 1986.

ad a. very cold, sunny and extremely dry month of February 1986

In general, Douglas fir suffers particularly from sunny and dry weather in winter. Consequently needle assimilation is stimulated, whereas the roots are still inactive for water supply. As a result the tree dehydrates and loses needles. This situation has been observed since 1983, and has greatly determined Douglas decline. Further, observations showed that frequently browning appeared on Douglas, which might be related to the occurrence of

frost. Because of the weather conditions in the period preceding the frost spell (a gradual fall in temperature with occasional light nightfrosts) twig ripening was much improved in the autumn of 1985. Unlike the preceding year in oak, no or few frosted buds and leading shoots were observed.

Like 1985, frost damage in the form of dying-off of cambium was observed in Corsican and maritime pine. This frost damage was also observed in Belgium and there, too, it is considered highly determinant of the health status of these trees.

ad b. late night frost in the month of May

As a result of late nightfrost many young buds and developing shoots were frosted in Douglas, Norway spruce, beech and native oak. Reports show that with the exception of some smaller areas the normally possible recovery has taken place.

ad c. dry summer months of July and the first two weeks of August

As a result of the low precipitation in this period it may be assumed that the course of the trees' vegetation period has been affected, in particular on drought-sensitive soils. Especially on Scots pine autumn phenomena were observed in the survey period, which "normally" only occur in late September and October and which presumably are brought about by this drought. Deciduous trees on drought-sensitive soils, too, will have been affected.

4.2 Insect damage

On the basis of the experiences gained in 1985 in relation to the damage caused by insects during the survey period the list of damage patterns to be surveyed has been changed. Table 17 shows what has been assessed for each observation plot.

Table 17 Insect damage per tree species based on damage patterns

damage pattern	t r e e s p e c i e s							
	Scots pine	Corsican /Austrian pine	Douglas	Norway spruce	oak	beech	other conif- erous	other decidu- ous

Tomicus piniperda	7%	1%	-	-	-	-	-	-
Blastesthia turionella	1%	-	-	-	-	-	-	-
Adelges cooleyi	-	-	4%	-	-	-	-	-
Pristiphora abietina	-	-	-	14%	-	-	1%	-
Cryptococcus fagisuga	-	-	-	-	-	13%	-	-
non-specified agents	4%	1.5%	2%	3%	52%	16%	21%	41%

no damage	88%	97.5%	94%	83%	48%	71%	78%	59%

The table shows that on most tree species insect damage has been observed to a limited extent. The high percentages in deciduous tree species are striking. In particular the high percentage in oak is remarkable. Only on 48% of the stands of oak assessed no insect damage has been observed. In spring this percentage must have been even higher as damage patterns in oak should be attributed almost completely to spring agents such as the great and small winter moth and the green leaf roller which cause heavy losses in spring. Damage by *Tomicus piniperda* has been observed on 7% of the Scots pine assessed, and on 1% of the Corsican/Austrian pine assessed. The former percentage is considered high, given the ideal circumstances for this insect to develop to pest level, because of the percentages of low-vital and

non-vital pine forest.

As in the preceding year a complementary study has been undertaken of the insect damage in oak. This study shows that in 1986, too, oak vitality has been greatly affected by the occurrence of insect damage, in particular by the small winter moth. This damage has been reported throughout the entire country. On many stands of oak this damage has been observed since several years, but this year damage has been mainly reported in older stands (> 20 years). Insect damage increasingly causes defoliation and a decline in shoot development. Therefore, the health status is readily judged as being low-vital.

Last year it has been determined that if insect damage would occur again this would have serious consequences for the health status of native oak in the Netherlands. Insect damage in combination with and perhaps also brought about by weather conditions (a.o. frost and drought) is at the moment of writing causing forest dieback. If these circumstances will be as determinant in the coming year, the downward trend in oak vitality will continue.

4.3 Branch and twig diseases

In order to gain an insight into the extent of prevalence of the fungi *Sphaeropsis sapinea* and of *Brunchorstia* these agents have once again been assessed.

Table 18 Fungal damage per tree species based on damage patterns

branch/twig disease	damage*	t r e e s p e c i e s			
		Scots pine	Cors. Austr. pine	other conifer- ous	deciduous

<i>Sphaeropsis</i>					
<i>sapinea</i>					
(shoot death)	slight	24%	14%	-	-
	moderate	-	1%	-	-
	severe	-	0.5%	-	-
(death of branches)	slight	4%	6%	-	-
	moderate	-	2%	-	-
	severe	-	0.5%	-	-
<i>Brunchorstia</i>	slight	-	12%	-	-
	moderate	-	0.5%	-	-
	severe	-	0.5%	-	-
other agents	slight	4%	4%	4%	7%
	moderate	-	-	-	2%
	severe	-	-	-	-

not infected		68%	59%	96%	91%

* slight : 1-40% of the shoots/needles/leaves per tree shows symptoms of damage.

moderate: 41-60% of the shoots/needles/leaves per tree shows symptoms of damage.

severe : > 60% of the shoots/needles/leaves per tree shows symptoms of damage.

After several years of damage, damage caused by *Sphaeropsis sapinea* and *Brunchorstia* cannot be clearly distinguished during field studies. The distinction made in the survey can only be assessed under laboratory conditions. The percentages are therefore not a true representation. It may be concluded, however, that Corsican pine has suffered from fungal damage, which in the case of *Sphaeropsis* and *Brunchorstia* greatly affects vitality and may destroy stands.

A light form of branch death in Scots pine has been observed throughout the entire country which is often mistaken for fungal damage caused by

Sphaeropsis. In most cases branches or part of the lower branches are concerned, which seem less vital to tree health. The coming year will have to show which meaning should be attached to this phenomenon.

From the table it may be concluded that damage in other coniferous and deciduous trees is restricted, as in the preceding year. The percentages in Scots and Corsican pine are 32% and 41% respectively. Given the health status of Corsican pine and the damage percentage of branch death by *Sphaeropsis*, this fungus cannot be considered the only factors responsible for Corsican pine decline. It is assumed that the frosts of 1985 and 1986 are determinants as well.

This year shoot death by the fungus *Sphaeropsis* appears to stabilize or to decrease. Damage research carried out under field conditions support the observations of surveyors. In the coming year (1987) research currently being undertaken may provide an insight into the link between causes and effects of N-emission levels and the prevalence of the fungus *Sphaeropsis sapinea*.

4.4 Disturbance of the mineral status

It is generally assumed that deficiency symptoms caused by air pollution, acid deposition and N-emissions will increase, especially when high N-emissions are concerned. This type of pollution disturbs, inter alia, the interrelationship between the elements and causes potassium and magnesium deficiencies (K and Mg).

For the first time attention was paid in the 1985 health survey to the discoloration of needles and leaves, and in particular to those discolorations typical of deficiency symptoms.

In 1986, discoloration of needles and leaves has been incorporated into the health classification according to the ECE-method. In the data bank of the health surveys these observations on individual trees were included separately. As the surveying methods used in 1985 differed from the methods used in 1986 the data of these two years cannot be compared.

Table 19 Needle and leaf discoloration in major tree species

tree species	occurrence of symptoms			
	none*	slight*	moderate*	frequent*
Scots pine	38.1	50.8	8.3	2.8
Corsican/Austrian pine	45.2	39.9	10.1	4.9
Douglas fir	44.9	48.5	5.7	0.9
Norway spruce	76.0	19.3	3.8	0.9
oak	62.3	29.6	7.0	1.1
beech	66.6	28.7	3.8	0.9
other deciduous trees	74.2	21.2	3.8	0.8
other coniferous trees	78.5	18.4	2.7	0.4

*none : normal colour of leaves and needles, no discolorations have been observed

*slight : typical leaf and needle discolorations, occurring in less than 25% of the needles and leaves

*moderate: typical leaf and needle discolorations, occurring in 25-60% of the needles and leaves

*frequent: typical leaf and needle discolorations, occurring in more than 60% of the needles and leaves

Most discolorations have been observed on coniferous trees. In comparison to other tree species high discoloration values are most common in Corsican and Austrian pine, Scots pine and Douglas.

As concerns deciduous forest, discoloration symptoms are particularly observed on native oak, notably on calcareous soils with iron deficiencies. Unlike coniferous trees, deciduous trees on acid sandy soils show less conspicuous symptoms. Leaf analyses may be decisive in this matter.

The leaf analyses which have been performed up to date have shown deficiencies of potassium, magnesium and phosphate. In contrast with previous analyses hardly ever a nitrogen deficiency is found.

Floristic changes due to eutrophication

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Towards the end of our Symposium in Bilthoven I was asked to present an abstract of my view on the effects of the deposition of nitrogen compounds from the atmosphere on wild living organisms at the population-, biocoenosis- and ecosystem levels. The main effect is nutrient input. Nitrogen supply has for long time been a critical factor for plant nutrition. More than 50% of the plant species in Central Europe can only compete on stands that are deficient in nitrogen supply. This is much more pronounced in the threatened species that are known from the "Red Data Lists": 75 to 80% of these species are indicators for biocoenoses with insufficient to very poor nitrogen supply. About 220 of the non-threatened plant species with indicator values for nitrogen deficiency (about 600 out of the total of 1274) are alpine in distribution, that is why they appear non-threatened. Otherwise the discrepancy would be even greater.

Threatened plants by definition are rare. Most of them have become rare in the very recent decennia. The discrepancy in the distribution of the threatened and the non-threatened plants over the gradient of nitrogen indicator values from very poor (1) over poor (3) and just sufficient (5) to rich (7 to 8) and surplus (9) is the most obvious of those that can be analysed. Other gradients of indicator values are light, temperature, continentality, moisture, acidity/alkalinity and salt tolerance. These gradients can be investigated on the basis of 2164 plant species for which

indicator values have been defined (Ellenberg sen. 1979, 1983). The comparison of threatened and non-threatened species gives the possibility to look at temporal trends.

As nitrogen is a main trigger of plant growth, nitrogen input to ecosystems means changes in the structure of plant stands. Plenty of influences on the competition equilibrium between plants in a stand are possible by this nutrient input. Tolerance of nitrogen deficiency is no longer important. Many of those low-growing, light-requiring hunger artists (niedrigwüchsige, lichtbedürftige Hungerkünstler) are outshadowed by faster and higher growing species. Plant stands become denser, higher.

They develop a sort of woodland climate under their canopy with dampened temperature oscillations higher moisture in the air at least during daylight hours, less wind speed, and so on, even if they are only growing up to knee height. The micro-climate this way is changing to more "atlantic" conditions. "Continental" plant species disappear, in an other view: they appear on the "Red Data Lists".

Plants that are pushed by nitrogen supply to grow fast, dense, and high need more kations like K, Mg, Ca for their growth, and they spend more water during growth.

Nutrient imbalances develop, tolerance of dry spells will diminish. As growth with good nutrient supply starts early in the season and lasts longtime in fall, there is more exposure to frost spells. Plant individuals rich in nitrogen, up to a certain degree, appear to be highly appreciated by herbivores, from aphids up to deer or caterpillars. Predators living from those species will thrive, too. Mycorrhizae and other fungi are affected by nitrogen inputs. The same is true for algae and lichens.

A special case is the development of large bodied insects like grasshoppers, some caterpillars and beetles. Many of them require relatively high temperatures in order to develop in time during the short seasons in Central and Northwestern Europe. Highest temperatures are observed in short grass and other open habitats with parts of the ground not covered by plants, mainly for some hours a day, only. Due to the eutrophication drafted above such habitats have become rarely available, nowadays. Many bird species that rely on those large insects have become scarce. Other species, like partridge, that need a high temperature microclimate for their own development at least for some critical early weeks in their ontogeny, appear to be affected directly.

Nitrogen has been supplied actively to many places by agriculture. An average hectare of cultivated land in Western Germany receives about 200 kgs N per year from different "active" sources. Emission density of NO_x in our country has been calculated to about 40 kgs N/ha/year from combustion leading to NO_x , mainly from industrial sources and from automobile traffic. The emission of NH_3 in many areas, mainly in Northwestern Central Europe, can be paramount from agricultural sources, as we have learned during this symposium. Wet deposition has been measured at many places giving figures of 10 to 50 kgs N/ha/year. In throughfall of plant stands, at forest edges, and under conditions of intensive husbandry N-input can be much higher.

Dry deposition of N and direct NH_3 uptake via the stomata in plant leaves are more difficult to investigate. Experience shows that in addition to wet N deposition (100%), there may be another 50 to 150%. And about 10% of the gaseous NH_3 is directly taken up via the stomata (Heil, pers. comments). So, N-deposition from the air may accumulate to significant uncontrolled input as compared to agricultural activities.

This input accumulates in biomass, litter or humus unless it is exported from the system by some sort of harvest. And some time in the future under

suitable conditions, the accumulated amount will become re-mineralized, changing the competition-equilibrium most effectively, then, at the latest.

Longtime before ion inputs to ecosystems developed toxic effects to some tissues or individuals, they influence competition between organisms in populations and biocoenoses. Nitrogen has been in poor supply, traditionally in former times at many places. That is why today ecosystems are reacting in such a significant way. Spruce and pine, the paramount forest - and plantation species, are adapted naturally to poor environments. Forestry is well advised to look for tree species that thrive under conditions that become more acidic and richer in nitrogen. As there are very few tolerant species (Betula, Sorbus, some Salix) and few stands sufficiently void of stress from frost and water deficiency, this is a hard task. But you can take the change of the plant cover, of the flora and fauna, as bioindication for significantly altered living conditions. They affect man, too. At least on the competition level, in case he has to make use of the ecosystems in a more efficient way than his close or worldwide neighbours.

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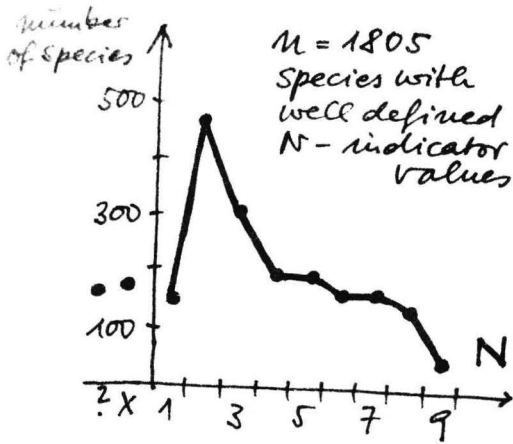
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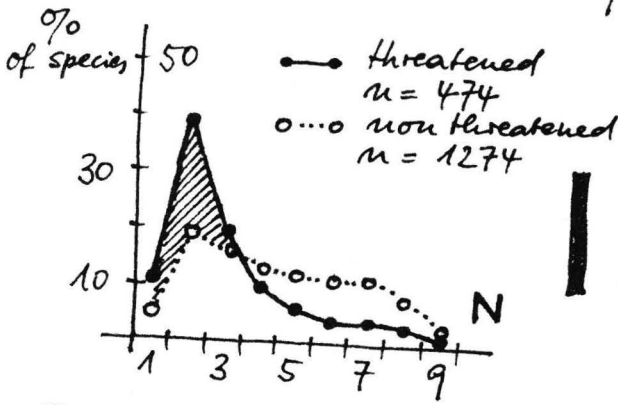
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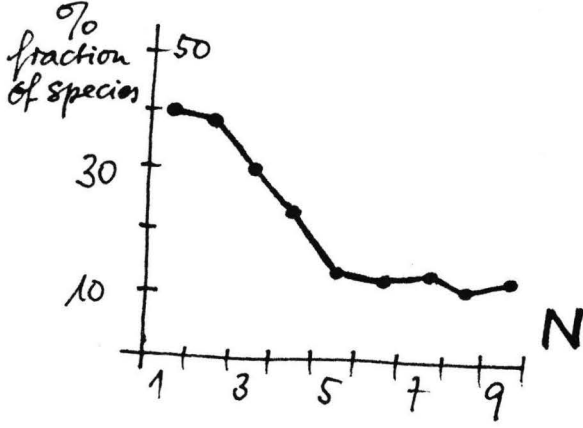
Fig. 1:



Distribution of 2164 Central European Plant species in the gradient of nitrogen indicator values.
 "2" not known; "x" indifferent
 "1" most pronounced nitrogen deficiency
 "3" poor in nitrogen
 "5" just sufficient in nitrogen
 "7" more often found at places rich in N
 "8" nitrogen indicator
 "9" surplus nitrogen to polluted with N
 "2", "4", "6" intermediate



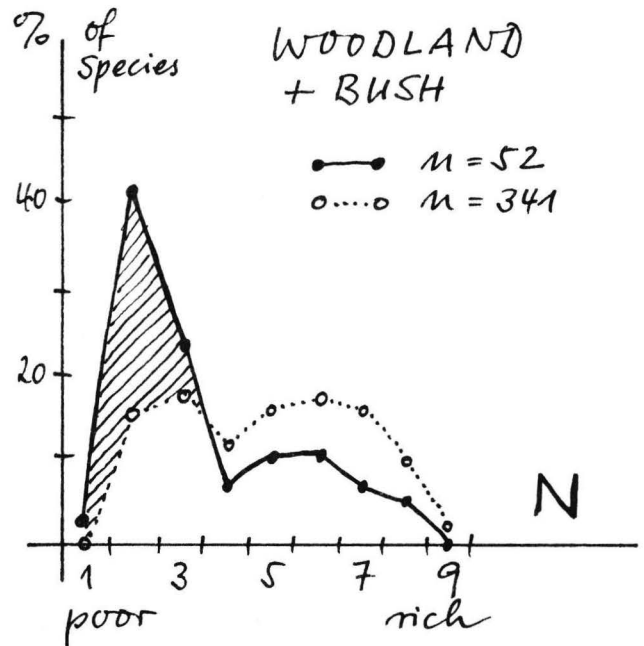
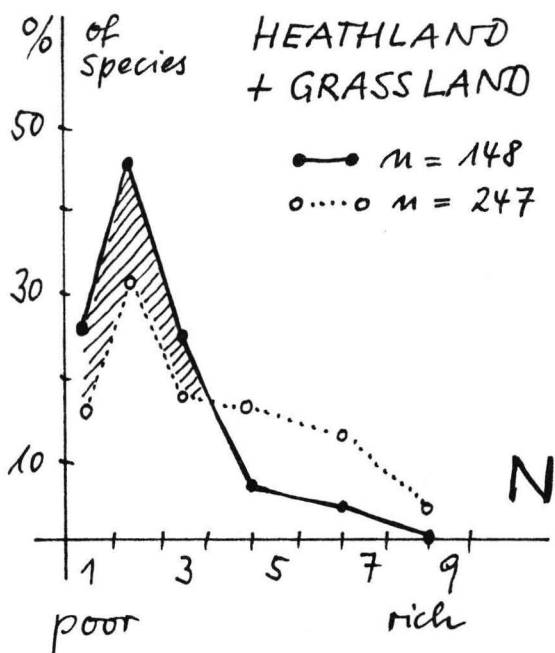
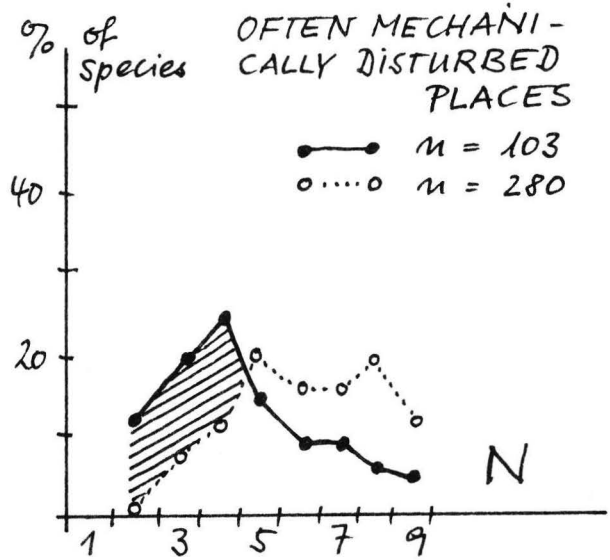
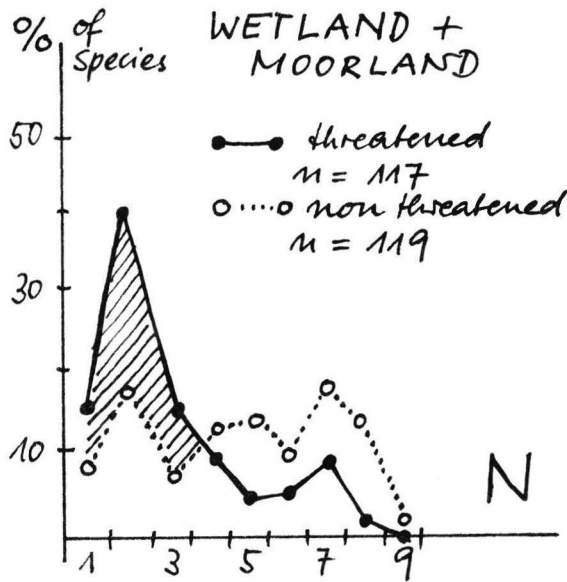
Most of the threatened species can only compete on nitrogen-deficient stands (57 "potentially threatened" species not regarded.)



The fraction of threatened species within the total of species in a given class of nitrogen indicator value is diminishing with better nitrogen supply. It remains constant from value "5" upwards (see above).

re-drafted from ELLENBERG jun. 1985

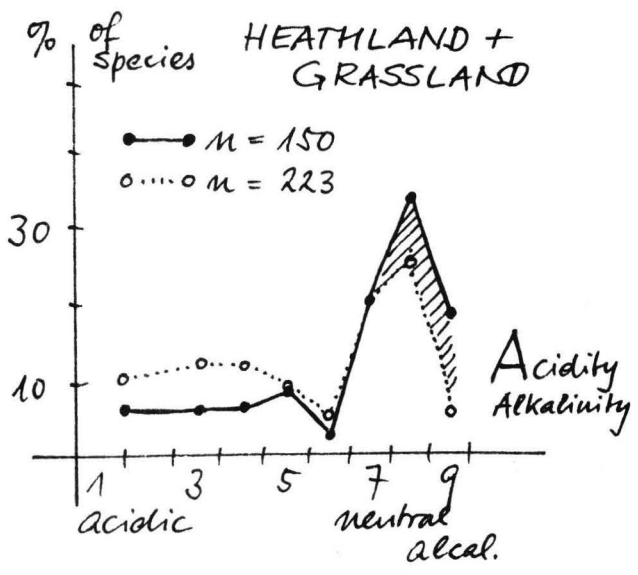
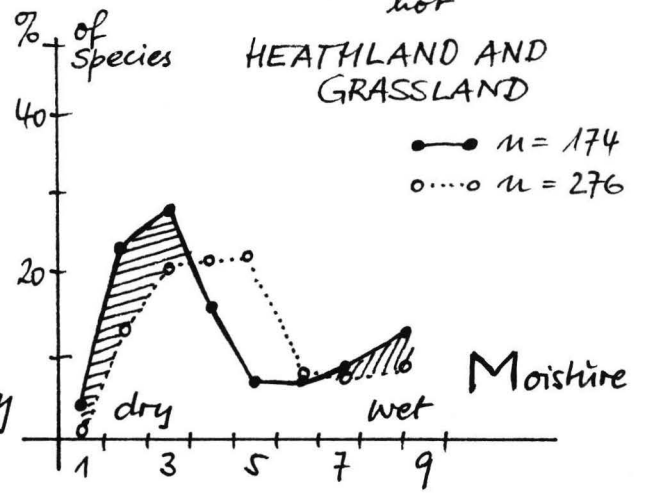
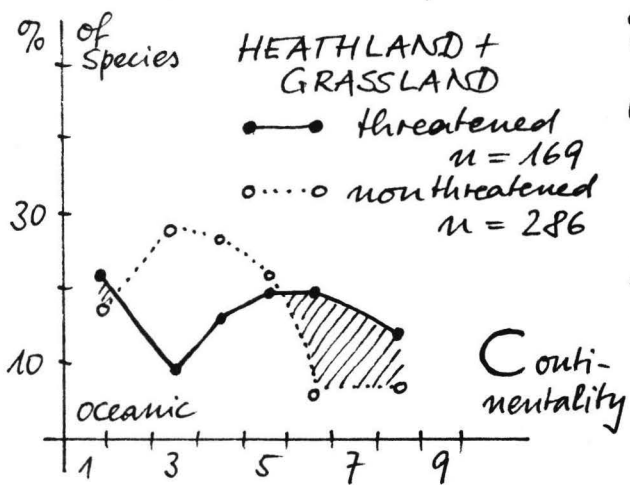
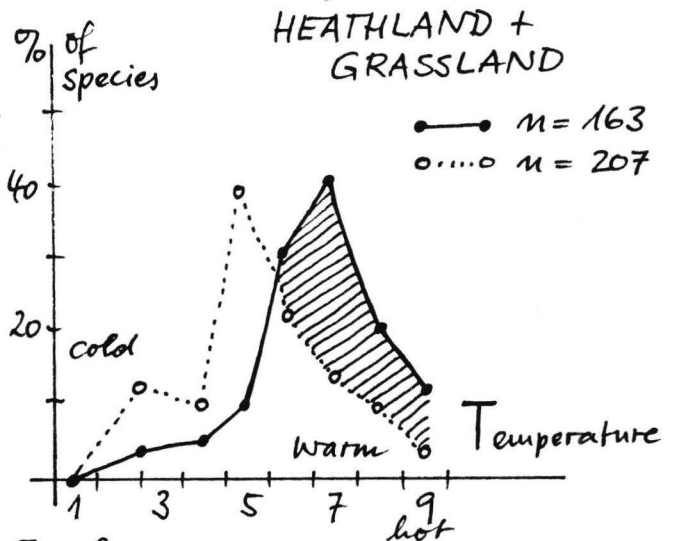
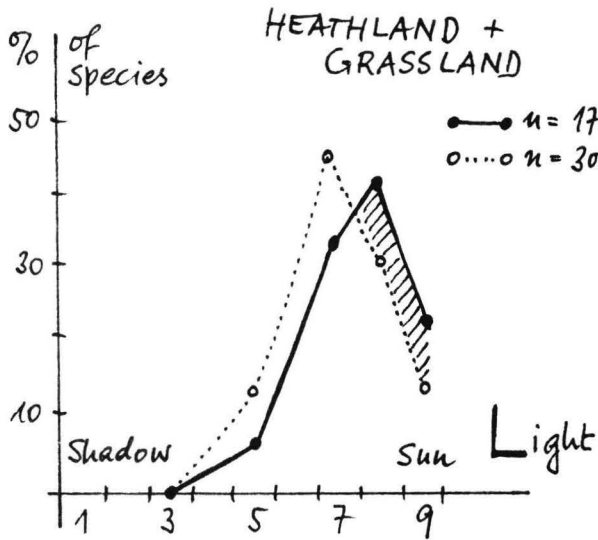
Fig. 2:



in every analyzable ecosystem type threatened plant species "concentrate" in the poor to very poor sector of the Nitrogen (N) gradient.

redrafted from ELLENBERG jun. 1985.

Fig. 3:



Threatened plants (●—●) in Central Europe require better Light and Temperature conditions than non threatened (○····○) species. They tolerate extrema better in the Continentality and Moisture gradients. Indicators for neutral or slightly alcalic soils are more threatened than acidity - indicators (A).

All these effects are influenced or even triggered by the Nitrogen factor. — The example refers to one ecosystem type, only.

Growth disturbances of forest trees close to fur animal farms

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Finland is one of the biggest producers of farmed furs in the world. Production has continuously increased, particularly during the last ten years. Last year over 6 million furs were sold. There are 5600 fur animal farms in Finland, most of them situating in a restricted region in the western coast. It is estimated that the excrements of fur-bearing animals contain app. 6,000.000 kg of nitrogen per year. The excrements lay in the open without almost any treatment. Although NH_3 emission from the fur farms has not been investigated so far, it may be considerably high.

Many macroscopic growth disturbance symptoms can be seen in forests close to fur animal farms: loss of apical dominance, die-back of the leader shoot, abnormal branch growth and needle fall. High foliar nitrogen content and nutrient deficiencies are hypothesized. Root damages and impairment of mycorrhizae vigour have been observed. Expansion of green algae on tree trunks and needles is visible.

A study on tree growth disturbances has been initiated, because forest owners and professionals were concerned about damages and death of trees, yield loss and regeneration problems. Permanent sample plots have been established in the forests (*Pinus sylvestris*) close to the fur animal farms. Tree growth is measured, growth disturbance symptoms are described and needle and soil samples are collected for nutrient analyses.

Early results suggest that high nitrogen content in the needles, connected with altered nutrient ratios (eg. Mg, B), contributes to the observed growth disturbances.

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