ATMOSPHERIC BEHAVIOUR OF AMMONIA AND AMMONIUM

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ter verkrijging van de graad van
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To all people who fight for a better environment all over the world.

STELLINGEN

1. Atmosferische chemie is de wetenschap die zich bezighoudt met het onderzoeken van het atmosferisch deel van de kringlopen van stoffen. De volgende processen worden hierbij onderzocht: emissie, transport, chemische omzetting en verwijdering. Tevens wordt de invloed van de chemische samenstelling van de atmosfeer op het klimaat bestudeerd.

2. Het door Hoell *et al.* (1982) gebruikte model om het vertikale koncentratieprofiel van ammoniak in de troposfeer te berekenen is onrealistisch omdat reaktie met zwavelzuur-bevattend aerosol niet expliciet in het model is opgenomen.
(Hoell, J.M., Levine, J.S., Augustsson, T.R., Harward, C.N. (1982) Atmospheric ammonia: Measurements and modeling, *AIAA Journal* **20**, 88-95.; zie ook hoofdstukken 3 en 5 van dit proefschrift)

3. De faktor β die door Eliassen (1978) in lange-afstand transportmodellen wordt gebruikt, geeft niet alleen de hoeveelheid geëmitteerd reaktieprodukt weer of dient om de overall-reaktiesnelheid te korrigeren voor een relatief grotere reaktiesnelheid dichtbij de bron. Het is in de eerste plaats een korrektiefaktor die ervoor dient om te kompenseren voor de onderschatting van de hoeveelheid reaktieprodukt die anders zou optreden als gevolg van de introduktie van de korrektiefaktor α.
(Eliassen, A. (1978) The OECD study of long range transport of air pollutants: long range transport modelling, *Atmospheric Environment* 12, 479-487; zie ook hoofdstuk 4 van dit proefschrift)

4. Het zou voor het overleven van de mensheid nuttig kunnen zijn te weten welke maatschappelijke processen ertoe geleid hebben dat "zure regen" van een reeds lang door wetenschappers gesignaleerd probleem tot een door de maatschappij ervaren probleem werd.

5. Meteorologische onderzoekers dienen hun weerzin voor de modellering van veel voorkomende, doch niet-ideale situaties te overwinnen.

6. Indien het zo is dat de produktiviteit van een wetenschapper het grootst is als deze jong is, wordt dit wellicht ten dele veroorzaakt door het feit dat men dan veelal geen relatie en/of kinderen heeft.

7. De nadruk die bij de beoordeling van de kwaliteit van wetenschappers wordt gelegd op de onderzoekskapaciteiten, heeft tot gevolg dat universiteiten beschikken over veel niet-overdraagbare kennis.

8. De benoeming van buitengewoon- en bijzonder-hoogleraren kan leiden tot een grote invloed van buiten-universitaire instellingen op het reilen en zeilen van universiteiten, hetgeen in strijd kan zijn met de belangen van deze universiteiten.

9. Overheidsinstellingen kunnen veel beter bestuurd worden, indien projektgewijze wordt gewerkt, een financiele verantwoording per projekt gegeven wordt en het beschikbare geld naar keuze voor materiële of personele kosten gebruikt mag worden, dan wel aan derden uitbesteed mag worden.

10. Voor het goed funktioneren van instellingen en de daar werkende mensen is het van belang, dat er serieus werk wordt gemaakt van karrière-afbouw, d.w.z. het tijdig in overeenstemming brengen van de werkinhoud met de kapaciteiten van de ouder wordende werknemer.

11. De Nederlandse samenleving zou ontwricht raken, indien alle vrijwilligers ineens met hun werk zouden stoppen.

12. De Nederlandse regering maakt een ernstige denkfout door impliciet aan te nemen dat een vermindering van het aantal ambtenaren automatisch leidt tot een financiële besparing, met name in die gevallen waar dan als gevolg werk aan derden uitbesteed moet worden.

13. De kinderopvang in Nederland dient snel verbeterd te worden.

14. De besparingen waar de Nederlandse regeringen weinig energie ingestoken hebben zijn energiebesparingen.

Willem A.H. Asman,
Atmospheric behaviour of ammonia and ammonium
Wageningen, 2 november 1987.

PREFACE

This thesis is the result of a process of learning atmospheric chemistry by trial and error. Most of the results presented here were obtained when I was working at the Institute for Meteorology and Oceanography, State University Utrecht (IMOU).
The research described in this thesis has been carried out in joint projects with the Netherlands Energy Research Foundation (ECN). This thesis consists mainly of articles based upon research done in co-operation with other persons at IMOU and ECN and would have been impossible without their contribution. Aart Vermetten, Jan-Willem Erisman, Willem Mulder, Elsbeth Pinksterboer (all formerly working at IMOU), Anita Waijers-Ypelaan and Sjaak Slanina (both at ECN) participated in the field measurements and/or participated in the evaluation of the results. Ton Janssen (ECN) contributed much to the parametrization and set-up of the long-range transport model and made all calculations. Bas Drukker helped to find obscure data on historical livestock statistics. Hans Maas (formerly IMOU) helped with some tables and figures. Marjolijn Verhoeven (IMOU) voluntarily typed part of this thesis and Eveline Plesman (IMOU) gave administrative support.

Last but not least: Ed Buijsman made this research possible by making an emission inventory for ammonia for Europe together with Hans Maas and a minor contribution of me. I am very grateful to him for having worked together in a good atmosphere (even without pipe-smoke) for so many years under conditions which would discourage most research-workers. I benefited much from his knowledge on atmospheric chemistry and from his philosophy of life. To me it is depressing to see that our society has no mechanisms by which it can profit enough from the experience and knowledge of unpretentious people.

I am much indebted to ECN for the way they have been co-operating from 1977 to 1987. Their willingness to co-operate was not only essential to this research itself but was also vital to obtain financial support from government agencies.

I am very grateful to the Netherlands Ministry of Housing, Physical Planning and Environment which supported my work financially since 1980, as the State University of Utrecht was no longer able to pay. I wish to thank Chiel Bovenkerk and Jaap Swager of this Ministry who allowed me to make "scientific excursions", pressed me to present results that had something to do with reality and stimulated my work by using the results in environmental policy.

Also I am indebted to Louk Conrads for his continuous interest in and support of my work. He started research on acid rain at IMOU in 1969, some 15 years before everybody seemed to be working on this subject. Furthermore, I wish to thank Piet Jonker (IMOU) who was always willing to help me with computational and statistical problems, Jeroen van der Hage who learned me how to construct scientific instruments from waste products and garbage and Wim Boot who helped to solve electronical problems.

It makes me very happy that I had the opportunity to co-operate with many other persons during earlier stages of my research. They contributed in this way to my education in atmospheric chemistry. From them I learned much and not only in scientific respect. I wish to thank them all, but in particular Joop van de Vate, Joop Luten, A.P. Datema, Han Möls, Frits Bakker, Walter Lingerak, Jan Baard, Wim Zijp, Roel Heijboer and Harry ten Brink (all ECN); Taeke Ridder, Joop den Tonkelaar, John Bernard, Jan Reiff, A. van den Hoek, Cecil Engeldal and Frank van Lindert (all Royal Netherlands Meteorological Institute, KNMI); Ferd Römer (KEMA), Frank de Leeuw and Hans Reijnders (National Institute of Public Health and Environmental Hygiene, RIVM); Gode Gravenhorst (formerly Insitute of Meteorology and Geophysics, Frankfurt F.R.G.); Tom Horst and Jake Hales (Battelle Pacific Northwest Laboratories, Richland WA, USA). Moreover, I wish to thank R.A. Wijsman and J. Westerik (KNMI) who helped to obtain meteorological data and H.M. van Zoest who printed our reports with the utmost care.

I am grateful to the students whom I helped and who forced me to express my thoughts much clearer: Ellen Velders, Jurriën Hooghiemstra, Myriam van Rooij and Elsbeth Pinksterboer.

I am much indebted to Eep Adema and prof. dr. H.-W. Georgii who were willing to act as supervisors for a thesis which was already nearly finished when I asked them to. I am grateful to my present employer, the National Institute of Public Health and Environmental Hygiene and to my colleagues who created a working environment in which I felt happy enough to be able to complete this thesis in the evening hours.

Finally, I wish to dedicate this thesis to all people who fight for a better environment all over the world. Without idealism there is no future! (this does not imply, however, that there exists a future for idealists).

CONTENTS

CHAPTER 1. INTRODUCTION

1.1 Why are ammonia and ammonium important components?

This study deals with the atmospheric behaviour of ammonia (NH_3) and ammonium (NH_4^+). Although ammonia and ammonium are important atmospheric components, also in a quantitative sense, the attention has until now mainly been focussed on SO_x and NO_x as being the main acidifying components. Ammonia and ammonium are important components both in the atmosphere and after having been deposited for several reasons:

a. Ammonia is the most abundant alkaline component in the atmosphere. In many parts of Europe up to 70% of the acid in precipitation is neutralized by ammonia (EMEP, 1984). Also a large fraction of the acid in aerosols at ground level is neutralized by ammonia (chapter 3). As a result the reaction product ammonium is an important component in aerosols at ground level and in precipitation.

b. When ammonia and ammonium are deposited and enter the soil as ammonium, nitrification can occur by Nitrosomas and Nitrobacter leading to the overall reaction (Van Breemen, 1982):

$$NH_4^+ + 2O_2 \rightarrow 2\ H^+ + NO_3^- + H_2O$$

As a result not only is acid formed by the oxidation, but also acid formed in the atmosphere is no longer neutralized by ammonia. In this way ammonia and ammonium can cause acidification of the soil which may lead to adverse effects on vegetation.

Nitrification can also occur after ammonia and ammonium have been deposited on water surfaces as has been observed in moorland pools in the southeastern part of the Netherlands (Schuurkens en Leuven, 1987).

c. Very high concentrations of ammonia (yearly average higher than about 75 $\mu g\ m^{-3}$) can cause direct damage to sensible plants (Van der

Eerden, 1982). But such high concentrations occur usually only nearby sources, as for example stables (Asman and Maas, 1986).

d. In forest ecosystems a high input of ammonia and ammonium leads to leaching of potassium, magnesium and calcium from the soil, often resulting in increased ratios of ammonium to potassium and magnesium and/or aluminium to calcium in the soil solution (Roelofs et al., 1987). Field investigations show a clear correlation between these increased ratios and the conditions of some plant species. Ecophysiological experiments proved that increased ratios of ammonium to potassium inhibit the growth of symbiotic fungi and the uptake of potassium and magnesium by the root system (Roelofs et al., 1987). Other experiments proved that coniferous trees take up ammonium by the needles and compensate for this by excreting potassium and magnesium. 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 (Roelofs et al., 1987). Moreover, trees may become more susceptible to other stress factors, such as ozone, drought, frost and fungal diseases.

   In the southern part of the Netherlands where perhaps the highest emission density of ammonia in Europe is, the damage of the forest seems to be clearly related to ammonia and ammonium, although other components may play a role as well (Den Boer, 1986).

e. Ammonia and ammonium are nitrogen components which can act as plant nutrients as nitrogen is often a limiting factor for plant growth in natural systems. If ammonia and ammonium are deposited in large enough quantities the nitrogen-poor species will disappear or even become extinct, because they are no longer able to compete with nitrophilous species, which will lead to a different ecosystem (Ellenberg, 1987). This phenomenon has caused a shift in the Netherlands from heath- and peatlands into grasslands (Roelofs et al., 1987).

f. A large part of the input of ammonia and ammonium to isolated lakes in the Netherlands, which are poor in calcium and nutrients originates from atmospheric deposition. This input can lead to acidification of the lakes and increase in the ammonium concentration in the water. This causes a change in vegetation. Moreover, it causes an increase in mortality of eggs and larvae of frogs (Schuurkes and Leuven, 1987).

g. If ammonia is absorbed by cloud droplets this will cause a rise in pH which enhances the rate of oxidation of dissolved sulphur dioxide by ozone (Maahs, 1983). The result of this effect is that somewhat more sulphur dioxide will be taken up by cloud droplets and will be oxidized to sulphate.

h. Uptake of ammonia by raindrops will also lead to a rise in pH, which enhances below-cloud scavenging of sulphur dioxide (Adewuyi and Carmichael, 1982).

i. The presence of ammonia at the earth's surface may decrease the surface resistance for the dry deposition of sulphur dioxide and in this way influence the dry deposition (velocity) of sulphur dioxide (Adema, 1986).

1.2 What should be known to describe the atmospheric behaviour of a component?

To understand the atmospheric behaviour of a component, information should be known on emission, transport, deposition processes, reactions and concentrations of the component. In the following these points are discussed with the emphasis on ammonia and ammonium.

1.2.1. Emission

The spatial variation of the emission should be known, also as a function of time if concentration/deposition patterns should be known as a function of time. Moreover, information is needed on the (effective) source height of the emissions. This because the source height influences the concentration, e.g. that at ground-level. It will therefore affect the amount of material being dry deposited and hence determine how much material is left for transport over longer distances. For ammonia only the geographical distribution of the yearly averaged emission is known. Ammonium is not emitted in significant quantities.

1.2.2. Transport

To describe the transport of airborne components it is necessary to have information on the windfield as a function of time. Windfields can be constructed or computed from meteorological observations. In the models described in this thesis only information is used which is extracted from windfields. To compute the values of effective removal parameters used in the long-range transport model (chapter 4) information is used on the frequency of occurrence of the wind speed during periods of different atmospheric stability. In the long-range transport model (chapter 5) backward-trajectories are used. A backward-trajectory is the path along which an air parcel travels before reaching a certain location (receptor point). Wind speed and wind direction are functions of height in the atmosphere. This is taken into account, as far as possible in both the parameterization and in the long-range transport model itself.

1.2.3 Deposition processes

Both dry and wet deposition processes should be known as they determine how much of a component is deposited and how much will be transported further away.

1.2.3.1 Dry deposition

The dry deposition process is described by using a dry deposition velocity, v (m s^{-1}). A linear relation is assumed between the flux F (mole m^{-2} s^{-1}) to the earth's surface and the concentration of a component (mole m^{-3}) at a certain height (reference height; in our model 1 m above the earth's surface): $v = F/c$.
This dry deposition velocity is determined by three subsequent processes (Fowler, 1980).

a. Transport from the reference height to a thin layer (laminar layer) just above the earth's surface. The transport is caused by turbulence and is hence influenced by meteorological conditions (wind speed, atmospheric stability), but also by the vegetation height. This transport is the same for all substances, apart from aerosols with diameter > 10 µm for which gravitation is also of importance. The resistance to transport by this process is called aerodynamic resistance.

b. Transport through the laminar layer. The thickness of this layer depends on meteorological circumstances. Gases are transported by molecular diffusion through this layer. Aerosols with a diameter < 0.1 µm are able to diffuse through the laminar boundary layer by Brownian diffusion. The efficiency of this mechanism decreases with increasing particle size. But in general Brownian diffusion is not an efficient process compared with molecular diffusion. Inertial impaction is another mechanism by which aerosols can be transported through this layer to the surface. For this mechanism the particle must have sufficient momentum to cross the laminar layer. This mechanism is only efficient for particles with diameter > 1.0 µm. As a result the transport of aerosols through the laminar layer shows a minimum in the size range 0.1 µm < particle diameter < 1.0 µm and in consequence this transport is a limiting factor to the overall dry deposition of aerosols of this size range. The size of ammonium containing aerosols is usually < 1.0 µm. The resistance to transport by this process is called boundary layer resistance.

c. Surface processes. After having reached the surface the mechanism of dry deposition depends on the physical and chemical properties of both the component and the surface. Moreover biological processes (e.g. opening of the stomata) may play a role if the surface consists of vegetation. Reactive gases are often attached well to the surface, depending e.g. on their (chemical) solubility in water. The resistance to transport by these processes is called surface resistance.
For ammonia which may already be present at the surface the transport will depend on the difference between the air concentration and the concentration at the surface. If the latter is higher no dry deposition will occur, but emission. The atmospheric part of the emission process depends on the same transport processes as the dry deposition, the only difference being the direction of the flux.

1.2.3.2 Wet deposition

in-cloud scavenging

Clouds are formed when air is lifted up or is mixed so that it becomes supersaturated with water vapour. Condensation takes place on aerosols, which act as condensation nuclei. As a result, components originating from these aerosols will turn up in cloud water. Most aerosols will act as condensation nuclei. The remaining aerosols may be exposed to scavenging by cloud elements.

The in-cloud residence time of cloud droplets is so large that they have taken up enough of a gas that there will exist equilibrium between the concentration in the droplet and the concentration in the interstitial air surrounding the droplet (this equilibrium may be influenced by other components present in the droplet). For a not very soluble gas (e.g. sulphur dioxide) a minor part will dissolve in the cloud water. But for a very soluble gas as ammonia most of the gas will dissolve in the cloud water, also because dissolved ammonia is partly depleted by reaction with protons to ammonium. Because of the long lifetime of cloud droplets, oxidation reactions can be of importance for some components like sulphur dioxide. Due to physical processes in the cloud involving the ice-phase, snow flakes and raindrops are formed which on their way to the earth's surface may take up both aerosols and gases below the cloud base. It should be mentioned here that most clouds will never precipitate, but continue to serve as "reactors" in which liquid phase reactions occur (Asman, 1986).

below-cloud scavenging

For aerosols the rate of below-cloud scavenging depends on the aerosol size distribution, the properties of the aerosol and the size distribution of the precipitation elements (snowflakes, raindrops). For not very soluble gases (e.g. sulphur dioxide) the concentration in raindrops leaving the cloud base will be in equilibrium with the air concentration in the cloud, which is not likely to be very different from the air concentration below the cloud. The uptake of such a gas below cloud base will generally not be substantial. Only when the concentration decreases strongly with height substantial below-cloud uptake may take place. For a very soluble gas like ammonia the situation is different. Most drops will not have reached equilibrium with respect to the air concentration below cloud base. This because the air concentration below cloud base is much higher than the interstitial air concentration within the cloud and the mass transfer rate through the air-drop interface is simply not large enough to cause equilibrium of the drops before they reach the ground. The rate of below-cloud scavenging of very soluble gases depends on the physical and chemical properties of the gas and the size distribution of the raindrops. On scavenging of gases by snowflakes not much is known (Asman, 1986).

Overall-scavenging

As precipitation is usually acidic, scavenged ammonia exists in precipitation as ammonium and cannot be distinguished from ammonium which originates from scavenging of ammonium aerosol. Moreover, measurements will not give any information of the relative importance of the scavenging process (below-cloud or in-cloud) involved. To model scavenging, geographically detailed information on the occurrence of precipitation (rate, time of duration) is needed. In this thesis six-hourly averaged precipitation fields are used.

1.2.3 Reactions

When a component reacts it will be transformed into a reaction product which may have different chemical and physical properties than the original component (precursor). In the atmosphere gaseous ammonia will react with acidic gases (nitric acid, hydrochloric acid) or acidic aerosols (e.g. containing sulphuric acid). The reaction product ammonium aerosol may be deposited at a different rate than the precursor and, e.g. as a result, be transported further away than would have been possible for its precursor as is the case for ammonium.

1.2.4 Measurements

Measurements may either be used to describe (a part of) a process involved, or may be used to check model results. There are a lot of problems associated with measurements, some of which will be discussed below.

Measurements involve sampling and analysis of chemical components. Some problems associated with the interpretation of measurements are:

a. Sometimes not only the component of interest is sampled but also another component at the same time which may be transformed into the component that is analysed in the sample. An example is ammonia which can be dry deposited in a bulk sampler and will be analysed as ammonium (Slanina and Asman, 1980).

b. The sample may be not representative. There exist many kinds of non-representativeness:
The sample may be taken during a short time-period, but the result is used to draw conclusions about periods associated with different circumstances.
The sample may be only representative of the concentration in a small area, whereas conclusions are drawn which are supposed to be valid for larger areas. An example is a precipitation sample which is contaminated by a bird-dropping, causing a high ammonium concentration (Asman et al. 1982). Although this concentration itself may be realistic enough, it will certainly not be representative of a larger area.
Another example is that concentrations are often only measured at ground level, but are sometimes assumed to be representative of the whole mixing layer, which may not be the case.

c. The analytical method is not only sensitive to the component of interest, but also to a limited extent to other components. This can give serious trouble if these other components are present in relatively high concentrations, without this being realized.

d. The sample may become contaminated during transport or in the laboratory, or the concentration of the component of interest may change during storage due to processes as adsorption, biological activity or reaction. Examples are the change in ammonium concentration in precipitation which occurs in not light-protected bottles (Ridder et al., 1984) and contamination ammonia is always present in the laboratory atmosphere and is emitted by human beings.

e. A non-systematic error is associated with all measurements. This should be taken into account when a conclusion is drawn from e.g. the difference between the values during two periods at one site. This means that such differences should be evaluated statistically which is very often not done.

f. Sometimes the effect of a process is completely masked by the variation of other processes occurring at the same time. This will often be the case during measurements in the field. An example is e.g. measurements of plume washout of a powerplant, where the spatial variation in the concentration of the component which was washed out was mainly caused by the spatial variation in rainfall rate and not by spatial variations in the efficiency of the washout process itself. By adopting a special procedure for correcting the concentrations for the variation of the rainfall rate it appeared to be possible to obtain information on the washout of the component (Slanina et al., 1983).

Sometimes one might not even be aware of another process which influences the observations. An example is perhaps the vertical concentration profile of ammonia measured by Hoell et al. (1982). They explain this vertical profile completely by diffusion of ammonia from the earth's surface and reaction with OH, O and $O(^1D)$, and some heterogeneous loss including rainout and dry deposition. They apparently completely ignore the certainly more important reaction with acidic components.

g. Laboratory experiments are not always representative of field conditions. E.g. measurements of the dry deposition velocity of a component in the laboratory are usually not representative of field conditions as no or reduced turbulence in air exists compared to field conditions.

h. Measurements sometimes give contradictory results.

The problems discussed above indicate that measured data can only be used with care and only after examination of all probable errors associated. This is sometimes difficult as the description of the methods used in literature is not always sufficient.

The measurement of ammonia and ammonium and related components is not easy as indicated by some examples given above.

1.3. Putting the pieces of a puzzle together

To describe the atmospheric behaviour of a component much more information should be known than is usually available. Not only a lack of information on processes and actual concentration patterns exists, but also part of the information available seem to be contradictory. To tackle this problem a systematic approach is necessary. A useful way to proceed is to use a model as a logical framework for the integration of the existing knowledge. Model results can then be used for the following purposes:

a. To get an indication of the probability of the results of measurements which then may lead to the rejection of doubtful results.
b. To get an indication about the strategy for obtaining additional information (what to measure, when and where?).
c. To interpolate measured data.
d. To give an indication of situations in the past or in the future or in other regions. This can be dangerous of course as one is never sure whether all important factors are included in the model, especially not if this situation is completely different from the situation for which the model was originally developed.
e. To get an indication of the variability in the atmospheric behaviour of a component caused by the uncertainty in the different processes involved (sensitivity analysis).

A useful way of applying models is using them in an iterative cycle combined with measurements both in the field and in the laboratory: using the model results to plan additional measurements and using those measurements to improve the model etc. One should be aware, however, of the inherent danger of looking for what one expects to find.

1.4 The ammonia and ammonium case

1.4.1 Scope of this thesis

A few models for ammonia and ammonium exist. Russell et al. (1983) made a multi-layer Lagrangian transport model describing the transport and formation of ammonium nitrate aerosol for California. They did not take reactions of ammonia and sulphuric acid into account, nor wet deposition. Their model was mainly used to compute diurnal variations of ammonium nitrate aerosol, ammonia and nitric acid concentrations, which were compared with measurements for one day.

De Leeuw et al. (1986) developed a multi-layer Lagrangian transport model with detailed chemistry including the reaction with sulphuric acid containing aerosol and wet deposition. Their model was especially designed to describe episodes with high aerosol concentrations.

More complicated models as discussed above have the advantage of giving more insight in detailed (chemical) mechanisms. But the results obtained with such models are often difficult to verify as components are involved which are not measured, or not at all levels the model gives results for. Moreover, more complicated models require relatively more computing time, which makes them less suitable to compute long-term average concentrations. At this moment no good information is available on seasonal variations in the ammonia emission. Moreover, much information on the variation both in time and space of other processes is also lacking. This means that some processes involved can be described in detail, whereas others cannot. Such models suffer then from an imbalance in the treatment of different processes, and the results of the models will be no better than is dictated by the weakest link in the chain. It should be mentioned here that such models still can be very valuable to study mechanisms and possible interactions between different processes and components. But because of the lacking information on e.g. short-time variation in emission no realistic short-term concentrations can be obtained.

Some information on the processes involved is available, but sometimes only on a yearly basis. It seems therefore most appropriate to integrate the existing knowledge by using a relatively simple model for the computation of yearly averaged concentrations. A first attempt to do this was made by Fisher (1984). He tried to compute deposition fields for ammonium in precipitation and the total deposition (sum of dry and wet deposition) of NH_x (sum of ammonia and ammonium) for Europe. But he had to conclude that his approach would remain limited until the main rates of removal of nitrogen compounds were better known.

The scope of this thesis is:

a. To evaluate the existing knowledge of all processes involved.
b. To acquire additional crucial information on some processes from own field measurements.
c. To integrate this knowledge by applying a model for the computation of long-term average (ground level) concentrations, with emphasis on the European scale. This model has been developed especially for ammonia and ammonium.
d. To show some new applications of models: computation of historical import/export balances and concentration patterns.

1.4.2. On the presentation

This thesis consists mainly of separate articles (chapters 3 to 6) which were submitted to Atmospheric Environment. This has some consequences:

a. Some information is presented in more than one article or part of this thesis.
b. A list of references appears after each chapter.
c. The articles have not been written at the same time. As a result some information was not yet known at the time of preparation of some articles, although this does not lead to any serious inconsequences.

In the following a preview is given of the contents of the different chapters.

Chapter 2

In this chapter some information is presented on the geographical distribution of the yearly averaged ammonia emission in Europe, which is essential to understand the model results.

Chapter 3

In this chapter field measurements are described. These measurements were performed for the following purposes:

a. To verify the estimated emission density
b. To get an indication on the vertical concentration profiles of ammonia, ammonium and related components in an area where emission occurs. This information is needed to model the horizontal transport.
c. To get an indication of the overall conversion rate of ammonia to ammonium.

Chapter 4

In this chapter is described how correction factors can be computed which can be used in a simple Lagrangian long-range transport model to describe the effects of turbulent mixing on concentration and deposition patterns. By using these correction factors more realistic results can be obtained.

Chapter 5

This chapter forms the basic part of the thesis and describes the evaluation and integration of the present knowledge, the setup of the model, numerical aspects of the model and comparison of model results with measurements. Although the model in principle would allow to vary most parameters as a function of time and space (e.g. dry deposition velocity, reaction rate, mixing height etc.) this was not done in practice in view of all uncertainties in the parameter values. Therefore, also no processes like escape into the reservoir layer were taken into account.

Chapter 6

In this chapter it is shown that it is not only possible to use a model to describe the present situation, but also to give estimates of concentrations in the past. These estimates make it possible to know where trends in concentrations measured in the past can be expected.

Chapter 7

In this chapter the conclusions of this study are summarized and discussed.

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CHAPTER 2. EMISSION

An emission inventory for NH_3 for Europe has been made by Buijsman et al. (1987). Table 1 and Figure 1 show the total anthropogenic NH_3 emissions in Europe around 1980. Buijsman et al (1987) showed that the natural emission of NH_3 in Europe is about 750×10^3 tonnes $year^{-1}$, which is about 10% of the anthropogenic NH_3 emission in Europe. No sources for the emission of NH_4^+ are known which means that all NH_4^+ found in the atmosphere originates from the emission of NH_3.

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Table 1.: Total antropogenic NH_3 emissions in Europe in the early 80's. All data in 10^3 t NH_3 y^{-1}, except the emission densities ($t\ NH_3\ km^{-2}\ y^{-1}$).

Country	Livestock wastes	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
FRG	329	35	6	371	2.4
GDR	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	

[*] Emission from ammonia. fertilizer and related plants.

[¶] Differences can occur due to rounding.

[†] Industrial emissions in the USSR not taken into account.

[§] Defined as: $\frac{\text{agricultural emissions}}{\text{agricultural area}}$

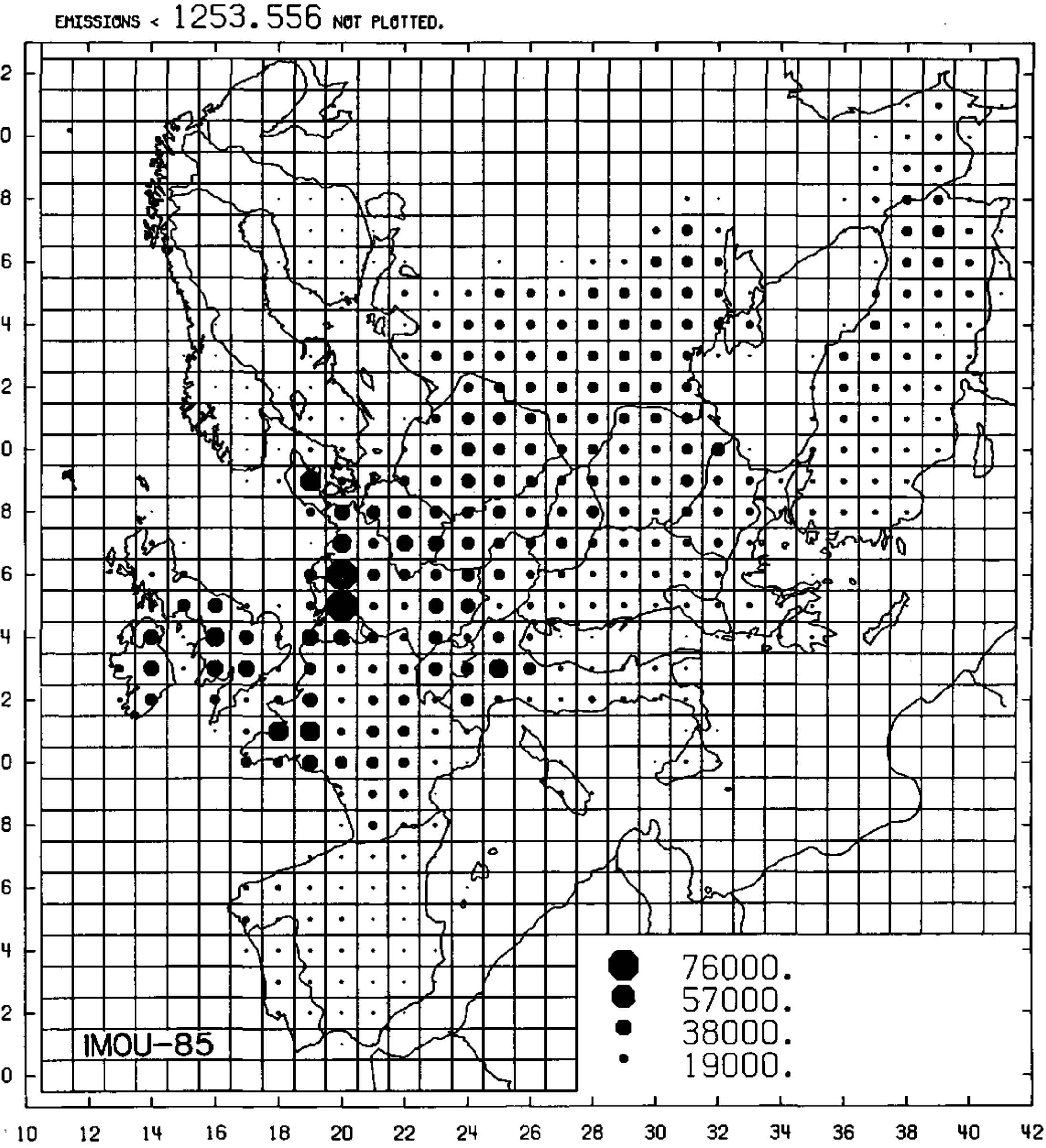

Figure 1. Ammonia emission from anthropogenic sources on EMEP-grid. Relative scale. Legenda in tons NH_3 a^{-1}.

CHAPTER 3.

(Submitted for publication in Atmospheric Environment)

VERTICAL DISTRIBUTION OF GASES AND AEROSOLS: THE BEHAVIOUR OF AMMONIA AND RELATED COMPONENTS IN THE LOWER ATMOSPHERE.

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Abstract.

Vertical concentration profiles for NH_3, HNO_3 and HCl-gas and for NH_4^+, NO_3^-, SO_4^{2-}, Cl^- and Na^+ aerosol were obtained from a meteorological tower in the central part of the Netherlands. An upward NH_3 flux of 0.12 $\mu g\ m^{-2}\ s^{-1}$ was calculated from the NH_3 profiles and meteorological data. From the HNO_3 profiles a maximum HNO_3 dry deposition velocity of 4 $cm\ s^{-1}$ was calculated. Good agreement was found between the measured concentration products $[NH_3]_{(g)} \times [HNO_3]_{(g)}$ and the theoretical values at temperatures above 0 °C and relative humidities below 80%. In other cases higher NH_3 and/or HNO_3 concentrations in the gasphase were measured than theoretically predicted.

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1. Introduction.

Ammonia and ammonium are important atmospheric components. Ammonia is the major neutralizing gas in the atmosphere, so it plays an important role in the neutralization of atmospheric acids generated by the oxidation of sulfurdioxide and nitrogen oxides. As a result ammonium is a major constituent of atmospheric aerosols.

Most of the ammonia is emitted near the earth's surface and in western Europe most of it will react irreversibly with H_2SO_4 containing aerosol. A smaller part of the atmospheric ammonia will react with gaseous HNO_3 and HCl to form aerosol compounds like NH_4NO_3 and NH_4Cl (Pio and Harrison, 1987) which can dissociate again by:

$$NH_4NO_{3(s)} \rightleftharpoons NH_{3(g)} + HNO_{3(g)}$$
$$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$$

To model the atmospheric behaviour of NH_3, NH_4^+ and related components, it is necessary to have information on the vertical distribution of these components. Some information on the vertical distribution of NH_3 and/or NH_4^+ can be found in the literature (Georgii and Müller, 1974; Böttger et al., 1978; Georgii and Lenhard, 1978; Lenhard and Gravenhorst, 1980; Hoell et al., 1980; Levine et al., 1980; Hoell et al., 1981; Alkezweeny et al., 1986). However, many of the measurements reported were made by aircraft and subsequently do not describe the distribution in the lowest part of the atmosphere where the most pronounced concentration gradients are likely to occur, as NH_3 is emitted at or near the earth's surface.

It was therefore decided to measure vertical gradients at the meteorological tower of the Royal Netherlands Meteorological Institute (KNMI) located at the rural site of Cabauw in the middle of the Netherlands. This had the added advantage, that usually detailed meteorological data were available, which can be very helpful to interpret the results. Not only NH_3 and NH_4^+ were measured, but also gaseous HNO_3 and HCl, and NO_3^-, SO_4^{2-}, Cl^- and Na^+ in aerosols.

Furthermore, information about the equilibrium involving NH_3 especially for the reaction with HNO_3, is also essential for modelling purposes. Therefore, the concentration products of NH_3 and HNO_3 are compared with theoretically derived concentration products pertinent to the dissociation equilibrium of NH_4NO_3. The relation between these concentration products and the temperature and relative humidity is also discussed.

2. Experimental.

The samples were taken at a meteorological tower which is 213 m high and is situated at Cabauw in the central part of The Netherlands (51.55 °N, 4.55 °E). The tower is surrounded by pastures where cattle are usually grazing. In the nearby surroundings of the tower no nitrogenous fertilizers are used. Cabauw is located in an area with an average ammonia emission density of approximately 0.20 μg NH_3 m^{-2} s^{-1} , which is somewhat higher than the average emission density in the Netherlands, 0.14 μg NH_3 m^{-2} s^{-1} (Buijsman et al., 1984).

The samples were taken at heights of 25, 100 and 200 m. At ground level the samples were taken at 2 m height at some distance from the tower building. The sampling system consists of two denuder tubes and a filterpack. The first tube is coated with NaF to collect acidic gases (HNO_3 and HCl), the second tube is coated with H_3PO_4 to collect gaseous NH_3. The filterpack consists of three filters. The first filter is a teflon filter (Mitex Millipore LS 5 μm, ϕ 47 mm) on which aerosol particles are retained. The other filters are paper filters (Whatman 41, ϕ 51 mm), impregnated with NaF and H_3PO_4 respectively. These are used to collect HNO_3 and NH_3, generated by evaporation of NH_4NO_3 from the first filter.

After sampling the filters are rinsed with deionized water, which is subsequently analysed for SO_4^{2-}, NO_3^-, Cl^- (ionchromatography), NH_4^+ (colorimetric method with nitroprussic-hypochloride with flow injection and UV detection) and Na^+ (AAS) at ECN. Details about sampling and analytical methods can be found in Ferm (1979), Slanina et al. (1981) and Slanina (1982). The accuracy for sampling and analysis is 5 - 10%. The detection limit for gases and aerosols is about 0.05 μg m^{-3} for a 12 hour sampling period at a flow rate of 10 l min^{-1}.

Measurements have been carried out during 30 day-time (9 a.m. till 9 p.m.) and 30 night-time (9 p.m. till 9 a.m.) periods. During the first 15 periods samples were taken only at 2, 100 and 200 m height. At the meteorological tower wind speed, wind direction, temperature and relative humidity are measured continuously at several levels (Driedonks et al., 1978). Unfortunately, however, no meteorological data for the tower were available for the first 12 sampling periods. For these periods ground level data for the nearby station De Bilt (20 km from Cabauw) were used. The samples were taken during different seasons and meteorological circumstances.

3. Vertical concentration profiles.

The averaged concentrations for measured components are presented in Table 1. The meteorological data are extensively described by Erisman et al. (1986B). The average day- and night-time concentration profiles are presented in Figures 1 and 2. These present the average concentrations for the last 15 sampling periods, including the 25 m sampling height. This was done because only concentrations measured at different heights at the same time can be compared.

For NH_3 a strong decrease in concentration with increasing height is observed. The NH_3 concentration gradient is much more pronounced during night-time than during day-time. At night (ground) temperature inversions were frequently observed. Together with increased atmospheric stability and lower windspeed the occurence of ground inversions is presumably the reason for the relatively high NH_3 concentrations at ground level during night-time. This in spite of the much lower emission rate of NH_3 observed during night-time (Beauchamp et al., 1982).

For HNO_3 a strong increase with height is observed. A stronger increase with increasing height was observed for HNO_3 concentrations during night-time than during day-time. This is presumably caused by the occurence of inversions during night-time. Inversions prevent downward transport of HNO_3 and upward transport of NH_3.The strong increase of HNO_3 concentration with

Table 1. The average concentrations for measured components.

Height (m)		Concentration ($\mu g\ m^{-3}$) NH_3	HNO_3	HCl	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-	Na^+
2	average	8.3	1.1	0.5	5.6	10.5	9.2	1.2	0.5
	min.	0.8	0.0	0.1	1.2	0.1	2.1	0.1	0.1
	max.	49.4	12.1	1.9	20.3	44.3	32.5	4.6	1.9
	number	56	55	55	53	53	53	53	46
25	average	6.2	0.8	0.4	5.0	10.1	9.4	1.4	0.5
	min.	0.7	0.0	0.1	1.2	1.0	1.6	0.1	0.1
	max.	19.0	6.3	3.0	15.6	41.1	25.0	5.0	1.6
	number	32	32	32	32	32	32	32	32
100	average	3.6	2.2	0.6	5.0	8.5	8.6	1.4	0.5
	min.	0.1	0.0	0.1	1.0	0.5	0.7	0.2	0.1
	max	12.1	23.3	3.0	15.4	26.7	26.1	12.1	1.7
	number	60	60	60	58	57	57	57	55
200	average	2.1	2.6	0.8	4.1	7.8	8.1	1.1	0.4
	min.	0.1	0.0	0.1	0.8	0.8	0.4	0.3	0.1
	max.	10.0	19.5	2.8	13.6	37.2	23.3	4.5	1.9
	number	58	58	58	56	56	56	55	53

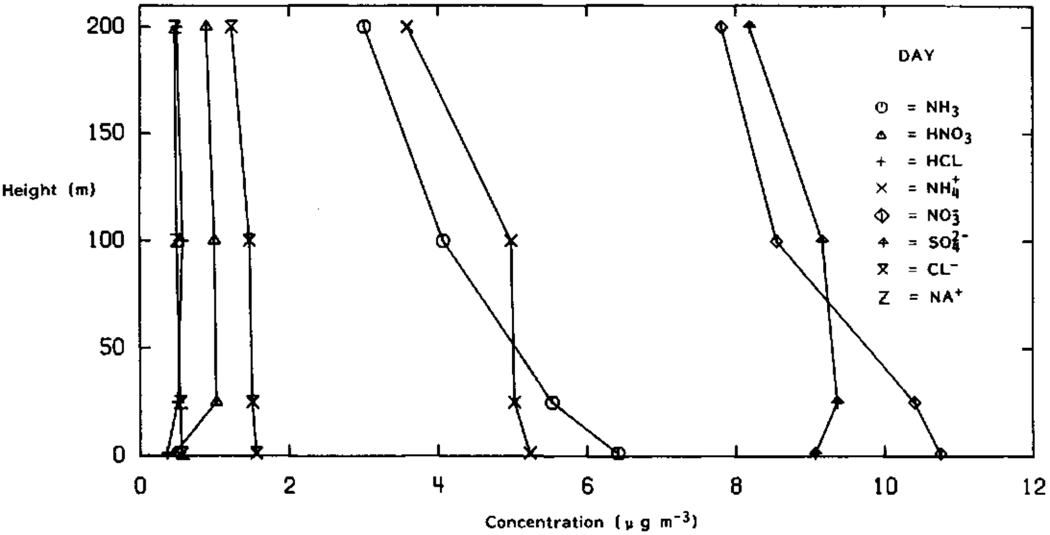

Figure 1. Average vertical profiles for the day-time sampling periods including 25 m sampling height.

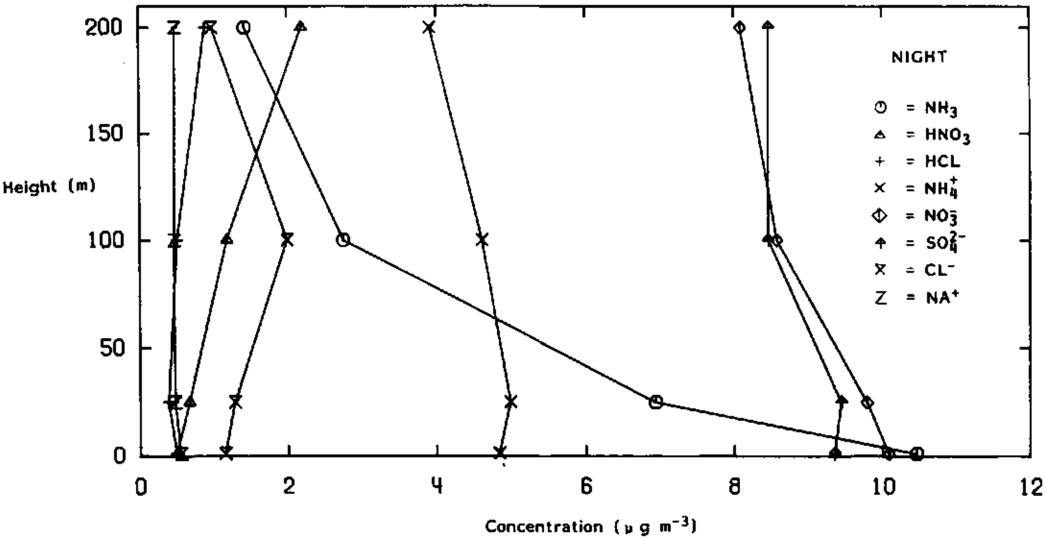

Figure 2. Average vertical profiles for the night-time sampling periods including 25 m sampling height.

height might be explained by two processes: a) reaction with NH_3 and b) dry deposition. The NH_3 concentration near NH_3 emitting surfaces can easily be so high that virtually all HNO_3 has reacted with NH_3 before it can be deposited at the earth's surface. It was not possible to deduce the relative importance of reaction from our measurements, because the HNO_3 concentrations at all heights are much lower than the NO_3^- concentrations. A significant increase in NO_3^- concentrations due to reaction of HNO_3 to NO_3^- aerosol could therefore not be detected. If the gradient is the result of the reaction with NH_3 it is possible that the dry deposition velocity of HNO_3 is lower, than calculated .

Two methods were applied to calculate the HNO_3 dry deposition velocity from the HNO_3 profiles and meteorological data, assuming that reaction with NH_3 is unimportant.

If equilibrium in the atmospheric boundary layer has been established, the dry deposition velocity, v_d, can be calculated according to Onderdelinden et al. (1986):

$$v_{d1}=([c_i(z_2)/c_i(z_2)]-1)/r_a(z_1,z_2) \qquad (1)$$

where $c_i(z_1)$ is the HNO_3 concentration at height z_1 and $r_a(z_1,z_2)$ is the difference between the aerodynamic surface resistances, controlled predominantly by turbulent mixing above a surface, at height z_1 and z_2.

The dry deposition velocity could also be calculated by assuming that v_d is inversily proportional to the sum of three resistance terms (Walcek et al., 1986):

$$v_{d2}=(r_a+r_b+r_s)^{-1} \qquad (2)$$

where r_a is the aerodynamic resistance, r_b is an additional resistance that accounts for pollutant transfer across the atmospheric near surface layer, and r_s is a resistance associated with pollutant-surface interaction. r_a and r_b were calculated according to Onderdelinden et al. (1984), r_s was assumed to be zero, due to its high miscibility on surfaces (Walcek et al., 1986). Both methods were applied for sampling periods where no inversions occured, the deposition velocities were found to be $v_{d1}= 4.0$ cm s^{-1} and $v_{d2}= 3.9$ cm s^{-1}. The agreement is very good. These dry deposition velocities are also in the same order of magnitude as the averaged HNO_3 dry deposition velocity in the Netherlands, $v_d = 3.4$ cm s^{-1}, calculated by Erisman (1987).

The NH_4^+, SO_4^{2-} and NO_3^- concentration decreased slightly with increasing height. This decrease was somewhat larger during day-time than during night-time. NH_4^+, SO_4^{2-} and NO_3^- are only formed by reaction of the emitted primary components: NH_3, SO_2 and NO_x. As the reaction is slow compared to atmospheric mixing processes, and the dry deposition velocities are low, no pronounced vertical gradients of NH_4^+, SO_4^{2-} and NO_3^- were observed. No significant gradients could be observed for HCl, Cl^- and Na^+.

The average concentrations given in Table 1 are not annual averages, because measurements were not carried out on an annual basis. However, the measurements were carried out during different seasons and meteorological conditions. These averages, therefore, might give a good picture of what the annual averages could be. This is supported by the fact that the average NH_3 concentration is in very good agreement with the emission - concentration relation given by Erisman et al. (1986) (see Figure 3). For measuring sites with different emission densities in the Netherlands a strong relation was found between the median concentration of NH_3 and the estimated local emission density. In Figure 3 this relation is presented including the average NH_3 concentration at Cabauw.

4. Ammonia flux.

Under steady state conditions, the vertical flux of a trace constituent into the first few hundred metres of the atmosphere is proportional to the gradient of the mixing ratios if it can be assumed that sources and sinks are homogeneously distributed at the earth's surface. The NH_3 flux can be represented by (Onderlinden et al., 1987):

$$F = -K_z \; (dc_i/dz) \qquad (3)$$

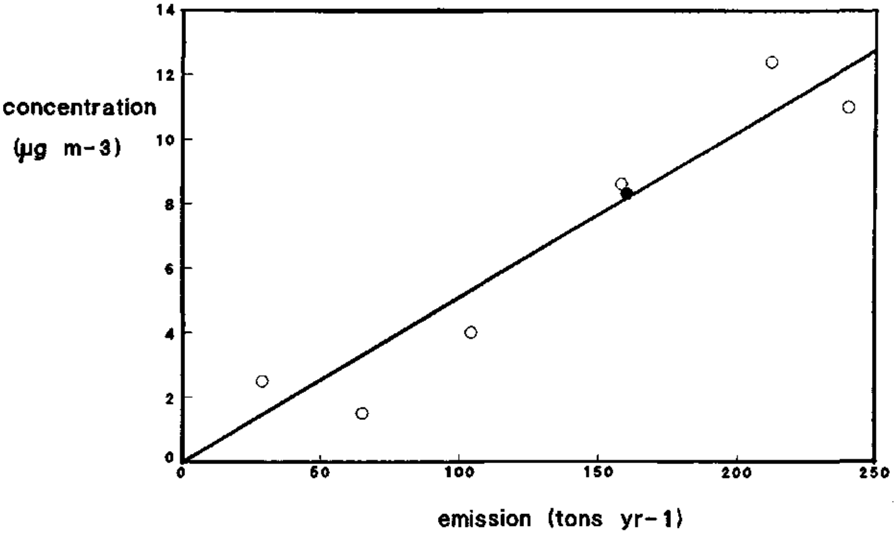

Figure 3. Measured NH_3 concentration vs. calculated NH_3 emission (5x5 km^2) for The Netherlands. Average NH_3 concentration at Cabauw is marked with (●).

where K_z is the average eddy diffusity, c_i is the concentration of NH_3 and z is the height.

An average net upward NH_3 flux of 0.12 $\mu g\ m^{-2}\ s^{-1}$ was calculated from the individual sampling periods. Buijsman et al. (1984) calculated an average net NH_3 emission flux of 0.20 $\mu g\ m^{-2}\ s^{-1}$, while the NH_3 deposition flux for this area was calculated by Asman and Maas (1986) to be 0.06 $\mu g\ m^{-2}\ s^{-1}$. From these two fluxes an average net upward NH_3 flux of 0.14 $\mu g\ m^{-2}\ s^{-1}$ can be calculated, which is in very good agreement with the average flux, calculated from the individual sampling periods. Although, the agreement is worse if we take into account that the emission could be higher by 30% to 40% as suggested by Buijsman (1987).

An estimate of the conversion rate of gaseous NH_3 to particulate NH_4^+ is useful for modelling atmospheric transport of NH_x. This conversion rate is the result of various reactions, diffusion to aerosols and vertical exchange processes in the atmosphere. It will be different under different circumstances as it will depend on e.g. concentrations of reaction agents involved, temperature, relative humidity and the rate of vertical mixing. The conversion rate R ($\mu g\ m^{-3}\ s^{-1}$) can be computed from equation (4), assuming steady state conditions:

$$\frac{d}{dz}\left(K_z \frac{dc_i}{dz}\right) + R = 0 \qquad (4)$$

where c_i is the NH_3 concentration ($\mu g\ m^{-3}$) and K_z is the eddy diffusity ($m^2\ s^{-1}$). For day-time periods R was calculated to be $5\ 10^{-4}$ $\mu g\ m^{-3}\ s^{-1}$ and for night-time periods $3\ 10^{-4}$ $\mu g\ m^{-3}\ s^{-1}$, sampling periods where inversions occured were not taken into account. In order to obtain a value of the overall conversion rate constant, k, commonly used in transport models, it was assumed that NH_3 is converted into NH_4^+ by one irreversible reaction with a first-order reaction mechanism:

$$R = k\ c_i \qquad (5)$$

k was calculated to be $1\ 10^{-4}\ s^{-1}$ for day-time periods and $5\ 10^{-5}\ s^{-1}$ for night-time periods. In fact the reaction mechanism is much more complicated, because many components are involved and different types of reactions take place in both the gasphase and in solutions.

5. Temperature and relative humidity dependence of the NH_4NO_3 dissociation constant.

Theoretical calculations of the formation of atmospheric nitrate aerosol based on thermodynamic equilibrium between NH_3, HNO_3 and aerosol constituents have been presented by several authors (see e.g. Stelson and Seinfeld, 1982A, 1982B, 1982C; Tanner, 1982; Bassett end Seinfeld, 1983, 1984; Russell and Cass, 1984). Pure NH_4NO_3 does not exist in the atmosphere but is present in particles of mixed composition. Stelson and Seinfeld (1982A) determined the dependence on temperature and relative humidity of the NH_4NO_3 aerosol dissociation constant: $K_e = P_{HNO3} \times P_{NH3}$, where P_i is the partial pressure of component i at equilibrium. Later they reported (Stelson and Seinfeld, 1982C) that addition of H_2SO_4 to the mixture does not lower the value of K_e to a large extend, unless the H_2SO_4/HNO_3 ratio is very large.

The product of measured NH_3 and HNO_3 concentrations, K_m, has been compared with the theoretically derived dissociation constant (Stelson and Seinfeld, 1982A). Most of the measurements were made in the United States, where in general NH_3 concentrations are lower and HNO_3 concentrations are higher than in most parts of Europe (Doyle et al., 1979; Stelson et al., 1979; Cadle et al., 1982; Tanner, 1982,1984; Hildemann et al., 1984; Jacob et al., 1986 and Lewin et al., 1986). In Japan measurements were carried out in an area far away from large emission areas (Chang et al., 1986). For Europe only measurements in the North-Western part of England exist (Harrison and Pio, 1983). From the measurements in the United States, Japan and Europe it can be concluded that K_m is in good agreement with K_e for temperatures above $0\,^oC$ and relative humidities below 80%. At temperatures below $0\,^oC$, K_m was found to be higher than K_e (Cadle et al., 1982). At relative humidities above 80% different authors, however, obtained different results. Hildemann et al. (1984), Harrison and Pio (1983), Chang

et al. (1986) and Lewin et al. (1986) found good agreement between K_m and K_e, whereas Stelson et al. (1979), Cadle et al. (1982), Tanner (1982) and Jacob et al. (1986) found K_m values which were higher than K_e.
Our measurements were carried out for a wider range of temperatures (-10 to 25 °C) and relative humidities (35 to 100% r.h.) than reported elsewhere in the literature. The sampling period was 12 hours. During such a long period the temperature, the relative humidity and the concentrations will change. As a result, the values of K_m derived from 12 hourly averaged NH_3 and HNO_3 concentrations might be different from the value of K_e computed from the 12 hourly averaged temperature and relative humidity. This effect has not yet been quantified. K_e derived from the 12 hour averaged temperature and relative humidity was estimated to be 10% lower on the average (max. 30%) than K_e derived from the temperatures and relative humidities for these 12 hours.
The concentration products K_m for all periods and heights were plotted versus the reciprocal temperature and are shown in Figure 4 (for relative humidities below 80%) and in Figure 5 (for relative humidities above 80%. In most cases where the relative humidity could not be determined, the temperature was below 0 °C. At these temperatures the relative humidity cannot be measured at the tower. The data for these conditions are plotted in Figure 5. In Figures 4 and 5 the relation given by Stelson and Seinfeld (1982A,1982B) are also plotted. In Figure 4 the regression function is plotted as well. From these figures it can be concluded that a reasonable agreement exist between K_m and K_e for temperatures above 0 °C and relative humidities below 80%. In other cases the measured concentration product K_m is larger than the value of K_e computed from the relation given by Stelson and Seinfeld (1982A). This means that more NH_3 and HNO_3 is present in the gasphase than predicted by using the theoretical relation.
We found that most discrepancies between field observations and theoretical considerations occur at night at 2 m sampling height, where highest relative humidities were observed. These discrepancies could probably occur because NH_3 and HNO_3 may not be well enough mixed and/or not enough time was allowed for reaction. Another explanation could be that under these circumstances the HNO_3 concentrations are close to the detection limit so that the concentration product K_m becomes more uncertain (measuring artefacts may not be excluded at such low concentrations). At high relative

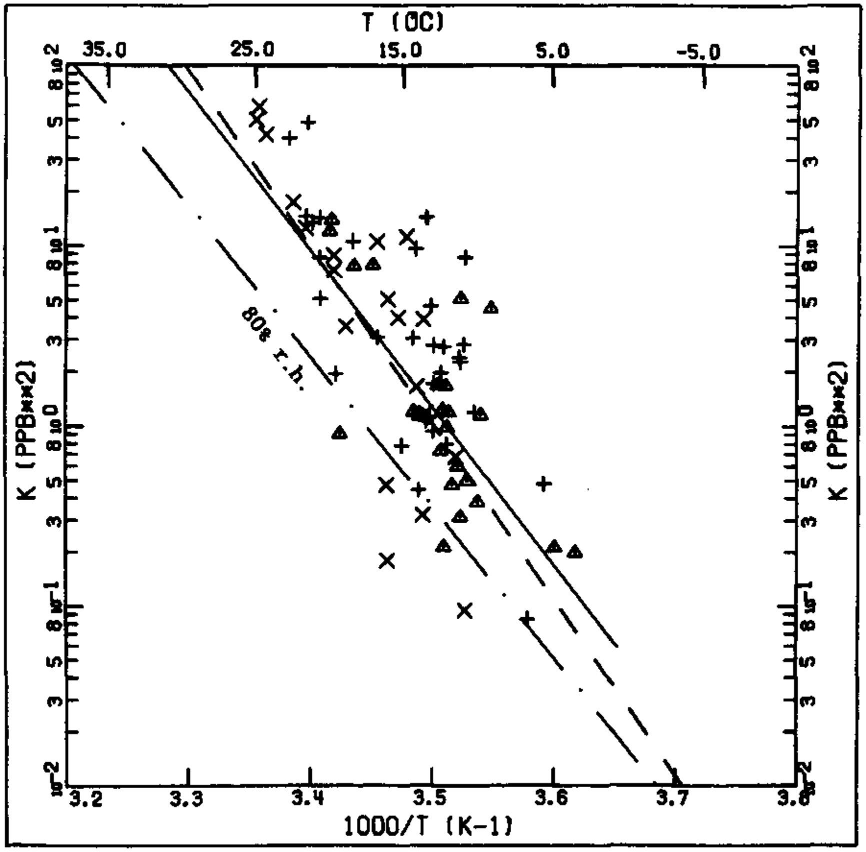

Figure 4. Comparison of the measured concentration product (K_m=[NH_3] x [HNO_3]) with the calculated dissociation constant K_e as a function of temperature at relative humidities below 80% and concentrations of HNO_3 above 0.1 µg m^{-3}.

▲ = 70 < r.h. ≤ 80%

\+ = 60 < r.h. ≤ 70%

× = r.h. ≤ 60%

— — — = thermodynamic equilibrium constant K_e for solid ammonium nitrate

— · — = thermodynamic equilibrium constant K_e for 80% r.h.

——— = regression line K_m (r=0.75; n=72).

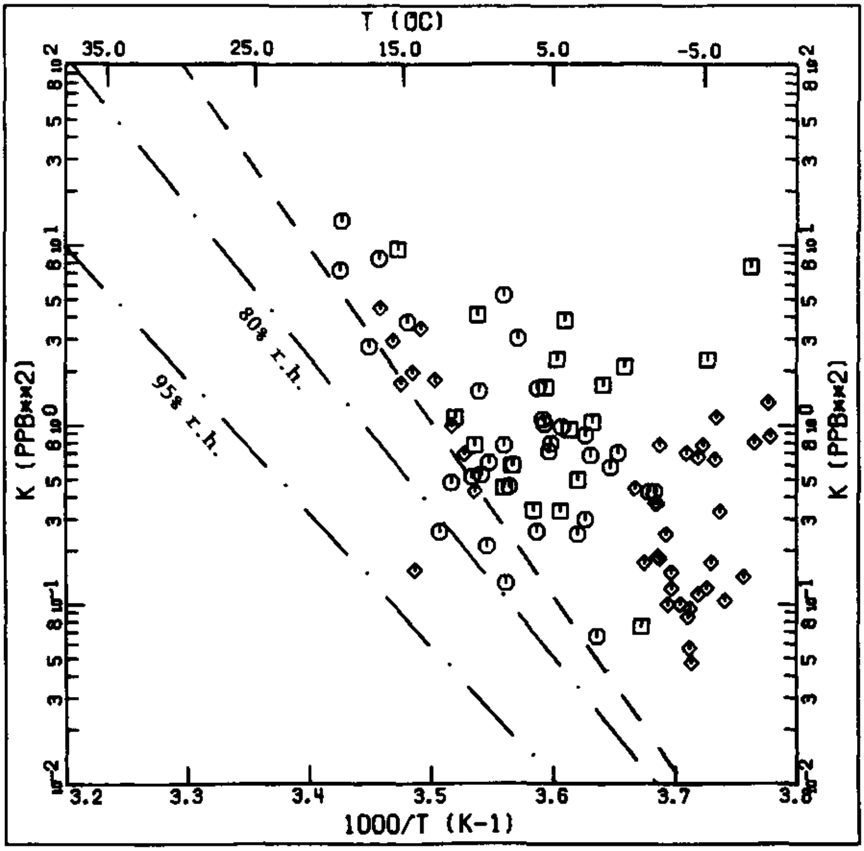

Figure 5. Comparison of the measured concentration product (K_m=[NH_3] x [HNO_3]) with the calculated dissociation constant K_e as a function of temperature at relative humidities above 80% and concentrations of HNO_3 above 0.1 μg m^{-3}.

⊡ - 90 < r.h. ≤ 100%

ʘ - 80 < r.h. ≤ 90%

◈ - no r.h. measurements available

— — — - thermodynamic equilibrium constant K_e for solid ammonium nitrate.

Other lines relate to solution droplets at the indicated relative humidity.

humidity all surfaces, even teflon as used in this study, can absorb waterlayers. This effect could lead to an underestimation of NH_3 and HNO_3 concentrations due to absorption in waterlayers, present in the inlet of the denuder-filterpack systems. Moreover, discrepancies may occur because 12 hourly averaged concentrations were used. For temperatures lower than 0 ^{o}C, the sampling equipment should be tested to see whether artefacts occur.

6. Conclusions.

From the vertical concentration profile measurements information on the processes in the lower part of the atmosphere was obtained. Some conclusions are:

- NH_3 concentration decreases strongly with increasing height, whereas an increase of HNO_3 concentration with increasing height was observed. The latter could be the result of dry deposition or reaction. If the reaction of HNO_3 with NH_3 is the most important, this could imply that the calcuted HNO_3 dry deposition velocity of 4 cm s^{-1} is a maximum.
  A small decrease of NH_4^+, SO_4^{2-} and NO_3^- concentrations with increasing height was observed. No significant gradient could be found for Na^+, Cl^- and HCl.
- An average net upward NH_3 flux of 0.12 $\mu g\ m^{-2}\ s^{-1}$ was calculated from the concentration measurements and meteorological data, which is in agreement with estimates from cattle statistics and calculation of the dry deposition.
  An overall conversion rate constant of 1 10^{-4} $\mu g\ m^{-3}\ s^{-1}$ for day-time periods and 5 10^{-5} $\mu g\ m^{-3}\ s^{-1}$ for night-time periods were calculated.
- A comparison was made between the concentration product of the measured NH_3 and HNO_3 concentrations and thermodynamic equilibrium between NH_4NO_3(s) and its precursor gases NH_3 and HNO_3, at a wide temperature and relative humidity range (-10 to 25 ^{o}C and 35 to 100% r.h.). Good agreement was found at temperatures above 0 ^{o}C and relative humidities

below 80%. In the other cases higher NH_3 and/or HNO_3 concentrations were measured in the gasphase than predicted.

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CHAPTER 4.

EFFECTIVE REMOVAL PARAMETERS IN LONG-RANGE AIR POLLUTION TRANSPORT MODELS

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ABSTRACT

In simple Lagrangian long-range transport models used for air pollution studies turbulent mixing is described in a very approximate way. This description has the effect that calculated concentrations and deposition patterns may not be realistic. However, correction factors, derived from more detailed diffusion theory calculations, can be introduced easily into these simple models so that an adequate account of the mixing process is taken. If such correction factors are applied in simple models, the increase in computing time is negligible, whereas the results are about as good as those of more sophisticated models which need much more computing time.

This paper describes how the necessary correction factors can be put into a simple model and how a reactive diffusion model is used to derive the values of these factors. Calculated values are given for the pollutants NH_3, SO_2 and NO_x and for their reaction products NH_4^+, SO_4^{2-} and NO_3^-, respectively.
Sensitivity calculations are made and results are compared with the results of other diffusion models.

1. INTRODUCTION

For long-range air pollution transport calculations fairly simple Lagrangian models are frequently used, e.g. the EMEP model (Eliassen et al., 1983). In these models instantaneous homogeneous mixing of emitted and produced components throughout the mixing layer is assumed. However, in reality this mixing process requires some time, thus affecting deposition patterns. This especially applies to species emitted at low height and/or exhibiting large deposition velocities. Yet the long-range transport and deposition processes can be described adequately with such simple models, provided two types of corrections are applied:

- A correction factor for the fact that near the source - with low emission height - ground level concentrations will be higher than average, resulting in faster depletion due to enhanced dry deposition. A reduced effective source strength should therefore be used in the long-range transport calculations. However, if this reduced source strength is used right from the point of emission, the rate by which reaction products are formed will be underestimated in the near-source area. This can be corrected by the introduction of a small direct emission rate of the reaction product.
- Correction factors for the fact that the dry deposition flux is overestimated at larger distances from the source, if it is calculated from height-averaged concentrations and the dry deposition velocity at reference height: the ground level concentration will be lower than average because depletion due to dry deposition takes place at ground level. This overestimation can be avoided by introducing modified (effective) depletion parameters: effective dry deposition velocities and effective reaction constants.

Some of the above-mentioned correction factors have been introduced in earlier model calculations. Eliassen et al. (1983) described EMEP model calculations in which a correction factor for additional local dry deposition of SO_2 was introduced, together with an effective dry deposition velocity of SO_2. The correction factors were derived from simple Gaussian plume dispersion calculations (Högström, 1979) and similarity theory (Eliassen et al., 1983). An identical approach has been adopted by Asman et al. (1986A), who used a similar Lagrangian model to study SO_2 and NO_x transport to and from the Netherlands. This model (IE model) was developed in a joint effort by IMOU and ECN.

Recently, we used the IE model to study the transport of ammonia and ammonium over Europe (Asman et al., 1986B, 1986C). Ammonia is mainly emitted at ground level and has a relatively large dry deposition velocity. A further complication arises from the relatively fast transformation of ammonia to ammonium. It was therefore felt necessary to pay further attention to the parameters introduced above. Scriven and Fisher (1975) described an analytical diffusion model (based on K-theory) which provides useful physical insight in effective parameters. However, it is rather limited with respect to, e.g., the vertical variations of wind velocity, eddy diffusivity and the concentration of reaction products. This may be an important restriction if a ground-level source like ammonia is considered. Asman and Maas (1986) developed a surface depletion model which could also be used to derive effective removal parameters. But this model also neglects the vertical variation of the reaction product concentration. Moreover, the dispersion parameters used in this model may be less adequate for ground-level sources.

We have chosen to derive parameter values from detailed numerical calculations based on the diffusion equation. In particular for ground-level sources this approach is quite adequate (Hanna et al., 1982).

This paper is intended to provide details of the numerical diffusion calculations and the way in which the results can be incorporated in a Lagrangian long-range model. Section 2 gives the mathematical details and in section 3 information is provided on model input data.

Finally, in section 4, several results are presented. Most results apply to NH_3/NH_4^+ as the effect of introducing effective depletion parameters is largest for these components. But for the sake of comparison other species like SO_2 and NO_x are considered as well.

2. BASIC EQUATIONS

2.1. Equations used in a Lagrangian model

According to the principles described in section 1 the equations used in a long-range transport model for the horizontal cross-wind integrated fluxes Q (mole s^{-1}) due to a point (or line) source Q_o (mole s^{-1}) can be formulated as follows:

$$u_t \frac{dQ_1}{dx} = -\left(\frac{v_{e1}}{H} + k_e\right) Q_1 \tag{1}$$

$$u_t \frac{dQ_2}{dx} = k_e Q_1 - \frac{v_{e2}}{H} Q_2 \tag{2}$$

where:

u_t = transport velocity of the air parcel (= x/t) (m s^{-1})
v = dry deposition velocity (m s^{-1})
k = (pseudo) first-order chemical reaction constant (s^{-1})
H = mixing layer height (m)

Subscripts 1 and 2 refer to the emitted component and its reaction product, respectively, and subscript e refers to "effective value".

The above equations apply to transport during dry periods, i.e. without scavenging.

The solutions of (1) and (2) are:

$$Q_1 = (1-\alpha_1-\beta)Q_o \exp\left[-\left(\frac{v_{e1}}{H} + k_e\right)t\right] \tag{3a}$$

$$Q_2 = (\beta-\alpha_2)Q_o \exp\left(-\frac{v_{e2}}{H}t\right) + $$
$$+(1-\alpha_1-\beta)Q_o \frac{k_e}{\frac{v_{e1}}{H}+k_e-\frac{v_{e2}}{H}} \left[\exp\left(-\frac{v_{e2}}{H}t\right)-\exp\left[-\left(\frac{v_{e1}}{H}+k_e\right)t\right]\right]. \tag{3b}$$

In (3) the correction factors α and β have been introduced (see section 1):

α = additional (or: apparent direct) local dry deposition (fraction of Q_o);

β = apparent direct emission of the reaction product (fraction of Q_o).

At a given distance x from the source the dry deposition rate d (mole s^{-1} m^{-1}) is:

$$d_i(x) = \frac{v_{ei}}{Hu_t} Q_i(x) \quad (i=1,2) \tag{4}$$

and the production rate p (mole s^{-1} m^{-1}) is

$$p(x) = \frac{k_e}{u_t} Q_1(x). \tag{5}$$

Up to this distance the integrated dry deposition D (mole s^{-1}) is:

$$D_i(x) = \alpha_i Q_o + \int_o^x d_i(x')dx' \quad (i=1,2) \tag{6}$$

and the integrated production (mole s^{-1}) is:

$$P(x) = \beta Q_o + \int_o^x p(x')dx'. \tag{7}$$

The following relations hold

$$Q_o = Q_1 + Q_2 + D_1 + D_2 \tag{8}$$
$$P = Q_2 + D_2. \tag{9}$$

Analytical evaluation of the integrals in (6) and (7) is straightforward, e.g.:

$$D_1(x) = \alpha_1 Q_o + \frac{v_{e1}}{H} \frac{1-\alpha_1-\beta}{\frac{v_{e1}}{H}+k_e} Q_o[1-\exp(-(\frac{v_{e1}}{H}+k_e)t)]. \tag{6a}$$

2.2. Equations used in the numerical diffusion model

The time-independent two-dimensional diffusion equations for the cross-wind integrated concentrations $C_i(x,z)$ (mole m^{-2}) are:

$$u \frac{\partial C_1}{\partial x} = \frac{\partial}{\partial z} (K \frac{\partial C_1}{\partial z}) - kC_1 \tag{10}$$

$$u \frac{\partial C_2}{\partial x} = \frac{\partial}{\partial z} (K \frac{\partial C_2}{\partial z}) + kC_1 \tag{11}$$

with given initial concentrations at the source (x=o), and boundary conditions:

$$K \left.\frac{\partial C_i}{\partial z}\right|_{z=z_r} = v_i C_i\Big|_{z=z_r} \qquad (i=1,2), \tag{12}$$

$$K \left.\frac{\partial C_i}{\partial z}\right|_{z=H} = 0 \qquad (i=1,2), \tag{13}$$

where the following new parameters have been introduced:

$u(z)$ = wind velocity (m s^{-1})
$K(z)$ = (eddy) diffusion coefficient (m^2 s^{-1})
z_r = reference height (*in this paper equal to 1 m above* ground level).

The horizontal fluxes Q_i (mole s^{-1}) are:

$$Q_i(x) = \int C_i(x,z)u(z)dz \qquad (i=1,2). \tag{14}$$

The dry deposition rates d_i (mole s^{-1} m^{-1}) are (the index r refers to reference height):

$$d_i(x) = v_{ri}C_i(x,z_r) \qquad (i=1,2), \tag{15}$$

and the production rate p is:

$$p(x) = \int k(z)C_1(x,z)dz. \tag{16}$$

Eqs. (10) and (11) are solved numerically. The finite difference scheme used in PLUVIUS (Easter et al., 1984) is adopted in our calculations. In view of the simplicity of the equations, high numerical accuracy can be achieved easily. Total dry deposition integrated up to distance x, D (mole s^{-1}),

$$D_i(x) = \int_o^x d_i(x')dx' \qquad (i=1,2) \tag{17}$$

is also evaluated numerically.

2.3. Combination of the two approaches

The results of the diffusion calculations are used in the following way. At any distance x the ratio $d_i(x)/Q_i(x)$ is determined (eqs. (14) and (15)), which gives us the effective dry deposition velocities v_{ei}, according to eq. (4). Similarly, the ratio $p(x)/Q_1(x)$ (eqs. (14) and (16)) gives us the effective reaction constant k_e, according to eq. (5). Finally, by putting $Q_i(x)$, eq. (14), equal to the expressions in (3a) and (3b), and by putting $D_1(x)$, eq. (17), equal to the expression in (6a), three independent equations are obtained from which α_1, α_2 and β can be determined.

All calculated values for v_{ei}, k_e, α_i and β will be dependent on x, but will tend to constants for sufficiently large x. These constant values are the parameter values to be used in the long range transport model.

2.4. Application to receptor-oriented models

Equations (1) and (2) apply to transport from a point or line source along forward trajectories. If backward trajectories to a fixed receptor point are to be used, the same effective parameter values can be introduced in the model equations, although in a slightly different way: In this case an air parcel of height H is considered, containing a pollutant load L (vertically integrated concentration, mole m^{-2}); this air column will be fed continuously by partly homogenized ("gridded") emissions E (mole m^{-2} s^{-1}). In this more general case the equivalents of eqs. (1) and (2) are:

$$\frac{dL_1}{dt} = -\left(\frac{v_{e1}}{H}+k_e\right)L_1 + (1-\alpha_1-\beta)E \tag{1a}$$

$$\frac{dL_2}{dt} = k_e L_1 - \frac{v_{e2}}{H}L_2 + (\beta-\alpha_2)E. \tag{2a}$$

The values of L_1 and L_2 at the receptor point, calculated with (1a) and (2a), give us the following information. At this point, supposed to be situated in an area with emission density E (mole m^{-2} s^{-1}), the total dry deposition fluxes are $\alpha_i E + (v_{ei}/H)L_i$, which gives us, by definition, the pollutant air concentrations at reference height:

$$C_{ri} = \frac{\alpha_i E + (v_{ei}/H)L_i}{v_{ri}} \qquad (i=1,2). \tag{18}$$

2.5. Including wet deposition

In Lagrangian models the wet deposition process is usually modelled by means of a single scavenging coefficient Λ (s^{-1}) (independent of the distance to the source), which is related to the (measured) scavenging ratio S (mole m^{-3} in precipitation / mole m^{-3} in air) by:

$$\Lambda = \frac{SI}{H} , \tag{19}$$

with

I = precipitation rate ($m\ s^{-1}$)
H = mixing height (m).

Λ includes in-cloud scavenging (rain-out) as well as below-cloud scavenging (wash-out). In the IE model (Asman et al., 1986A, 1986B, 1986C) use is made of gridded time-dependent data on the precipitation rate. With the inclusion of wet deposition eqs. (1a) and (2a) are transformed into:

$$\frac{dL_1}{dt} = -\left(\frac{v_{e1}}{H}+\frac{S_1 I}{H}+k_e\right)L_1 + (1-\alpha_1-\beta)E \tag{1b}$$

$$\frac{dL_2}{dt} = k_e L_1 - \left(\frac{v_{e2}}{H}+\frac{S_2 I}{H}\right)L_2 + (\beta-\alpha_2)E. \tag{2b}$$

Wet deposition fluxes (mole $m^{-2}\ s^{-1}$) at the receptor point are equal to $(S_i I/H)L_i$ (i=1,2), where I is the precipitation rate on arrival of the considered air parcel. Strictly speaking, the values of α, β and v_e are dependent on the precipitation rate. This effect can in principle be taken into account. However, this refinement does not seem to be justified, in view of the approximate way in which the wet deposition process is modelled. For instance, by the use of a scavenging coefficient in the Lagrangian model which is independent of the distance to the source, near-source effects on the wet deposition rate are ignored. (Fortunately, this will lead to two compensating effects: use of the reduced source strength in eq. (1b), i.e. $(1-\alpha_1-\beta)E$ instead of E, will lead to an underestimation of wet deposition near the source; on the other hand, in this same area the wash-out process is dominant but is less effective than the rain-out process which dominates at larger distances).

3. METEOROLOGICAL INPUT DATA

Calculations have been made for neutral atmospheric conditions (Pasquill class D), which prevail in the Netherlands (about 70% of the time).
Similarity theory gives us the profiles in the surface layer of wind velocity u and diffusivity K (Pasquill, 1974):

$$u(z) = \frac{u_*}{\kappa} \ln\left(\frac{z}{z_o}\right) , \qquad (20)$$

with

u_* = friction velocity
κ = Kármán's constant (0.35-0.40)
z_o = surface roughness length, in all calculations assumed to be equal to 0.2 m, corresponding to moderately flat terrain.

According to Dutch recommendations (TNO,1984) the logarithmic profile was extended up to 200 m, above which a constant value was assumed: $u(z>200\ \text{m}) = u_t = u(200)$.

$$K(z) = \kappa u_* z. \qquad (21)$$

This linear variation was assumed valid for $z_r \leq z \leq 50$ m; above 50 m K was kept constant (Hanna et al., 1982). Decrease of K near the top of the mixing layer was not considered; instead, the zero net flux boundary condition (13) was applied.

Combination of (20) and (21) gives:

$$K(z) \approx 0.04\ u(10).z \quad (z \leq 50\ \text{m}). \qquad (22)$$

The constant value of K for z>50 m may be evaluated from a different point of view. For constant u and K and no depletion the diffusion equation gives a Gaussian plume with coefficient of vertical dispersion (Pasquill, 1974):

$$\sigma_z(x) = (2Kx/u)^{\frac{1}{2}}. \qquad (23)$$

For Pasquill class D Briggs (1973) evaluated $\sigma_z(x)$ for open-country conditions:

$$\sigma_z = 0.06x(1+0.0015x)^{-\frac{1}{2}} \text{ , } (10^2\text{m}<x<10^4\text{m}) \tag{24}$$

which, for large x, tends to

$$\sigma_z \approx 1.55\ x^{\frac{1}{2}} \text{ .} \tag{25}$$

From (23) and (25) we find:

$$K \approx 1.2\ u. \tag{26}$$

(For distances larger than 10 km data for σ_z presented by Pasquill (1974) suggest a somewhat larger value, up to $K \approx 2u$).
In our model calculations $K(z>50)$ is equal to $50\ \kappa u_*$, see (21). With (20) we have the following relation between K and u:

$$\frac{K(z>50)}{u(z)} = \frac{50\ \kappa^2}{\ln(z/z_o)} \text{ ,} \tag{27}$$

with $\kappa^2 \approx 0.15$ and $z_o = 0.2$ m.
The ratios of K and u (according to (27)) presented below show that our adopted values for K fit in quite reasonably with (26).

$\frac{K(z>50)}{u(10)}$	$\frac{K(z>50)}{u(50)}$	$\frac{K(z>50)}{u(100)}$	$\frac{K(z>50)}{u(z\geq 200)}$
1.9	1.3	1.2	1.1

4. RESULTS

4.1. An example: NH_3/NH_4^+

Diffusion calculations have been performed for a ground-level NH_3 source, with a wind velocity of 4 m s^{-1} at 10 m height. Dry deposition velocities v_r are 8.0×10^{-3} and 1.0×10^{-3} m s^{-1} for NH_3 and NH_4^+, respectively, the adopted reaction constant k is 8.0×10^{-5} s^{-1}, independent of z, and the mixing height is 800 m (Asman et al., 1986B). For the initial condition (at x=o) the emission was assumed to take place at $z = z_r$ ($\approx$ 1 m).

Calculated parameter values are: $\alpha_1 = 0.255$, $\alpha_2 = 0.0079$, $\beta = 0.099$, $v_{e1} = 5.4\times10^{-3}$ m s^{-1}, $v_{e2} = 9.9\times10^{-4}$ m s^{-1} and $k_e = 8.2\times10^{-5}$ s^{-1}. Figure 1 shows the calculated horizontal flux Q as a function of the distance from the source, both according to diffusion theory and according to the Lagrangian model if the above parameter values are incorporated. Near the source the Lagrangian model underestimates the sum of airborne NH_3 and NH_4^+. This sum is, in case of precipitation, proportional to the wet deposition flux calculated with the Lagrangian model (Asman et al., 1986B). However, scavenging near the source will be less effective than assumed in the model, since the more efficient in-cloud scavenging cannot yet be active. As mentioned earlier, there is thus a certain compensation of approximations.

Figure 2 shows the dry deposition D, integrated up to distance x. From Fig. 2a it can be seen that the additional local dry deposition of NH_3 indeed takes place quite near the source: two thirds of it are deposited within 5 km distance from the source and 90% within 30 km. The - very small - additional dry deposition of NH_4^+ is extended over a larger area, because the formation of NH_4^+ by reaction takes time.

The use of an accurate value for the additional (or: apparent direct) local dry deposition factor α of NH_3 is quite important in Lagrangian models. This can be demonstrated by the following example. Consider an area with a homogeneous emission density E (mole m^{-2} s^{-1}) and assume that this area is large enough so that an equilibrium situation can be established, i.e. $dL_1/dt = 0$ in eq. (1a) (see section 2.4). We may then derive the total NH_3 dry deposition flux,

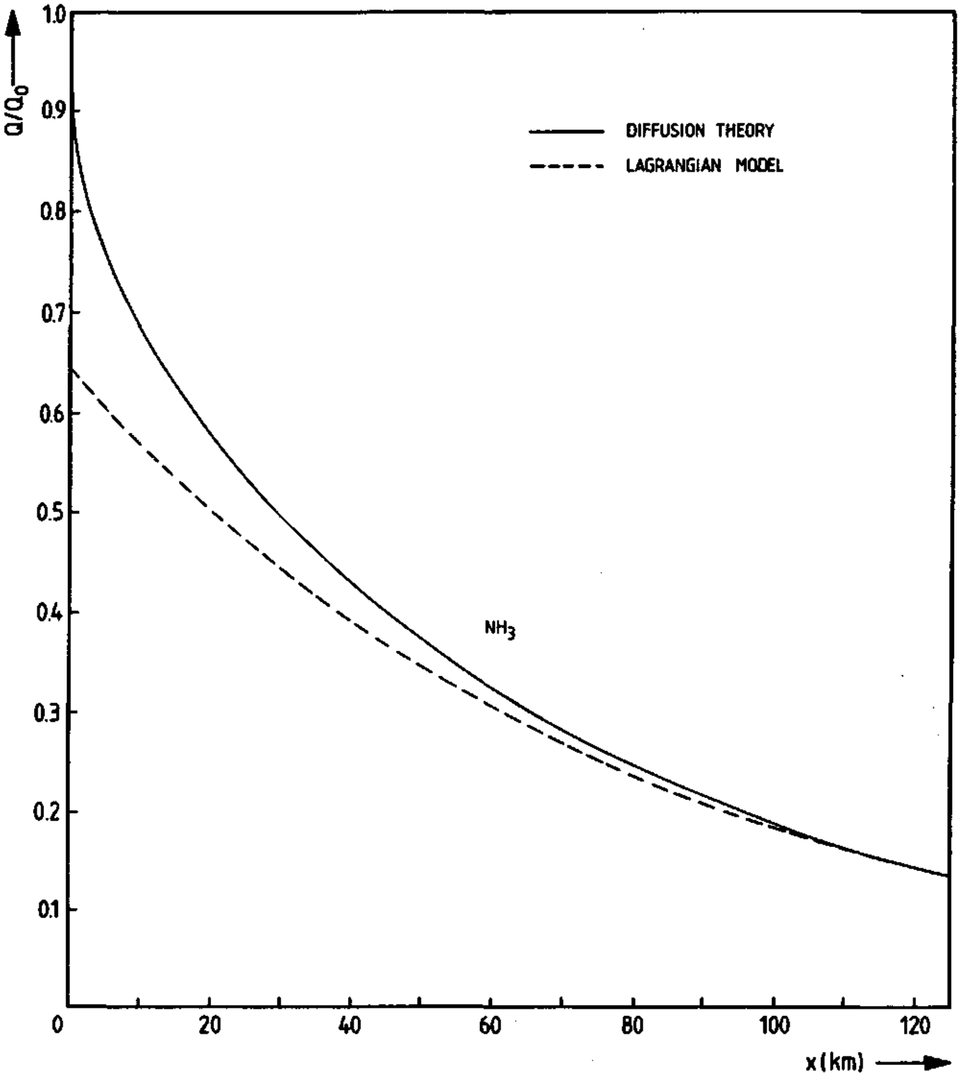

Fig. 1a. Normalized horizontal flux Q/Q_0 as a function of distance x from the source, according to diffusion (K-theory) calculations and according to the simple Lagrangian model if correction factors and effective removal parameters, derived from the diffusion calculations, are incorporated. Shown are values for NH_3. Compare with Fig. 1b which shows values for NH_4 and the sum of NH_3 and NH_4.

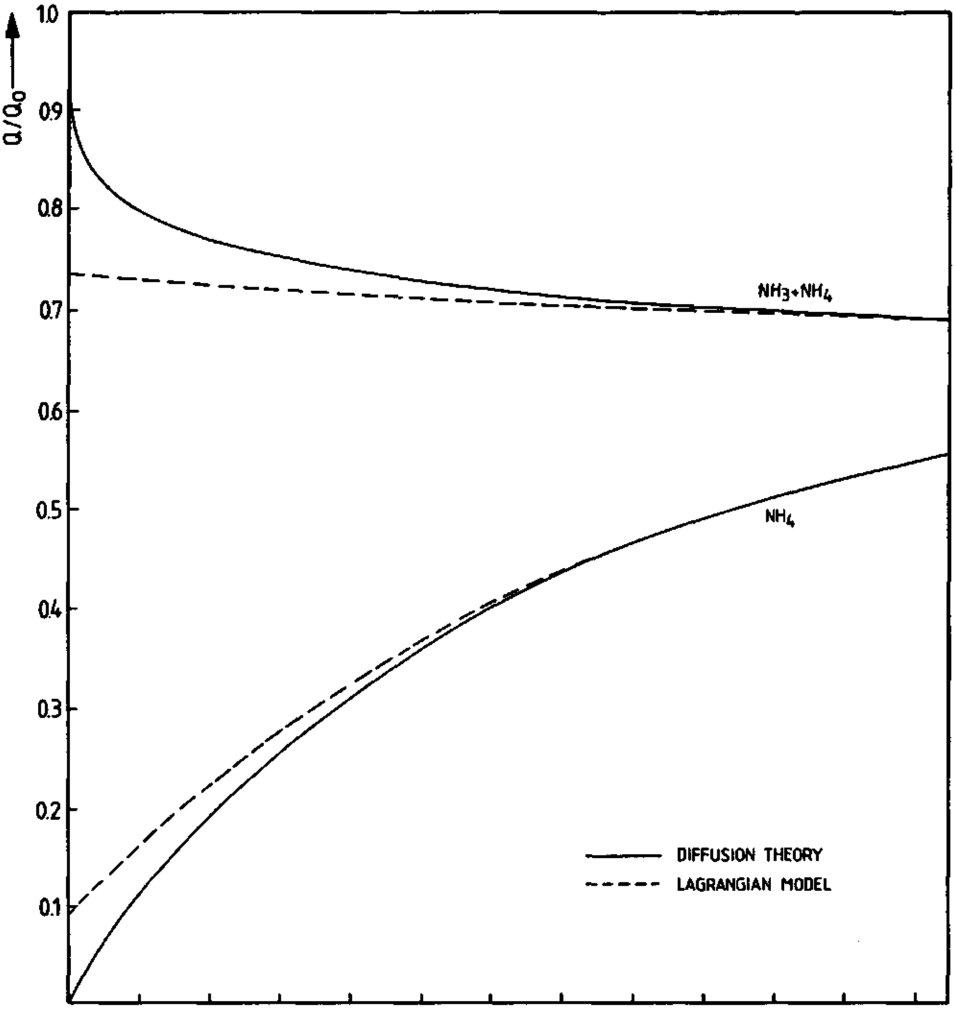

Fig. 1b. Normalized horizontal flux Q/Q_o of NH_4 and the sum of NH_3 and NH_4 as a function of distance x from the source. See text Fig. 1a.

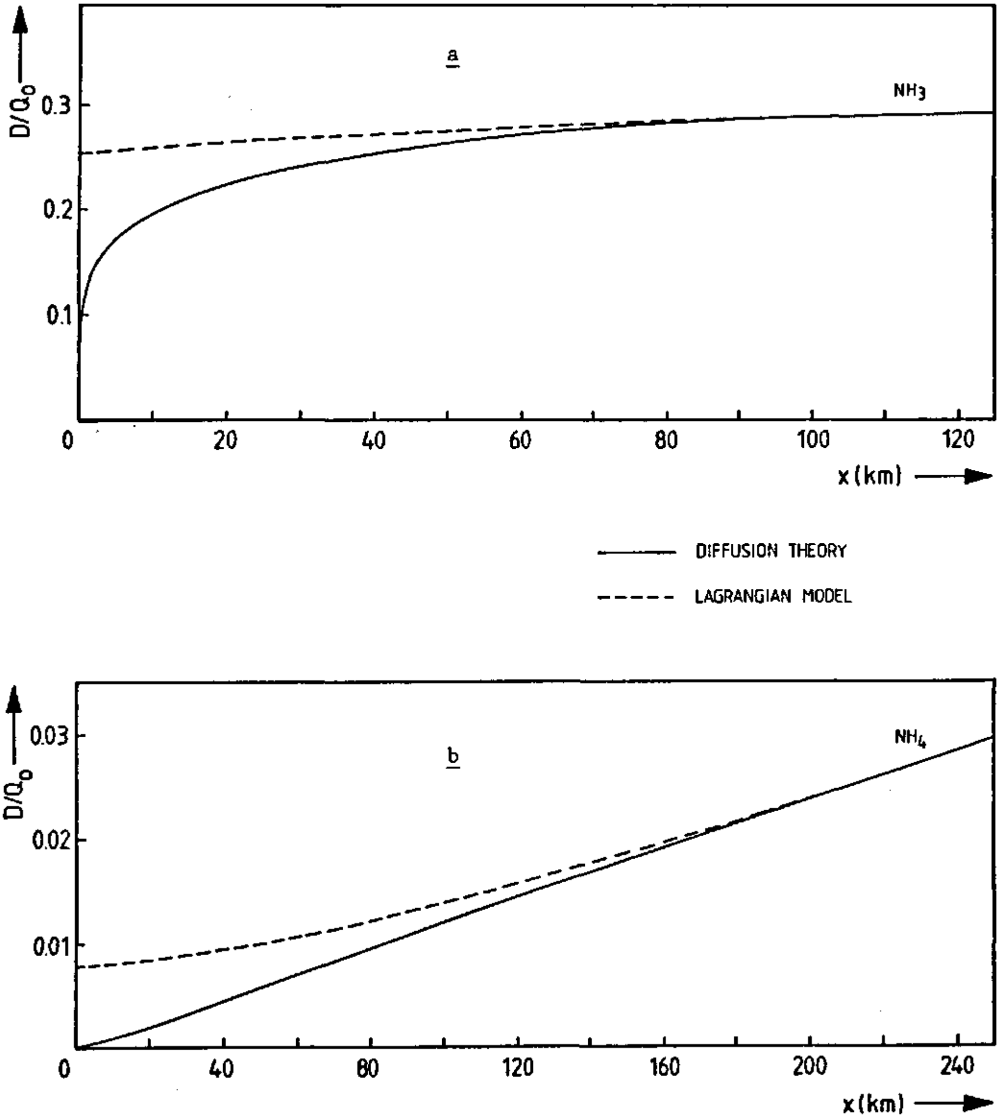

Fig. 2. Normalized dry deposition D/Q_o integrated up to distance x from the source, of NH_3 (Fig. 2a) and NH_4 (Fig. 2b). Correction factors and effective removal parameters, derived from the diffusion calculations, were used in the Lagrangian model calculations. Note the different scales in the two figures.

which is made up of two contributions, viz. the apparent direct local dry deposition $\alpha_1 E$ from local sources and the term $(v_{e1}/H)L_1$. With the parameter values mentioned above the term $\alpha_1 E$ appears to contribute nearly 84% to the total NH_3 dry deposition. Furthermore, a variation of 10% in α_1 would change total dry deposition by nearly 8%. The same sensitivity applies to the equilibrium NH_3 concentration at reference height, see eq. (18). On the other hand, complete ignorance of the correction factors in a Lagrangian model would result in a severe underprediction of the equilibrium NH_3 ground-level concentration, by almost 65%. The sensitivity to the other effective parameter values (β, k_e and v_{e1}) appears to be much less.

In this example the effective source strength of NH_3 is $(1-\alpha_1-\beta)Q_o$ = 0.65 Q_o (eq. 3a). It is interesting to note that the analytical model of Scriven and Fisher (1975), assuming a height-independent eddy diffusivity, would give 0.76 Q_o. Neglecting the suppression of turbulence near ground-level leads to an underprediction of local dry deposition. A similar underprediction has been found with the surface depletion model of Asman and Maas (1986).

4.2. Climatologically averaged parameter values

For long-term calculations with a Lagrangian model we have tried to determine climatological averages of the effective parameters. Diffusion calculations have been performed for Pasquill class D for three wind velocity classes, viz. 1.45, 4 and 8 $m\ s^{-1}$ at 10 m height; these values have been recommended for long-term pollution studies in the Netherlands (TNO, 1984).

Results are presented in Table 1. Calculated values for v_{e2} and k_e are in all cases almost equal to the reference values and are not presented in the table. Furthermore, weighted averages of the parameter values are given, in accordance with climatological conditions in the Netherlands (TNO, 1984). These averages have been used in our long-range transport calculations for NH_3/NH_4^+ (Asman et al., 1986B, 1986C). Clearly, there is a strong dependence of most parameter values on the wind velocity (or turbulence level), and one may wonder whether this dependence should be taken into account in a Lagrangian model. On the other hand, in reality the dry deposition velocity of NH_3 at reference height is itself dependent on the wind velocity (Asman et al., 1986B), tending to lower values at

Table 1. Calculated parameter values for the long-range transport model of NH_3/NH_4^+.

$u(10)$ $m\ s^{-1}$	$u(z \geq 200)$ $m\ s^{-1}$	$K(1)$ $m^2\ s^{-1}$	$K(z \geq 50)$ $m^2\ s^{-1}$	α_1	α_2	β	v_{e1} $m\ s^{-1}$	w.f. [1)]
1.45	2.6	0.054	2.7	0.436	0.0265	0.192	3.24×10^{-3}	0.16
4.0	7.1	0.15	7.5	0.255	0.0079	0.099	5.44×10^{-3}	0.39
8.0	14.1	0.30	15.0	0.157	0.0029	0.050	6.61×10^{-3}	0.45
weighted average:				0.240	0.0086	0.092	5.61×10^{-3}	

1) Weighting factor according to Dutch climatological data (TNO, 1984)

lower wind velocities and/or turbulence levels. If this variation is taken into account, the variation of, e.g., the apparent direct local dry deposition of NH_3 with wind velocity would be reduced substantially (see section 4.3).

4.3. Effect of variation of input data

Many input data for the diffusion calculations (and also for the Lagrangian model calculations) are uncertain and/or dependent on various conditions (e.g. atmospheric). They are at best reasonable estimates of space and time averaged values. In order to evaluate these uncertainties a series of diffusion calculations for NH_3/NH_4^+ has been made in which each input parameter has been varied separately. Results are presented in Table 2. As should be expected, the important parameter α_1 (the apparent direct local dry deposition of NH_3) is strongly dependent on the dry deposition velocity v_{r1} and on the turbulence level. It may be mentioned that the surface depletion model of Asman and Maas (1986) predicts a variation in α_1 of about a factor 2 if very stable or very unstable stratification is considered instead of neutral conditions. However, meteorological conditions in the Netherlands are such that on average these variations with stability are almost completely balanced. The data in Table 2 have been used in a sensitivity study with our Lagrangian model (Asman et al., 1986C).

4.4. Results for various pollutants

Pollutants like NH_3, SO_2 and NO_x exhibit significantly different chemical and physical behaviour. Moreover, concentration patterns of these substances are affected by the source height. We made some diffusion calculations for these species in order to show the possible variations in effective parameters for the Lagrangian model. One wind velocity was considered, viz. 5.4 $m.s^{-1}$ at 10 m height, which is the weighted average for Pasquill class D, according to Table 1. Dry deposition velocities v_r and reaction constants k were taken from Asman et al. (1986A). The results are presented in Table 3. The emission height and the dry deposition velocity have a large influence on the calculated value of α_1. The lower the emission height or the larger the dry deposition velocity, the larger α_1 will be. The average emission height of SO_2 is rather large in the Netherlands; this leads to a relatively low value of α_1, despite the rather large dry

Table 2. Calculated parameter values for NH_3/NH_4^+ for various model input data. The parameter values are "climatological averages", i.e. weighted averages over 3 wind velocity classes (cf. Table 1).

Variant	α_1	α_2	β	v_{e1} m s^{-1}
Standard	.240	.0086	.092	5.6×10^{-3}
H x ½	.196	.0026	.039	6.6×10^{-3}
k x ½	.259	.0053	.052	5.8×10^{-3}
v_{r1} x ½	.138	.0107	.090	3.2×10^{-3}
v_{r2} x ½	.240	.0044	.092	5.6×10^{-3}
K x ½	.351	.0187	.145	4.3×10^{-3}
u x 1.15	.217	.0071	.081	5.9×10^{-3}

deposition velocity. The dry deposition velocity of NO_x is relatively small which leads to a relatively low value of α_1, despite the low emission height. But for NH_3 the emission height is low and the dry deposition velocity is rather large, which explains the large value of α_1. The results indicate that, for the prevailing meteorological conditions and emission heights in the Netherlands, accurate knowledge of the effective parameter values for SO_2 and NO_x is less urgent than for NH_3.

In an earlier stage we computed α_1 of SO_2 with a simple Gaussian plume dispersion model which took dry deposition into account by means of the source depletion concept. For this pollutant, which in the Netherlands is emitted predominantly at high source heights, we found reasonable agreement between the source depletion model and the K-model used in this paper, provided the constant value of the eddy diffusivity K_z above the surface layer is in accordance with the dispersion parameter σ_z, as in eq. (23). Calculations by Högström (1979) of α_1 of SO_2, also made with a Gaussian model with source depletion, confirm this conclusion.

Eliassen and Saltbones (1983) derived an expression for the effective dry deposition velocity of SO_2, based on similarity theory, which for neutral atmospheric conditions reads:

$$v_e = v_r \left[1+\frac{v_r}{\kappa u_*} \ln\frac{z_e}{z_r}\right]^{-1}, \tag{28}$$

where z_e should be taken equal to 50 m.

With eq. (20) and taking $u(10) = 5.4$ m s^{-1}, $z_0 = 0.2$ m and $\kappa = 0.4$, we find that $v_e \approx 7.0\times10^{-3}$ m s^{-1} for SO_2, which is 10% higher than the value given in Table 3. Still better agreement would be obtained if a somewhat larger value of K_z above the surface layer would be used in the diffusion calculations, which would be in accordance with σ_z values for distances larger than 10 km from the source given by Pasquill (1974) (see section 3).

Table 3. Calculated parameter values for different pollutants, emitted at various heights. The parameter values are not not "climatologically averaged": $u(10)=5.4$ m s^{-1}.

Pollutants primary	Pollutants secondary	v_{r1} m s^{-1}	v_{r2} m s^{-1}	k s^{-1}	Emission height m	α_1	α_2	β	v_{e1} m s^{-1}	v_{e2} m s^{-1}
NH_3	NH_4	8.0×10^{-3}	1.0×10^{-3}	8.0×10^{-5}	0	.21	.0053	.076	6.0×10^{-3}	1.0×10^{-3}
					10	.16	.0055	.078	6.0×10^{-3}	1.0×10^{-3}
SO_2	SO_4	8.0×10^{-3}	1.0×10^{-3}	3.9×10^{-6}	50	.15	.0004	.004	6.3×10^{-3}	1.0×10^{-3}
					100	.12	.0004	.004	6.3×10^{-3}	1.0×10^{-3}
					200	.07	.0003	.003	6.3×10^{-3}	1.0×10^{-3}
					400	-.01	.0002	.0	6.3×10^{-3}	1.0×10^{-3}
NO_x	NO_3	3.0×10^{-3}	2.8×10^{-3}	1.2×10^{-5}	10	.08	.0052	.011	2.8×10^{-3}	2.6×10^{-3}
					100	.05	.0042	.009	2.8×10^{-3}	2.6×10^{-3}

5. CONCLUSIONS

The very approximate description of turbulent mixing in simple long-range transport models can introduce large errors in calculated ground-level concentrations and deposition patterns. Correction factors have been defined which can be used in these models to reduce the errors. Values for these correction factors have been derived in a consistent way with an efficient and flexible numerical reactive diffusion model based on K-theory. Some of the results could be checked with other models and theories.

The results show that the correction factors are very important for ground level sources of pollutants with relatively high dry deposition velocities, such as NH_3. The factors are dependent on meteorological conditions and have therefore an inherent uncertainty. However, by applying the proposed combination of diffusion theory and simple long-range transport a substantial improvement is obtained in calculated ground-level concentrations and deposition patterns. Results are thus obtained which are about as good as those of more sophisticated models which require much more computing time.

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CHAPTER 5.

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

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Abstract

This paper reviews available data on ammonia emission and other parameters used in the model, viz. dry deposition velocities, scavenging coefficients and the pseudo-first order reaction rate . There are some striking differences in emission and subsequent behaviour of ammonia and sulphur dioxide. Ammonia is predominantly emitted near or at ground level, whereas sulphur dioxide is mainly emitted from higher sources. Moreover, the conversion rate of ammonia to ammonium is higher than for sulphur dioxide to sulphate. The approximate treatment in the Lagrangian model of turbulent mixing (instantaneous homogeneous mixing over the whole mixing layer) had to be modified by the introduction of several correction factors derived from detailed diffusion calculations. Contrary to sulphur dioxide, the concentration at ground-level of ammonia will be determined to a large extent by local sources, which hinders model verification. For this purpose only measurements in the Netherlands could be used. The model has been run for the year 1980. The computed ammonium concentrations in air and precipitation are in agreement with the available measured data. The model results show that the dry deposition of ammonia in any country is mainly caused by inland sources, whereas the dry and wet deposition of ammonium is to a considerable extent caused by foreign sources. Moreover some numerical aspects of the model are discussed and the results of a sensitivity analysis are shown.

1. Introduction

Ammonia and ammonium are important atmospheric components. Ammonia is the most abundant alkaline component in the atmosphere. A substantial part of the acid in the atmosphere generated by the oxidation of sulphur dioxide and nitrogen oxides is neutralized by ammonia (see e.g. Asman et al., 1982). As a result ammonium is a major component in aerosols and in precipitation. Ammonia and ammonium are also important components in biological cycles. Nitrogen can be a limiting factor for growth in oligotrophic ecosystems. In many ecosystems a substantial part of the N-input is caused by deposition of ammonia and ammonium from the atmosphere. Very high concentrations of ammonia can cause direct damage to vegetation (Van der Eerden, 1982). After deposition ammonia and ammonium may be taken up by the needles of trees. This results often in the excretion of potassium and magnesium by the needles, which may lead to potassium and/or magnesium deficiencies, depending on the soil conditions (Roelofs et al., 1985). These deficiencies may lead to premature shedding of needles.

When ammonia and ammonium are deposited and enter the soil as ammonium, nitrification can occur :

$$NH_4^+ + 2\ O_2 \rightarrow 2\ H^+ + NO_3^- + H_2O \quad .$$

As a result not only is acid formed by the oxidation, but also acid formed in the atmosphere is no longer neutralized by ammonia (Van Breemen et al., 1982; Asman et al., 1982). In this way ammonia and ammonium can cause acidification of the soil. It should be mentioned, however, that nitrification does not always occur and sometimes is incomplete. If ammonia is absorbed by cloud droplets this will cause a rise in pH which enhances the rate of oxidation of dissolved sulphur dioxide by ozone (Maahs, 1983). The result of this effect is that somewhat more sulphur dioxide will be taken up by cloud droplets and will be oxidized to sulphate. Uptake of ammonia by raindrops will also lead to a rise in pH, which enhances below-cloud scavenging of sulphur dioxide.

Different kinds of transport models exist for different purposes. There are, for example, models with very detailed chemistry, which include ammonia and ammonium (Russell et al., 1983; De Leeuw et al., 1986). These are more suited to determine the relative importance of different reaction mechanisms and the extent of non-linear behaviour. They can also be used to interpret measurements during relatively short periods (episodes). They are however not well suited for computing long-term (annual average) concentrations, because this would require too much computing time. For this purpose relatively simple linear models may be used, which at very least lead to an objective spatial interpolation between measured concentrations (Eliassen, 1978; Eliassen and Saltbones, 1983). Moreover, simple import-export matrices can be calculated with such models, which are useful for policy makers. An attempt to model ammonia and ammonium over Europe has been made by Fisher (1984). His work was severely handicapped by lack of information on the emission of ammonia, on the transformation rate of ammonia to ammonium and on the dry deposition velocity of ammonia.

IMOU and ECN have been engaged in a project together with the Netherlands Organization for Applied Scientific Research TNO and the Kernforschungsanlage-Jülich (F.R.G.) to study the atmospheric behaviour of ammonia and ammonium. With the information gained from this project it is possible to make a considerable step forward in the modelling of the atmospheric behaviour of ammonia and ammonium on a European scale. The model applied here is a linear Lagrangian receptor-oriented model of the EMEP-type (Eliassen, 1978). In the following sections information is given concerning the parameters used in the model, which is followed by the presentation of the main results of a complete model run.

2. Emissions

The gridded (net) NH_3 emission data used in the model are based upon the work of Buijsman et al. (1985A) and include emissions caused by animals, by the use of fertilizers and by some industrial processes. Some other aspects of the emission that can be of importance in modelling will also be presented in this section.

2.1. Emission data used

The major part of the NH_3 emission is caused by decomposition of animal manure. The mineral inorganic part of the nitrogen in manure (about 50% of the total N-content) is easily lost as NH_3. Data on the mineral part of nitrogen in manure were used to calculate the emissions. The other part of the nitrogen in manure consists of organic nitrogen. The emission of, for example, amines is unimportant compared to the emission of NH_3. Sluijsmans and Kolenbrander (1976) and Commission of the European Communities (1978) estimate that the remaining nitrogen also can be taken up by plants over longer periods, up to 100 years. It is not yet clear whether this part of the nitrogen can cause any NH_3 emission. It was therefore assumed that this part would not lead to any emission. No important sources for NH_4^+ aerosols are known. This means that all NH_4^+ found in the atmosphere originates from the conversion of emitted NH_3. The emissions computed by Buijsman et al. (1985A) are conservative estimates. This is partly because some emission may occur more than one week after spreading of the manure (Asman,1986), whereas the emission estimated by Buijsman et al. (1985A) is derived mainly from measurements during the first week after spreading. In addition some sources of NH_3 could not be included in the gridded part of their emission survey. To take account of these sources we used gridded emission data in the model which are 20% higher than their gridded emission data. Furthermore, ammonia emissions in Iceland, Marocco, Algeria, Tunesia, Libya and an extended part of the USSR were estimated from cattle statistics and were used in the calculations. Although we computed concentrations for each central point of an EMEP grid element (about 150 x 150 km^2), the emissions used in the computations are for IE grid elements (about 75 x 75 km^2).

For Europe as a whole the amount of potential acid emitted is much larger than the amount that can be potentially neutralized. In Europe (Iceland, USSR and Turkey excluded) 1.3 x 10^{12} equivalent SO_2 is emitted each year, 3.1 x 10^{11} equivalent NO_x and 3.1 x 10^{11} equivalent NH_3 (Dovland and Saltbones, 1979; Eliassen et al., 1982). Asman and Janssen (1986) examined the geographical distribution of SO_2, NO_x and NH_3 emissions in Europe and found that it is very likely that in most places the conversion rate of NH_3 to NH_4^+ aerosol is not limited by the amount of acid present in the atmosphere.

2.2. Diurnal and seasonal variations in the emission rate

Because of diurnal variations in wind-speed and temperature, the emission rate of NH_3 from manure and urine in the field is higher during day-time than during night-time (Beauchamp et al., 1978, 1982; Hoff et al., 1981; Harper et al., 1983; Lockyer, 1984; Ryden and McNeill, 1984). For the same reasons it is also likely that the emission from stables and during storage will show the same pattern. The ground-level concentration, however, tends to be higher during night-time than during day-time (Alkazweeney et al., 1986). This is confirmed by measurements undertaken by IMOU and ECN in an area in the Netherlands where emission occurs. This phenomenon can be explained by a combination of effects. During night-time the atmosphere is usually more stable, the mixing height tends to be lower and even inversions may occur at ground level. Moreover, because of the reduced turbulence, the dry deposition velocity will in general be lower than during day-time. It is difficult to take all these effects into account in the model.

Seasonal variations in the emission rate are likely to be caused by the application of manure and fertilizer. Application will usually occur before the growing season starts. In the Netherlands a maximum in the NH_3 concentration was clearly observed in March, which could be attributed to the spreading of manure collected during wintertime when cattle are kept indoors (Vermetten et al., 1985). There is some indication that a less pronounced peak occurs in autumn as well. Lenhard and Gravenhorst (1980) found from measurements by aircraft in Western Germany a flux density of NH_3 which was substantially higher in summer than in winter. Fluctuations in the emission rate will depend on the local agricultural practices and are also affected by soil and weather conditions. As a result seasonal variations in the emission rate are likely to vary from region to region and will be different for different years. Because most of the above mentioned effects and variations could not be quantified, any diurnal or seasonal variation in the emission rate has been neglected in our model.

3. Dry deposition

When evaluating publications on the dry deposition velocity of a component it must be noticed that this velocity can be defined in different ways. It can be determined by experiments in the laboratory, during which the circumstances are not always representative of field conditions (e.g. wind-speed and turbulence). Moreover it does not represent the dry deposition velocity for a certain reference height. The dry deposition velocity deduced from laboratory and field experiments may not be representative of other surfaces and circumstances. Often the surface is not well defined as it consists of both soil and vegetation. This may be important e.g. because an acid soil is likely to absorb NH_3 very well. The overall dry deposition velocity used in our model should represent the loss rate in the mixing layer due to dry deposition averaged over a large area, which often consists of surfaces with different properties. This loss rate can be influenced by other factors than just the dry deposition velocity near ground level (e.g. reduced exchange due to inversions). This means that the dry deposition velocity used in our model under certain circumstances is not necessarily the same as the dry deposition velocity measured in the field under the same circumstances.

3.1. Dry deposition of ammonia

Malo and Purvis (1964) used filter paper as a surrogate for soil under field conditions and compared the rate of absorption of ammonia by soils and filter paper in a gas chamber. From these measurements a dry deposition velocity of 3×10^{-3} m s^{-1} can be deduced. The procedure used is rather doubtful, because the measured cumulative deposition was related to ambient concentrations measured during only 1 hr a day. Hannawalt (1969A, 1969B) determined the adsorption of NH_3 by soils in a gas chamber. From his experiments a dry deposition velocity of 5×10^{-3} $m\ s^{-1}$ can be deduced. This is certainly an underestimate of the dry deposition velocity under atmospheric circumstances as the air flow in the gas chamber was reduced compared to field conditions. Rodgers (1978) measured the deposition of NH_3-N to different soil samples under field conditions. From his measurements a dry deposition velocity of 6×10^{-4} to 5×10^{-3} $m\ s^{-1}$ can be deduced if it is assumed that no dry deposition of NH_4^+ aerosol occurred at the same time. Hutchinson et al. (1972) measured the uptake rate of NH_3 by plants in a gas chamber. From their measurements a dry deposition velocity of 2×10^{-3} to 6×10^{-3} $m\ s^{-1}$ on the leaf of soybean, sunflower, corn and cotton can be deduced. The air flow in their experiment was not representative of field conditions. The uptake rate was 3 times higher in the light than in the dark. According to Hutchinson et al. (1972) this would suggest that uptake occurs through the stomata. Their measurements imply a rather high deposition velocity of probably 1×10^{-2} to 3×10^{-2} $m\ s^{-1}$ under field conditions. Horvâth (1982, 1983) determined the dry deposition velocity of NH_3 by the gradient technique. He found deposition velocities of 5×10^{-3} to 1×10^{-2} $m\ s^{-1}$ on soil, but emission occurred on occasions. Van Aalst (1985A, 1985B) using the same technique found during day-time a deposition velocity of 1.8×10^{-2} $m\ s^{-1}$ on heather (and soil) and long grass (and soil) in a nature reserve. Van Aalst (1986A) states that, although the long grass seemed to be almost dead, the deposition velocity was still high. This could indicate that the uptake of NH_3 does not only take place through the stomata of the plants or that the absorption by soil is very important. Van Aalst (1986B) found a dry deposition velocity of 2.2×10^{-2} $m\ s^{-1}$ over a forest.

If NH_3 (or NH_4^+ aerosol) is present in or on the surface onto which dry deposition takes place, the observed (net) dry deposition velocity can be reduced (or even net emission can occur), as it depends on the difference in ambient and surface concentrations. A reduction of the dry deposition velocity may also have occurred during the experiments discussed before. Farquhar et al. (1980), Lemon and Van Houtte (1980) and Horvâth (1982, 1983) found that below a certain ambient NH_3

concentration ("compensation point") emission occurred and above this concentration deposition occurred. This means for example that plants can absorb NH_3 when the ambient concentration is high, but that the absorbed NH_3 can be released if the ambient concentration drops. This mechanism could even lead to "secondary transport" of NH_3 to areas with a low surface concentration of NH_3 (e.g. nature reserves). Farquhar et al. (1980) found that the compensation point of Phaseolus vulgaris L. ranged from 1μg m^{-3} (15°C) to 3 μg m^{-3} (25°C). This does not necessarily mean that the NH_3 concentration in air should have the same value, because during the transport from the leaves to the reference height where the concentration is measured dilution will occur. The "compensation point" has only been determined for a few plant species under a few conditions and often when fertilizers containing NH_4^+ were applied. As a result no general quantitative conclusions can yet be drawn on the influence of the existence of a "compensation point" on the dry deposition flux over large areas. But the existence of NH_3 in or on the surface will lead to a certain reduction of the overall dry deposition velocity representative of a larger area, as should be used in our model. For water surfaces some information on the existence of this phenomenon is also available (Horvâth, 1982; Georgii and Gravenhorst, 1977). They found that both deposition and emission could occur, depending on the difference between the atmospheric ammonia concentration and the equilibrium concentration in water.

During part of the time (net) emission will occur in areas where manure and fertilizer are applied or cattle are grazing. Then no (net) dry deposition can take place. As a result the overall dry deposition velocity for such areas will be less than the dry deposition velocity for ammonia-free surfaces. This effect is potentially important in European countries as a substantial part of the land (10-85%) is used for agricultural purposes. Asman (1986) estimated that the reduction of the overall dry deposition velocity is of the order of 20% if a half-life of 4 days is used for the rate of volatilization of NH_3. However, in some areas consisting mainly of grassland where cattle are grazing this reduction could be up to 50%. The reduction of the dry deposition velocity to account for the effects described above, is small compared to the large uncertainty in the dry deposition velocity itself.

Therefore, this effect is not taken into account yet. The concept of a reduced dry deposition velocity is, however, in principle more correct to compute realistic annual ammonia fluxes for areas for which only the net annual ammonia emission is known and where both emission and deposition can occur.

We adopted a value of 8 x 10^{-3} m s^{-1} for the overall dry deposition velocity of NH_3 in our model. This value lies in the middle of the - wide - range of values found in the literature. The consequence of applying an overall dry deposition velocity in the model is that the dry deposition of NH_3 in agricultural areas might be overestimated (the dry deposition velocity will be relatively low there because of the presence of ammonia at the surface). This will lead to underpredictions of concentrations in these areas. The dry deposition of NH_3 onto forests might be underestimated (it will be relatively high there because it will be mainly determined by the aerodynamic resistance), at least close to agricultural areas. The spatial resolution of the model however is not suited to treating such refinements.

3.2. Dry deposition of ammonium aerosol

NH_4^+ is mainly found in fine particles (Lenhard and Gravenhorst, 1980 ; Stevens et al., 1984 ; Clarke et al., 1984). This arises because coarse particles generally originate from resuspended soil and are therefore more likely to be alkaline. As a result absorption of NH_3 cannot occur. Fine particles are likely to be more acid, e.g. as a result of the formation of H_2SO_4 from SO_2, and absorption of NH_3 by these particles can easily occur.

Gmur et al. (1983) measured the dry deposition velocity of $(NH_4)_2SO_4$-aerosols onto plants in the laboratory. They found a dry deposition velocity of 3.2 x 10^{-5} m s^{-1}. This is certainly an underestimate as the air flow was much lower than that in typical field conditions. Gravenhorst et al. (1983) derived indirectly a dry deposition velocity of 5 x 10^{-3} to 1.5 x 10^{-2} m s^{-1} over a spruce and a beech forest. These values are very high, however, and are at least not likely to be representative of other surfaces. A dry deposition velocity for NH_4^+

aerosol of 1×10^{-3} m s^{-1} was adopted for the overall dry deposition velocity used in our model. Although quite a range in deposition velocities is reported for fine particles, the value does not seem to be unreasonable (Sehmel, 1980; Davies and Nicholson, 1982).

4. Wet deposition of ammonia and ammonium

It should be pointed out that for NH_3 no equilibrium exists between the air concentration and the concentration in raindrops, like that usually assumed for SO_2. The solubility of NH_3 is much larger than for SO_2 (Hales and Drewes, 1979) and is enhanced by the reaction with H^+ in the drop. As a result the mass transfer rate through the air/drop interface is not high enough for drops of most sizes to reach saturation before they reach the earth's surface. As the ground level concentration in areas with emission is much higher than the concentration aloft, no equilibrium between the ground level air concentration and the concentration in precipitation will exist. Asman (1985A) deduced from the computations of Levine and Schwartz (1982) a function for the below-cloud scavenging coefficient of NH_3 of the form $\Lambda_{bc} = 2.64 \times I^{0.68}$ (where Λ_{bc} in s^{-1} at temperature 25°C, I the precipitation rate in m s^{-1}). This value is in agreement with that of Janssen and Ten Brink (1985). At a rainfall rate of 1 mm hr^{-1}, Λ_{bc} takes the value 9.2×10^{-5} s^{-1}.

NH_3 within cloud will dissolve mainly in the acid cloud droplets. The in-cloud scavenging of NH_3 will therefore proceed at about the same rate as the in-cloud scavenging of SO_4^{2-} aerosol particles which act as condensation nuclei. From measurements within the EMEP-project (Whelpdale, 1981) it is known that the overall scavenging ratio, S, for SO_4^{2-} is of the order of 10^5 to 10^6, where S = concentration in precipitation/concentration in air (mole m^{-3})/(mole m^{-3}). The average value is about 10^6. This reflects mainly in-cloud scavenging. The average liquid water content of clouds is higher at higher rainfall rates. The scavenging ratio will therefore be lower at a higher rainfall rate, because the dissolved NH_3 and NH_4^+ is then more diluted. Although this might be relatively unimportant, this effect is accounted for by using a value for the in-cloud scavenging ratio S_{ic} of NH_3 deduced from Liu et al. (1982), namely: $S_{ic} = 5000 \times I^{-0.36}$. This leads to a value of 1.1×10^6 for S_{ic} at a rainfall rate of 1 mm hr^{-1}. The in-cloud scavenging coefficient is $\Lambda_{ic} = S_{ic}.I/H$, where H is the height of the mixing layer (m). At a rainfall rate of 1 mm hr^{-1} and a height of the mixing layer of 800m Λ_{ic} takes the value 4.0×10^{-4} s^{-1}.

Ammonia is emitted at or near ground level. The cloud base is generally a few hundred metres above ground. This means that very near a source, when the plume is under the cloud base, scavenging will occur at a much lower rate than at some distance from the source, where the remaining NH_3 is scavenged mainly by in-cloud processes. Computations show, however, that the results of the model calculations are not very sensitive to this effect and therefore a value of $S = 5000 \times I^{-0.36}$ is used for the overall scavenging coefficient of NH_3.

For NH_4^+ aerosol the same overall scavenging coefficient is used because NH_4^+ containing aerosols will act as condensation nuclei and hence will be scavenged in the cloud at about the same rate as NH_3.

5. Reactions of ammonia and ammonium

Under European conditions most ammonia will react with acid aerosol (e.g. containing H_2SO_4). A minor part will react with gaseous HNO_3: $NH_3 + HNO_3 \rightleftarrows NH_4NO_3$ (See for these reactions: Stelson and Seinfeld, 1982). Temperature and relative humidity have a great influence on the equilibrium concentration of NH_4NO_3. Ammonia is mainly released from the earth's surface whereas HNO_3 and acid aerosol are formed throughout the whole mixing layer. It is therefore likely that the pseudo first order reaction rate k is a function of height. Moreover k is likely to be dependent on time of the day and season. Lenhard and Gravenhorst (1980) measured concentrations of NH_3 and NH_4^+ aerosol over western Germany at 100m and at 700m above ground level. From their measurements and vertical eddy diffusivity coefficients they estimate an average value for k at 400m of 1.2×10^{-5} s^{-1} in winter and 2.1 x 10-5 s-1 in summer.

They note also that k is likely to be greater at a lower level. Vermetten et al. (1985) measured NH_3 and NH_4^+ aerosol concentrations at a meteorological tower in the Netherlands. They calculated values of k between 10^{-5} and 10^{-3} s^{-1}, which should be representative of the lowest 100m of the atmosphere. The concentration profiles of all components involved as well as the temperature, relative humidity and mixing height are different at different sites and under different circumstances. As a result k will not be a constant, but will vary with time and place. As insufficient information was available on the factors influencing k, a constant value for k was adopted. This value was chosen in such a way that realistic concentrations were calculated. NH_3 and NH_4^+ aerosol concentrations at ground level are very sensitive to the value of k chosen, whereas NH_4^+ in precipitation is not influenced very much in areas with relatively high emissions, as the scavenging coefficients for NH_3 and NH_4^+ aerosol are the same. This means that a value of k should be taken which is representative of the lowest part of the atmosphere. We adopted a value of 8×10^{-5} s^{-1}, partly based on the results of sensitivity studies.

Ammonia also can react with OH, O and $O(^1D)$. Levine et al. (1980) found that the reaction with OH was most important. When adopting a constant, relatively high, OH-concentration of 4×10^6 molecules cm^{-3} (Logan et al., 1981) a pseudo first order reaction rate of 5.4×10^{-7} s^{-1} for ammonia is found. This value is much lower than the pseudo first order rate for the reaction of NH_3 with acid aerosol and nitric acid. Therefore the reaction with OH is neglected in our model. However outside areas with high emissions the reaction with OH may play a more important role over a larger scale.

6. 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 in reality 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:

Near the source, at or near the earth's surface, ground level concentrations 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}) of a point source used in such a 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 βQ of the reaction product (where $\alpha + \beta + \gamma = 1$; Janssen and Asman, 1986).

At larger distances from a point source when 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. Therefore, the dry deposition flux would 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 parameterization of this phenomenon is important as α determines the amount of NH_3 that is available for long-range transport. Moreover, the calculated ground-level concentration is to a large extent determined by α. The values of the parameters introduced above have been calculated with a numerical reactive diffusion model using K-theory (Janssen and Asman, 1986).

The following equations are used for the height-averaged concentrations of NH_3 and NH_4^+ aerosol (subscript 1 refers to NH_3; subscript 2 refers to NH_4^+ aerosol; see Table 1 for the list of symbols)

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

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

The operator $\frac{D}{Dt}$ is the total time derivative, I is the precipitation rate (m s^{-1}) and E is the ammonia emission rate averaged over the grid element (moles m^{-2} s^{-1}). The remaining parameters are presented in Table 1 together with their values. The ground-level concentration c_g of a component in a receptor point in a grid element with emission rate E_g can be computed from: $c_g = (v_e.\bar{c} + \alpha.E_g)/v$ (Janssen and Asman, 1986).

In the model a constant mixing height of 800 m is applied, being the approximate harmonic mean mixing height in N.W.-Europe at 00 and 12 GMT (Buch, 1984). The mixing height is defined by Buch as the height up to the lowest stable layer (with $dT/dz > -5.0 \times 10^{-3}$ K m^{-1}) with base above 200 m. A harmonic mean is taken because the height-averaged concentration is proportional to H^{-1}. This definition of the mixing layer is in fact not very satisfactory as stable surface layers cannot be taken into account (H = 0 then and hence H^{-1} is undefined). Buch found that stable surface layers occur about 30-40% of the time in N.W.-Europe and as expected they occur mainly during night-time. The best way to tackle this problem is perhaps to adapt the correction factors α and β while not taking into account mixing heights lower than 200 m.
The 850 hPa isobaric 4-day backward trajectories arriving at the centres of each EMEP-grid element every six hours in the year 1980 were provided by EMEP and used in the calculations. From measurements it is known that the NH_3-concentration decreases very rapidly with height (Georgii and Müller, 1974; Georgii and Lenhard, 1978; Lenhard and Gravenhorst, 1980; Vermetten et al., 1985; Alkazweeny et al., 1986). In general the concentration weighted transport height will be much lower than the 850 hPa level (about 1500 m). Therefore we reduced the 850 hPa wind-speed by 15% and backed the wind-direction by 15 degrees. In this way a wind-vector representative of a 200 m level is obtained (Asman, 1985B).

Six-hourly gridded precipitation fields for the year 1980 were also

Table 1. Parameter values used in the model.

symbol	explanation	parameter value
v_1	Dry deposition velocity for NH_3	8.0×10^{-3} m s^{-1}
v_{1e}	Effective dry deposition velocity for NH_3	5.6×10^{-3} m s^{-1}
v_2	Dry deposition velocity for NH_4^+	1.0×10^{-3} m s^{-1}
v_{2e}	Effective dry deposition velocity for NH_4^+	1.0×10^{-3} m s^{-1}
S_1	Scavenging ratio for NH_3	$5000.I^{-0.36}$ (mole m^{-3} prec)/(mole m^{-3} air)[a]
S_2	Scavenging ratio for NH_4^+	$5000.I^{-0.36}$ (mole m^{-3} prec)/(mole m^{-3} air)[a]
k	Pseudo first order reaction rate NH_3 to NH_4^+	8.0×10^{-5} 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})

obtained from EMEP. These data were compared with the annual precipitation amounts found in "Monthly climatic data for the World" (NOAA,1981) (Maas and Van der Veen, 1986). It was found that the data obtained from EMEP were about 15% higher than the climatic data. Therefore, a correction factor of 0.85 was applied to the EMEP-data.

7. Measurements used to test the model

7.1. Ammonia

There are few reliable measurements of the NH_3 concentration in air. Older measurements are most abundant, e.g. those presented by Egner, Eriksson (1955). However, in view of the long sampling times, possible influences of bacterial processes and the presence of NH_3 in the laboratory we prefer not to use these older measurements. In recent years the denuder technique has been developed to measure NH_3 (Ferm, 1979). If daily samples are taken using this technique and any contact with NH_3 after sampling is avoided, reliable data can be obtained. As the NH_3 emission can be highly variable in time, the NH_3 concentration in air can be highly variable in time as well. This means that concentrations can only be used where sampling has been undertaken for a long period of at least one year. There are only a very few stations in Europe where such measurements are available.

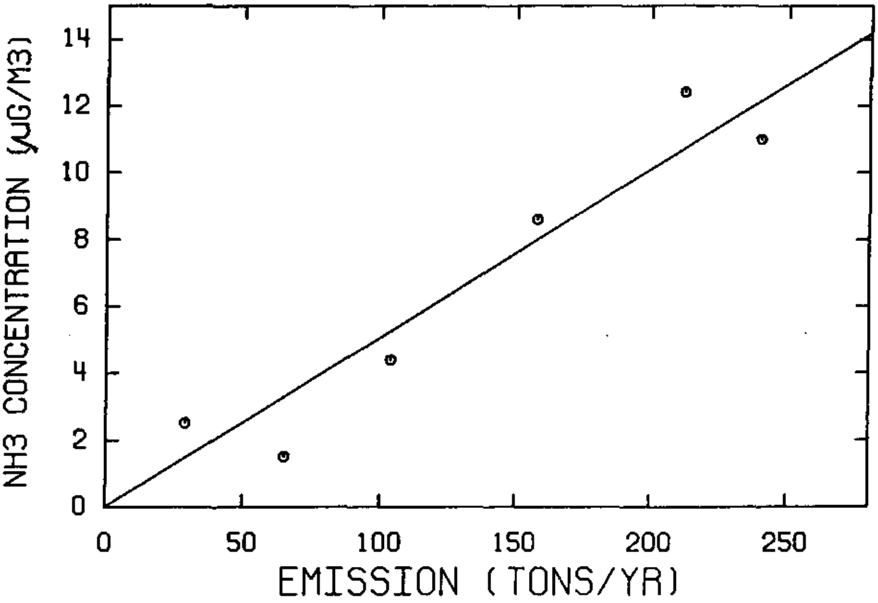
Another problem arises from variability of concentrations in space. If measurements at only one point in a grid element (150 x 150 km^2) are available, these measurements will usually not be representative of such a large grid element and cannot be used then to check the model.
For the Netherlands, there are measurements (Diederen, 1984; Erisman et al., 1986) that can be related to emissions on a 5 x 5 km^2 grid (Buijsman et al., 1984). Computations with the surface depletion model of Horst (1977) made by Asman and Maas (1986B) show that the contribution to the annual average concentration caused by emission from one relatively large point source usually drops to a very low value within a few hundred metres of the source. Other computations (Asman and

Maas, 1986A) show that the NH_3 concentration not too near a point source is affected to a large extent by local emissions (over a scale of about 5-30 km). The Dutch measuring sites are located in such a way that generally no influence of nearby permanent point sources could be expected. Occasionally, however, daily concentrations up to 250 µg m^{-3} can be found, if manure spreading occurs in the near surroundings. To avoid the influence of such high values, median concentrations are used instead of mean concentrations. Figure 1 shows the relation between the measured median concentration and the local emission of NH_3. Using this relation and the average emission rate in the Netherlands, a median NH_3 concentration in the Netherlands of about 5 µg m^{-3} is computed. This is only a rough estimate of the ammonia concentration but it is the only one available to check the model. The background concentration of NH_3 is likely to be negligible compared to concentrations usually found in areas with some emission and may be of the order of a few tenths of a µg m^{-3}. Georgii and Gravenhorst (1977) report a background concentration in marine areas of approximately 0.1 µg m^{-3}.

7.2. Ammonium aerosol

For NH_4^+ aerosol more measurements exist although some interference with NH_3 cannot be excluded. There are measurements from the Netherlands (Diederen, 1984; Erisman et al., 1986), from the United Kingdom (Harrison and McCartney, 1980), from Poland (Pruchwicki, 1984) and from EMEP-stations in Denmark, Hungary, the USSR and Poland (EMEP, 1983A, 1983B; Mészáros and Horváth, 1984). Although some of the measurements were made in years other than 1980, these will still be used to check the model (see section 8). As NH_4^+ aerosol is a reaction product, the spatial variation in the average concentration will be much less than for NH_3. Computations made by Asman and Maas (1986B) show that the average concentration does not vary much within a grid element of 150 x150 km^2. This means that the measured concentrations referred to above can be used to check the model results. Georgii and Gravenhorst (1977) reported NH_4^+ aerosol concentrations between 0.2-1 µg m^{-3} for maritime

Figure 1. Relation between measured concentration and calculated emission for NH_3.
Emissions are given in tons y^{-1} for the 5 x 5 km^2 area in which the station is located.



background locations. Buijsman et al. (1985B) found a NH_4^+ concentration in precipitation on the Atlantic Ocean of about 5 µmole l^{-1}. Adopting a low scavenging ratio of 10^5 and assuming that all NH_4^+ in precipitation is caused by scavenging of NH_4^+ aerosol an upper limit of 0.9 µg m^{-3} is found. A more realistic value would be 0.1-0.2 µg m^{-3}.

7.3. Ammonium in precipitation

NH_4^+ in precipitation has been measured at many sites in Europe. These data offer a good possibility to test the model. Precipitation is often still collected with bulk samplers that are not covered with a lid during dry periods. Thus some dry deposition is sampled in addition to the wet deposition and the real concentration will be overestimated when these results are used (Galloway and Likens, 1978; Slanina and Asman, 1980; Söderlund, 1982; Ridder et al., 1984). The composition of the sample can also change during storage in the field and in the laboratory (Ridder et al., 1984, 1985). The magnitude of this change depends on the conditions and duration of storage. Buijsman and Erisman (1986) examined and corrected recent data for 210 stations in Europe. Not all the data are for 1980. As meteorological conditions are different in different years, it is not strictly correct to use data for other years than 1980. However, the exclusion of this data will lead to a larger uncertainty in the deposition pattern than would otherwise occur. The measurement sites are not evenly distributed over Europe. Their density is highest in N.W.-Europe. Buijsman et al. (1985B) found a background concentration in precipitation of about 5 µmole l^{-1}.

8. Results of the model calculations and discussion

Figures 2, 3 and 4 show computed concentrations in air and precipitation without any added background concentration. In the model the emissions are spread evenly over a grid element, even if no emission occurs in part of the grid element. Together with the geographical resolution of the statistical data used to calculate the emissions, this will

Figure 2. Computed NH_3 concentration in air (μg m^{-3}).

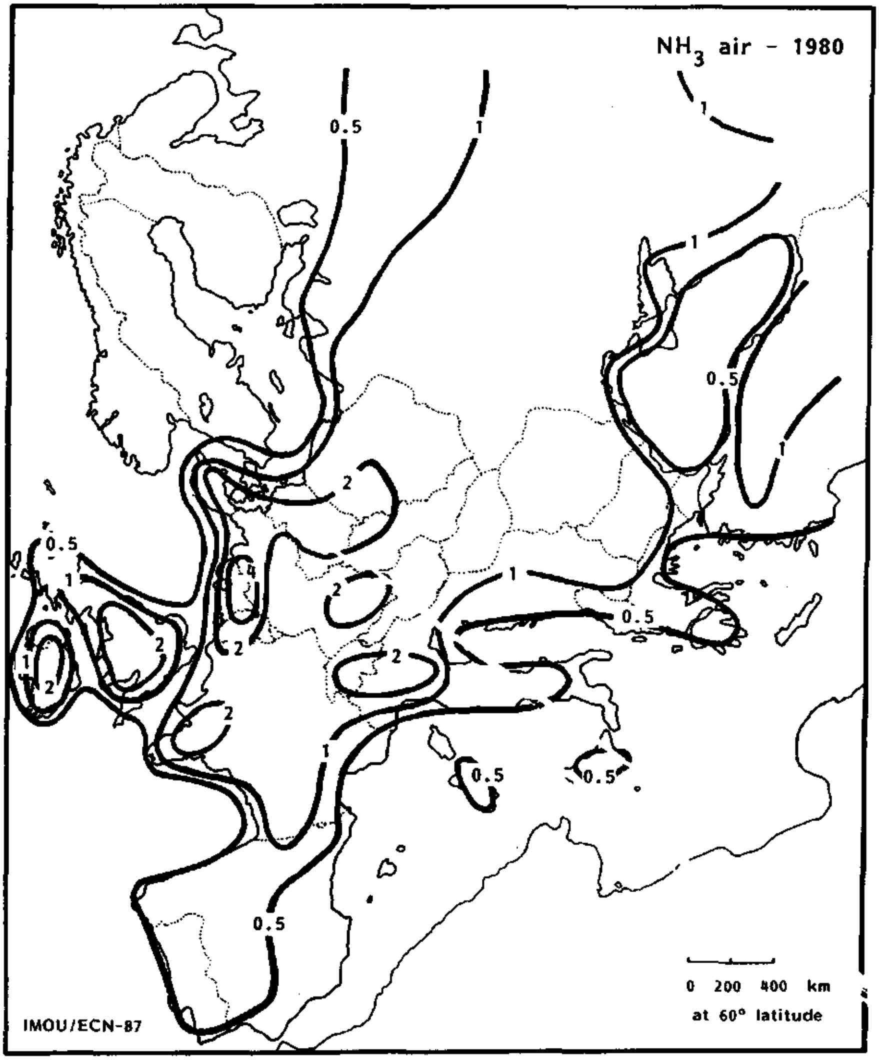


Figure 3. Computed NH_4^+ aerosol concentration ($\mu g\ m^{-3}$).

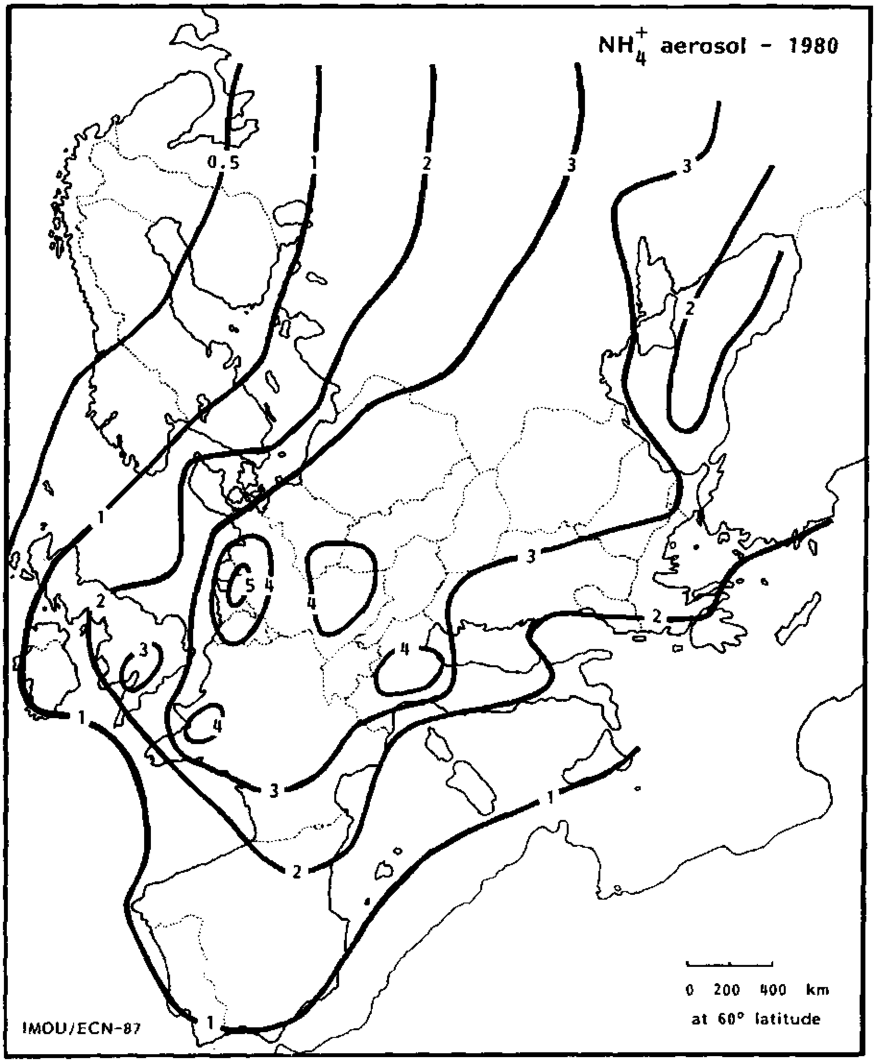
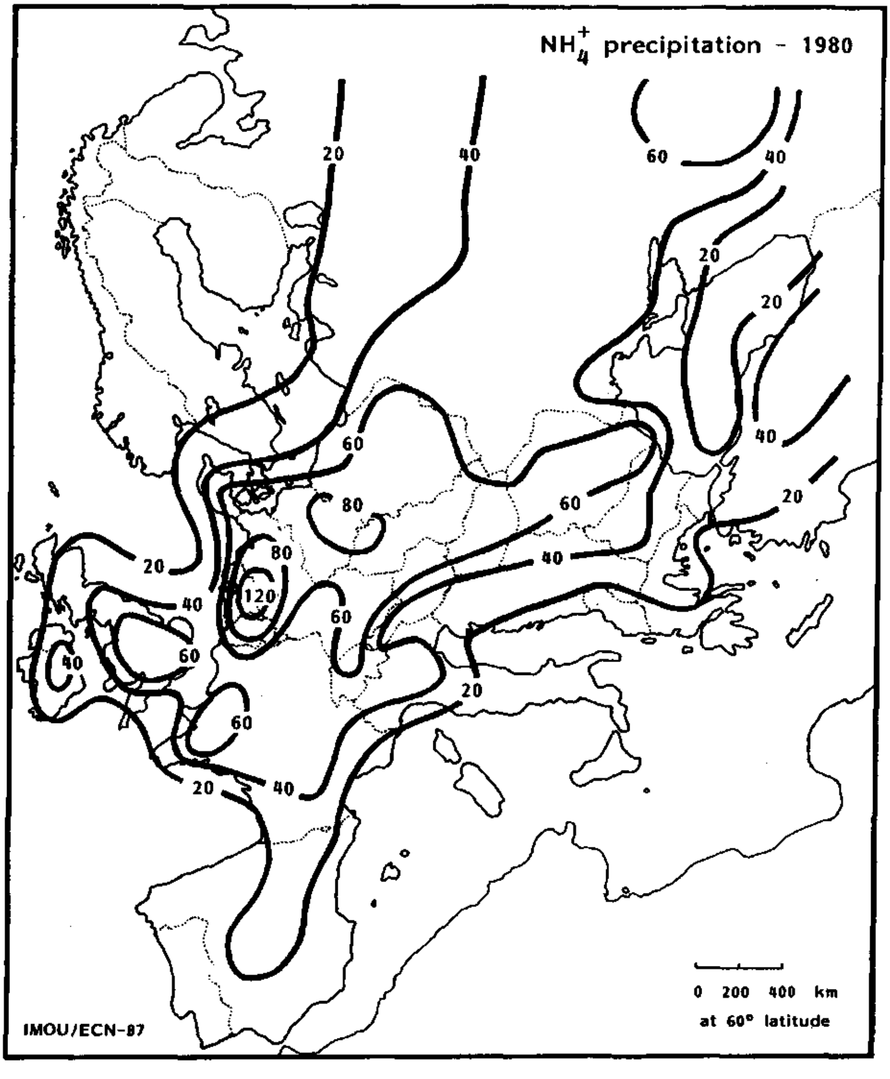


Figure 4. Computed NH_4^+ concentration in precipitation (μmole l^{-1}).



influence the concentration gradients computed with the model. Moreover, concentrations are only computed for the central point of each grid element. Figures 5 and 6 show the relations between computed and measured concentrations of NH_4^+ in air and precipitation for EMEP grid elements (no background concentrations added). For NH_4^+ in aerosols a significant correlation exists between computed and measured concentrations, although not many measurements are available ($r = 0.71$, $n = 16$). For NH_4^+ in precipitation the agreement between model results and measurements is good, the correlation coefficient for 90 EMEP-grid elements is 0.73, which is statistically significant.

Table 2 shows the country by country budget for total deposition of NH_x (=dry plus wet deposition of both NH_3 and NH_4^+) and country averaged concentrations in air and precipitation. The total deposition caused by a country is somewhat smaller than the emission of that country as not all emitted material is deposited within the receptor area. Country by country budgets for dry deposition of NH_3, dry deposition of NH_4^+ aerosol and wet deposition of NH_4^+ were also computed (see Asman and Janssen, 1986). From these results it appears that over 90% of the NH_3 dry deposition in a country is caused by emissions within the country itself. This arises for two reasons. Firstly NH_3 is emitted at ground level and has a relatively high dry deposition velocity. Secondly the conversion of NH_3 to NH_4^+ aerosol relatively rapid (compared to the conversion of SO_2 to SO_4^{2-} aerosol). (For the latter a pseudo first order reaction rate of 3.9×10^{-6} s^{-1} has been used by Asman et al., 1986). A substantial part (20-80%) of NH_4^+ in air and precipitation in most countries appears to come from foreign sources, which points to true long-range transport.

Figure 5. Computed vs. Measured NH_4^+ aerosol concentration (μg m^{-3}).

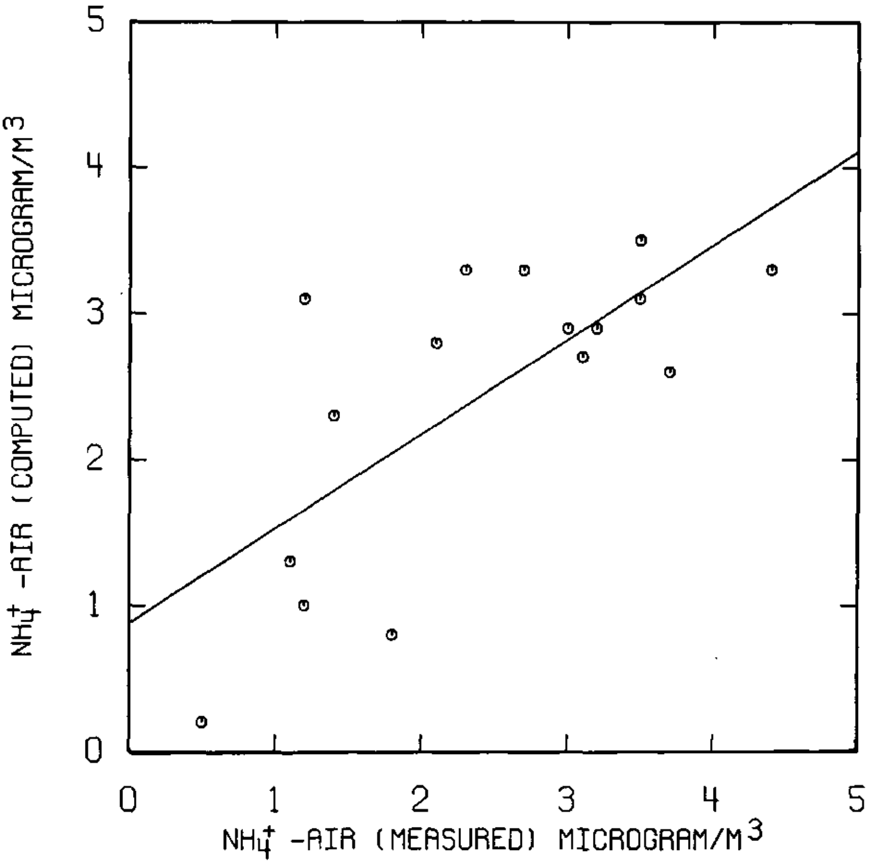


Table 2. Country by country budget total deposition of NH_x (NH_3 + NH_4^+) (10^6 mole $year^{-1}$)

emitter countries →

receiver countries →

	Alban	Austr	Belgi	Bulga	Czech	Denma	Finla	Franc	GermD	GermF	Greec	Hunga	Icela	Irela	Italy	Luxem	Nethe
Albania	557	4	1	8	5	0	0	12	2	5	57	8	0	0	124	0	0
Austria	1	2496	18	5	415	13	1	274	90	839	6	139	0	6	698	2	32
Belgium	0	2	1976	0	15	12	0	771	33	146	0	1	0	14	8	13	300
Bulgaria	48	28	7	4745	40	2	0	38	14	31	329	95	0	0	123	1	6
Czechoslovakia	1	399	43	16	5789	41	4	390	878	1094	8	504	0	10	232	4	74
Denmark	0	2	20	0	12	3113	1	62	112	248	0	3	0	15	6	1	69
Finland	0	6	10	10	27	49	1762	35	50	49	3	3	0	6	1	1	14
France	1	25	582	0	60	74	0	30322	146	630	0	9	0	151	360	43	261
German Dem. Rep.	0	27	110	1	197	133	4	455	6880	1467	0	22	0	18	54	8	235
German Fed. Rep.	0	186	860	4	272	265	4	2493	850	14319	1	27	0	60	274	75	2308
Greece	144	8	1	251	13	0	0	33	3	8	2687	24	0	0	207	0	1
Hungary	4	244	8	24	511	6	0	118	39	118	12	4084	0	2	375	1	12
Iceland	0	0	3	0	0	3	1	6	0	9	0	0	146	4	0	0	4
Ireland	0	0	6	0	0	10	0	118	3	9	0	0	0	3797	0	0	7
Italy	3	133	14	2	54	6	0	715	31	162	2	35	0	5	12991	1	14
Luxemburg	0	1	24	0	1	1	0	97	2	16	0	0	0	1	1	87	3
Netherlands	0	2	366	0	12	27	0	282	49	323	0	1	0	22	10	4	3649
Norway	0	7	27	1	47	243	20	113	107	140	0	11	1	25	28	1	68
Poland	2	151	88	29	1385	252	14	467	1923	907	11	231	0	18	164	6	223
Portugal	0	0	4	0	0	0	0	40	4	8	0	0	0	5	1	0	8
Romania	29	108	18	898	329	20	1	117	72	128	102	997	0	4	288	1	21
Spain	0	0	37	0	1	10	0	773	29	62	0	0	0	24	9	3	43
Sweden	0	22	34	9	64	609	107	125	224	301	0	32	0	28	37	1	113
Switzerland	0	42	17	0	20	8	1	696	24	267	0	2	0	5	405	2	18
Turkey	22	9	1	395	25	1	0	23	5	12	379	35	0	0	99	0	2
UK	0	1	113	0	9	74	3	796	63	190	0	1	1	778	18	4	204
USSR	46	304	96	729	1238	332	552	643	1002	969	213	860	0	45	553	6	260
Yugoslavia	176	369	18	225	266	9	0	214	72	187	182	895	0	5	1418	1	15
North Africa	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
North Sea	0	8	544	1	85	971	15	3211	328	1068	0	25	2	1464	94	14	1112
Atl. Ocean N.	0	4	42	0	11	90	17	314	58	146	0	0	37	636	14	2	86
Atl. Ocean S.	0	0	39	0	3	6	0	1201	35	75	0	0	0	68	4	1	64
Baltic Sea	1	21	73	16	102	1256	317	249	1017	955	6	43	0	36	37	5	254
Black Sea	19	25	4	711	72	3	2	52	15	36	191	98	0	0	105	1	4
Mediterranean	154	75	29	260	71	5	0	1742	62	141	1051	83	0	17	4080	2	33
Sum	1208	4711	5233	8339	11152	7644	2826	46998	14219	25063	5241	8269	189	7270	22817	292	9519
Emission in receptor domain	1443	5026	5552	8661	11761	7771	3000	49498	14252	25770	6587	8910	296	8162	25046	325	10008

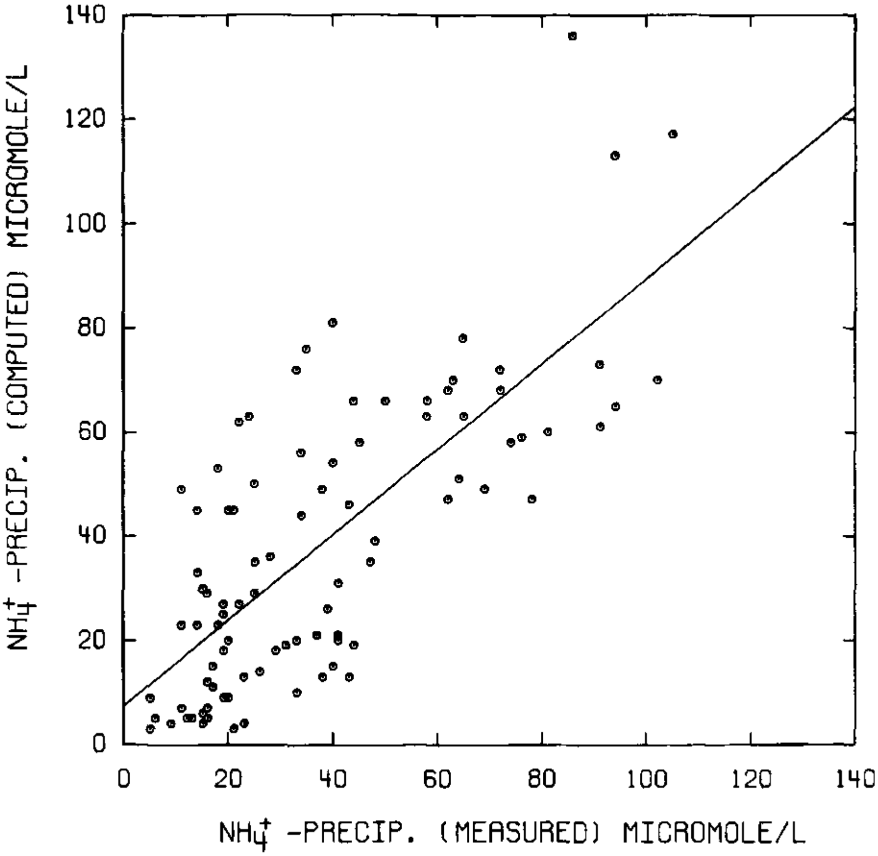
Table 2. continued

emitter countries →

receiver countries ↓

	Norwa	Polan	Portu	Roman	Spain	Swede	Switz	Turke	UK	USSR	Yugos	N.Afr.	Sum	average concentrations NH_3-air µg m^{-3}	NH_4^+-air µg m^{-3}	NH_4^+-precip. µmole l^{-1}
Albania	0	5	0	6	6	0	2	0	1	3	111	14	932	0.9	2.2	12
Austria	0	101	6	16	51	4	215	0	34	25	192	1	5679	1.2	3.3	45
Belgium	1	11	3	0	17	2	3	0	185	3	1	0	3515	3.5	4.4	77
Bulgaria	0	41	0	815	6	1	6	168	7	191	704	12	7458	1.5	3.2	44
Czechoslovakia	2	858	4	100	48	16	90	1	73	172	147	2	10999	1.8	3.6	71
Denmark	10	68	1	2	10	41	11	0	117	39	0	0	3964	3.2	2.9	52
Finland	40	103	0	20	1	94	1	4	27	999	3	0	3317	0.2	0.5	10
France	6	52	102	0	1201	12	205	0	1005	10	9	28	35297	1.7	3.4	45
German Dem. Rep.	7	361	5	10	42	32	39	0	150	98	7	2	10365	2.5	3.9	79
German Fed. Rep.	17	252	18	18	152	39	585	0	559	99	16	3	23755	2.0	3.9	70
Greece	0	19	1	63	9	0	4	50	4	44	280	50	3904	0.9	2.3	18
Hungary	0	127	1	381	16	2	22	0	11	57	538	4	6717	1.8	3.6	61
Iceland	1	0	0	0	0	1	0	0	21	2	0	0	202	0.1	0.1	2
Ireland	1	4	2	0	19	3	0	0	334	3	0	0	4317	2.1	1.4	28
Italy	0	52	15	10	171	2	241	0	42	12	115	140	14968	1.5	2.8	28
Luxemburg	0	1	0	0	2	0	1	0	6	0	0	0	244	2.2	3.8	56
Netherlands	2	23	3	2	17	3	3	0	266	7	0	0	5073	5.1	4.8	82
Norway	1245	140	0	12	9	114	10	0	269	187	0	0	2826	0.1	0.5	7
Poland	13	16518	8	180	70	75	50	4	176	1370	98	3	24436	1.7	3.3	67
Portugal	0	1	1297	0	238	0	0	0	12	0	0	1	1618	0.7	1.2	11
Romania	1	377	2	12245	25	7	17	72	27	1256	858	8	18027	1.6	3.6	60
Spain	2	7	392	0	8067	2	5	0	88	1	0	39	9592	0.6	1.6	16
Sweden	236	380	1	54	11	1946	13	2	189	688	8	0	5237	0.2	0.7	13
Switzerland	0	16	4	0	50	2	1854	0	34	3	1	2	3474	1.7	3.6	52
Turkey	0	19	0	214	7	0	3	14985	1	329	130	71	16768	1.1	2.7	30
UK	12	40	9	1	63	21	6	0	14111	44	0	0	16561	2.1	2.2	42
USSR	70	6133	16	3940	114	251	93	2403	268	150662	587	15	172400	1.0	2.2	36
Yugoslavia	0	155	4	249	45	4	43	3	28	77	8160	29	12848	1.0	2.8	31
North Africa	0	0	1	0	8	0	0	0	0	0	0	18	28			
North Sea	200	301	32	13	221	132	29	0	6770	263	1	0	16903			
Atl. Ocean N.	197	59	7	0	52	32	5	0	727	154	1	0	2691			
Atl. Ocean S.	2	36	217	0	780	1	5	0	179	11	0	8	2737			
Baltic Sea	63	1023	4	60	33	683	22	5	241	1582	16	0	8120			
Black Sea	0	65	1	1020	15	2	8	2979	3	3364	157	14	8965			
Mediterranean	0	67	66	127	1097	4	97	319	119	124	587	636	11049			
Sum	2130	27414	2224	19558	12671	3527	3686	20997	26083	161880	12728	1098	474987			
Emission in receptor domain	2416	28137	3223	20589	16029	3625	3680	27447	28126	174483	13828	63	513712			
Emission outside receptor domain								13664		98381		19317				

Figure 6. Computed vs. measured NH_4^+ concentration in precipitation (μmole l^{-1})



9. Numerical aspects of the transport model

9.1. Time interpolation

Equations (1) and (2) describing the ammonia transport model are mass-consistent. As a result the computation using one backward trajectory to one receptor point will be mass consistent. This does not necessarily mean that the results for Europe as a whole are mass-consistent, when many backward trajectories, arriving at receptor points at 6 hour intervals, are used. One reason is that the yearly integrated time a grid-element is crossed by trajectories is not the same for every grid element. As a result there may be differences between the actual amount of ammonia emitted and the emitted amount of ammonia used in the calculations. This effect can be avoided by using forward-trajectories with a point source in the centre of each grid element which releases a puff every 6 hours, representative of all emissions in that grid element. This has, however, the disadvantage that the concentration patterns computed with the model are sensitive to the assumed location of the point sources within the grid elements.

A second reason why the model might not be mass-consistent is that the depositions obtained every 6 hours at a receptor point have to be interpolated in time to compute the annual deposition. This is not likely to be a big problem during a dry period, as the dry deposition rate (amount deposited per unit time) is not likely to vary much over 6 hours. A linear interpolation would then give reasonable results. However, it can pose a major problem during wet periods as a large fraction of the airborne components can be removed within a few hours. In our model we use precipitation data with a time resolution of 6 hours. This means that a grid element is either wet or dry during a 6-hour period. As a consequence the period during which a moving air parcel is exposed to precipitation will usually be so long that no linear interpolation can be applied. Different ways of interpolation are shown in Figure 7. The physically most probable interpolation should lie in between the stepwise variation and the linear variation and is indicated by the dotted curve. In Table 3 the results of several model

Figure 7. Interpolation of 6-hourly concentration data.

Wet depositions are derived from the time-dependent product of concentration and precipitation rate.

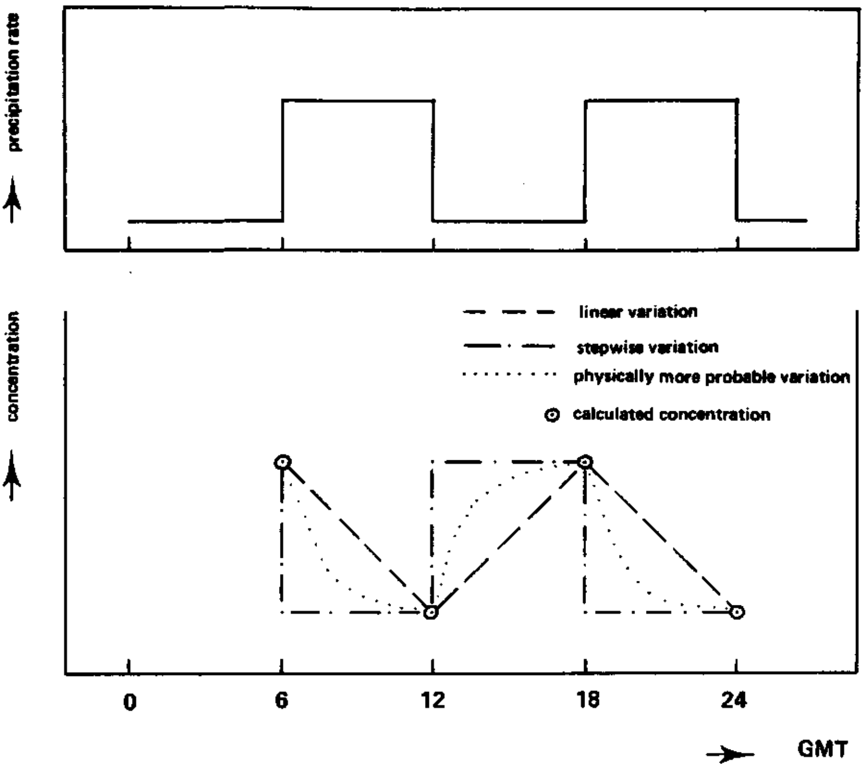


Table 3. Influence of various numerical approximations on the concentrations and depositions in the Netherlands.

No.	Version	Average concentrations NH_3 air $\mu g\ m^{-3}$	NH_4^+ air $\mu g\ m^{-3}$	NH_4^+ precip. $\mu mole\ l^{-1}$	Dry deposition $NH_3 + NH_4^+$ Ind. $10^8 mole\ y^{-1}$	Imp.	Exp.	Wet deposition $NH_3 + NH_4^+$ Ind. $10^8 mole\ y^{-1}$	Imp.	Exp.
1	Standard	5.1	4.8	82	27	2	9	10	12	50
2	As no.1, but direct dry deposition distributed homogeneously over grid cell	3.0	4.2	82	12	6	25	10	12	50
3	As no.1, but with linear time variation of concentrations	5.1	4.8	103	27	2	9	11	16	62
4	As no.1, but with step-wise time variation of concentrations	5.1	4.8	62	27	2	9	8	8	37
5	As no.1, but with backward trajectories to midpoints of IE cells	5.2	5.0	101	28	2	-	15	12	-
6	As no.5, but direct dry deposition distributed homogeneously over grid cell	4.4	4.8	101	22	4	-	15	12	-
7	As no.5, but with linear time variation of concentrations	5.2	5.0	123	28	2	-	17	15	-
8	As no.5, but with step-wise time variation of concentrations	5.2	5.0	78	28	2	-	13	8	-
9	As no.1, but with forward trajectories from midpoints of EMEP cells	-	-	-	27	-	8	10	-	51
10	As no.9, but direct dry deposition distributed homogeneously over grid cell	-	-	-	12	-	23	10	-	51

Ind.: depositions from indigenous sources
Imp.: depositions from foreign sources
Exp.: depositions outside source country

versions for the Netherlands are presented.In version 1 (standard) backward trajectories to midpoints of EMEP grid elements are used applying the physically most probable interpolation. In version 3 the linear interpolation is applied and in version 4 the stepwise interpolation is applied. In version 9 forward trajectories are used; emissions are assumed to take place in the midpoint of EMEP grid elements and the apparent direct local dry deposition is calculated as in the standard run. In version 9 there are no problems with interpolation in time, because for each puff integration of wet and dry depositions per grid element can be carried out without numerical approximations. The results of version 9 were used to find out which interpolation procedure should be adopted. It appeared that the average of the versions 3 and 4 gave about the same results as version 9. This average is used as the standard version (no. 1) (no forward trajectories were available for regions outside the Netherlands).

Table 3 shows that the method of interpolation has a great influence on results, especially the way in which NH_4^+ in wet deposition may be attributed to source regions. This is of major importance in policy decisions. If linear interpolation was applied, the total calculated deposition originating from any country was usually about 10% higher than the emission from the same country. This unrealistic phenomenon is absent when the standard version of the model is used. This also supports our adopted interpolation scheme.

The effect discussed above is different from the effect caused by space and time smoothing of precipitation data as discussed by Eliassen and Saltbones (1983).

9.2. Area integrated apparent direct local dry deposition

After the calculations have been performed for a one year period with equations (1) and (2), dry depositions for NH_3 (D_{1g}) and for NH_4^+ aerosol(D_{2g}) are obtained for the central point of each grid element. Then the apparent direct local dry depositions of NH_3 and NH_4^+ aerosol have to be added, being $\alpha_1.E_{yg}$ and $\alpha_2.E_{yg}$ respectively.

(E_{yg} is the emission density in the grid element in moles m^{-2} year^{-1}). In this way total dry depositions for each central point of a grid element are obtained (D_{1gt} and D_{2gt} respectively). To calculate the total dry deposition in a country two different methods can be followed, which will be illustrated for the dry deposition of NH_3:

a. The dry deposition is computed from the added values D_{1gt} for the central points of the grid elements that lie in this country. (If more than one country is situated in a grid element a fraction of the deposition should be added proportional to the area occupied by the country).

b. The dry deposition is computed from the added values D_{1g} for the central points of the grid elements that lie in this country. Then the apparent direct local dry deposition for the whole country is added: $\alpha_1.E_{yc}$, where E_{yc} is the emission of the whole country in moles year^{-1}.

By applying method (a) the apparent direct local dry deposition is spread out evenly over the whole grid element, whereas by applying method (b) the apparent direct local dry deposition is assumed to take place directly at the source. From Figure 8 it can be seen that the enhanced dry deposition of NH_3 in reality occurs relatively close to the source. Computations show that 65% of it takes place within 5 km distance from the source and 90% within 30 km (Janssen and Asman, 1986). Method (b) is therefore better and is used to calculate the dry deposition in a country.

The concentration maps (Figures 2 and 3) can only be calculated by using method (a), while the average concentration for a country is obtained by applying method (b). This may lead to an apparent discrepancy when comparing average concentrations for a country (Table 2) and the concentrations estimated from the maps. The discrepancy between the two methods will be most apparent for a country when:

- the relative contribution of the apparent direct local dry deposition is large.
- there are large emission variations across its frontiers, e.g. in coastal areas.
- it is a small country (large ratio of circumference and area).

The Netherlands is an extreme example, which is demonstrated in Table 4. (Compare also versions 1 and 2 in Table 3).

9.3. Spatial resolution

To investigate the influence of the density of the receptor points a version of the model was made for the Netherlands with receptor points in each centre of an IE grid element (4 IE grid elements form one EMEP grid element). The results are presented in Table 3 (version 5). A better preservation of concentration gradients is obtained, which - for the Netherlands with its extremely high emissions - results in higher calculated average concentrations and depositions, because all central points of EMEP grid elements covering the Netherlands happen to lie near its frontiers. The two different ways to account for the apparent direct local dry deposition discussed in section 9.2 now give results which are closer to each other (compare versions 5 and 6 in Table 3 with versions 1 and 2). The reason is that in version 6 this deposition is spread evenly over a four times smaller area (75 x 75 km^2) than in version 2, which - according to Figure 8 - is closer to reality. The effect of different time integrations on concentrations in precipitation remains the same (see versions 5, 7 and 8).

10. Sensitivity analysis

To investigate the influence of uncertainties in the parameters used in the model a sensitivity study was made. This could be done by simply changing the value of one of the parameters and running the model again. The values of α_1, α_2, β and v_{1e}, however, are not independent,
but are chosen by reference to numerical reactive diffusion model in which the independent variables are H, k, v_1, v_2, K_z (eddy diffusivity) and u_t (transport velocity). In fact v_1 and v_2 will be a function of K_z, but this could not be taken into account. Therefore, it was decided to change the independent variables and then to use the derived values of the computed dependent variables in the model. Table 5 shows the

Table 4. Effect of different ways of accounting for the apparent direct local dry deposition.

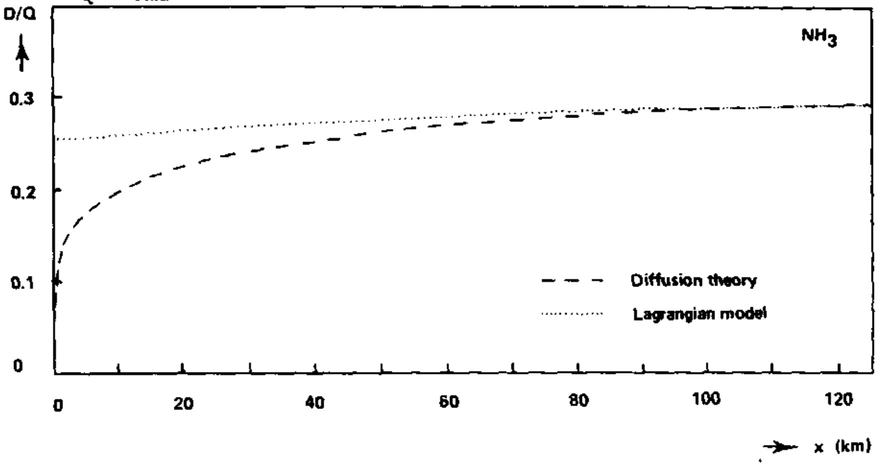
Country	Apparent direct local dry deposition at source location					Apparent direct local dry deposition distributed homogeneously over grid cell				
	Air conc. NH_3 µg m^{-3}	Air conc. NH_4^+ µg m^{-3}	Dry depositions Ind. 10^8 mole y^{-1}	Dry depositions Imp. 10^8 mole y^{-1}	Dry depositions Exp. 10^8 mole y^{-1}	Air conc. NH_3 µg m^{-3}	Air conc. NH_4^+ µg m^{-3}	Dry depositions Ind. 10^8 mole y^{-1}	Dry depositions Imp. 10^8 mole y^{-1}	Dry depositions Exp. 10^8 mole y^{-1}
Albania	0.9	2.2	4	1	2	0.6	2.1	2	2	3
Austria	1.2	3.3	14	5	4	1.4	3.4	11	11	8
Belgium	3.5	4.4	15	2	5	2.9	4.2	6	9	13
Bulgaria	1.5	3.2	26	5	7	1.5	3.2	20	10	13
Czechoslovakia	1.8	3.6	34	7	9	1.9	3.6	25	19	18
Denmark	3.2	2.9	21	1	7	1.8	2.5	12	2	17
Finland	0.2	0.5	9	2	2	0.1	0.5	7	3	4
France	1.7	3.4	158	11	30	1.5	3.3	137	18	53
GDR	2.5	3.9	41	5	11	2.1	3.8	30	10	23
GFR	2.0	3.9	76	14	17	2.1	4.0	62	34	32
Greece	0.9	2.3	19	4	6	0.7	2.2	12	6	13
Hungary	1.8	3.6	26	5	8	1.6	3.6	18	10	15
Iceland	0.1	0.1	1	0	0	0.0	0.1	1	0	0
Ireland	2.1	1.4	23	1	4	1.6	1.3	16	2	11
Italy	1.5	2.8	78	5	21	1.1	2.7	58	6	39
Luxemburg	2.2	3.8	1	0	0	1.8	3.7	0	1	1
Netherlands	5.1	4.8	27	2	9	3.0	4.2	12	6	25
Norway	0.1	0.5	7	2	2	0.1	0.5	5	2	4
Poland	1.7	3.3	86	11	16	1.7	3.3	75	20	26
Portugal	0.7	1.2	10	1	3	0.6	1.2	7	3	5
Romania	1.6	3.6	63	10	12	1.6	3.6	53	18	22
Spain	0.6	1.6	53	5	10	0.5	1.6	46	7	18
Sweden	0.2	0.7	11	4	3	0.1	0.7	8	6	6
Switzerland	1.7	3.6	11	2	3	1.8	3.7	8	6	6
Turkey	1.1	2.7	95	6	11	1.0	2.7	87	7	19
UK	2.1	2.2	81	3	19	1.6	2.0	61	5	41
USSR	1.0	2.2	599	24	24	0.9	2.2	578	34	40
Yugoslavia	1.0	2.8	43	9	10	1.0	2.8	37	16	15
North Africa			0	0	2			0	0	2
Sea areas			0	108	0			0	225	0
Sum			1633	258	258			1393	494	494

Ind.: depositions from indigenous sources
Imp.: depositions from foreign sources
Exp.: depositions outside source country

Figure 8. Dry deposition of NH_3 integrated up to distance x from the source. Wind-speed at 10 m height: 4 m s^{-1}. Calculations with a numerical reactive diffusion model gave an apparent direct local deposition of $\alpha_1 = 0.26$. The Lagrangian model would produce the dotted line if this enhanced dry deposition is assumed to take place at the source.

D = integrated dry deposition rate.

Q = emission rate.



calculated parameter values used in the sensitivity study. The sensitivity study was done for a receptor point in an area with a high emission density in S.E. Netherlands (Table 6; 51.8°N, 5.6°E) and for a receptor point in an area with a low emission density (Table 7; Central Sweden; 58.6°N, 14.8°E). In version 2 the mixing height was multiplied by a factor ½. In version 2a both the scavenging ratios and the mixing height were multiplied by a factor ½. Version 2a seems to be physically more reasonable for evaluating the variation of the mixing height, as the wet removal rate remains the same as in the standard version.

Table 7 shows that the computed origin of NH_4^+ in precipitation over Central Sweden can be rather sensitive to the turning of the trajectories (compare version 13 with the standard version). This may be caused by the existence of a strongly prevailing wind-direction associated with precipitation periods. The sensitivity analysis indicates further that a wide range of possible parameter values would give acceptable agreement with measured concentrations.

11. Concluding remarks

Although the model calculations give satisfactory results this does not mean that our present knowledge of the atmospheric behaviour of ammonia and ammonium is sufficient. Parameter values in a model are chosen either using empirical evidence or physical reasoning independent of the model or by adjusting parameters to give the best agreement with measured concentrations. A wide range of possible parameter values would give acceptable agreement with measured concentrations. Long-range transport modelling of ammonia and ammonium requires not only an adequate description of processes on a large scale, but it also requires an adequate description of the processes on a local scale as they determine the fraction of NH_x which can be transported over longer distances. Further research should be undertaken in the following areas:

- the emission of NH_3. The importance of organic nitrogen compounds to the emission of NH_3 should be determined. In addition the emission

Table 5. Calculated parameters used in the sensitivity study.

No.	Version	α_1	α_2	β	v_{1e}(m s^{-1})
1	Standard[1)]	0.240	0.0086	0.092	5.6×10^{-3}
2	H * ½	0.196	0.0026	0.039	6.6×10^{-3}
3	k * ½	0.259	0.0053	0.052	5.8×10^{-3}
4	v_1 * ½	0.138	0.0107	0.090	3.2×10^{-3}
5	v_2 * ½	0.240	0.0044	0.092	5.6×10^{-3}
8	K_z * ½	0.351	0.0187	0.145	4.3×10^{-3}
14	u_t * 1/0.85	0.217	0.0071	0.081	5.9×10^{-3}

1) Standard parameter values have also been used in versions no. 6, 7 and 9 to 13 of Tables 6 and 7.

Table 6. Sensitivity study for receptor point in SE-Netherlands[1]

No.	Version	Air conc. $\mu g\ m^{-3}$		Precip. conc. NH_4^+ $\mu mole\ l^{-1}$	Dry deposition of $NH_3 + NH_4^+$ $10\ mole\ ha^{-1}\ y^{-1}$		Wet depositions NH_3 $10\ mole\ ha^{-1}\ y^{-1}$		Wet depositions NH_4^+ $10\ mole\ ha^{-1}\ y^{-1}$						
		NH_3	NH_4^+		Imp.	Total	Imp.	Total	B	F	FRG	NL	UK	Others	Total
1	Standard	7.2	6.0	142	10	117	7	46	9	8	6	23	6	7	58
2	$H * \frac{1}{2}$	7.1	7.0	188	14	118	9	75	10	8	6	27	5	7	63
2a	$(H, S_1, S_2) * \frac{1}{2}$	7.2	7.8	140	16	121	7	50	8	7	5	20	5	6	52
3	$k * \frac{1}{2}$	8.1	4.5	136	10	128	11	57	6	6	4	14	5	6	42
4	$v_1 * \frac{1}{2}$	8.4	7.1	164	9	75	8	54	10	9	6	25	7	8	66
5	$v_2 * \frac{1}{2}$	7.2	6.3	145	8	112	7	46	9	8	6	23	6	8	61
6	$S_1 * \frac{1}{2}$	7.2	6.1	125	10	118	5	29	10	8	6	25	6	7	63
7	$S_2 * \frac{1}{2}$	7.2	6.5	120	11	118	7	46	6	7	4	14	5	5	42
8	$K_z * \frac{1}{2}$	9.8	7.8	121	10	159	5	35	8	7	5	23	5	6	54
9	$I * \frac{1}{2}$	7.2	6.4	231	11	118	6	34	8	7	5	18	6	6	50
10	Tr=3 days[2]	7.2	5.9	141	10	117	7	46	9	8	6	23	6	6	57
11	Tr=2 days	7.2	5.5	137	9	116	7	46	9	7	5	23	6	5	54
12	Tr=1 day	7.2	4.7	126	8	115	7	46	9	5	4	22	5	2	47
13	$\Delta\phi = 15°$[3]	7.2	5.8	134	9	116	5	45	7	5	5	24	7	5	53
14	$u_t * 1/0.85$[4]	6.6	5.3	138	10	107	8	46	8	8	5	20	6	8	55

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1) Imp. = Import; B = Belgium; F = France; FRG = Federal Rep. Germany; NL = The Netherlands; UK = United Kingdom.

2) Length of trajectories reduced to 3 days.

3) Transport wind direction veered by 15° to 850 hPa value.

4) Transport wind velocity increased to 850 hPa value.

Table 7. Sensitivity study for receptor point in Central Sweden1).

No.	Version	Air conc. $\mu g\ m^{-3}$		Precip. conc. NH_4^+ $\mu mole\ l^{-1}$	Dry deposition of $NH_3 + NH_4^+$ mole $ha^{-1}\ y^{-1}$		Wet depositions									
							NH_3 mole $ha^{-1}\ y^{-1}$	NH_4^+ mole $ha^{-1}\ y^{-1}$								
		NH_3	NH_4^+		Imp.	Total	Total	DK	F	GDR	FRG	PL	S	USSR	Others	Total
1	Standard	0.32	1.1	21	14	67	24	19	11	10	12	13	31	10	26	133
2	$H * \frac{1}{2}$	0.34	1.4	20	18	75	36	18	7	6	6	14	34	7	20	112
2a	$(H,S_1,S_2)*\frac{1}{2}$	0.35	1.7	19	22	81	26	17	8	8	10	11	29	8	21	112
3	$k * \frac{1}{2}$	0.38	0.9	20	14	73	34	17	10	9	11	12	21	10	23	112
4	$v_1 * \frac{1}{2}$	0.38	1.3	25	16	51	28	22	13	12	14	15	35	12	30	154
5	$v_2 * \frac{1}{2}$	0.32	1.2	23	8	59	24	20	13	11	13	14	32	12	28	143
6	$S_1 * \frac{1}{2}$	0.33	1.1	21	14	68	17	20	12	10	13	14	35	11	26	140
7	$S_2 * \frac{1}{2}$	0.32	1.3	21	17	71	24	19	11	11	16	10	24	11	25	128
8	$K_z * \frac{1}{2}$	0.43	1.1	18	12	83	18	17	10	8	11	11	28	9	22	116
9	$I * \frac{1}{2}$	0.33	1.2	42	16	70	19	20	11	11	16	11	28	11	27	135
10	Tr=3 days2)	0.32	0.9	20	11	64	24	19	6	10	11	12	31	9	24	121
11	Tr=2 days	0.32	0.7	17	7	60	24	19	3	6	8	11	31	5	17	99
12	Tr=1 day	0.32	0.4	11	2	55	24	13	0	2	3	7	29	1	3	58
13	$\Delta\phi=15^\circ$3)	0.32	1.0	16	12	65	24	17	0	4	6	12	30	9	17	96
14	$u_t*1/0.85$4)	0.30	1.2	21	16	65	25	18	8	11	11	15	29	12	26	130

1) Imp. = import; DK = Denmark; F = France; GDR = German Democratic Rep.; FRG = Federal Rep. Germany; PL = Poland; S = Sweden.

2) Length of trajectories reduced to 3 days.

3) Transport wind direction veered by 15° to 850 hPa value.

4) Transport wind velocity increased to 850 hPa value.

rate as a function of time should be determined over longer periods, especially for meadows.

- the dry deposition velocity of NH_3. This should be determined for different surfaces and circumstances (including during the night) to obtain a more realistic overall dry deposition velocity for NH_3. In this respect the uptake of NH_3 by representative plants should be studied to determine the value of the compensation point. The mutual influence of emission and dry deposition of NH_3 may require a more sophisticated modelling of the dry deposition process.
- the apparent reaction rate for the conversion of NH_3 to NH_4^+ aerosol as a function of height. It should be determined at sites with different chemical and climatological regimes and for different seasons.
- the influence of the patchy nature of precipitation on the wet removal rates to be used in a model.
- the dependence of dry deposition velocities on the resistance of the atmosphere needs to be better defined (via K_z and the atmospheric stability).

Moreover, one should realize that the quality of the measurements used to check the model is often poor. For NH_3 and NH_4^+ aerosol, measurements should be undertaken at more stations in such a way that the results can be used to verify model results. For NH_3 this means that one should be able to relate the concentration with the local emission.

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CHAPTER 6.

Estimated historical concentrations and depositions of ammonia and ammonium in Europe (1870-1980)

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Abstract

Ammonia emissions in Europe have increased by at least a factor 2.3 since 1870. The deposition of ammonia and ammonium in Europe has also increased considerably over this period, but the relative increase in deposition varies regionally.

1. Introduction

Ammonia and ammonium are important atmospheric components and are involved in the acid rain problem. When ammonia and ammonium are deposited and enter the soil as ammonium, nitrification can occur which results in the formation of acid. Ammonia can also influence the uptake of SO_2 by droplets and in this way influence the removal of SO_2 from the atmosphere. Moreover, nitrogen can be a limiting factor for growth in oligotrophic ecosystems. After deposition ammonia and ammonium may be taken up by the needles of trees. This results often in the excretion of potassium and/or magnesium by the needles which may lead to potassium and/or magnesium deficiencies followed by premature shedding of needles (Roelofs et al., 1985).

In the past these adverse effects were not found or not noticed. It would therefore be interesting to know the historical ammonia and ammonium concentrations and depositions. The purpose of this study is to estimate these historical concentrations and depositions.

The main source of ammonia is the decomposition of animal manure (Buijsman et al., 1987). After World War II application and production of fertilizers give a minor contribution to the emission of ammonia. Fortunately, historical data of livestock statistics are available from which emissions can be computed (Buijsman, 1986). As a first approximation one could state that the concentrations/ depositions in a country will show the same trend as the emission of that country. For the ammonia concentration this can be a very acceptable approach as the ammonia concentration is mainly determined by local sources, i.e. by sources within the country itself (Asman and Janssen, 1987). Model results show, however, that for many countries the contribution of foreign sources to the concentration of ammonium in air and precipitation is dominating. This means that for those countries such an approach may be unacceptable, at least if the trend in the emission of the neighbouring countries is not the same as for the country itself. The best approach would be to compute the trend in concentrations and depositions with a model by using very detailed geographical information on the historical emission of ammonia. For many countries such very detailed information is not available for before World War II. Moreover, converting the emission data from historical geographical units (municipalities, provinces) to grid-elements, as was done for 1980 (Buijsman et al., 1987), would be very time-consuming. It was therefore decided to use only historical emission data for a country as a whole to estimate historical concentrations and depositions. This had the disadvantage that it is then implicitly assumed that the trend in the emission is the same for different regions within a country, which is not necessarily true. Source-receptor matrixes derived from previous model calculations for 1980 (Asman and Janssen, 1987) were used to compute the historical concentrations/depositions, using historical emissions for areas which correspond to countries with boundaries as they were in the year 1980.

By using these previous model calculations it is also implicitly assumed that the historical meteorological circumstances are the same as in 1980. This has the advantage that trends become more clear. Moreover, it is assumed that other model parameters in the past have the same values as in 1980. This is of course not true. E.g., the (overall) dry deposition velocities for NH_3 and NH_4^+ could be different from those in 1980 as the vegetation type could be different from that in 1980. Also the pseudo-first order reaction rate constant for the reaction of ammonia to ammonium could be different, especially if not enough acid would be available to neutralize the ammonia. The data of Fjeld (1976) and Buijsman (1986) show that the emissions of anthropogenic SO_2 and NH_3 in 1900 were 33% respectively 61% of those in 1980. The NO_x emission is likely to show the same trend as that of SO_2. In 1980 1.3×10^{12} eq. SO_2, 3.1×10^{11} eq. NO_x and 3.1×10^{11} eq. NH_3 were emitted in Europe (Iceland, USSR and Turkey excluded; Asman and Janssen, 1987). This means that in 1900 the amount of potential anthropogenic acid emitted was still larger than the amount that could be potentially neutralized by NH_3. This was also presumably the case in 1870, but it cannot be excluded that earlier in history more NH_3 was emitted in Europe than could be neutralized by potential anthropogenic acid. Apart from anthropogenic emissions, emissions of sulphur dioxide and nitrogen oxides emitted from natural sources exist which are rather uncertain. It seems therefore reasonable to apply the same pseudo-first order reaction constant for the whole period 1870-1980.

In view of all uncertainties both in the parameters and in the emissions it was felt not worth while to run the model with parameter values different from those given by Asman and Janssen (1987) for 1980. Concentrations and depositions were computed for around the years 1870, 1920, 1950 and 1980 by using previously calculated source-receptor relationships.

2. Emissions

Buijsman et al. (1987) computed the ammonia emission in Europe by using livestock statistics and emission factors for different categories of animals. If available they used information on livestock statistics with regard to age and/or weight, on the local nitrogen content in manure and urine and on the housing period of cattle. The latter information was only available for some countries for 1980 and it would be difficult to obtain this information for the past. Moreover, if this information were available for some years for a country and one would use more general information to compute the emission for the other years because of lack of detailed information, this could result in an unrealistic estimate of the trend in the emission. The emission factors are also likely to be a function of time, as e.g. the average weight of cattle was presumably somewhat lower in the past, the nitrogen content of animal fodder was lower and the way the manure was stored could be different. It is therefore likely that the emission factors were somewhat lower in the past than they are today. In view of all these uncertainties it was decided to use the same emission factor for all countries for all years, implicitly assuming a certain constant age distribution for each animal category for all countries. To get a good estimate of the trend in the concentrations/depositions these same emission factors were used for the year 1980, although the estimates of Buijsman et al. (1987) for 1980 are of a better quality. The emission factors used are from Buijsman (1986) and are shown in Table 1.

Table 1. Ammonia emission factors for domestic animals (kg NH_3 y^{-1} $animal^{-1}$)*

animal type	ammonia emission
horses	9.43
cattle	18.2
pigs	2.83
sheep	3.08
goats	3.08
asses	3.08
poultry	0.26

* Average values based upon age or weight distribution within an animal category for 1980 (Buijsman et al., 1986).

Not for all reference years (1870, 1920, 1950, 1980) information was available on the animal statistics for all countries. The number of animals was then estimated by interpolation or extrapolation. To be able to use previous model calculations it was necessary to have estimates of the emission for areas which correspond to countries with boundaries as they were in the year 1980. This was relatively easy for the year 1950, as the boundaries in Europe have not changed since World War II. But many countries had different boundaries in the past or did not even exist. The emissions for those areas for 1870 and 1920 had to be computed. If available, geographically detailed statistics were used for this purpose. Otherwise the emission was estimated using trends in neighbouring countries. In the Appendix detailed information is given on the way the historical emissions were computed. In Tables 2 to 4 the livestock numbers are given for around 1870, 1920 and 1950 respectively. The livestock numbers for 1980 can be found in Buijsman et al. (1987).

The emission of ammonia from fertilizers and fertilizer production was taken from Buijsman (1986), who adopted a constant emission factor of 50 kg NH_3 ton^{-1} N in fertilizer due to the application and 5 kg NH_3 ton^{-1} N in fertilizer caused by production. The production and consumption of nitrogeneous fertilizers for 1950 is given in Table 5. The data for 1980 can be found in Buijsman et al. (1987). The emission of ammonia from fertilizers and fertilizer production was computed only for 1950 and 1980 as it was unimportant before World War II. The emission of ammonia from coal combustion was not taken into account as data before 1920 were lacking and the emission factors are rather uncertain.

The ammonia emission caused by animal manure, application of fertilizers and production of fertilizers for 1870-1980 are shown in Figure 1 and are partly adopted from Buijsman (1986). To take account of other ammonia sources the emission used in the calculations was taken 20% higher than the data presented in Figure 1. Furthermore, ammonia emissions of Morocco, Algeria, Tunesia and Libya were estimated and used in the calculations to get realistic concentrations/depositions in southern Europe. The model area includes only the western part of the USSR. The historical trend in the emission in this part was estimated from livestock statistics of the Ukraine, White-Russia, Lithuania, Moldavia, Latvia and Estonia.

Table 2. Total number of animal around 1870 for "countries" with 1980 boundaries (1000 heads)

"country"	horses	cattle	pigs	sheep	goats	asses	poultry	camels	reindeer
Albania	63	326	12	2310	1647	33	1160	0	0
Austria	18[illegible]	1995	877	465	170	0	2976	0	0
Belgium	27[illegible]	1383	646	365	197	0	4461	0	0
Bulgaria	[illegible]	1970	497	7426	1643	148	4755	0	0
Czechoslovakia	[illegible]131	3535	1508	6842	261	13	20552	0	0
Denmark	338	1379	500	1976	147	0	5732	0	0
Finland	269	1029	149	886	15	0	401	0	130
France	2935	13463	7556	23904	1931	745	48932	0	0
G.D.R.	518	2426	1229	8395	612	2	8759	0	0
G.F.R.	989	8229	3002	10017	1262	8	21864	0	0
Greece	297	961	237	5895	4506	249	2868	0	0
Hungary	703	1333	1559	2597	8	12	4277	0	0
Iceland	30	19	0	366	0	0	70	0	0
Ireland	426	3234	1268	3694	0	0	8047	0	0
Italy	461	3797	3896	8927	2291	937	13348	0	0
Luxemburg	20	89	119	16	4	0	328	0	0
Netherlands	252	1411	329	900	137	0	4564	0	0
Norway	152	1017	101	1686	323	0	808	0	97
Poland	1487	5610	2409	11330	0	0	20022	0	0
Portugal	80	520	777	2707	937	189	1284	0	0
Romania	752	3333	1299	6814	357	1	11640	0	0
Spain	310	1460	1162	13773	2650	995	4744	0	0
Sweden	428	1966	354	1595	124	0	1414	0	0
Switzerland	101	1036	335	368	396	0	3183	0	0
Turkey	661	6969	0	18334	17397	719	30283	69	0
United Kingdom	1374	5969	2364	29041	0	0	22372	0	0
Yugoslavia	1453	3838	3406	13461	2906	123	21745	0	0

Table 3. Total number of animals around 1920 for "countries" with 1980 boundaries (1000 heads)

"country"	horses	cattle	pigs	sheep	goats	asses	poultry	camels	reindeer
Albania	47	365	12	1228	893	53	730	0	0
Austria	283	2165	1473	597	382	1	5609	0	0
Belgium	243	1603	1176	186	158	2	14086	0	0
Bulgaria	467	2384	1118	9462	1357	184	10118	0	0
Czechoslovakia	702	4487	2470	744	1225	1	17108	0	0
Denmark	562	2523	2855	374	9	0	20029	0	0
Finland	400	1865	382	1550	0	0	1151	0	61
France	2848	13749	5406	9925	1353	294	88708	0	0
G.D.R.	829	3105	3103	2130	1035	15	16174	0	0
G.F.R.	1602	10646	7233	2222	2008	10	37007	0	0
Greece	194	671	334	5643	3674	355	5956	0	0
Hungary	815	1819	2133	1587	45	7	21931	0	0
Iceland	50	26	0	550	5	0	22	0	0
Ireland	487	4278	1286	2666	116	158	17278	0	0
Italy	982	6755	2644	11947	3077	1435	48913	0	0
Luxemburg	18	107	213	8	3	0	531	0	0
Netherlands	364	2063	1519	668	131	0	9661	0	0
Norway	193	1131	237	1525	249	0	2638	0	0
Poland	2872	9063	6284	2429	1190	24	36436	0	0
Portugal	80	768	1117	3684	1557	325	7326	0	0
Romania	1198	3885	2176	10295	454	7	36986	0	0
Spain	626	3435	4728	18550	3804	2132	25940	0	0
Sweden	620	2899	1387	708	41	0	9504	0	0
Switzerland	134	1425	640	245	330	4	3247	0	0
Turkey	486	7801	0	9745	9435	1140	19050	0	0
United Kingdom	1607	7765	2994	21085	35	7	55903	0	0
Yugoslavia	1070	4296	3456	7155	1576	195	14382	0	0

Table 4. Total number of animals around 1950 (1000 heads)

country	horses	cattle	pigs	sheep	goats	asses	poultry	camels	reindeer
Albania	51	434	47	1707	830	67	660	0	0
Austria	283	2281	2523	362	323	2	6972	0	0
Belgium	227	2020	1234	116	73	2	17778	0	0
Bulgaria	473	1625	1058	7569	952	214	11592	0	0
Czechoslovakia	605	4303	3802	596	982	0	18206	0	0
Denmark	502	3053	3235	59	4	0	24548	0	0
Finland	409	1782	446	1220	2	0	3524	0	87
France	2397	15801	6824	7511	1297	195	85000	0	0
G.D.R.	723	3615	5705	1085	1628	1	22726	0	0
G.F.R.	1570	11149	11890	1643	1347	4	51801	0	0
Greece	279	815	582	6905	3710	621	9050	0	0
Hungary	712	2222	5542	1049	115	0	28782	0	0
Iceland	42	45	1	416	0	0	98	0	0
Ireland	391	4322	645	2385	48	106	21132	0	0
Italy	799	8354	4058	10295	2495	1169	68570	0	0
Luxemburg	15	119	96	4	1	0	493	0	0
Netherlands	256	2726	1864	390	76	0	23465	0	0
Norway	191	1237	422	1812	131	0	3912	0	0
Poland	2800	7200	9350	2199	595	0	46240	0	0
Portugal	75	895	1398	2901	706	309	9622	0	0
Romania	971	4309	2211	9834	542	0	17507	0	0
Spain	642	3112	2688	16344	4135	1821	23819	0	0
Sweden	440	2648	1263	279	15	0	12241	0	0
Switzerland	134	1530	908	170	180	2	6300	0	0
Turkey	1109	10909	7	23992	17724	1775	19142	177	0
United Kingdom	549	10620	2986	20431	37	0	96109	0	0
Yugoslavia	1097	5248	4295	10046	1098	184	20207	0	0

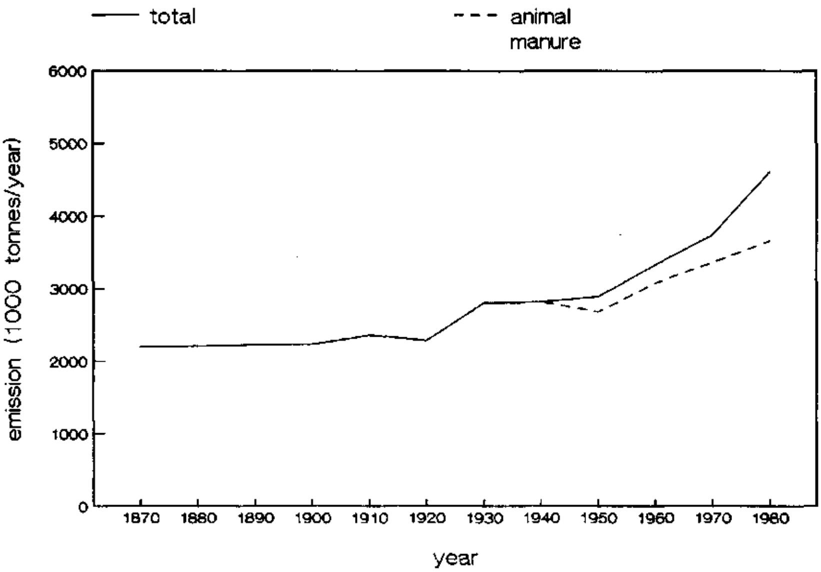
Table 5. Production and consumption of nitrogeneous fertilizers around 1950 (10^3 tonnes N year)*

country	production	consumption
Albania	0	0
Austria	75	23
Belgium	173	78
Bulgaria	0	0
Czechoslovakia	30	40
Denmark	0	70
Finland	0	17
France	259	262
G.D.R.	205	184
G.F.R.	465	362
Greece	0	22
Hungary	4	1
Iceland	0	0+
Ireland	0	8
Italy	177	157
Netherlands	189	166
Norway	161	31
Poland	65	75
Portugal	0	32
Romania	0	0
Spain	6	57
Sweden	25	68
Switzerland	14	9
Turkey	0+	0+
United Kingdom	275	219
Yugoslavia	4	6
total	2127	1887

* Buijsman (1986)

\+ No information available

Fig. 1. Ammonia emission in Europe from animal manure, application and production of fertilizers (excl. Turkey and the U.S.S.R.).



3. Results and discussion

The results of the computations are shown in Tables 6 and 7 and Figures 2 to 5. NH_x in the figures means the sum of NH_3 and NH_4^+. No "background concentrations or depositions" are added. Asman and Janssen (1987) estimated for around 1980 background concentrations for NH_3 in air and NH_4^+ aerosol of 0.1 - 0.2 µg m^{-3} and for NH_4^+ in precipitation 5 µmole l^{-1}. They estimated a background deposition for around 1980 of about 50 mole ha^{-1} $year^{-1}$. It is likely that the background concentration/deposition was lower in the past as it is partly caused by far away anthropogenic sources. The geographical resolution of the results within a country depends on the spatial resolution of the emission data for 1980 (Buijsman et al., 1987), as no shifts in emission pattern within a country before 1980 were taken into account. The geographical resolution of the emission data is different for different countries. The more detailed the emission is known, the more detailed the concentration and deposition pattern can be computed.

The computed NH_3 concentration in air is representative of a large area (150 × 150 km^2), whereas a measured NH_3 concentration can be influenced to a large extent by local sources. This makes it difficult to compare measurements of NH_3 with model results (Asman and Janssen, 1987). The NH_4^+ concentrations in air and precipitation are less influenced by local emissions, which makes a comparison of computed and measured concentrations possible. Asman and Janssen (1987) found a good agreement between computed and measured concentrations of NH_4^+ in air and precipitation for around 1980. Comparison with measured historical concentrations is rather doubtful because of the poor quality of these data. But the results presented here may indicate where the trend may be large enough to be detectable. The figures show a large increase in concentrations and depositions, especially for the period 1950-1980. The increase in deposition since 1870 has been largest in The Netherlands (by a factor 3.7) and relatively moderate in Scandinavia. More detailed information, also on historical import/export balances for the separate components, can be found in Asman et al. (1987). The results show for example that, although the Swedish ammonia emission decreased by 17% in the period 1950-1980, the wet deposition of NH_4^+ increased by 30%. This

Table 6. Emission and deposition budget (total NH_x) of European countries 1870-1980 (10^8 mole $year^{-1}$)[1)]

	1870				1920				1950				1980			
"country"	Deposition			Emission	Deposition			Emission	Deposition			Emission	Deposition			Emission
	Ind.	Imp.	Exp.		Ind.	Imp.	Exp.		Ind.	Imp.	Exp.		Ind.	Imp.	Exp.	
Albania	5	2	6	14	4	2	4	10	5	3	5	12	6	4	7	14
Austria	15	16	13	31	18	19	16	36	20	22	18	40	25	33	22	50
Belgium	8	8	13	23	10	8	16	28	13	9	22	37	21	17	34	58
Bulgaria	27	14	21	50	34	14	26	62	26	16	20	47	47	27	36	86
Czechoslovakia	37	25	34	75	37	30	34	75	37	34	35	76	59	54	55	120
Denmark	11	4	16	27	19	5	27	46	22	6	33	56	30	9	44	75
Finland	10	7	6	18	18	8	11	31	18	9	11	31	17	16	11	30
France	168	23	92	274	152	31	84	248	170	35	94	278	303	54	167	495
G.D.R.	28	18	30	58	30	21	32	62	38	24	41	79	69	37	73	143
G.F.R.	82	41	61	147	99	47	74	178	116	57	87	208	158	100	119	285
Greece	16	7	15	38	13	7	13	33	16	8	16	40	27	12	26	66
Hungary	14	14	15	31	19	16	19	41	24	17	25	52	41	27	42	89
Iceland	1	0	0	1	1	0	0	2	1	0	0	2	1	1	0	3
Ireland	26	3	24	56	33	3	30	70	32	4	30	69	48	6	44	104
Italy	46	10	35	88	74	11	56	143	88	13	67	170	131	20	99	252
Luxemburg	0	1	1	2	1	1	1	2	1	1	1	2	1	2	2	3
Netherlands	9	7	14	24	13	8	21	35	19	10	31	52	42	15	68	116
Norway	10	8	7	19	11	10	8	21	13	11	9	25	13	17	9	24
Poland	68	38	45	115	96	42	63	163	86	49	57	147	165	81	109	282
Portugal	7	1	5	17	10	2	8	26	11	2	8	26	13	3	9	32
Romania	41	29	24	68	55	32	33	92	55	35	33	92	123	58	73	207
Spain	31	8	18	62	58	9	33	116	53	10	30	104	81	16	46	161
Sweden	18	15	14	33	26	19	21	48	24	22	20	45	20	34	16	37
Switzerland	9	8	8	17	11	9	11	22	12	11	12	25	17	17	17	34
Turkey	56	9	22	153	47	10	19	130	77	10	31	211	131	18	53	360
United Kingdom	79	13	67	158	87	16	74	173	109	17	92	217	173	27	147	345
USSR	569	96	42	1030	637	119	47	1153	694	127	52	1257	1507	217	112	2729
Yugoslavia	62	21	35	106	54	26	30	91	66	30	37	112	82	47	46	139
North Africa	0	0	4	69	0	0	5	88	0	0	5	94	0	0	11	194
Sea Areas	-	243	-	-	-	287	-	-	-	328	-	-	-	530	-	-
Sum	1452	689	689	2804	1664	815	815	3223	1846	917	917	3606	3352	1496	1496	6534

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1) The emissions of (parts of) "countries" outside the receptor domain are used to calculate the deposition within the receptor domain.

Ind.: depositions from indigenous sources

Imp.: depositions from foreign sources

Exp.: depositions outside source country but within Europe

Table 7. Average concentrations in European "countries" 1870-1980 (no background contribution added).

"country"	NH_3-air (µg m^{-3})				NH_4^+ -aerosol (µg m^{-3})				NH_4^+-precip. (µmole l^{-1})			
	1870	1920	1950	1980	1870	1920	1950	1980	1870	1920	1950	1980
Albania	0.8	0.6	0.7	0.9	1.4	1.4	1.6	2.2	8	7	9	12
Austria	0.7	0.8	0.9	1.2	1.7	2.0	2.3	3.4	24	29	33	46
Belgium	1.5	1.8	2.3	3.7	2.0	2.3	2.8	4.6	36	39	48	82
Bulgaria	0.9	1.1	0.8	1.5	1.7	1.9	1.9	3.2	24	27	25	44
Czechoslovakia	1.1	1.1	1.1	1.8	1.9	2.1	2.3	3.7	38	42	46	73
Denmark	1.1	1.9	2.3	3.1	1.2	1.7	2.0	3.0	21	31	37	53
Finland	0.1	0.2	0.2	0.2	0.3	0.4	0.4	0.5	5	7	8	10
France	0.9	0.9	1.0	1.7	1.8	1.8	2.0	3.4	24	24	26	45
G.D.R.	1.0	1.1	1.4	2.5	1.8	2.0	2.4	4.0	37	42	50	82
G.F.R.	1.1	1.3	1.6	2.2	2.0	2.3	2.7	4.2	35	41	49	76
Greece	0.5	0.5	0.6	0.9	1.3	1.3	1.5	2.3	11	10	12	18
Hungary	0.7	0.8	1.1	1.8	1.7	2.0	2.3	3.7	28	33	38	61
Iceland	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1	1	1	1	2
Ireland	1.4	1.8	1.8	2.7	0.9	1.1	1.2	1.8	19	23	23	36
Italy	0.5	0.9	1.0	1.5	1.1	1.6	1.9	2.8	11	16	18	28
Luxemburg	1.1	1.4	1.3	2.2	2.0	2.2	2.4	4.0	29	30	34	58
Netherlands	1.2	1.8	2.7	5.9	1.8	2.3	2.9	5.3	32	39	51	92
Norway	0.1	0.1	0.1	0.1	0.3	0.3	0.4	0.5	4	5	6	7
Poland	0.7	1.0	0.9	1.7	1.5	1.8	1.9	3.3	29	37	38	67
Portugal	0.4	0.5	0.5	0.7	0.6	0.9	0.9	1.2	5	8	8	11
Romania	0.6	0.7	0.7	1.7	1.5	1.8	1.9	3.6	24	30	31	60
Spain	0.2	0.4	0.4	0.6	0.7	1.1	1.1	1.6	7	11	11	16
Sweden	0.1	0.2	0.2	0.2	0.4	0.5	0.5	0.7	7	10	10	13
Switzerland	0.8	1.0	1.1	1.6	1.8	2.1	2.4	3.6	25	30	34	52
Turkey	0.4	0.3	0.5	0.9	1.1	1.0	1.4	2.5	12	11	16	27
United Kingdom	1.2	1.3	1.6	2.6	1.2	1.3	1.6	2.6	24	26	32	51
USSR	0.4	0.4	0.4	1.0	0.9	1.0	1.1	2.2	14	16	17	36
Yugoslavia	0.8	0.7	0.8	1.0	1.6	1.7	2.0	2.8	19	19	22	31

Figure 2. NH_3 concentration in air (10^{-6} g m^{-3})

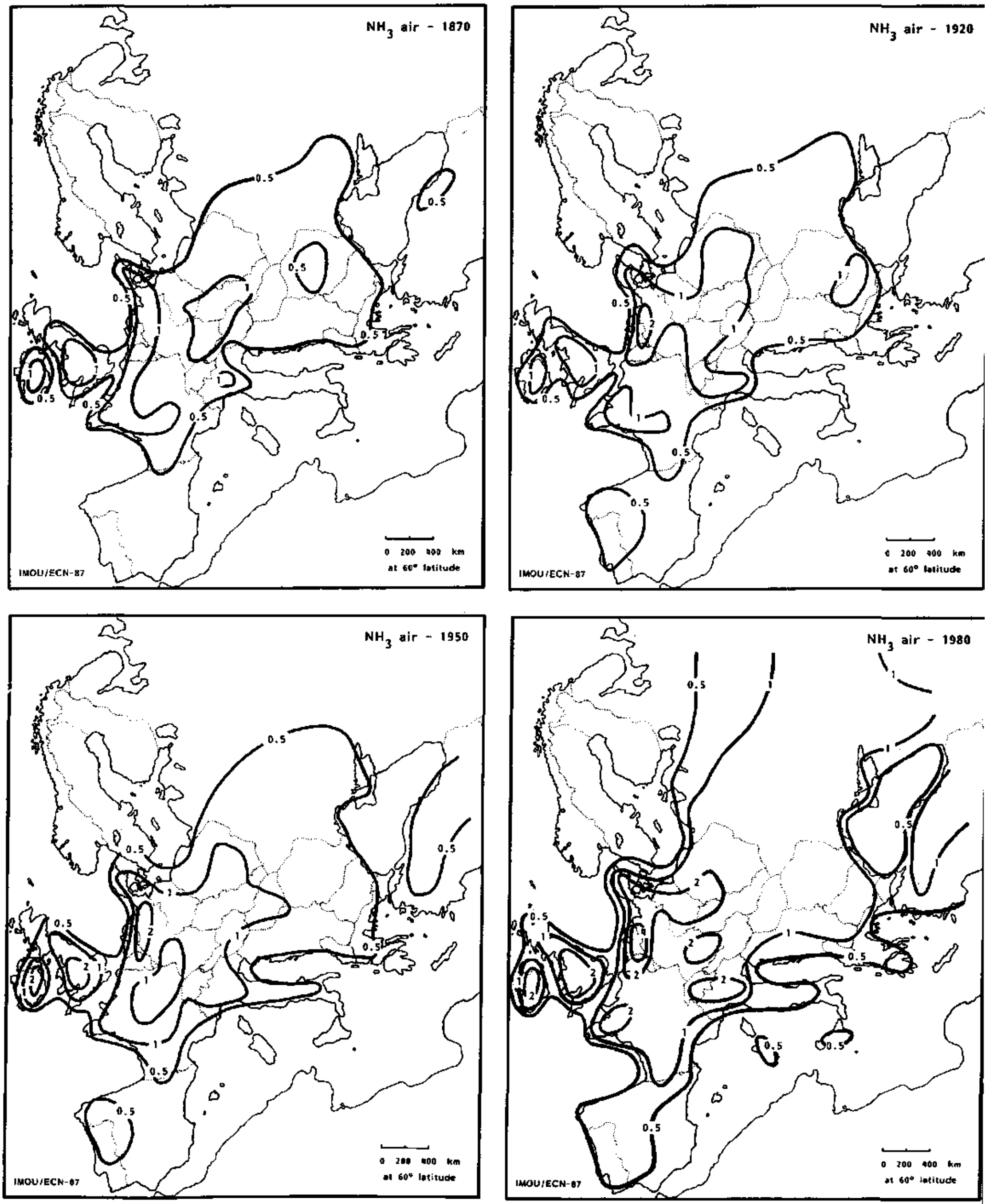


Figure 3. NH_4^+ aerosol concentration (10^{-6} g m^{-3})

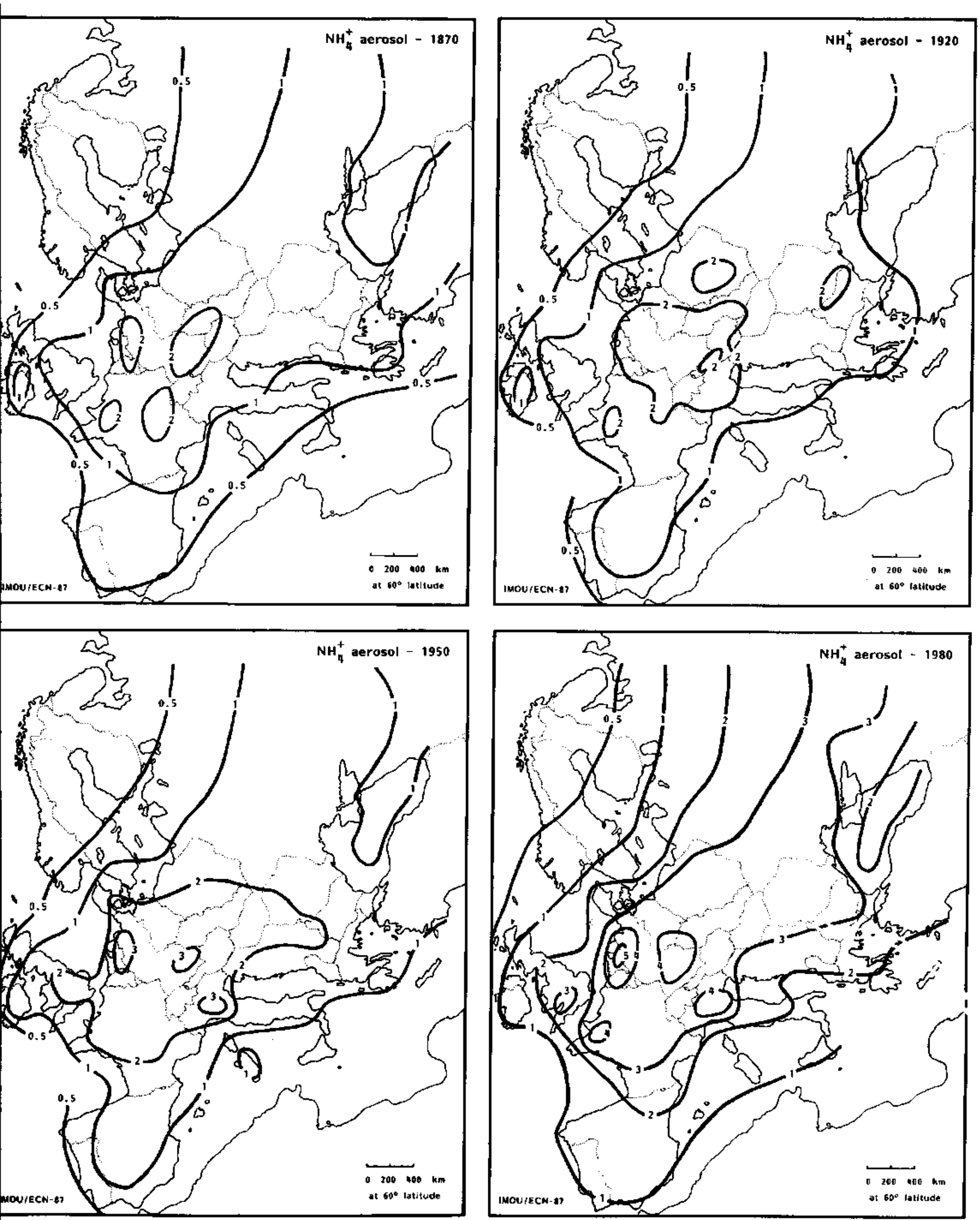


Figure 4. NH_4^+ concentration in precipitation (10^{-6} mole l^{-1})

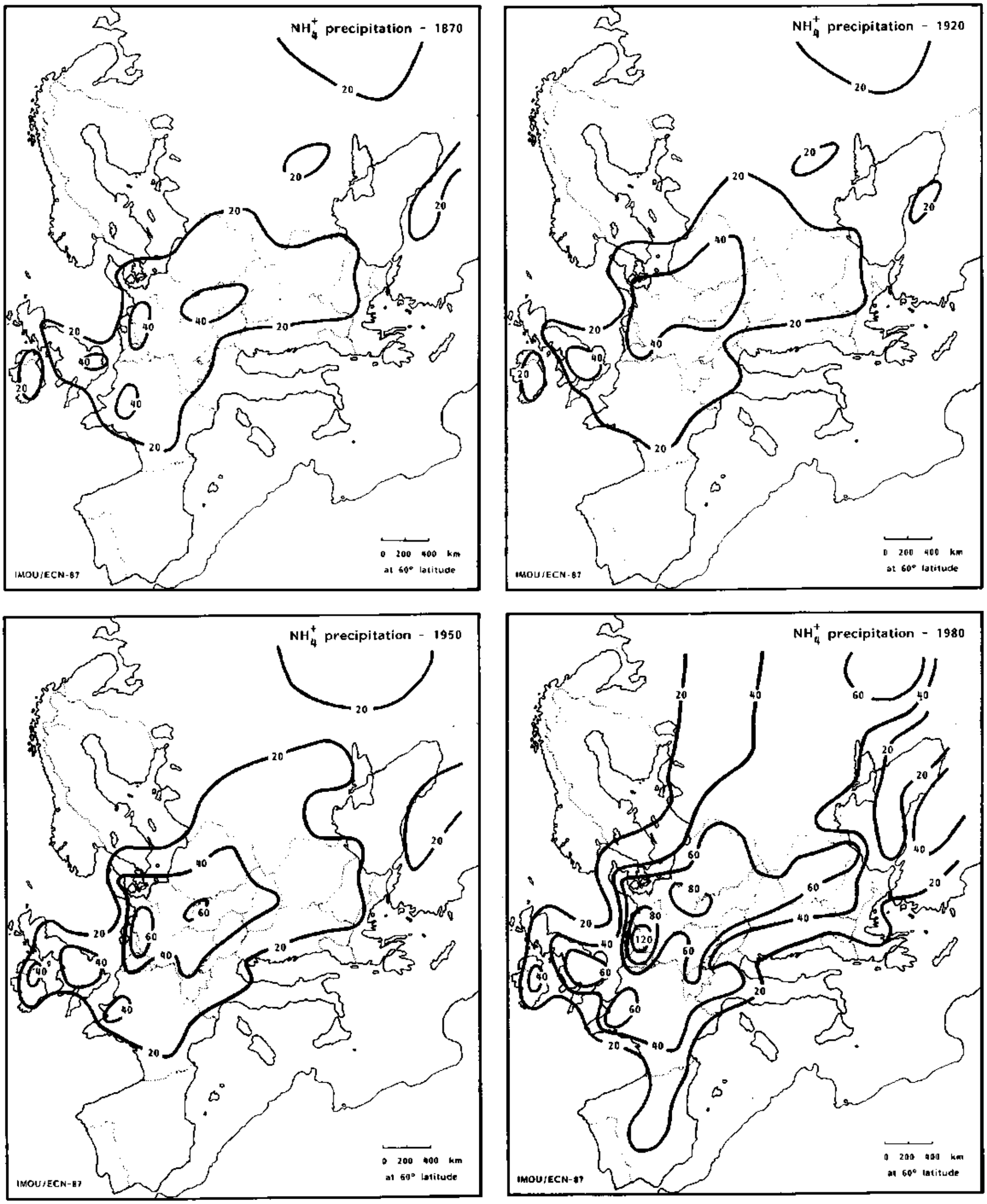
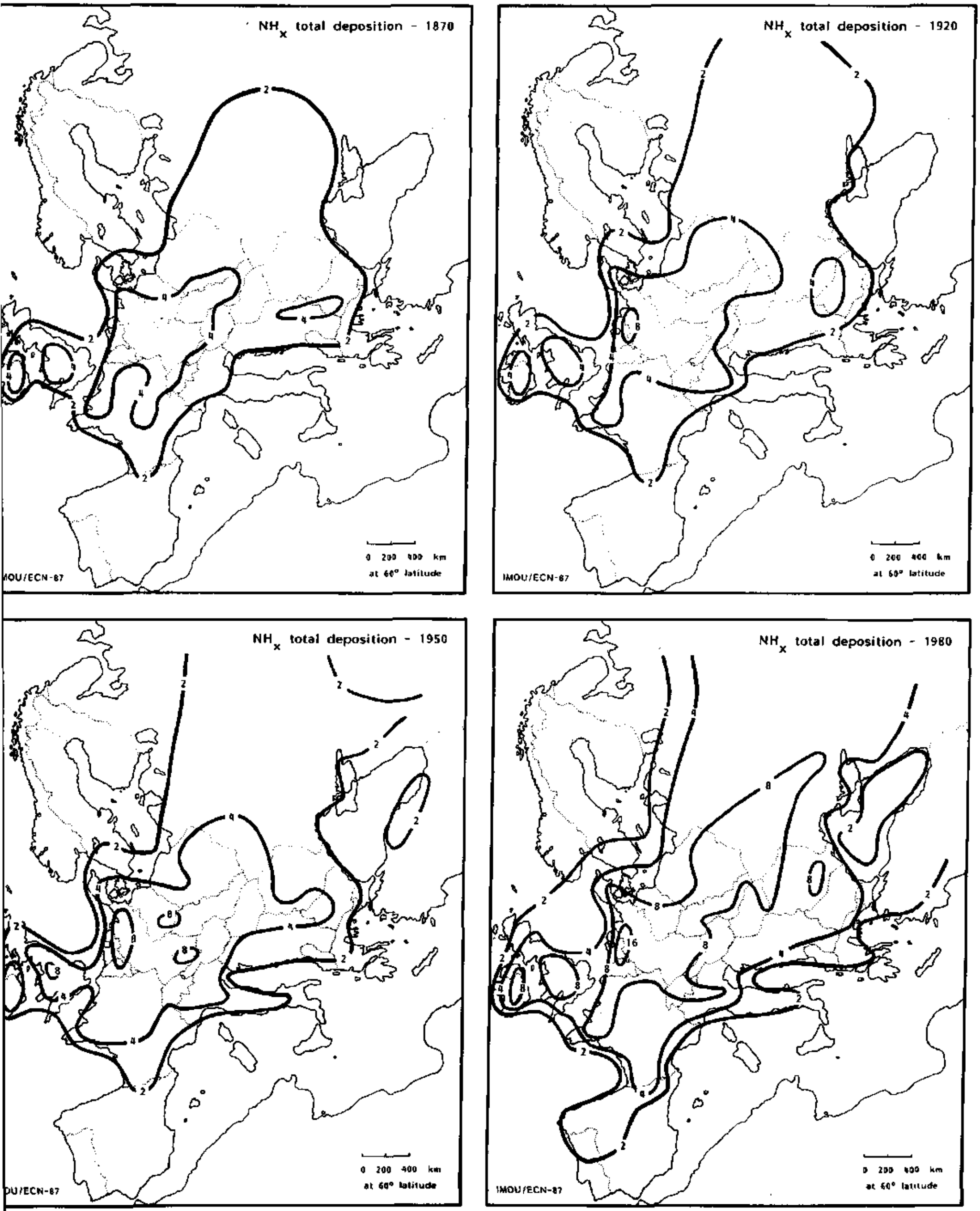


Figure 5. Total NH_x deposition (10^2 mole ha^{-1} $year^{-1}$)



is the result of a relative increase in the import from 63% of the wet deposition of NH_4^+ in 1950 to 76% in 1980 (Asman et al., 1987). For the Netherlands the situation is opposite: the ammonia emission increased by 122% in the same period, whereas the wet deposition of NH_4^+ increased only by 80%. This is the result of a relative decrease in the import from 62% of the wet deposition of NH_4^+ in 1950 to 53% in 1980 (Asman et al., 1987). These examples indicate that considerable long-range transport of NH_x occurs. It also demonstrates that, at least for NH_4^+ in air and precipitation, a large error can be made by estimating concentration trends in one country just by using trends of the emission for only that particular country.

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Appendix

Procedure followed to compute historical livestock numbers for countries with 1980 boundaries from livestock numbers for countries with historical boundaries.

Remarks:

- The livestock numbers for the year 1980 were taken from Buijsman et al. (1987).

- The livestock numbers for around 1920 were mostly for 1923 for practical purposes (new official borders for some countries).

- Data for poultry 1920: The numbers for Czechoslovakia and the western part of the USSR were estimated from the data for 1950 for these countries and the trend 1923-1950 for Bulgaria, Finland, Hungary, German Democratic Republic, Poland, Romania and Yugoslavia.

- Data for poultry 1870: The numbers for Belgium, France, Hungary, Ireland, Italy, Luxemburg, Netherlands, Poland, Portugal, Romania, Spain, Switzerland, United Kingdom and the western part of the USSR were estimated from the data for 1870-1923 for the other countries.

In the following the procedure is given for separate countries for the different years. If data are not known/estimated for these years, but data for an other year are used, this is indicated.

Albania

1950: Drejtoria e Statistikës (1959). For buffaloes the same emission factor is taken as for cattle.

1920: Data are estimated from the trend in Yugoslavia (1923-1938) and the data for Albania from Drejtoria e Statistikës (1959).

1870: The estimate for 1923 and the trend for Yugoslavia 1863-1923.

Austria

1950: Mitchell (1980). Data for asses from Capone (1953).

1920: Mitchell (1980). Data for asses used for 1938 (Capone,1953).

1870: Data are computed for 1880 from data for 1902 (Oesterreiches Statistisches Zentralamt, 1932) for Austria with 1980 boundaries and the trend 1880-1902 for Austria with historical boundaries (Mitchell, 1980). Data for asses lacking.

Belgium

1950: Mitchell (1980). Poultry from Landbouw Economisch Instituut (1986) and goats and asses from Capone (1953).

1920: Mitchell (1980). Data for goats, asses and poultry for 1929 from Capone (1953).

1870: Data are for 1880. Data for goats for the year 1866 (Valpy, 1874-1914). Data for asses lacking.

Bulgaria

1950: Mitchell (1980).

1920: Data are for 1920. Data for former parts of Romania added (Colescu, 1925).

1870: Data are for 1890. The same trend assumed as for Bulgaria with historical boundaries.

Czechoslovakia

1950: Mitchell (1980).

1920: Data are for 1925. From Mitchell (1980) minus Ruthenia (Auerhau, 1932). Data for asses are for 1939 (Capone, 1953).

1870: Data for 1910 were reconstructed from K.K. Statistischen Zentralkommission (1914) and Office de Statistique du Royaume de Hongrie (1921). Data for 1870 were computed from these data and the trend 1870-1910 for Austria-Hungary (Mitchell, 1980).

Denmark

1950: Mitchell (1980). Data for goats from Capone (1953).

1920: Mitchell (1980). Data for goats are for 1939 (Capone, 1953).

1870: Mitchell (1980), data for the southern part of Jutland added (Kaiserliches Statistisches Amt, 1910). Data for goats and poultry from Valpy (1874-1914).

Finland

1950: Mitchell (1980). Data for goats from Capone (1953).

1920: Mitchell (1980). Data for goats for 1939 (Capone, 1953).

1870: Data are for 1881 (Mitchell, 1980). Reindeer, goats and poultry from Institut International d'Agriculture (1939).

France

1950: Mitchell (1980). Data for asses and poultry from Capone (1953).

1920: Mitchell (1980). Data for asses and poultry for 1929 (Capone, 1953).

1870: Mitchell (1980), data for Alsace-Lorraine for 1873 added. These data were computed from the data for 1907 (Kaiserliches Statistisches Amt, 1910) and the trend 1873-1910 (Bundesministerium für Ernährung, Landwirtschaft und Forsten, 1956).

German Democratic Republic

1950: Mitchell (1980). Data for asses from Capone (1953).

1920: Reconstructed for 1925 (Statistisches Reichsamt, 1929).

1870: Data are for 1873 and were computed from reconstructed data for 1907 (Kaiserliches Statistisches Amt, 1910) and the trend 1873-1907 for Germany with historical boundaries (Bundesministerium für Ernährung, Landwirtschaft und Forsten, 1956).

German Federal Republic

1950: Mitchell (1980). Data for asses from Capone (1953).

1920: Reconstructed for 1925 (Statistisches Reichsamt, 1929).

1870: Data are for 1873 and were computed from reconstructed data for 1907 (Kaiserliches Statistisches Amt, 1910) and the trend 1873-1907 for Germany with historical boundaries (Bundesministerium für Ernährung, Landwirtschaft und Forsten, 1956).

Greece

1950: Mitchell (1980).

1920: Ministère de l'Economie Nationale (1930).

1870: Data are for 1860 (Ministère de l'Economie Nationale, 1930). Data for Tessalia, Crete, eastern Thracia, Ionic Islands, Aegean Islands, Epiros and southern Macedonia added, using geographically detailed statistics for 1923 and the trend 1860-1923 for the part of Greece that already existed in 1860.

Hungary

1950: Mitchell (1980). Data for poultry for 1935 (Capone, 1953).

1920: Office Central Royal Hongrois de Statistique (1927).

1870: Data are for 1863 and were computed from the data for 1911 (K.K. Zentral Kommission, 1864) and the trend 1863-1911 for Hungary with historical boundaries.

Iceland

1950: Hagstofu Islands (1952).

1920: Hagstofu Islands (1914, 1932).

1870: Hagstofu Islands (1914).

Ireland

1950: Mitchell (1980).

1920: Mitchell (1980).

1870: Computed from the data for 1920 and the trend for the whole of Ireland (Mitchell, 1980).

Italy

1950: Mitchell (1980) with additional data for Triest (Capone, 1953).

1920: Mitchell (1980), minus data for Istria, Rijeka and Zadar for 1929 (Instituto Centrale di Statistica del Regno d'Italia, 1933).

1870: Data are for 1864 (Instituto Centrale di Statistica, 1878).

Luxemburg

1950: Service Central de la Statistique et des Etudes Economiques (1982). Data for goats from Capone (1953).

1920: Estimated from the data for 1939 (Capone, 1953) and the trend 1923-1939 for Belgium.

1870: Data are for 1880. Estimated from the data for 1923 and the trend 1880-1923 for Belgium.

Netherlands

1950: Mitchell (1980).

1920: Data are for 1921. From Mitchell (1980). Data for goats from Institut International d'Agriculture (1939).

1870: Mitchell (1980). Data for goats from Valpy (1874-1914).

Norway

1950: Mitchell (1980).

1920: Mitchell (1980). Data for goats for 1939 from Capone (1953).

1870: Data are for 1875 (Mitchell, 1980). Data for goats for 1875 from Valpy (1874-1914).

Poland

1950: Mitchell (1980).

1920: Weinfeld (1922-1925) for 1921. Data for parts of Poland that were German then were taken from Statistisches Reichsamt (1929).

1870: Data for 1910 were computed from Weinfeld (1922-1925). Data for the parts of Poland that were German were taken from Kaiserliches Statistisches Amt (1910) and are for 1907. The trend 1870-1910 is assumed to be the same as for the Old Kingdom of Poland (Weinfeld, 1922-1925).

Portugal

1950: Instituto Nacional de Estatística (1959).

1920: Instituto Nacional de Estatística (1959).

1870: Instituto Nacional de Estatística (1959).

Romania

1950: Mitchell (1980).

1920: Colescu (1925) and Colescu (1931) which give geographically detailed data for 1924 and 1930. Corrected for the parts of Boekowina, Bessarabia, Transsylvania which belong to the USSR now and corrected for a part that belongs to Bulgaria now.

1870: Data are for 1888. From Colescu (1903) which gives geographically detailed data for 1900 and the trend 1888-1900 for Romania with historical boundaries. Data for 1871 for the parts of Transsylvania and Boekowina which then belonged to Hungary were added (Königliches Ungarisches Statistisches Bureau, 1872).

Spain

1950: Mitchell (1980).

1920: Mitchell (1980).

1870: Data are for 1888 (Mitchell, 1980).

Sweden

1950: Mitchell (1980). Data for goats from Capone (1953).

1920: Mitchell (1980). Data for goats for 1937 (Capone, 1953). Data for poultry for 1927 (Capone, 1953).

1870: Mitchell (1980). Data for goats and poultry for 1880 (Valpy, 1874-1914)

Switzerland

1950: Mitchell (1980). Data for asses from Capone (1953).

1920: Data are for 1921 (Mitchell, 1980).

1870: Data are for 1876 (Mitchell, 1980).

Turkey

1950: Central Statistical Office (1955).

1920: Office Central de Statistique (1927) for 1927. Data for poultry are for 1927/1930 (Capone, 1953).

1870: Data are for 1863, computed from the data for 1923 assuming the same trend 1863-1923 as for Yugoslavia.

United Kingdom

1950: Mitchell (1980). Data for goats from Capone (1953).

1920: Mitchell (1980). Data for goats, asses and poultry for 1938 (Capone, 1953).

1870: Mitchell (1980). The contribution from Northern-Ireland is computed from the data for 1923 and the trend 1870-1923 for Ireland as a whole.

Yugoslavia

1950: Mitchell (1980). Data for asses from Capone (1953).

1920: Mitchell (1980). Data for Istria, Rijeka and Zadar which then belonged to Italy for 1929 added (Instituto di Statistica del Regno d'Italia, 1933).

1870: Reconstructed from data for Istria, Dalmatia, part of Styria and Croatia/Slavonia for the year 1863 (K.K. Statistischen Zentralkommission, 1864) from data for the "Kroatische Militärgrenze" (Königliches Ungarisches Statistisches Bureau, 1872) for 1871 and data for Serbia for 1900/1905 (Direction de la Statistique de l'Etat du Royaume de Serbie, 1901, 1906). It was assumed that the ratio of livestock numbers in Montenegro, Macedonia, Bosnia-Hercegovina, Vojvodina and Kossovo to the livestock numbers for whole of Yugoslavia was the same in 1870 and in 1980.

CHAPTER 7. FINAL COMMENTS AND DISCUSSION

7.1 Summary of major findings of this study

- The average NH_3 concentration at Cabauw, an area where emission occurs, decreases strongly with height in the lowest 100 m of the atmosphere, whereas the average concentration of NH_4^+, SO_4^{2-} and NO_3^- in aerosols does not.
- The average HNO_3 concentration at Cabauw increases with height. A possible reason for this increase apart from dry deposition at the earth's surface, may be the reaction with NH_3 emitted from the earth's surface.
- The net average upward flux of NH_3 during different meteorological conditions at Cabauw was 0.12 $\mu g\ m^{-2}\ s^{-1}$.
  In aerosols at Cabauw somewhat more SO_4^{2-} (equivalents) is present than NO_3^- up to 200 m height.
- The first order conversion rate constant for gaseous NH_3 to particulate NH_4^+ in the lowest 200 m of the atmosphere at Cabauw was $5 \times 10^{-5}\ s^{-1}$ for nighttime periods and $1 \times 10^{-4}\ s^{-1}$ for daytime periods. These values are rather uncertain as part of the assumptions that had to be made in the calculation are violated.
- Good agreement was generally obtained between the product of measured concentrations of NH_3 and HNO_3 and the product derived from thermodynamics. At temperatures below 0°C and relative humidities above 80%, however, no good agreement was obtained.
- Correction factors are derived which can be used in relatively simple atmospheric transport models. These correction factors account for the fact that mixing of emitted components over the whole mixing layer takes some time and does not occur instantaneously as assumed in the simple models. A simple model with correction factors gives as good results for a larger scale (> 100 km) as a more sophisticated model, but with less computing time. If no correction factors are used in a simple model for NH_3 the computed NH_3 concentration at ground level becomes much too low.

- A long-range transport model was developed based on emissions and parameter values which seem to be realistic in view of the present knowledge. Concentrations computed with this model are in good agreement with measured concentrations.
- A substantial part (20-80%) of NH_4^+ in air and precipitation in most countries appears to come from foreign sources, which points to true long-range transport.
- It was demonstrated that for NH_3 a historical emission inventory can be constructed which can be used to estimate historical concentration and deposition patterns.
- The largest relative increase in concentration and deposition of NH_x compounds in Europe since 1870 must have occurred in the Netherlands.

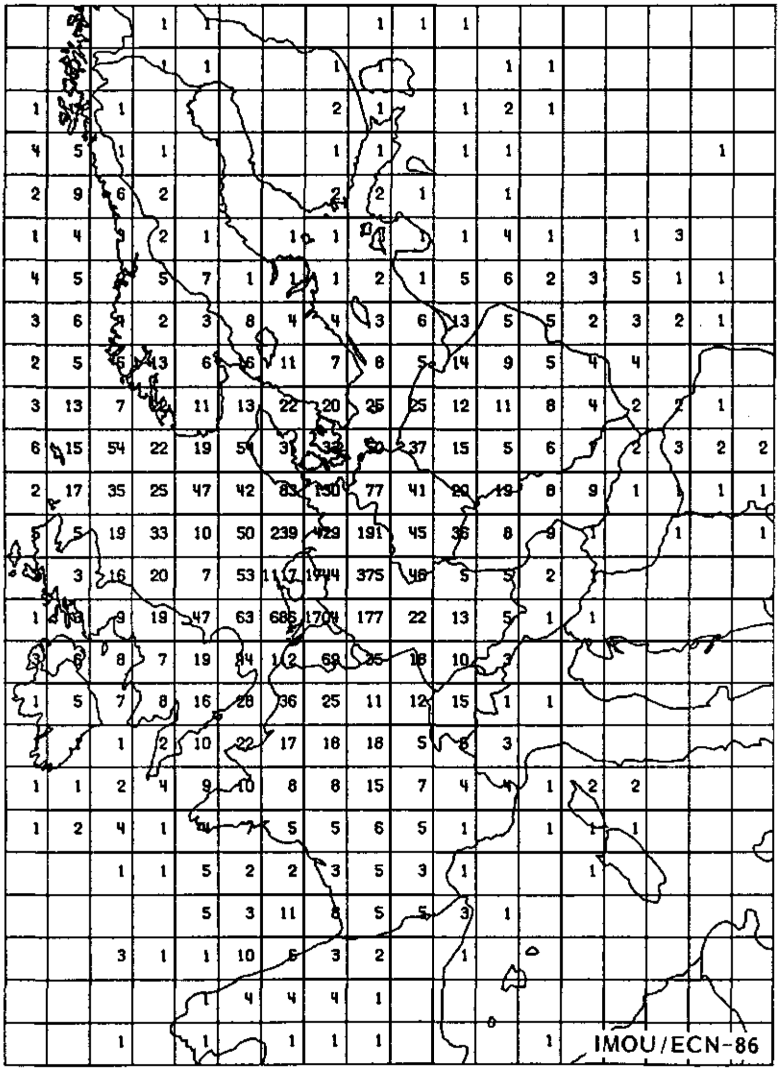
7.2 Discussion

As indicated in chapter 5 uncertainty exists on the parameter values (including emission) used in the model. This means that parameter values may differ within certain limits from the values used in the model, even if no regional or seasonal variations are taken into account. In this model the combination of parameter values is chosen in such a way that the results obtained are in good agreement with the available measurements. This means that, if future research would indicate that some parameter values should have somewhat different values or better measurements would become available, not only one parameter value should be changed but also other parameter values should be changed at the same time to give the best possible fit to the measurements. In this way the parameters are interdependent. It must be mentioned, however, that the model results are not very sensitive to changes in parameter values (chapter 5). In this chapter the budget of NH_x in Europe is considered and some additional remarks are made on the flux of NH_3 and the conversion rate of NH_3 to NH_4^+.

7.2.1 Budget considerations

The interdependence of parameter values is illustrated by budget considerations for a larger area such as e.g. western Europe. The atmpospheric lifetime of NH_x is relatively short. This is illustrated by Figure 1 which shows a map with contributions of NH_3 sources in the Netherlands to the deposition of NH_x in grid elements in Europe (these results are obtained with an export-version of the model, using forward trajectories; Asman and Janssen, 1986). Because of the relatively short lifetime of NH_x the yearly average deposition in western Europe should be almost equal to the yearly average emission in that area. It would in principle be possible to use this relation to compute the emission if the deposition were known or vice versa. The deposition consists of the contributions of dry deposition of NH_3 and the dry and wet deposition of NH_4^+. These contributions will be discussed here as well as the possibilities of getting some information from budget considerations and wet deposition of NH_4^+.

Figure 1. Contribution of NH_3 sources in the Netherlands to the deposition of NH_x in grid elements in Europe (10^6 mole $year^{-1}$)



			1	1				1	1	1							
			1	1			1	1			1	1					
1		1					2	1		1	2	1					
4	5	1	1				1	1		1	1					1	
2	9	6	2				2	2	1		1						
1	4	9	2	1		1	1		1	1	4	1		1	3		
4	5		5	7	1	1	1	2	1	5	6	2	3	5	1	1	
3	6	9	2	3	8	4	4	3	6	13	5	5	2	3	2	1	
2	5	5	13	6	6	11	7	8	5	14	9	5	4	4			
3	13	7	[illegible]	11	13	22	20	25	25	12	11	8	4	2	2	1	
6	15	54	22	19	54	31	32	50	37	15	5	6	7	2	3	2	2
2	17	35	25	47	42	83	130	77	41	20	19	8	9	1	1	1	1
5	5	19	33	10	50	239	429	191	45	36	8	9	1		1		1
	3	16	20	7	53	1117	1944	375	48	5	5	2					
1	18	9	19	47	63	686	1704	177	22	13	5	1	1				
3	6	8	7	19	84	112	69	35	18	10	3						
1	5	7	8	16	28	36	25	11	12	15	1	1					
	1	1	2	10	22	17	18	18	5	6	3						
1	1	2	4	9	10	8	8	15	7	4	4	1	2	2			
1	2	4	1	4	7	5	5	6	5	1		1	1	1			
		1	1	5	2	2	3	5	3	1			1				
				5	3	11	8	5	5	3	1						
		3	1	1	10	6	3	2		1							
				1	4	4	4	1									
		1		1		1	1	1				1					

The only contribution which is really measured is the wet deposition of NH_4^+. The measured wet deposition is representative of an area which varies from perhaps 20 × 20 km^2 in an area with relatively high emission density and a strong gradient in emission density to much larger than 150 × 150 km^2 in other areas. Although the measurement of wet deposition of NH_4^+ is not always easy (Buijsman and Erisman, 1986), it is possible to compute a realistic wet deposition field for NH_4^+ for western Europe. At least if additional measurements become available in areas which are not well covered by precipitation networks.

The dry deposition of NH_4^+ aerosol is computed from the NH_4^+ aerosol concentration and an adopted dry deposition velocity. NH_4^+ is a reaction product which is formed some time after NH_3 is released from the earth's surface. Its dry deposition velocity is low, which means that once it is formed it will remain in the air for a long time (during precipitation the NH_4^+ aerosol is removed very fast, but this will not affect the yearly averaged NH_4^+ aerosol concentration as it is mainly determined by the concentration during dry periods). Moreover, even if the dry deposition velocity would vary somewhat because of a spatial difference in surface properties this would not much affect the average vertical concentration profile, and hence the ground level concentration, because the dry deposition velocity is relatively low. This means that the NH_4^+ aerosol concentration is representative of a large area, i.e. an area which is larger than the area of which a NH_4^+ concentration in precipitation is representive, as this is partly determined by the more local contribution of NH_3. Although the NH_4^+ aerosol concentration is not measured at many locations yet, it must be possible to do so in the future and to obtain a realistic NH_4^+ aerosol concentration field for western Europe. This means that the uncertainty that will remain then is the uncertainty in the dry deposition velocity of the NH_4^+ aerosol.

The dry deposition of NH_3 is computed from the NH_3 concentration in air and an adopted dry deposition velocity. Emission occurs from many diffuse sources mainly in agricultural areas. This means that in those areas often sources are nearby. Moreover, the sources are at or near ground level. As a result the NH3 concentration in areas where emission occurs is usually only representative of a relatively small area, maybe

5 × 5 km^2 or less. As a consequence a tremendous number of stations would be required to measure a realistic concentration field in agricultural areas in western Europe. The measured concentration in an area where no emission occurs is likely to be representative of a larger area. One should, however, be aware of the fact that the vertical concentration profile and hence the ground level concentration can change if a spatial difference in dry deposition velocity occurs (e.g. the dry deposition velocity over heather would be different from the dry deposition velocity over forests). The only way to obtain a better estimate of the concentration pattern of NH_3 is to do measurements in a limited area, then to develop a model for this area and to apply the model then to a larger area. The dry deposition velocity of NH_3 is not well known and in fact one may question the use of the concept of a dry deposition velocity for NH_3 (see 7.2.2). It can be concluded that a large uncertainty will always remain in the dry deposition of NH_3 for western Europe.

Buijsman et al. (1987) mention that the emission they estimated is a conservative one and has an uncertainty of approximately 30%. The emission seems to be difficult to determine.

Computations made by Asman and Janssen (1986) show that, with the adopted parameters, 30% of the NH_3 emitted in the Netherlands is dry deposited as NH_3, about 8% is dry deposited as NH_4^+ and about 62% is wet deposited as NH_4^+. This means that, in order to know the total deposition of NH_x in western Europe it seems to be less important to know the dry deposition of NH_4^+. It is still very important, however, to know the concentration pattern of NH_4^+ for other purposes. It can be used e.g. to check conversion rate of the reaction NH_3 to NH_4^+. As wet deposition of NH_4^+ seems to contribute most to the total NH_x deposition it can still be worth while to undertake additional measurements or to improve these measurements to get a better estimate of the total NH_x deposition. The remaining uncertainty in the total NH_x deposition will then be caused by the uncertainty in the dry deposition of NH_3, which is difficult to get rid of. If we consider the budget of NH_x it appears that there will remain uncertainty on both sides of the balance: in the emission of NH_3 and in the total deposition of NH_x (which is partly due to the uncertainty in the contribution of the dry deposition of NH_3). If e.g. the emission were higher than assumed, some parameter values in the model would have to be changed to leave the computed wet deposition of NH_4^+ unchanged. This means in that case that the dry deposition of NH_3 should be higher than previously computed.

7.2.2 Modelling the flux: emission and dry deposition of ammonia

The treatment of the net flux of NH_3 in the model is somewhat primitive, which is caused by a lack of information. Emission of NH_3 (upward flux) is caused by degradation of livestock waste in the stable, during storage and in the field. An important additional source is the use of fertilizers. As discussed in chapter 5 only the (net) emission is known to some extent (e.g. during a few weeks after spreading). The dry deposition of NH_3 (downward flux) in the model is calculated by using a constant dry deposition velocity which is no function of meteorological circumstances or surface properties. The net (annual) flux is then the difference between the annual emission and the annual deposition in a grid element.

In reality the flux will show a variation in time and space which is, directly or indirectly, caused by changes in meteorological conditions, by the changes in the difference in partial pressure of NH_3 in the air just above surface and the partial pressure of NH_3 in the surface itself and by changes in the properties of the surface. The partial pressure of NH_3 in the earth's surface or in plants is usually not known as it depends on many factors (amount of ammoniacal N present, temperature, humidity, pH of the surface, microbial activity etc.). It is therefore in practice not possible to model the flux itself; only the variation caused by a variation in temperature, aerodynamic and boundary layer resistance could perhaps be taken into account if the necessary meteorological information is available.

7.2.3 The pseudo first order reaction rate

The conversion constant k, used in the model (8×10^{-5} s^{-1}), is somewhat different from the value derived from the measurements at Cabauw (about 5×10^{-5} s^{-1} to 1×10^{-4} s^{-1}). The value for k used in the model was partly based on the results of sensitivity studies. The reason for this difference may be explained by one or more of the following facts:

a. The value of k at Cabauw describes the reaction in the lowest 200 m of the atmosphere, whereas the value of k used in the model should describe the reaction in the whole mixing layer.

b. To calculate values for k for Cabauw assumptions have been made which are not fulfilled (Chapter 3).

c. The value of k is likely to have a different value at other locations than at Cabauw (Chapter 5).

It is recommended that the value for k of 8×10^{-5} s^{-1} should be used, as the model results then give a much better fit to the measured concentrations over the whole modelling area.

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Samenvatting van het proefschrift

"ATMOSFERISCH GEDRAG VAN AMMONIAK AND AMMONIUM"

Waarom zijn ammoniak en ammonium belangrijk?

Deze studie beschrijft het gedrag van ammoniak en ammonium in de atmosfeer in Europa. Ammoniak (NH_3) en ammonium (NH_4^+) zijn belangrijke stoffen in de atmosfeer om verschillende redenen:

a. Ammoniak (gas) is de meest voorkomende zuur-neutraliserende stof in de atmosfeer in West-Europa.

b. Ammonium komt in grote hoeveelheden voor in zwevende stofdeeltjes (aerosolen) en in regenwater.

c. Wanneer ammoniak en ammonium op de bodem of op het oppervlaktewater terechtkomen kan het door mikro-organismen tot zuur worden omgezet. Hierdoor kan bodem- en waterverzuring ontstaan, hetgeen nadelige gevolgen voor de planten kan hebben.

d. Erg hoge concentraties van ammoniak kunnen direkte schade veroorzaken bij planten.

e. Komen ammoniak en ammonium in bossen terecht, dan kunnen bomen gebrek aan magnesium en kalium krijgen, waardoor b.v. de naalden bij naaldbomen te vroeg gaan afvallen. Ook kunnen bomen gevoeliger worden voor andere stoffen zoals ozon of voor droogte, vorst of schimmelziekten.

f. Ammoniak en ammonium zijn stikstofhoudende voedingsstoffen en kunnen wanneer ze op de bodem op in het water terechtkomen de groei van plantensoorten bevorderen die van veel stikstof houden. Daardoor kunnen plantensoorten achteruitgaan of zelfs uitsterven die niet zo goed tegen veel stikstof kunnen. Een voorbeeld hiervan is de vergrassing van heide.

g. Ammoniak kan zuur in wolkendruppels (gedeeltelijk) neutraliseren, waardoor de reaktie, waarbij opgelost zwaveldioxidegas in zwavelzuur wordt omgezet, sneller kan verlopen.

h. De opname van ammoniak door regendruppels veroorzaakt een verhoogde uitwassing van zwaveldioxide.

i. Als zich aan het aardoppervlak ammoniakgas bevindt kan dit wellicht bewerkstelligen dat zwaveldioxidegas met een verhoogde snelheid op het aardoppervlak terecht kan komen.

Het gedrag van stoffen in de atmosfeer

Om het gedrag van een stof in de atmosfeer te kunnen beschrijven, is het nodig te weten:

a. Waar de stof in de lucht geloosd wordt en in welke hoeveelheid (emissie).
b. Hoe de stof in de atmosfeer getransporteerd wordt (richting, snelheid, hoogte).
c. Met welke snelheid de stof door wervels in de lucht naar het aardoppervlak getransporteerd wordt en daarop blijft vastzitten (droge depositie).
d. Met welke snelheid de stof door de regen uit de atmosfeer verwijderd wordt (natte depositie).
e. Met welke snelheid de stof reageert tot welke reaktieprodukten of met welke snelheid hij uit welke stoffen onstaan is (reaktiesnelheid).

Informatie over deze deelprocessen apart kan men te weten komen uit metingen, zowel in het laboratorium als in het veld. Daarnaast kan men informatie over de resultaten van alle processen die tegelijkertijd optreden ook uit metingen halen. Aan alle metingen kleven fouten en bovendien lijken de resultaten niet altijd met elkaar in overeenstemming te zijn. Bovendien is veelal niet alle informatie bekend die nodig is om het gedrag van een stof volledig te kunnen beschrijven.

Om alle beschikbare kennis op een systematische wijze op waarde te schatten en te integreren is het nuttig een model te ontwikkelen en toe te passen. Door modelresultaten met meetresultaten te vergelijken kan men een indruk krijgen van de waarde van de metingen en de modelresultaten. Vindt men aanzienlijke verschillen dan kan aangegeven worden waar welke aanvullende metingen verricht kunnen worden om meer zekerheid te verkrijgen.

Doel van het onderzoek

Doel van het in dit proefschrift beschreven onderzoek naar het atmosferisch-chemisch gedrag van ammoniak en ammonium in de atmosfeer is:

a. De beschikbare kennis over alle betrokken processen en stoffen inventariseren en op waarde schatten.
b. Aanvullende informatie over sommige processen verschaffen m.b.v. metingen in het veld.
c. De beschikbare kennis integreren door modellen te maken voor de berekening van lange-termijn gemiddelde koncentraties op grondniveau, i.h.b. voor Europa.
d. Nieuwe toepassingen van modellen te laten zien.

In hoofdstuk 1 wordt aangegeven waarom ammoniak en ammonium belangrijke stoffen zijn en wat het doel van het onderzoek is.

In hoofdstuk 2 wordt informatie gegeven over de ruimtelijke verdeling van de uitworp van ammoniak in Europa. Ammoniak ontstaat voornamelijk uit ontleding van dierlijke mest. Ook het gebruik van kunstmest en industriële processen kunnen tot uitworp van ammoniak leiden. Ammonium wordt in de atmosfeer gevormd uit de reaktie van ammoniak met zuur, maar het wordt niet in de atmosfeer geloosd.

In hoofstuk 3 worden metingen in het veld beschreven. Hieruit wordt de emissiesterkte van ammoniak in de omgeving van Cabauw berekend en wordt deze vergeleken met schattingen op grond van kennis over het aantal dieren in de omgeving. De koncentratie van ammoniak en ammonium tussen 0 en 200 m werd gemeten. Met behulp van deze gegevens kan men een idee krijgen van het horizontale transport van de stoffen, dat zich immers niet alleen aan de grond afspeelt. Daarnaast wordt een indruk verkregen van de snelheid waarmee ammoniak reageert tot ammonium.

In hoofdstuk 4 wordt besproken hoe korrektiefaktoren berekend kunnen worden. Deze zijn nodig indien men gebruik wil maken van relatief eenvoudige lange-afstand transportmodellen, waarbij aangenomen wordt dat een eenmaal geloosde stof in één klap over de gehele menglaag (ca. de onderste 800 m van de atmosfeer) verdeeld wordt. In de praktijk is dit niet het geval en zal er sprake zijn van een pluim die zich geleidelijk uitspreidt over de gehele menglaag. Door nu deze korrektiefaktoren in een eenvoudig model toe te passen verkrijgt men een resultaat dat even goed is als van meer ingewikkelde modellen, echter tegen een fraktie van de rekentijd. Deze korrektiefaktoren zijn niet alleen afgeleid voor ammoniak en ammonium, doch ook voor zwaveldioxide en stikstofoxiden en volgprodukten.

In hoofdstuk 5 wordt alle beschikbare informatie over de verschillende processen geïnventariseerd en onderling vergeleken. Deze processen worden geïntegreerd tot een model waarmee de koncentratie van ammoniak en ammonium in lucht alsook die van ammonium in regenwater berekend wordt. In het model worden de in hoofdstuk 4 afgeleide korrektiefaktoren toegepast. Vervolgens wordt nog een onderzoek gedaan naar hoe de resultaten van het model veranderen bij verandering van de verschillende processnelheden (gevoeligheidsanalyse). Dit wordt gedaan om te kijken hoe groot de variatie in de modelresultaten kan zijn t.g.v. onzekerheden in de processnelheden. Uiteindelijk worden de processnelheden binnen de grenzen van de onzekerheid zo gekozen dat de berekende koncentratiepatronen zo goed mogelijk overeenkomen met de gemeten patronen. Het blijkt dat het lukt de modelresultaten goed in overeenstemming te brengen met de meetresultaten.
Vervolgens wordt m.b.v. het model voor elk land in Europa aangegeven uit welke landen de daar terechtgekomen hoeveelheid ammoniak en ammonium afkomstig is. Het blijkt dat in veel landen een aanzienlijk deel van de depositie wordt veroorzaakt door bronnen in het buitenland. Het blijkt dat met name ammonium over grote afstanden getransporteerd kan worden. Voor ammoniak is dit niet het geval omdat dit vrij snel (ca. 30% per uur) in ammonium wordt omgezet. Uit de berekeningen blijkt dat ca. 72% van de depositie van ammoniak en ammonium in Nederland wordt veroorzaakt door emissie in Nederland. Ook blijkt dat Nederland ca. 4,5 maal zoveel van deze stoffen exporteert, als dat het importeert. Dat komt omdat Nederland t.o.v. de omringende landen een hoge emissiedichtheid heeft en omdat het aan één kant aan de zee grenst, waar geen emissie plaatsvindt.

In hoofdstuk 6 wordt gegeven hoe groot de toename in de ammoniakemissie voor de verschillende landen in Europa was in de periode 1870-1980. Het blijkt dat de Europese emissie in 1980 ca. 2 maal hoger was dan in 1870 (voor Nederland was dat ca. 5 maal). Vervolgens worden voor geheel Europa koncentratiepatronen berekend voor de jaren 1870, 1920, 1950 en 1980. Het blijkt dat de depositie van ammoniak en ammonium in elk land in Europa sinds 1870 is toegenomen, het sterkst echter in Nederland (met een faktor 3,7). Het berekenen van historische koncentraties en deposities is een nieuwe toepassing van dit soort modellen.

In hoofdstuk 7 wordt een samenvatting van de belangrijkste konklusies van deze studie gegeven en worden deze bediskussieerd.

CURRICULUM VITAE

Willem Albert Hajo Asman was born on August 15th 1948 in Laren (N.H.). He finished the secondary school in 1966 and started to study at the State University of Utrecht (RUU). He took a B.Sc. in chemistry in 1969 and a M.Sc. in chemistry in 1973 with analytical chemistry as a main subject ("The oxygen balance of running surface waters") and meteorology as a subsidiary subject ("The washout of sulphur dioxide from the atmosphere").

From 1973-1976 he taught chemistry at the evening courses in "laboratory practice" at the Dr. ir. W.L. Ghijssen Institute in Utrecht and in 1976 became state supervisor for these courses. Besides he read Danish language and literature during a few years.

In 1973/1974 he was scientific editor of a report on landscape ecology at the Institute of Systematic Botany of the State University of Utrecht.
Besides his work he was also participating in various environmental groups.

In 1974 he started as a volunteer to do research on atmospheric chemistry (precipitation chemistry) at the Institute of Meteorology and Oceanography (IMOU) of the State University of Utrecht, thereby relinquishing his claim on any unemployment benefit. From 1976-1980 the research was partly financed by the State University. From 1980-1987 the research was financed almost completely by the Netherlands Ministry of Housing, Physical Planning and Environment.

The number of people working in the Atmospheric Chemistry Groep of IMOU led by Ed Buijsman and him increased in this period from 2 to 6 (not including a part-time secretary). The group produced more than 90 articles and reports often in co-operation with other institutes. The field of research extended from experimental work to modelling the atmospheric transport and precipitation scavenging.

He taught voluntarily atmospheric chemistry at IMOU, at the Institute of Environmental Studies and at the Institute of Physical Geography of the State University of Utrecht. He also contributed to postdoc courses in Wageningen and Delft. Besides he was a member of several national committees on acid rain and standardization of chemical analysis of precipitation.

For 13 years he was working on temporary contracts (average duration about 6 months) at the University of Utrecht, which hindered planning of research to a large extent. In 1986 the University of Utrecht intended to start a co-operation with another institute, which made his financial and scientific future even more uncertain.

Since December 1986 he is working at the National Institute of Public Health and Environmental Hygiene (RIVM), Bilthoven, The Netherlands. From January 1988 he will also be working part-time at the National Agency of Environmental Protection, Air Pollution Laboratory, Risø National Laboratory, Roskilde, Denmark.

LEVENSOVERZICHT

Willem Albert Hajo Asman werd op 15 augustus 1948 geboren te Laren (N.H.). In 1966 behaalde hij het diploma HBS-B aan het Nieuwe Lyceum te Hilversum en schreef hij zich in aan de Rijksuniversiteit te Utrecht. Het kandidaatsexamen scheikunde legde hij af in 1969. Het doktoraalexamen scheikunde werd behaald in 1973 met als hoofdvak analytische scheikunde (onderwerp: "De zuurstofhuishouding in stromend oppervlaktewater") en als bijvak Meteorologie (onderwerp: "Uitwassing van zwaveldioxide uit de atmosfeer"). Daarnaast behaalde hij de lesbevoegdheid in de scheikunde.

Van 1973-1976 was hij docent scheikunde aan de avondopleiding MBO-Laboratoriumtechniek van het Dr. ir. W.L. Ghijsen Instituut te Utrecht en is sinds 1976 rijksgekommiteerde bij deze opleiding. Daarnaast studeerde hij enige jaren Deense Taal- en Letterkunde.

In 1973/1974 was hij in dienst van het Instituut voor Systematische Plantkunde van de Rijksuniversiteit te Utrecht, waar hij zich bezighield met de wetenschappelijke redaktie van een rapport van een interdisciplinair landschapsekologisch projekt (titel rapport: "Het Kromme-Rijnlandschap, een ekologische visie").
Naast zijn werk was hij aktief in verschillende milieugroepen, o.a. de Stichtse Milieufederatie, waarvan hij van 1981-1987 bestuurslid was.

In 1974 startte hij als vrijwilliger met verlies van uitkering atmosferisch-chemisch onderzoek naar de chemische samenstelling van de neerslag aan het Instituut voor Meteorologie en Oceanografie (IMOU) van de Rijksuniversiteit Utrecht (RUU). Van 1976-1980 werd het onderzoek gedeeltelijk door de RUU gefinancierd. Van 1980-1987 werd het onderzoek vrijwel geheel door de Direktie Lucht van het Ministerie VROM gefinancierd.
De groep atmosferisch-chemische onderzoekers breidde zich onder leiding van Ed Buijsman en hem uit tot 6 onderzoekers en een part-time sekretaresse. Door de groep werden meer dan 90 artikelen en rapporten geschreven veelal in samenwerking met andere instituten. Zijn onderzoek breidde zich uit van zuiver experimenteel onderzoek tot onderzoek op het gebied van transport- en uitwasmodellen.

Aan het IMOU werd op vrijwillige basis mede door hem kollege in de chemie van de atmosfeer gegeven. Daarnaast werden op vrijwillige basis kolleges in de chemie van de atmosfeer gegeven t.b.v. studenten Milieukunde en Fysische Geografie aan de RUU. Tevens werd door hem meegewerkt aan postakademiale kursussen in Wageningen en Delft. Bovendien had hij zitting in diverse kommissies op het gebied van "Zure regen" en standaardisatie van analysemethoden voor neerslag.

Gedurende 13 jaar was hij in tijdeljke dienst bij de RUU met slechts korte aanstellingperioden van ca. 6 maanden, waardoor een planning van onderzoek van enige betekenis ernstig bemoeilijkt werd. Doordat de RUU in 1986 een samenwerking met een buiten-universitair instituut aanging werd zijn toekomst zowel financieel als wetenschappelijk nog onzekerder. Sinds december 1986 werkt hij bij het Rijksinstituut voor Volkgezondheid en Milieuhygiëne te Bilthoven. Vanaf januari 1988 zal hij tevens part-time verbonden zijn aan het National Agency of Environmental Protection, Air Pollution Laboratory, Risø National Laboratory, Roskilde, Denemarken.

ABSTRACT

This study describes the atmospheric behaviour of ammonia and ammonium on a European scale. The concentrations of ammonia, ammonium and related components were measured at different levels of a 200 m high tower in the central part of the Netherlands. From these concentration profiles the ammonia flux into the atmosphere and the overall pseudo first-order reaction constant for the reaction of ammonia to ammonium are calculated. Moreover, the measured concentration product $[NH_3] \times [HNO_3]$ is compared with the theoretically derived product.

Correction factors are derived which can be used to describe the atmospheric behaviour of ammonia and ammonium adequately with a relatively simple long-range transport model. The present knowledge on the atmospheric behaviour of ammonia and ammonium is evaluated and is integrated in a model which produces concentration and deposition patterns of these components for the whole of Europe. Also import/export balances for these components for all European countries are presented. Moreover, emission and concentration patterns are given for the whole of Europe for the period 1870-1980.