Modelling the Atmospheric Nitrogen Deposition to Løgstør Bredning

Model results for the periods April 17 to 30 and August 7 to 19 1995

NERI Technical Report No. 195

Erik Runge, Ole Hertel, Lise Frohn
National Environmental Research Institute
Department of Atmospheric Environment
Frederiksborgvej 399, 4000 Roskilde, Denmark

Jens Havskov Sørensen
Danish Meteorological Office, Lyngbyvej 100
2100 Copenhagen, Denmark

Søren Larsen
Risø National Laboratory, Department of
Meteorology and Wind Energy, Frederiksborgvej 399
4000 Roskilde, Denmark

Ministry of Environment and Energy
National Environmental Research Institute
July 1997

Data sheet

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Authors:	Erik Runge[1], Ole Hertel[1], Jens Havskov Sørensen[2], Søren Larsen[3], and Lise Frohn[1]
Departments:	[1] National Environmental Research Institute, Department of Atmospheric Environment, [2] Danish Meteorological Office [3] Risø National Laboratory, Department of Meteorology and Wind Energy
Serial title and no.:	NERI Technical Report No. 195
Publisher:	Ministry of Environment and Energy. National Environmental Research Institute ©
URL:	http://www.dmu.dk
Date of publication:	July 1997
Referee:	Thomas Ellermann
Layout:	Lise Frohn, Bodil Chemnitz
Computer graphic:	Lise Frohn, Bjarne Jensen, Thomas Ellermann,
Please quote:	Runge, E., Hertel, O., Sørensen, J.H., Larsen, S.E. & Frohn, L.M. (1997): Modelling the Atmospheric Nitrogen Deposition to Løgstør Bredning. Model results for the periods April 17 to 30 and August 7 to 19 1995. National Environmental Research Institute. Denmark 50 pp. - NERI technical Report No. 195. Reproduction is permitted, provided the source is explicitly acknowledged.
Abstract:	Nitrogen deposition to the Løgstør Bredning in the fjord system Limfjorden has been computed, using the ACDEP-model. Meteorological input data from the DMI-HIRLAM Model was used for the calculations. The calculations covered two campaign periods 17 to 30 April and 7 to 19 August 1995.
Keywords:	Nitrogen deposition, atm. nitrogen load of fjord system, Løgstør Bredning, ACDEP, HIRLAM, SMP
ISBN:	87-7772-330-9
ISNN:	0905-815X
Paper quality	100 g Micra
Printed by:	Klæbel's offset tryk a-s
Number of pages:	50
Circulation:	200
Price:	DKK 65,- (incl. 25% VAT, excl. freight)
For sale at:	National Environmental Research Institute PO Box 358 Frederiksborgvej 399 DK-4000 Roskilde Denmark Tel.: +45 46 30 12 00 Fax: +45 46 30 11 14
	Miljøbutikken Information and Books Læderstræde 1 DK-1201 Copenhagen K Denmark Tel.: +45 33 37 92 92 (books) Tel.: +45 33 92 76 92 (info) Fax: +45 33 92 76 90

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National Environmental Research Institute

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Preface

The present work represents the results of the subproject 'Løgstør Bredning' within the framework of the Marine Centre under the Danish Environmental Research Programme (In Danish: Det Strategiske Miljøforskningsprogram - SMP).

The project is carried out as an interdisciplinary co-operation between three research institutions : The National Environmental Research Institute (NERI), Risø National Laboratory (RISØ) and The Danish Meteorological Institute (DMI).

Measurements from the project "Atmospheric Deposition and Ion fluxes in Forest Ecosystems" and from the Nation-wide Danish Monitoring Programme were kindly made available for this project by Mads F. Hovmand and Henrik Skov, both NERI.
Thomas Ellermann is acknowledged for valuable comments to the manuscript.

Summary

Modelling the Atmospheric Nitrogen Deposition to Løgstør Bredning

Model results for the periods April 17 to 30 and August 7 to 19 1995

Erik Runge, Ole Hertel, Lise Frohn
National Environmental Research Institute
Department of Atmospheric Environment
Frederiksborgvej 399, 4000 Roskilde, Denmark

Jens Havskov Sørensen
Danish Meteorological Office
Lyngbyvej 100, 2100 Copenhagen, Denmark

Søren Larsen
Risø National Laboratory,
Department of Meteorology and Wind Energy,
Frederiksborgvej 399, 4000 Roskilde, Denmark

NERI Technical Report No. 195, July 1997, 50 pp.

The present project is carried out under the Danish Environmental Research Programmes (SMP) Center for Environmental Research in Marine Environments. One of the aims of the center has been to model the temporal changes, transport, and accumulation of nutrients in the south-western part of Kattegat with adjacent fjord areas.

Calculation of Nitrogen deposition

In the present report the atmospheric deposition of nitrogen to Løgstør Bredning in Limfjorden has been estimated for two periods in 1995. During these two periods (April 17 to 30 and August 7 to 19) a number of biological experiments were carried out in the fjord system. The estimated nitrogen deposition together with the results of the experiments will be used as input data for the hydrographic water quality model MIKE 21.

ACDEP-model

The calculations of the nitrogen deposition have been performed with the transport-chemistry model ACDEP (Atmospheric Chemistry and DEPosition). ACDEP is a Lagrangian transport-chemistry model in which an air parcel is followed along 96 hours of transport to a given receptor point (Hertel et al., 1995).

Chemistry in the model

The chemical reactions in the model are based on a modified version of the chemical mechanism Carbon Bond Mechanism IV (CBM-IV) (Gery et al., 1989a,b). The modifications apply to the nitrogen chemistry, which in the ACDEP version of CBM-IV is substantially enlarged (Asman et al., 1993; Hertel et al., 1995).

Meteorological input

In general air pollution can be transported over large distances (several thousand kilometres). The pollution is spread over large areas by the three-dimensional atmospheric flow, and mixed in

the turbulent atmospheric boundary layer, which has a varying height. Furthermore the different components undergo chemical reactions, which are dependent on the meteorological parameters. In order to calculate the concentrations of the chemical components, it is necessary to employ meteorological data of high quality and with high resolution.

For the present calculations atmospheric trajectories and meteorological data calculated with a three-dimensional Lagrangian model (Sørensen, 1993; Jensen et al., 1996; Sørensen et al., 1997b) has been used. This model is again based on model results from one of the operational numerical weather prediction models (DMI-HIRLAM) currently used at the DMI (Sass, 1994).

Emission inventories

The emission inventories are other important input parameters for calculations of deposition with ACDEP. Since the deposition of nitrogen compounds to Danish areas not only originates from Danish sources, but also from long range transported pollution, it is necessary to have emission inventories for the entire Europe.

The emission inventories for Europe, that are used for the calculation of deposition to Løgstør Bredning, are the official national data submitted to the Geneva Convention of Long Range Transboundary Air Pollution. These data are given on a 50 km times 50 km grid.

The emissions of the compounds NH_3, SO_2, NO_x and NMVOC (Non-Methane Volatile Organic Compounds) from Danish sources were in connection with the Danish Sea 90 project compiled on a much more detailed grid (15 km times 15 km).

Coverage of Løgstør Bredning

The nitrogen concentration and deposition has been calculated for Feggesund, Løgstør, Nykøbing and Hvalpsund that cover the in- and outlets of Løgstør Bredning. Further calculations have been performed for the monitoring stations at Anholt, Tange and Ulborg in order to evaluate the model results.

For Løgstør Bredning a total nitrogen deposition of approximately 15 kg nitrogen per day per km^2 in the April campaign period and approximately 3 kg nitrogen per day per km^2 in the August campaign period has been calculated.

The distribution between dry and wet deposition is 5/95 in the April period and 28/72 in the August period. This reflects the difference in precipitation for the two periods. Furthermore the calculations show that the dry deposition is dominated by locally emitted ammonia (NH_3).

Sammenfatning

Det foreliggende projekt er udført under Det Strategiske Miljøforsknings Programs (SMP) center for marin miljøforskning. Centerets mål har bla. været at modellere tidslige ændringer, transport og akkumulation af næringssalte i den sydvestlige del af Kattegat med tilhørende fjordområder.

Beregning af kvælstofdeposition

I den foreliggende rapport er den atmosfæriske deposition af kvælstof til Løgstør Bredning i Limfjorden estimeret for to perioder i 1995. I disse to perioder (17. til 30. april og 7. til 19. august) blev en del biologiske eksperimenter udført i fjordsystemet. Den estimerede kvælstofdeposition indgår sammen med resultaterne fra eksperimenterne som inddata til den hydrografiske vandkvalitets model MIKE 21.

ACDEP-modellen

Beregningerne af kvælstofdepositionen er udført med ACDEP (Atmospheric Chemistry and DEPosition) modellen. ACDEP er en Lagrangsk transport-kemi model i hvilken en luftpakke følges langs 96 timers transport til et givet receptorpunkt (Hertel et al., 1995).

Kemi i modellen

De kemiske reaktioner i modellen er baseret på en modificeret udgave af den kemiske mekanisme Carbon-Bond Mechanism IV (CBM-IV) (Gery et al., 1989a,b). Modifikationerne gælder kvælstofkemien, der i ACDEP versionen af CBM-IV er væsentligt udbygget (Asman et al., 1993; Hertel et al., 1995).

Meteorologiske parametre

Luftforurening transporteres generelt over store afstande (adskillige tusind kilometer). Forureningen spredes over store områder af den tre-dimensionelle atmosfæriske strømning, og blandes op i det turbulente atmosfæriske grænselag, der har en meget varierende højde. Endvidere underkastes de forskellige komponenter fotokemiske reaktioner, der i høj grad er betinget af de meteorologiske parametre. For at beregne koncentrationerne af de kemiske komponenter er det derfor nødvendigt at anvende meteorologiske data af høj kvalitet og med høj opløsning.

Til de nærværende beregninger er anvendt atmosfæriske trajektorier og meteorologiske data beregnet med en tredimensional Lagrange´sk model (Sørensen, 1993; Jensen et al., 1996; Sørensen et al., 1997b) som igen er baseret på modelresultater fra en af de operationelle numeriske vejrprognosemodeller (HIgh Resolution Limited Area Model - HIRLAM) (Sass, 1994).

Emissionsopgørelser

Emissioner er ligeledes væsentlige inputs til beregningerne med ACDEP. Idet depositionen af kvælstof komponenter til danske områder ikke kun har sit udspring i danske kilder, men også i langtransporteret forurening, er det nødvendigt at have emissionsopgørelser for hele Europa.

De anvendte emissionsopgørelserne for Europa, er de officielle nationale data indleveret under Geneve konventionen om grænseoverskridende luftforurening. Disse data er givet på et 50 km x 50 km grid.

Emissionerne fra danske kilder blev i forbindelse med det danske Hav 90 projekt opgjort mere detaljeret (15 km x 15 km grid) for komponenterne NH_3, SO_2, NO_x og NMVOC (Non-Methane Volatile Organic Compounds).

Dækningen af Løgstør Bredning

Kvælstofkoncentrationen og -depositionen er beregnet til Feggesund, Løgstør, Nykøbing og Hvalpsund som dækker ind og udløb for Løgstør Bredning. Desuden er der foretaget beregninger for målestationerne på Anholt, ved Tange og ved Ulborg som er anvendt til at evaluere modelresultaterne.

For Løgstør Bredning er beregnet en samlet kvælstofdeposition på ca. 15 kg kvælstof per dag per km^2 under kampagneperioden i april, og ca. 3 kg kvælstof per dag per km^2 under kampagneperioden i august.

Fordelingen mellem tør- og våddeposition er 5/95 i april perioden og 28/72 i august perioden. Dette afspejler forskellen i nedbør for de to perioder. Endvidere viser beregningerne at tørdepositionen domineres af deposition af lokalt emitteret ammoniak (NH_3).

1 Introduction

SMP CERME

The present project is carried out within the framework of the Danish Environmental Research Programme. It is a part of one of the main themes in subprogram 4 "Marine and Fresh Waters" under 'The Center for Environmental Research in Marine Environments' (CERME).

CERME has as one of its aims to model temporal changes, transport, and accumulation of nutrients in the south-western part of Kattegat with adjacent fjord areas. These modelling activities are carried out on the basis of data from the Monitoring Programme under the Danish Action Plan for the Aquatic Environment 1990-1995 and data from the earlier accomplished Danish Marine Research Programme (Sea-90) as well as data collected in new campaigns.

Aim of the work

The aim of the present project is to estimate the atmospheric nitrogen deposition to Løgstør Bredning in Limfjorden during two periods in 1995. During these two periods biological experiments were carried out in the fjord system. Furthermore the results should contribute to an understanding of the nitrogen dynamics on local scale in the fjord area.

ACDEP - model

The calculations of nitrogen deposition to Løgstør Bredning are performed with the Atmospheric Chemistry and Deposition Model (ACDEP) (Hertel et al., 1995). The ACDEP-model was developed at the National Environmental Research Institute under the framework of the Sea-90 project (Asman et al., 1993) with the purpose of estimating nitrogen deposition to the Danish Seas. The model was tested using measurements from 6 Danish and 1 Swedish monitoring stations (Asman et al., 1993). This test was later supplemented with comparisons to other European stations (Hertel et al., 1995).

Atmospheric contribution to Kattegat

Within the framework of the Sea-90 project calculations were performed for the Kattegat Strait for the year 1990. The results from these calculations showed that the atmosphere contributes to approximately 30 % of the total nitrogen load for this area (Asman et al., 1993; 1994).

Routine calculations of N - deposition

Recently routine calculations with the ACDEP-model have been included in the Nation-wide Monitoring Programme (Skov et al., 1995). Within the framework of the monitoring programme, model calculations have been performed for all the Danish marine waters for the period 1989-1995 (Skov et al., 1996). These calculations include separate nitrogen deposition calculations for all Danish fjords, creeks and bays, and are carried out with a spatial resolution of 30 km × 30 km. The results are presented as monthly mean values (calculations are performed with a time resolution of 6 hours).

Typical levels for N - deposition

In general the calculations presented in Skov et al. (1996) show that the nitrogen deposition to Danish waters vary from 0.6 to 1.6 tonnes nitrogen per km^2 per year with only minor development during the period 1989 to 1995 (a slight decrease is estimated). The highest deposition is found for the coastal areas where especially the dry deposition of ammonia from local sources on land contributes to the atmospheric deposition. For the open waters the nitrogen deposition is dominated by wet deposition of nitrogen containing aerosols. Generally it has been found that aerosols contribute to between 60 and 70 % of the atmospheric nitrogen deposition to these waters (Hertel et al., 1996b). The meteorological input data used for these calculations are on a 6 hour time resolution and a coarse 150 km × 150 km grid. A considerably better resolution is used in the present study (see later sections).

2 Structure of the ACDEP-model

Brief description of ACDEP

Only a brief description of the ACDEP-model will be given here, the model is described in details in Hertel et al. (1995) and Asman et al. (1993), and further a short description in Danish can be found in Ellermann et al. (1996). Parts of the following chapter are taken from these references.

Type of transport-chemistry model

The ACDEP-model is a variable scale Lagrangian transport-chemistry model, in which an air parcel is followed along 96 h transport (trajectories) to a given receptor point. The air parcel is represented as a collumn with 10 vertical layers extending from the surface and up to 2 km above ground. The trajectories are calculated based on wind fields (wind speed and wind direction) for the period in question, see section 3.2. During the transport vertical diffusion and chemical transformations take place, concentrations are depleted by dry and wet deposition and the column receives emissions, see figure 2.1.

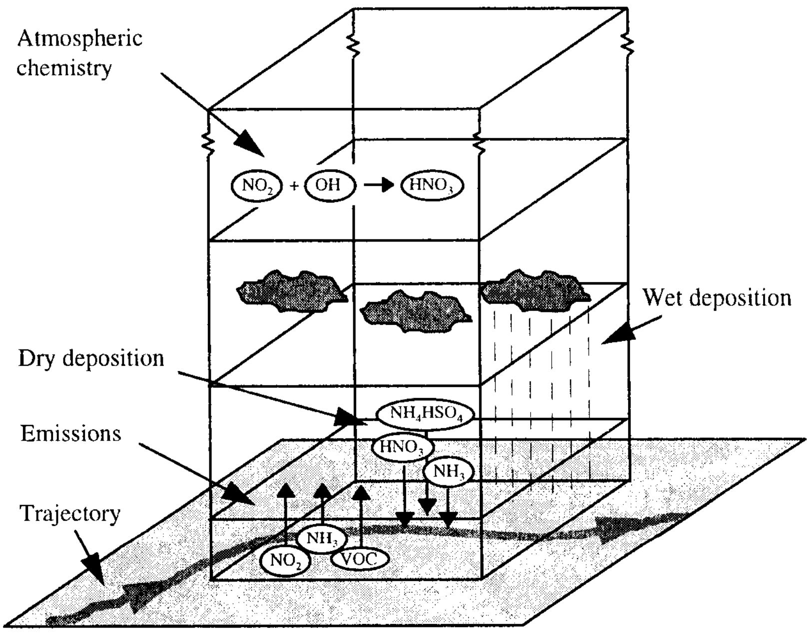

Figure 2.1 An illustration of the concept in the ACDEP-model. A one dimensional vertical air column is advected along 96 h back-trajectories. During the advection the column receives emissions, vertical mixing takes place, species are chemically transformed and/or removed by dry and wet deposition

2.1 Chemical reactions

Chemical mechanism

In any kind of air pollution model simplifications concerning the description of the chemical reactions in the atmosphere are necessary, since the number of chemical compounds (at present more than 3000 species are known) and chemical reactions simply are too large to be handled by computer simulations. The chemical reaction mechanism in the ACDEP-model is based on a slightly modified version of the Carbon-Bond-Mechanism IV (CBM-IV) (Gery et al., 1989a,b). The CBM-IV is originally developed with the aim of describing photochemical pollution episodes, but the mechanism contains also a relatively detailed nitrogen chemistry. The principle in CBM-IV is to let a single model specie represents a group of chemical compounds or a reactive chemical group contained in several chemical compounds. An example is the group of aldehydes, where formaldehyde is described explicitly and a model specie represents all other aldehydes in the model. The main part of alkanes and alkenes are similarly described in model by only two compounds each. The advantage of this procedure is that the calculation time is reduced significantly as the number of compounds is kept at a minimum.

Modified CBM-IV

The modifications of the original CBM-IV concern mainly the addition of the compounds ammonia and ammonium and their heterogeneous chemistry in the atmosphere. This was necessary since these compounds contribute significantly to the nitrogen deposition over sea (Asman et al., 1994; Skov et al., 1996; Hertel et al., 1996a). However, the present description of the heterogeneous reactions (reactions involving both gas phase and aerosol phase compounds) is highly simplified, since aerosol size distributions are not included in the model. Compounds in aerosol phase are assumed all to be contained in aerosols with a diameter of 1 µm. This is a rather crude simplification (see e.g. the discussion in Vignati and Hertel (1996)). Totally the chemical mechanism in the ACDEP-model contains 37 species of which the nitrogen compounds are represented by: ammonia (NH_3), ammonium nitrate (NH_4NO_3), ammonium bisulphate (NH_4HSO_4), ammonium sulphate ($(NH_4)_2SO_4$), nitric acid (HNO_3), nitrogen dioxide (NO_2), nitrate radical (NO_3), dinitrogen pentoxide (N_2O_5), nitrous acid (HONO), peroxy nitric acid (HO_2NO_2), peroxy acetyl nitrate (PAN; $CH_3COO_2NO_2$), organic nitrates and inorganic nitrates different from ammonium nitrate (the complete reaction mechanism can be found in Hertel et al. (1995)).

The NH_3 - NH_4^+ system

For the ammonia and ammonium system a special procedure has been developed (Asman et al., 1994; Hertel et al., 1995). In the model gas phase ammonia reacts with aerosol phase sulphuric acid (H_2SO_4) and gas phase nitric acid (HNO_3) resulting in aerosols containing ammonium (NH_4^+). Therefore ammonium appears in the model as ammonium bisulphate, ammonium sulphate, and ammonium nitrate. A common model assumption is that the reaction between ammonia and sulphuric acid is irreversible, since ammonium in sulphate containing aerosols cannot be released as ammonia again.

$$NH_3 + H_2SO_{4,aerosols} \rightarrow NH_4HSO_4 \qquad (2.1)$$

$$NH_3 + NH_4HSO_{4,aerosols} \rightarrow (NH_4)_2SO_4 \qquad (2.2)$$

The reaction between ammonia and nitric acid is on the other hand a reversible process (Seinfeld, 1986):

$$NH_3 + HNO_3 \rightleftharpoons NH_4NO_3 \qquad (2.3)$$

Assumed saturation in gas phase

Saturation concentration in the gas phase of ammonia and nitric acid is here assumed using an equilibrium product of the gas phase concentrations given by Stelton et al. (1979) and Stelton and Seinfeld (1982). An arbitrary delay before establishment of equilibrium is implemented in the model (see Hertel et al., (1995) for more details). The model contains other inorganic nitrates on or in aerosols besides ammonium nitrate, and these are assumed produced by simple first order processes.

Distribution of NH_4^+ on aerosols

A qualitative analysis has shown that ammonium mainly is associated with sulphate containing aerosols in the Danish background atmosphere (Hertel et al., 1996c). Hertel et al. (1996c) found that typically about 80 % of the ammonium is associated with sulphate containing aerosols and only about 20 % is bound to nitrate containing aerosols. This analysis, that was made on data from the Frederiksborg station in the Ion balance Forest Monitoring Programme, was used to evaluate results from the ACDEP model. The analysis indicate that the ACDEP calculations tend to overpredict the ammonium fraction associated with the sulphate containing aerosols due to a slight overprediction of the sulphate levels. However, this overestimation was not major and is therefore not expected to lead to any significant bias in the model calculations.

Numerical treatment of chemistry

Chemical reactions are numerically solved independently of transport, dispersion and dry and wet deposition, using a splitting procedure. Considering chemistry separately from other processes, the following set of differential equations appear:

$$\frac{dC_i}{dt} = P - LC_i \qquad (2.4)$$

where P and L are the chemical production (including emissions) and loss terms respectively and C_i is the concentration of the i'th chemical component.

The EBI method

For solving mathematically the chemical system in the model, a numerical solver, the Eulerian Backward Iterative (EBI) method, has been developed (Hertel et al., 1993). This method has proven to be both precise and efficient with respect to calculation time. The last is very important as nearly 90% of the calculation time in ACDEP and many other transport-chemistry models is spent on solving the chemical system. The time step used for solving the chemistry is 900s (for more details see Hertel et al. (1993)).

2.2 Horizontal transport and dispersion

In the ACDEP-model a vertical air-column is advected along 96 h back-trajectories. For the calculations in the Danish Nation-wide

Monitoring Programme (see Skov et al., 1996), a 2-D trajectory calculation programme developed at the Norwegian Meteorological Institute (for use in the EMEP-model) was applied on σ-level 0.925 winds (approximately 800 m above the surface) on EMEP grid. However, for the present calculations another procedure (in 3-D) is used, see chapter 3.

Assumptions concerning Horizontal transport

In the treatment of horizontal transport and dispersion a number of different simplifications are made. The total one dimensional air parcel is transported in the same direction and at the same speed. Thereby the model can not account for the variation in wind direction and speed with height, which may be significant. This is therefore a crude simplification of the real conditions in the atmosphere. However, these variations are to some extent accounted for in the applied procedure using 10 different trajectories, see section 3.2. In addition, and also in order to somewhat account for the horizontal dispersion, a simple procedure is applied. The emissions the model column receives at a specific point are calculated as an average over a surface area which increases with distance to the receptor point. The side length of the averaged area is 1/10 of the distance to the receptor point calculated along the trajectory.

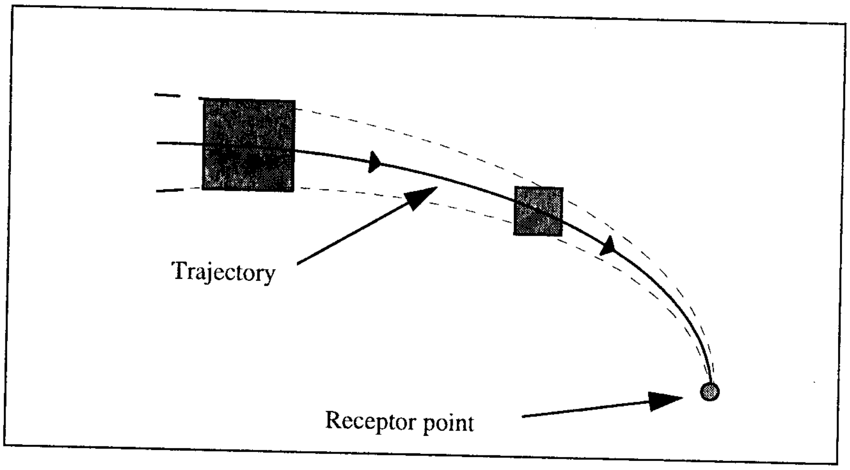

Figure 2.2 The procedure for simulation of horizontal dispersion. The full-drawn line is the trajectory of the model air column. The grey squares illustrate the areas over which the emissions are averaged and added to the air column.

2.3 Vertical dispersion

The vertical mixing of chemical compounds in the atmosphere depends obviously on the meteorological conditions. In the ACDEP-model, the vertical mixing is described by the commonly used K-theory:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left(K_z \cdot \frac{\partial C}{\partial z}\right) \qquad (2.5)$$

where C is the concentration of the compound in question, K_z is the vertical eddy diffusion coefficient, t is the time and z is the height above the surface. The variation of the pressure is disregarded.

Calculation of eddy diffusion coefficients

The eddy diffusion coefficient is computed using the Monin-Obukhov similarity theory with a simple extrapolation to the whole boundary layer:

$$K_z(z) = \kappa u* \frac{z}{\Phi_n\left(\frac{z}{L}\right)}\left(1 - \frac{z}{z_{mix}}\right) \tag{2.6}$$

where u* is the friction velocity, ϕ_n is the similarity function for heat flux (a function of L and z and assumed to be valid also for the chemical compounds), L is the Monin-Obukhov length, κ is von Karmans constant and z_{mix} is the boundary layer height.

Numerical treatment of vertical diffusion

The eddy diffusion coefficient expresses the ability of the atmosphere to mix pollutants. The turbulence vary with height and meteorological conditions (stability). Equation (2.6) is solved numerically using a semi-implicit method (the θ-method; see e.g. Lambert (1991)). Two diffusion time steps are performed for each advection time step to ensure numerical stability of the vertical diffusion algorithm. This is needed due to the fine vertical resolution of the model close to the surface.

2.4 Dry deposition

In the ACDEP-model, the dry deposition flux to the surface is defined as the lower boundary condition for equation (2.5):

$$K_z \frac{\partial C}{\partial z} = V_d C, \quad z = 2m \tag{2.7}$$

where V_d is the dry deposition velocity.

Resistance method

The dry deposition velocity is specific for each chemical compound, and is calculated on the basis of the physical and chemical characteristics of the species in question. The dry deposition velocities are computed using the resistance method, as given in Wesely and Hicks (1977):

$$V_d = \frac{1}{(r_a + r_b + r_c)} \tag{2.8}$$

where r_a is the aerodynamic resistance, r_b is the laminar sublayer resistance and r_c is the surface resistance. The resistance method is based on an analogy to a series of electric resistances. For the calculation of the different resistances, see chapter 5.

Dry deposition of compounds in aerosol phase

At present the ACDEP-model contains only a very simplified description of the processes related to dry deposition of nitrogen species in aerosol phase. The model does not contain aerosol size distributions and for the dry deposition calculations all compounds associated with aerosols are therefore assumed to be contained in aerosols with a fixed diameter of 1 μm. The calculation of the dry deposition of aerosols to water surfaces is based on the parameterization given by Slinn and Slinn (1980). Dry deposition velocities and the resulting removal rates of the different compounds can be seen in Asman et al. (1995) and Ellermann et al. (1996).

2.5 Wet deposition

In-cloud and below-cloud scavenging

The wet deposition is calculated in the ACDEP-model taking into account both in-cloud and below-cloud scavenging (Asman and Jensen, 1993). The in-cloud scavenging is the uptake of gases and aerosols in cloud droplets, and below-cloud scavenging is the similar uptake of gases and aerosols in raindrops during the fall through the atmosphere. Generally the in-cloud scavenging is the most important process due to the longer residence time in the atmosphere of cloud droplets compared to rain drops. When the cloud droplets evaporate without precipitation, the species taken up in the cloud droplets are released back to the surrounding air. Therefore, it is a good approximation to assume that species are effectively removed from the atmosphere during rain events only. In-cloud oxidation reactions are not taken explicitly into account in the model, but simple first order reaction rates are applied to account for wet phase transformations (Hertel et al., 1995).

Height of cloud base

It is assumed that in-cloud scavenging takes place in the model layers between 250 m and 2 km, while below-cloud scavenging takes place in the layers below 250 m (Asman et al., 1993). The anticipated height of the cloud base reflects conditions typical for precipitation events and is estimated from Danish and Dutch synoptic data (Asman and Jensen, 1993).

Skov et al. (1996) found in some cases large differences between model results and observed wet depositions. This was concluded to be due to large uncertainties in the local precipitation (due to the very coarse resolution in meteorological input data). A much finer resolution in precipitation data is used in the present study (see the next chapter).

3 Meteorological input

High quality and resolution in meteorological data

In general, air pollution can be transported over large distances (several thousand kilometres). The pollution is spread by the three-dimensional atmospheric flow over large areas. And the pollution becomes well mixed in the turbulent atmospheric boundary layer (ABL) which has a highly varying height. During the transport, air pollution undergoes photo-chemical reactions which to a large extent are influenced by the meteorological conditions. Thus, in order to calculate the concentrations of the chemical compounds, it is important to employ meteorological data of high quality and resolution.

Earlier calculations performed on EMEP data.

Previously calculations with the ACDEP model have been performed using a 2-D trajectory model and meteorological data from EMEP MSC-W at the Norwegian Meteorological Institute. For the present calculations for Løgstør Bredning, a new version of the model has been developed. This version is based on atmospheric back-trajectories and additional meteorological data calculated by a three-dimensional Lagrangian model (Sørensen, 1993; Jensen et al., 1996; Sørensen et al., 1997b) which again is based on model output from one of the operational numerical weather-prediction (NWP) models (DMI-HIRLAM) at the DMI (Sass, 1994).

3.1 DMI-HIRLAM

The weather forecast model HIRLAM

The HIgh Resolution Limited Area Model (HIRLAM) is a primitive-equation NWP model using a grid-point representation with second-order difference approximations for the spatial derivatives. The horizontal grid is a regular spatially staggered latitude/longitude grid (the Arakawa C grid) in a rotated spherical co-ordinate system. The vertical co-ordinate is a terrain-following hybrid co-ordinate which at the surface is identical with the σ co-ordinate ($\sigma = p/p_s$), where p_s is the surface pressure, and at increasing height approaches the pressure p.

Co-operation concerning HIRLAM

The HIRLAM project (Källén 1996; Kållberg, 1990) was initially started by the Nordic countries and the Netherlands. The project was later joined by Ireland, and partly by France and Spain.

Different model versions of HIRLAM

At the DMI several versions of the HIRLAM model are operational (Sass, 1994), see Figure 3.1. The boundary fields for the large-area Greenland Version (GRV) model are obtained from the global model run by the European Center for Medium-range Weather Forecast (ECMWF). The small-area Danish Version (DKV) is nested in the large-area version (GRV) which provides the boundary values for DKV. Both models are run with the same vertical resolution (31 hybrid levels), cf. figure 3.2. The time step is 4 minutes for GRV and 3 minutes for DKV, and the forecast length is 48 and 36 hours for the GRV and DKV models, respectively.

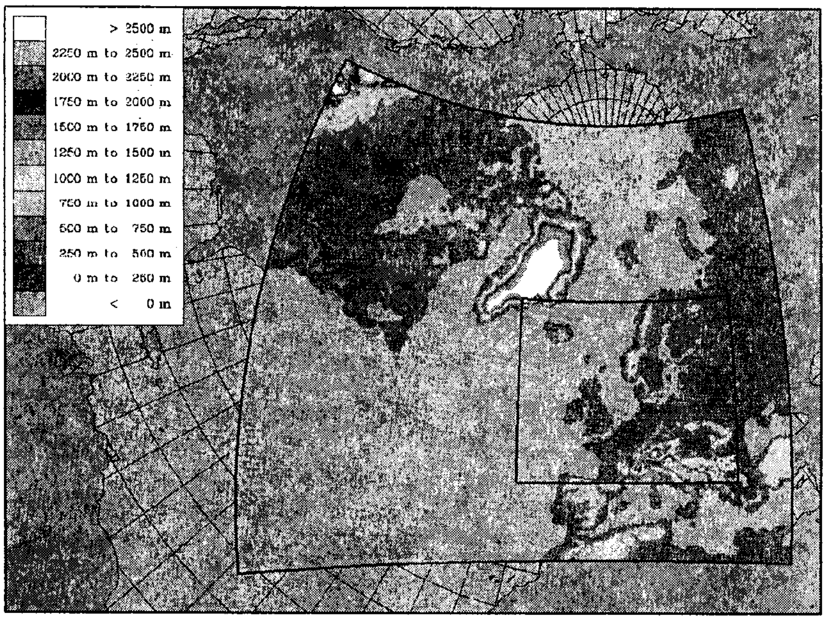

Figure 3.1 Illustration of areas covered by the HIRLAM model operated by DMI. The version with the large area (GRV) is used for forecast in Greenland, and supply the higher-resolution version (DKV) with boundary values. GRV has a horizontal resolution of about 46 km with 194x163 points at each vertical level, and for DKV the numbers are 23 km and 162x136 points.

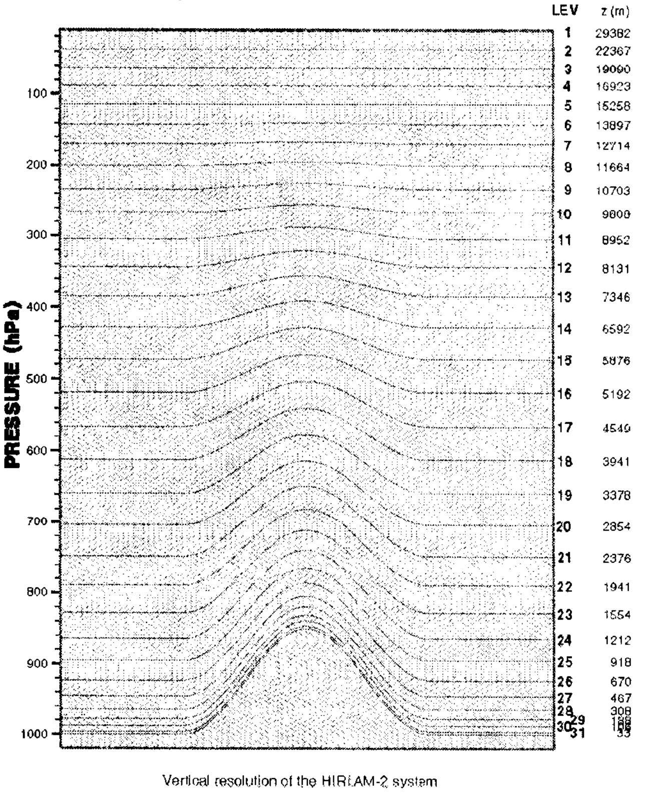

Figure 3.2 Vertical resolution of the DMI-HIRLAM models for a standard atmosphere.

The Forecasting system

The HIRLAM forecasting system consists of pre-processing, analysis, initialisation, forecast, post-processing and verification. Both models (GRV and DKV) are run with their own 6-hourly data-assimilation cycle.

3.2 Trajectories and Meteorological Data

The trajectory receptor points for ACDEP

In order to calculate the nitrogen deposition to Løgstør Bredning for the two campaign periods in 1995, trajectories were calculated arriving each hour at four receptor points in the Løgstør Bredning: Hvalpsund, Løgstør, Feggesund and Nykøbing. Furthermore calculations were performed for measuring stations near Løgstør Bredning: Ulborg, Tange and Anholt. This was done in order to validate the model calculations against observations from the monitoring programme at these stations.

Trajectory model

The atmospheric back-trajectories and additional meteorological data are calculated by a three-dimensional Lagrangian model (Sørensen, 1993; Jensen et al., 1996; Sørensen et al., 1997b) based on model output from the DKV version of the operational DMI-HIRLAM NWP model (Sass, 1994).

Input data for trajectory model

The calculations are based on analysed DKV-HIRLAM data, which are present at each 6 hours. The advection time step for the trajectory calculations is 15 minutes.

Meteorological parameters provided for the transport-chemistry model

In total 15 meteorological parameters were provided for the calculations with the ACDEP model. The position of an air parcel is described by the latitude and longitude co-ordinates as well as the height above ground. The temperature, the relative humidity and the horizontal wind (speed and direction) at the position of the air parcel is used by the ACDEP model. For the vertical profiles, also the surface temperature and the 10-m height wind is necessary. Finally, the height of the boundary layer, the total cloud cover, the precipitation intensity, the sum of latent and potential surface heat flux, and the surface momentum flux corresponding to the position of the air parcel is utilised. The ABL height is calculated by a method based on a bulk Richardson number approach (Sørensen et al., 1997a; Sørensen et al., 1997b). The meteorological parameters used for the ACDEP-model are given in Table 3.1.

Table 3.1 Meteorological data used in the ACDEP-model

Symbol	Description	Height
lon	longitude (radian)	-
lat	latitude (radian	-
z	present height (m)	-
u	wind component (m/s)	z
v	wind component (m/s)	z
tk	temperature (K)	z
rh	relative humidity (%)	z
u10	wind vector (m/s)	10 m
v10	wind vector (m/s)	10 m
ts	temperature (K)	surface
zi	mixing height (m)	-
prep	precipitation (mm/h)	-
cl	cloud cover (%)	-
fh	heat flux (W/m^2)	-
fm	momentum flux (kg/m/s^2)	-

Trajectories at 10 heights

The turn-over time of the large vertical eddies in the atmospheric boundary layer is approximately 15 minutes which is also the basic time step of the meteorological calculations. For a given receptor point and a given arrival time, any back-trajectory arriving at a point within the boundary layer above the receptor point is thus a valid representation of the large-scale transport of the boundary-layer air masses. Such trajectories may vary considerably due to the dependence of the wind on the height above ground. For this reason, a set of ten trajectories is calculated for a given arrival time and a given receptor point. These trajectories arrive at equidistant heights between the ground and the top of the boundary layer above the receptor point.

In figure 3.3 an example is shown of back-trajectories arriving at Tange. The arrival time is 00 UTC on April 25, 1995. Along the trajectories, the ratio of the height above ground to the boundary-layer height is indicated each 6 h.

Atmospheric Dispersion based on DMI-HIRLAM

Run time : 30.08.95, 19:52 UTC

Trajectories:
Arrival point : (9.60, 56.36)
Arrival time : 25.04.95, 00:00 UTC
Period : -4 days 0 hours 0 minutes
Marks each 6 hours

Height/ABL height
a : < 0.1
b : 0.1-0.2
c : 0.2-0.3
d : 0.3-0.4
e : 0.4-0.5
f : 0.5-0.6
g : 0.6-0.7
h : 0.7-0.8
i : 0.8-0.9
j : 0.9-1.0
k : 1.0-1.1
l : 1.1-1.2
m: > 1.2

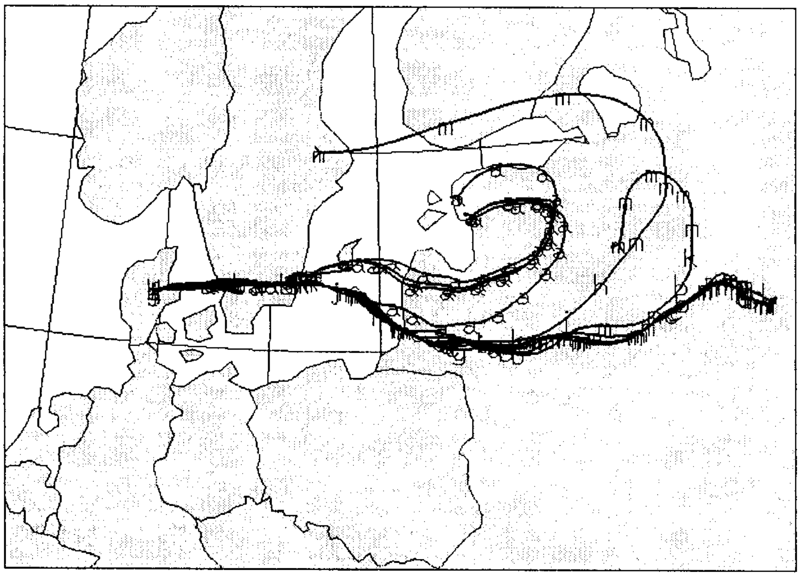

Figure 3.3 Back-trajectories corresponding to ten arrival heights inside the atmospheric boundary layer in a column above the receptor point (Tange). The arrival time is 00 UTC on April 25, 1995. Along the trajectories, the ratio of the height above ground and the boundary-layer height is indicated every 6 hours according to the table on the figure.

A back-trajectory calculation covers at least the four days preceding the arrival time with the exception of trajectories traversing the boundaries of the DKV-HIRLAM area during the calculation.

4 Inventories of emissions to the atmosphere

European emissions provided by DNMI

Inventories of emissions are one of the main input parameters to the model calculations. As the deposition of nitrogen compounds over Denmark does not only originate from Danish sources, inventories for all of Europe is needed. The inventories used in the calculations are the official national submitted data to the Geneva Convention on Long Range Transboundary Air Pollution. These data have kindly been placed at our disposal by the Norwegian Meteorological Institute (Barrett and Berge (1996)). The inventories are covering all of Europe.

The Danish part of the inventories have been compiled by The National Environmental Research Institute. The used emission inventories are based on evaluation of measured data as far as possible, otherwise on calculations from relevant statistics and emission factors.

4.1 Emissions used in the model calculation

Original emission inventories

As a part of the Danish Sea-90 project special emission inventories for NH_3, SO_2, NO_x and NMVOC (Non-Methane Volatile Organic Compounds) for the year 1990 compiled for use in the ACDEP model. These emission inventories contained a detailed 15 km times 15 km grid database for the Danish area. For the surrounding European countries the EMEP emission inventories on 150 km times 150 km grid were used. All used emission inventories are given as yearly emissions grid by grid.

Difference between 1990 and 1994 inventories

The calculations performed under the Nation-wide Danish Monitoring Programme for 1994 showed that the ACDEP-model in general gave an overestimation of the long range transport contribution, due to the fact that the emission inventories for 1990 was used, it was thus decided to update the emission inventories.

Procedure used for updating to 1994

For the model calculations emission data on a regular grid are required. The latest gridded inventories is for the year 1990. But as the inventories for 1990 is rather old, an update using the 1994 inventories has been performed. The update of the gridding were done in the following way. The original distribution of the emissions from the 1990 inventories was kept, and the emissions were updated by multiplying the ratio between the countrywise emissions in 1990 and 1994 from the EMEP (European Monitoring and Evaluation Programme) inventories. This procedure was chosen for simplicity since the new EMEP inventories is given on a new 50 km times 50 km grid (instead of the previous 150 km times 150 km grid, which is slightly shifted from the former grid). A more detailed description is given in Ellermann et al. (1996).

In table 4.1 is shown the emission inventories for the European countries for ammonia and nitrogen oxides. The inventories for 1990 and 1994 are shown, as well as the difference between the two years. It is seen that the differences are small, main differences (reductions) are seen for many of the Eastern European countries. It is assumed that the uncertainty of the distribution of the 1994 inventories over the grid using the 1990 grid, is insignificant, especially taking into account that the uncertainty of the national yearly totals is in the order of 30-40%.

Table 4.1 Inventories for emissions of ammonia and nitrogen oxides, for European countries, 1990 and 1994, and the difference between the two inventories. (Barrett and Berge (1996))

	Ammonia (NH_3)				Nitrogen oxides (NO_x)			
	Gg NH_3				Gg NO_2			
	1990	1994	Diff.	Pct	1990	1994	Diff.	Pct
Albania	30	30	0	0	30	30	0	0
Austria	99	101	2	2	222	177	-45	-20
Belarus	257	257	0	0	285	103	-182	-64
Belgium	79	80	1	1	343	350	7	2
Bosnia & Herzegovina	36	36	0	0	54	54	0	0
Bulgaria	323	146	-177	-55	376	327	-49	-13
Croatia	44	31	-13	-30	83	59	-24	-29
Czech Republic	105	92	-13	-12	742	369	-373	-50
Denmark	140	126	-14	-10	269	272	3	1
Estonia	29	29	0	0	72	43	-29	-40
Finland	41	41	0	0	300	283	-17	-6
France	700	666	-34	-5	1590	1521	-69	-4
Georgia	97	97	0	0	188	188	0	0
Germany	759	622	-137	-18	3071	2872	-199	-6
Greece	78	78	0	0	306	306	0	0
Hungary	176	140	-36	-20	238	183	-55	-23
Iceland	3	3	0	0	20	22	2	10
Ireland	126	126	0	0	115	122	7	6
Italy	384	384	0	0	2053	2050	-3	0
Kazakhstan 1)	18	18	0	0	76	76	0	0
Latvia	38	38	0	0	93	93	0	0
Liechtenstein	0,15	0,15	0	0	0,63	0,54	-0,09	-14
Lihuania	84	84	0	0	158	158	0	0
Luxembourg	7	8	1	14	23	21	-2	-9
Netherlands	236	172	-64	-27	575	526	-49	-9
Norway	39	41	2	5	230	225	-5	-2
Poland	508	384	-124	-24	1280	1105	-175	-14
Portugal	93	92	-1	-1	221	254	33	15
Republic of Moldova	50	50	0	0	35	35	0	0
Romania	371	371	0	0	883	443	-440	-50
Russian Federation 1)	1191	772	-419	-35	2675	1995	-680	-25
Slovakia	62	47	-15	-24	227	173	-54	-24
Slovenia	27	27	0	0	53	66	13	25
Spain	353	345	-8	-2	1188	1227	39	3
Sweden	61	58	-3	-5	411	392	-19	-5
Switzerland	62	60	-2	-3	166	140	-26	-16
The FYR Macedonia	18	18	0	0	2	2	0	0
Turkey 1)	415	415	0	0	175	175	0	0
Ukraine	926	926	0	0	1097	568	-529	-48
United Kingdom	320	320	0	0	2702	2219	-483	-18
Yogoslavia	99	99	0	0	66	52	-14	-21
Sum	8484	7430	-1054	-12	22694	19277	-3417	-15

1) Only the European part

In the present project the best solution would have been to use data for the same year as the measuring campaigns, but data for 1995 were not available at the time, the model calculations had to be made. Emission data for 1994 were then used in the model calculations, knowing that this could introduce an error in the model results.

4.2 The geographical distribution of the Danish emissions

Distribution of Danish emissions on 15 x 15 km^2 grid

The distribution on a 15 km x 15 km grid has been made by dispersing the national totals on administrative units (counties), using available statistics. Within each county the emissions have been distributed using relevant keys, e.g. the emissions of ammonia have been distributed over the agricultural areas and the emissions from individual heating have been distributed over the urban areas.

Detailed information concerning NH_3 releases

In order to get an even better distribution of the ammonia emissions in the counties close to the model area (Viborg and Nordjylland counties), information on the geographical placement of the farm houses and the number of animals at each farm, within the two counties, were obtained from the Ministry of Agriculture. Using this information it would be possible to calculate the emissions from each farm, and thus get a better geographical distribution of the emissions.

Incomplete datasets concerning number of farms and household

However, as it is seen from Table 4.2, the statistics of total animals as registered by the Danish Statistical Office and by the Ministry of Agriculture are rather different. A difference could be expected regarding the number of animals due to differences in the way the numbers are gathered. The Danish Statistical Office uses a sample test on one specific day and uses this to calculate the number of animals in the county. The Ministry of Agriculture base their registration on information from the farmers using questionnaires. However a difference of about 48% in the counts of cattle and of about 83% in the counts of pigs is substantial. Also surprising is a difference in the number of farms with cattle's or pigs. It was not possible, within the available time of the project, to clarify the reasons for these differences, and it was decided to use the statistics from the Statistical Office in the compilation of the ammonia emission inventories, as it is done for the rest of the country. Taking this decision it was not possible to calculate detailed ammonia inventories for the two counties close to the model area.

The used geographical distribution

In the figures 4.1 and 4.2 are shown the geographical distribution of the ammonia and nitrogen oxide emissions, respectively. The more detailed grid for Denmark and closer surroundings is framed in the figures.

The NH_3 emissions reflects the intense farming in Denmark as well as in the Netherlands (these two countries have the highest NH_3 emission per area in Europe).

Due to the high resolution for Denmark, the urban areas can be recognised and therefore only main emission areas in the detailed grid for Denmark is seen in the plot for the NO_x emissions. The high resolution leads to high emission density for these grids.

Table 4.2 Comparison number of animals and farms in Viborg County and the County of Northern Jutland. Data from The Danish Statistical Office (DS) and The Ministry of Agriculture's General Livestock Register (GLR).

Number of animals

	Viborg county			Nordjyllands county		
	DS	GLR	%diff	DS	GLR	%diff
Cattle	281493	145768	-48	397472	221080	-44
Pigs	1377708	233403	-83	1704230	315068	-82

Number of farms with cattle and pigs respectively

	Viborg county			Nordjyllands county		
	DS	GLR	%diff	DS	GLR	%diff
Cattle	4499	1869	-58	5730	2433	-58
Pigs	3808	693	-82	4131	915	-78

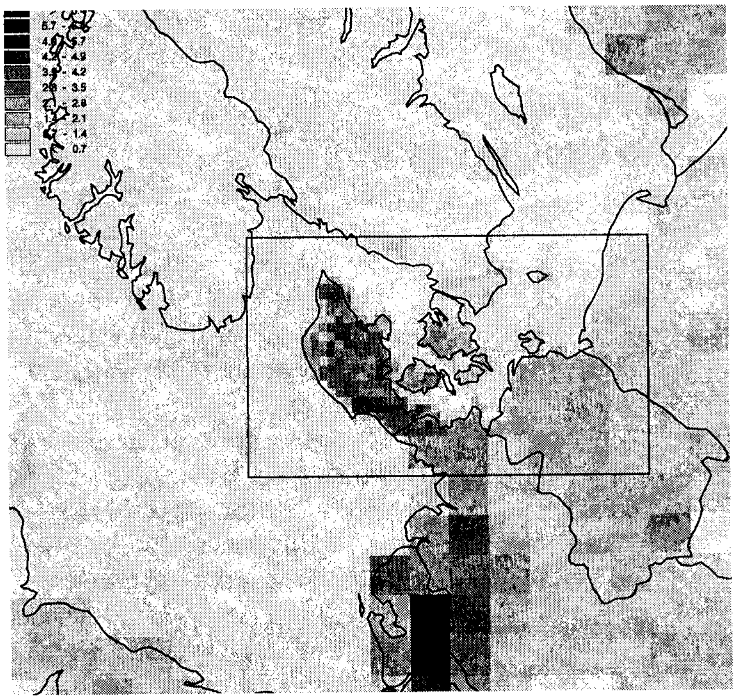

Figure 4.1 Emissions in 1994 of NH_3 (Tonnes (NH_3) per km^2 per year) for a sector including Denmark. The framed area has a finer resolution (15 x 15 km^2) than the rest of Europe (150 x 150 km^2).

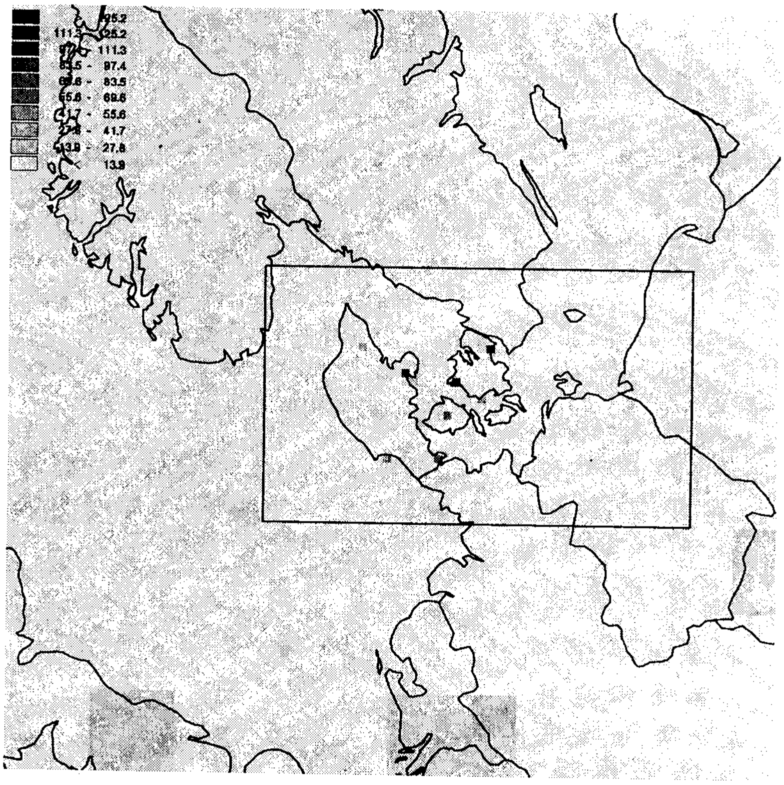

Figure 4.2 Anthropogenic emissions in 1994 of NO_x(Tonnes (NO_2) per km^2 per year) for a sector including Denmark. The framed area has a finer resolution than the rest of Europe.

4.3 The temporal distribution

Seasonal and diurnal variation

The emission inventories are, as mentioned, compiled as national totals with no information regarding the temporal distribution. This has been parameterized, using different simple functions (mainly obtained from the EMEP model) in the atmospheric transport model (see Asman et al. (1993) and Ellermann et al. (1996) for details). The procedures have been used in order to simulate seasonal and diurnal variations of the emissions. The implemented procedures for seasonal variation gives a higher emission of sulphur and hydrocarbons from combustion processes during wintertime and a higher emission of ammonia from agriculture during summertime. The nitrogen oxide emissions are assumed to be evenly distributed over the year. The procedures for diurnal variation generally gives a higher emission during the day.

5 Dry Deposition to the sea

Surface exchange of gases and aerosols

The dry deposition to the sea is part of the wider subject of exchange between the atmosphere and the Earth's different surfaces. A wide variety of processes are involved dependent on characteristics of the surface and the atmosphere and on the species considered. The modelling of surface-atmosphere exchange must be parameterized based on the available information. Presently the sea-atmosphere exchange shall mostly be considered, focusing on the input to the sea.

Section 5.1 is concentrated on the general deposition processes. Løgstør Bredning is, however, a shallow enclosed water for which reason a horizontal inhomogeneity might be relatively more important compared to the situation for larger expanses of sea. Section 5.2 considers the modifications that could be necessary due to this fact.

5.1 General deposition processes

Layers at the air-sea interface

Figure 5.1 shows schematically the different layers of the atmosphere and the sea that must be considered, when estimating the air-sea exchange. The atmospheric boundary layer interacts at the top with the lower part of the free troposphere. The flux, F, continues through the different atmospheric and oceanic sublayers until the deep ocean at the very bottom is reached. The subdivision in layers allows one to focus on the dominant processes in each layer, and then determine the overall flux by matching at the layer interfaces.

Governing differential equation

For detailed evaluation of the fluxes and concentrations of a given species, it is convenient to consider the governing differential equation, that describe the Lagrangian change of concentration of a given species due to changes of flux, divergence and transformations:

$$\frac{dC}{dt} = -\frac{\partial}{\partial z}\left(\langle cw\rangle - V_g C - D_c \frac{\partial C}{\partial z}\right) + \alpha C, \qquad (5.1)$$

where the concentration and the wind velocity vector have been separated into a mean value, C, and a fluctuating part, c, for velocity respectively (U+u,V+v,W+w), where u,v,w is along a x,y,z co-ordinate system with z vertical. In (5.1) only the vertical gradient on the right hand side have been retained, since it almost always is larger than the horizontal ones. Further, a fall velocity, V_g, is allowed for particles (Fairall and Davidson, 1986), and all the concentration changes, due to chemical or other transformation processes, are modelled as first order processes (Geernaert et al., 1997), which then leaves the job of describing α including the relevant processes for the individual species. The Brownian diffusion coefficient is denoted D_c and the turbulent diffusion is described by the eddy correlation, <cw>.

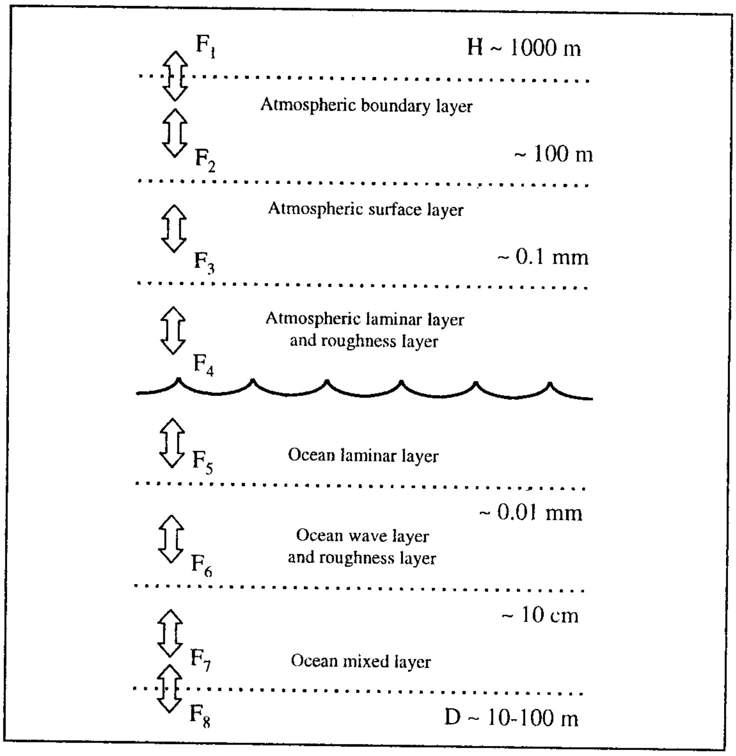

Figure 5.1. Characteristic regimes of and associated fluxes in the atmospheric and oceanic boundary layers (modified from Larsen et al, 1994).

Common assumptions

The common method of deriving the flux from (5.1) is to assume stationary and horizontal homogeneity, forcing the left hand side to zero, and to try to describe the terms on the right hand side in each of the layers of figure 5.1, with matching at the interfaces between the different layers.

In general this approach cannot be carried out analytically. However, a number of special cases, being of interest for the deposition questions reported on here, will be discussed in the following.

Approach in ACDEP

ACDEP models the concentration fields down to two meters above the surface, and calculates the dry deposition based on the concentration at this height. The reference height (in ACDEP the just mentioned two meters) for determination of the deposition flux is in the following denoted z_r.

Parameterization of the flux

In practice the vertical flux is often formulated in terms of concentrations and parameterization coefficients, such as:

$$F_r = v_a\left(C_r - C_\delta\right) = \frac{C_r - C_\delta}{r_a} = V_d C_r, \qquad (5.2)$$

where the flux at reference level is described by the concentrations at reference level and at the top of the laminar atmospheric layer coinciding with the bottom of the turbulence layer, δ. The transfer velocity and the transfer resistance are denoted by V_a and r_a, respectively. They are both denoted subscript a to indicate that they refer to the turbulent atmospheric surface layer. V_d is the deposition velocity and is seen to be operationally simple. Comparison of V_d and the other two parameters show that the information about the gradient of the concentration, not only the transfer characteristics, must be included in V_d, since it is multiplied with a concentration and not a concentration difference.

Transformations

From (5.1) it is seen that if chemical reactions are neglected, the vertical flux becomes constant with height for stationary conditions (dC/dt = 0). Considering the most important layers (the atmospheric surface layer, atmospheric laminar layer and oceanic laminar, wave and mixed layers) the vertical flux can be written as:

$$\begin{aligned} F &= \frac{C_r - C_\delta}{r_a} = \frac{C_\delta - C_{aos}}{r_\delta} = \frac{C_{aos} - C_{wos}}{r_s} \\ &= \frac{C_{wos} - C_{\delta o}}{r_{\delta o}} = \frac{C_{\delta o} - C_{\delta w}}{r_w} = \frac{C_{\delta w} - C_{ro}}{r_o}, \end{aligned} \tag{5.3}$$

which constrains the concentration differences across the different relevant layers, from a point in the atmospheric turbulence layer, z_r, to a point in the ocean mixed layer - z_0. The subscripts refer to atmospheric laminar layer, δ, the two sides of the water interface, aos, wos, the laminar ocean layer, δo, the ocean wave layer, δw, and the ocean mixed and turbulence layer, o.

Resistances are additive

From (5.3) two important conclusions can be drawn: The resistances are additive, that means that if an estimate of the concentrations at heights zr and zr_0 can be obtained , the air-sea exchange can be determined from:

$$F = \frac{C_r - C_{ro}}{r_a + r_\delta + r_s + r_{\delta o} + r_{\delta w} + r_o} \tag{5.4}$$

which shows the modelling convenience of the resistance concept. Another aspect appearing in (5.3) is that for layers, where the resistance is relatively large, the concentration gradient will be large as well, and for layers with small resistances the gradients will be small as well.

Surface resistance for slowly soluble gases

In (5.3) appears also the flux across the interface between air and water phase, involving the surface resistance, r_s. This term reflects the difference in partial pressure of C in air and water phase. For a number of slowly soluble gases, this resistance is very high, and is considered to dominate the sum resistance in (5.4), and hence a large part of the concentration gradient is found here. Examples of such gases are: ozone (O_3), carbon dioxide (CO_2), nitrogen oxide (NO), nitrogen dioxide (NO_2) and dimethylsulphide (DMS).

Resistance to deposition of soluble gases

For some species the water surface represent an ideal sink. This means that r_s is small for these species and C_{wos} is close to zero, keeping C_{aos} close to zero as well. For these species the deposition depends only on atmospheric mixing conditions, and the oceanic layers can be neglected. Examples of such species are: particles and soluble gases such as sulphur dioxide (SO_2) and nitric acid (HNO_3).

Other soluble gases can have an appreciable partial pressure in the water and C_{wos} must be accounted for, when the air-water flux is estimated. Ammonia (NH_3) is an example of such a gas.

Resistance to deposition of particles

For particles, the largest resistance is situated in the atmospheric laminar layer, since the particles must use their small Brownian diffusion coefficient to get through this layer, where therefore most of the gradient is concentrated. Since the diffusion coefficient is reversibly proportional to the particle diameter, while the fall velocity, V_g, is proportional to diameter squared, the exchange rate of particles show a strong dependency on diameter, see figure 5.2, and the deposition rate of particulate species becomes strongly dependent on the size distributions of the species.

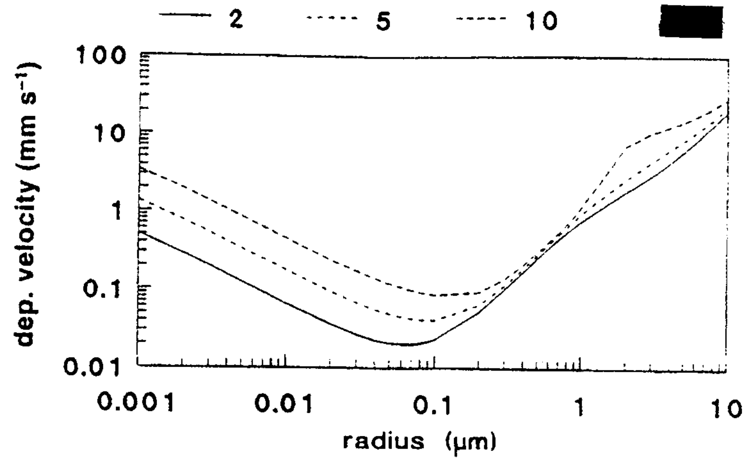

Figure 5.2 Dry deposition velocity, v_D, for particles at sea as function of their radius and wind speed in m s^{-1} (Asman and Larsen, 1996, and Asman et al,1994).

Resistance to deposition of in-soluble gases

For some species the transformation term, αC, in (5.1) cannot be neglected. Examples here are size fractionated descriptions of hygroscopic particles, that change size in response to the humidity gradients (Fairall and Larsen, 1984), HNO_3 and NH_3 that interacts with marine spray (Geernaert et al., 1996 and Geernaert, 1996), and exchange of O_3 in the presence of NO and NO_2.

Treatment of passive tracers

It is instructive to consider the simpler case of passive tracers under homogeneous and stationary conditions, because the exchange processes under these conditions are completely dominated by the turbulence of the atmospheric surface layer, that also for the less simple cases plays an important role for the exchange. For such conditions the relation between the concentration profile and the flux can be described by the standard surface layer concentration profiles (e.g. Larsen, 1993).

$$C(z) - C_0 = -\frac{\langle c'w\rangle}{\kappa u*}\left(\ln\frac{z}{z_o} - \Psi_c\left(\frac{z}{L}\right)\right), \quad (5.5)$$

with the corresponding expression for the velocity:

$$U(z) = \frac{u*}{\kappa}\left(\ln\frac{z}{z_0} - \Psi\left(\frac{z}{L}\right)\right). \quad (5.6)$$

In (5.5) and (5.6) u* is the friction velocity, describing the flux of momentum to the ground, κ is the von Karman constant. z_0 and z_{0c} are the roughness lengths for U and c respectively. This is the height at which the described profiles are assumed to have the surface values of U and c respectively. Ψ are stability corrections (named similarity functions) to the logarithmic profiles. z/L is the stability measure, with L being the Monin-Obukhov length. When the surface is warmer than the air masses above the surface, the atmosphere is thermally unstable, L is negative and Ψ positive. For a surface colder than the air masses stable conditions can be observed, positive L and a negative Ψ. For neutral conditions z/L = 0, Ψ(0) is equal to zero, and the logarithmic profiles prevail.

Aerodynamic resistance as formulated in ACDEP

Comparison between (5.2) and (5.5) shows that r_a for such cases is given by:

$$r_a = \frac{1}{\kappa u*}\left(\ln\frac{z}{z_{0c}} - \Psi_c\left(\frac{z}{L}\right)\right), \quad (5.7)$$

which illustrates the importance of the friction velocity for determination of r_a, and thereby for the turbulent transport governing the atmosphere-ocean exchange. In ACDEP r_a is applied for the lowest 2 m's of the boundary layer.

5.2 Special considerations for smaller enclosed waters

The Løgstør Bredning site

The parameterization of the atmosphere-surface exchange, presented above, have all been integrated in the ACDEP-model used for estimating the atmospheric load of nutrients to Løgstør Bredning, to the extent it has been practically possible. This means that over the Løgstør Bredning the exchange processes are considered to take place over a surface area which includes as well water as land surfaces (the applied land use database has a resolution of 15 km x 15 km). Since the description above has as one of its basic assumptions that the processes are stationary and horizontally homogenous, the fairly small horizontal scale of the Bredning, 20-50 km makes it worth considering the possible modifications of the exchange rate due to transition processes between the land and water surfaces. Some of the exchange rates are so small that the whole stationarity assumption must be considered in serious doubt. However, here the focus is on the possible effect of the abrupt change in surface roughness and stability taking place as the air moves across the coast line.

Internal boundary layers for land - sea wind flow

The response of the flow to a roughness change is usually described in terms of growth of an internal boundary layer within which the flow adapt to the new surface. The characteristics of such a situation can for land-sea situations be described in terms of the deviation between the upstream and the downstream u* values in the wind direction, as depicted in Figure 5.3. Here comparison between the equilibrium values, where the flow close to the surface have fully adapted to the new surface and the initial excursions are shown. As seen the stress initially is smaller than it will be at equilibrium conditions, when the air flow moves from land to sea, while it is opposite when the flow moves from the smoother sea to the rougher land surface. Through (5.7) this translates to the fact that the exchange will be smaller in the transition zones over the sea than predicted by the equilibrium models summarised in section 5.1, while correspondingly it will be enhanced over the coastal land surfaces. The magnitude is difficult to estimate, since it will depend on the local climatology, and moreover it will also vary from one species to another, depending on to what the exchange is controlled by r_a or any of the other resistances in the chain depicted by (5.4).

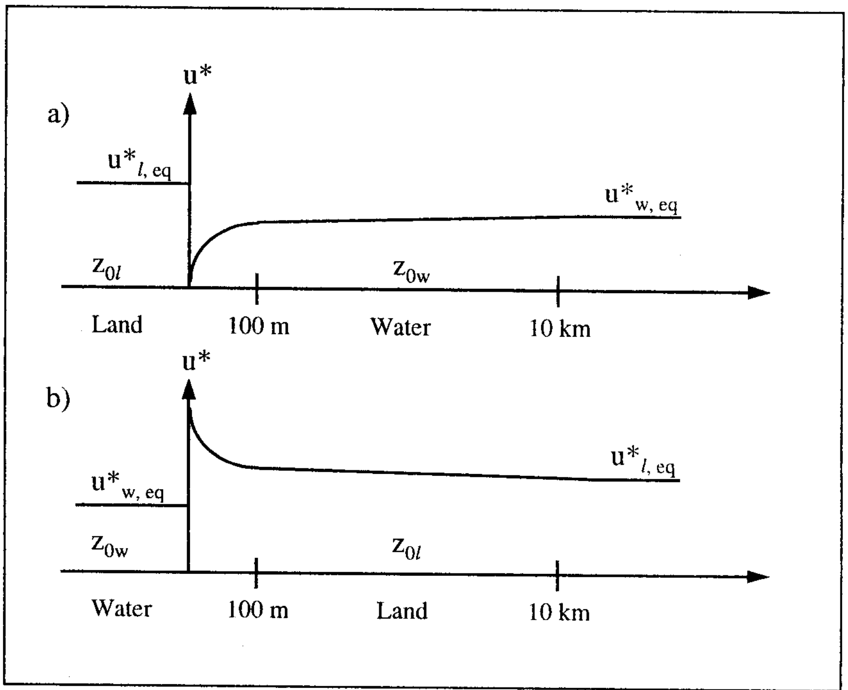

Figure 5.3. Change in the u* values when the air flow moves from a) land across sea and b) sea across land. u* is indicated by w (water) and l (land) on both plots. The equilibrium values of u* are indicated by subscript eq.

Internal boundary layer due to temperature changes

As internal boundary layers grow up due to abrupt change in surface roughness, similarly a change in surface temperature produces growth of internal boundary layers, with similar effects on the friction velocity. Due to the different thermal properties of water and land a fairly abrupt change in surface heat flux and thereby stability will often occur at the shore line. Water will tend to retain its temperature better than the land surface. Hence in the daytime, the stability over land will tend more towards unstable than over water, while at night the land conditions will be more stable. Being in Denmark the condition will most often be close to neutral, meaning that the land-sea transitions are mostly but not completely dominated by roughness changes as described above (Barthelmie et al, 1996).

Cold air mass over warmer water surface and vice versa

When cool air blows over a relatively warm surface a thermally induced internal boundary layer will develop, being much the same over land and water, and hence this induces little average difference between the two surfaces. Correspondingly, when relatively warm air blows across a cooler surface the stratification becomes stable and the turbulence diminishes. Over land the roughness is usually large enough for turbulence to continue to be produced, but the combination of small roughness and stable thermal stratification might initially diminish u* strongly and hence diminish as well the deposition as seen from (5.7). Eventually the air adapt to the underlying surface temperature and the stability approaches neutral again, but initially the exchange rate over water can be strongly reduced relative to the equilibrium conditions described in section 5.1.

In summary of the above, it can be stated that in a transition zone, of widths from a few to tens of kilometres, the exchange rates are likely to be smaller over the water than predicted by the equilibrium expressions used in ACDEP. It is difficult to predict how much without a closer modelling as well as more detailed climatological data. Conversely the coastal land surfaces are likely to experience enhanced exchange relatively to the exchange estimated from the equilibrium expressions.

ACDEP has a special dry deposition procedure for water surfaces

For the calculations of dry deposition of both gases and aerosols, taking into account the special conditions over sea, a special procedure was developed during the Sea90 project. In this routine the roughness length and the friction velocity over the sea surface is determined using an iterative procedure, (see Hertel et al. 1995, for details). As it was mentioned in the introduction the parameterization of the dry deposition of aerosols to sea surfaces has been revised in the ACDEP-model. Routine comparisons to the generally accepted dry deposition velocities (Slinn and Slinn, 1980) have previously shown a general underestimation by the ACDEP-model. The change of the model was introduced in the National Background Air Quality Monitoring Programme calculations (Skov et al., 1995) and resulted in considerably higher dry deposition of aerosols than earlier estimated, and thereby also in much higher nitrogen depositions.

6 Calculation, verification and analysis of the model results

Model output produced for water quality model

The ACDEP-model calculates the air concentrations (at the various altitudes corresponding to the 10 layer heights) and the dry and wet depositions of 37 chemical compounds (Hertel et al., 1995). The air concentrations at surface level of the sulphur and nitrogen compounds are used to test the model calculations against measurements, while the deposition of nitrogen is passed on as input to the hydrographic water quality model MIKE 21.

Calculation period

Calculations have been performed for the campaign periods (17 - 30 April and 7 - 19 August 1995) for receptor points representing the 7 localities: Ulborg, Tange, Anholt, Feggesund, Løgstør, Nykøbing and Hvalpsund.

Test sites from monitoring programmes run by NERI

The first site is a station under the programme 'Atmospheric Deposition and Ion fluxes in Forest Ecosystems', the next two sites coincide with monitoring stations that are common to The Nation-wide Danish monitoring program and the Monitoring Programme of the Action Plan for the Aquatic Environment, and the model results are compared with measurements made at these stations. The position and characterisation of these three stations are given in table 6.1.

Table 6.1 Position and characterisation of the monitoring stations for air concentrations.

Station	UTM x co-ordinate	UTM y co-ordinate	Landscape
Anholt	657	6287	coast
Tange	537	6246	forest
Ulborg	465	6239	forest

Receptor points at Løgstør Bredning

The last four localities cover the hydrological in- and outflows to Løgstør Bredning (Feggesund and Løgstør to the North, Nykøbing and Hvalpsund to the South - see fig 6.1), for which reason they are used as receptor points in MIKE 21.

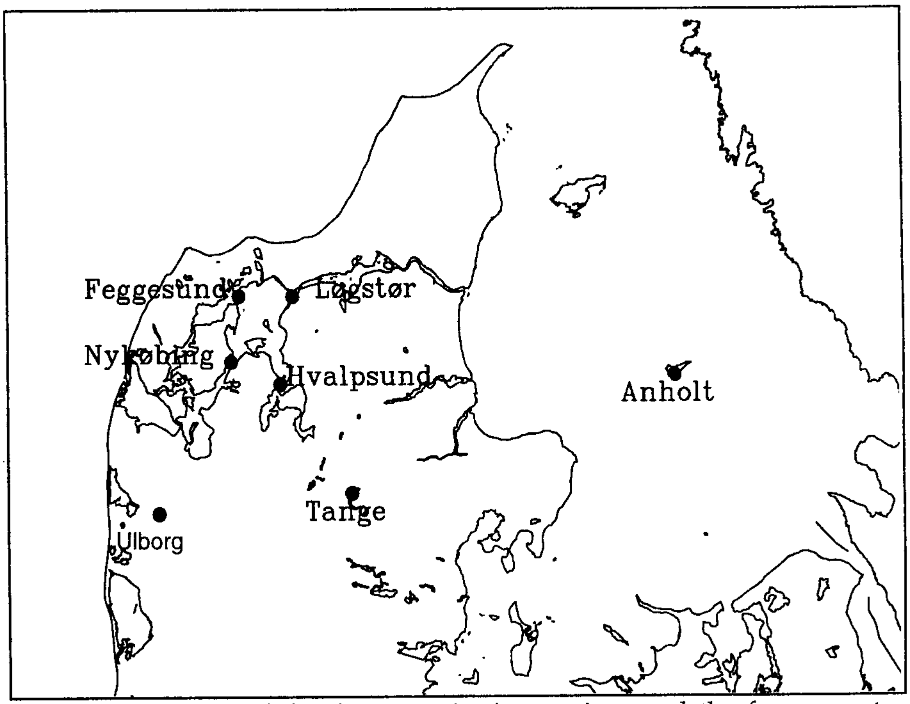

Figure 6.1 Position of the three monitoring stations and the four receptor points in Løgstør Bredning.

Measured compounds used for the comparison

At the monitoring stations the following compounds (among others) are collected in gas- and aerosol samples on a daily basis using the filterpack network (for an extensive treatment of the measuring methods see Ellermann et al. (1996)).

Gas phase compounds

Ammonia (NH_3), nitrogen dioxide (NO_2), nitric acid (HNO_3) and sulphur dioxide (SO_2).

Aerosol phase compounds

Ammonium (NH_4^+) nitrate (NO_3^-) and sulphate (SO_4^{--}).

No separation between HNO_3 in gas phase and NO_3^- in aerosol phase

The filterpack method does not allow for a proper separation of nitric acid (HNO_3) and particulate nitrate (NO_3^-) (Ellermann et al. 1996) and therefore comparison is performed for the sum of these two compounds (hereafter named total nitrate).

Wet deposition measurements

Monitoring data regarding the wet deposition of ammonium and nitrate are collected using precipitation collectors - bulk sampling collectors (see Ellermann et al., 1996). The precipitation samples are half month samples. These data are therefore not useful in a comparison between calculated and measured data for such short periods as the campaign periods in this project.

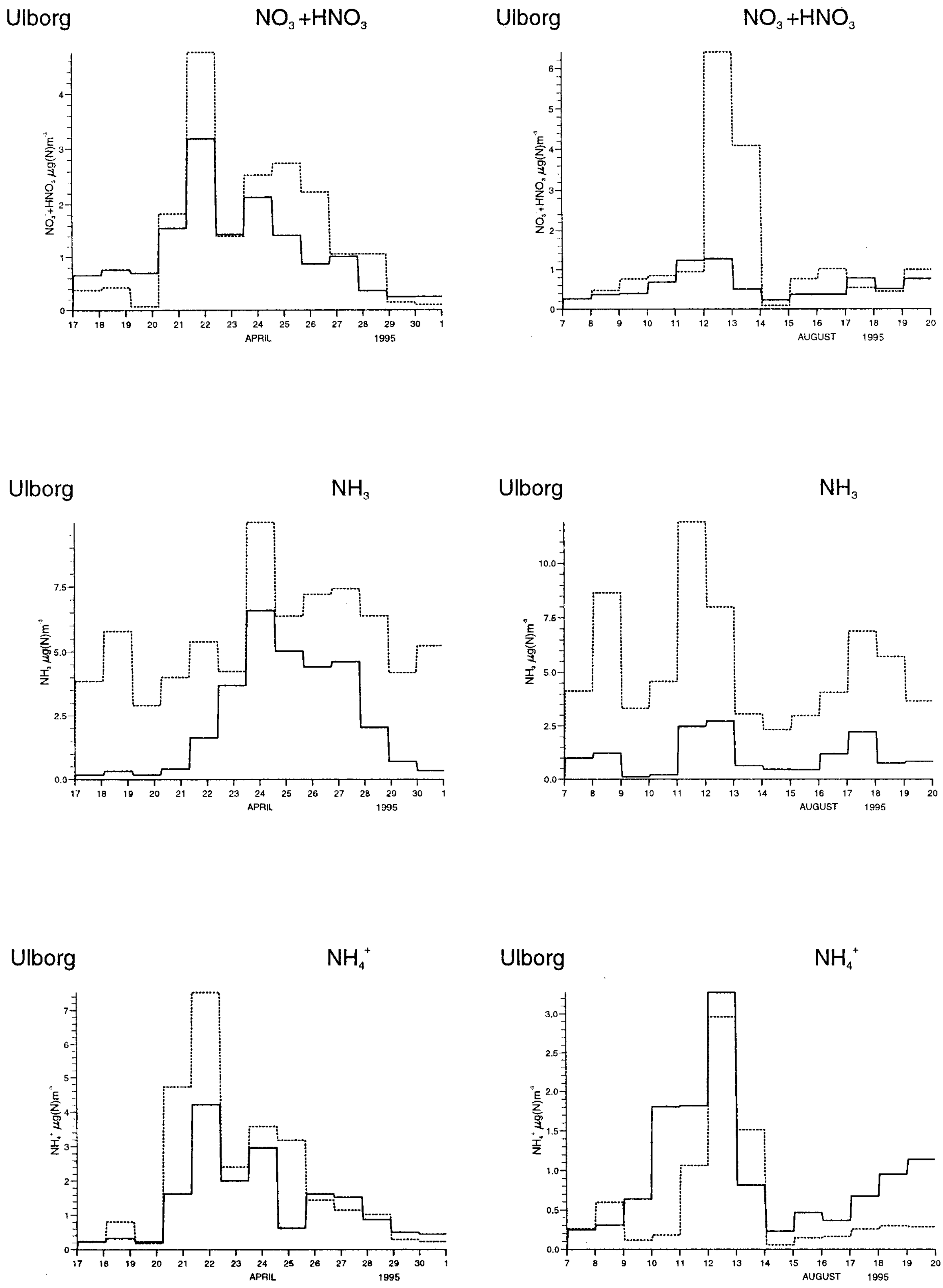

Figure 6.2 Comparison between calculated (---) and observed (—) levels of total nitrate (HNO_3 + NO_3^-), ammonia (NH_3), ammonium (NH_4^+), nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and sulphate (SO_4^{2-}) for the monitoring station Ulborg during the periods 17 to 30 April and 7 to 19 August 1995.

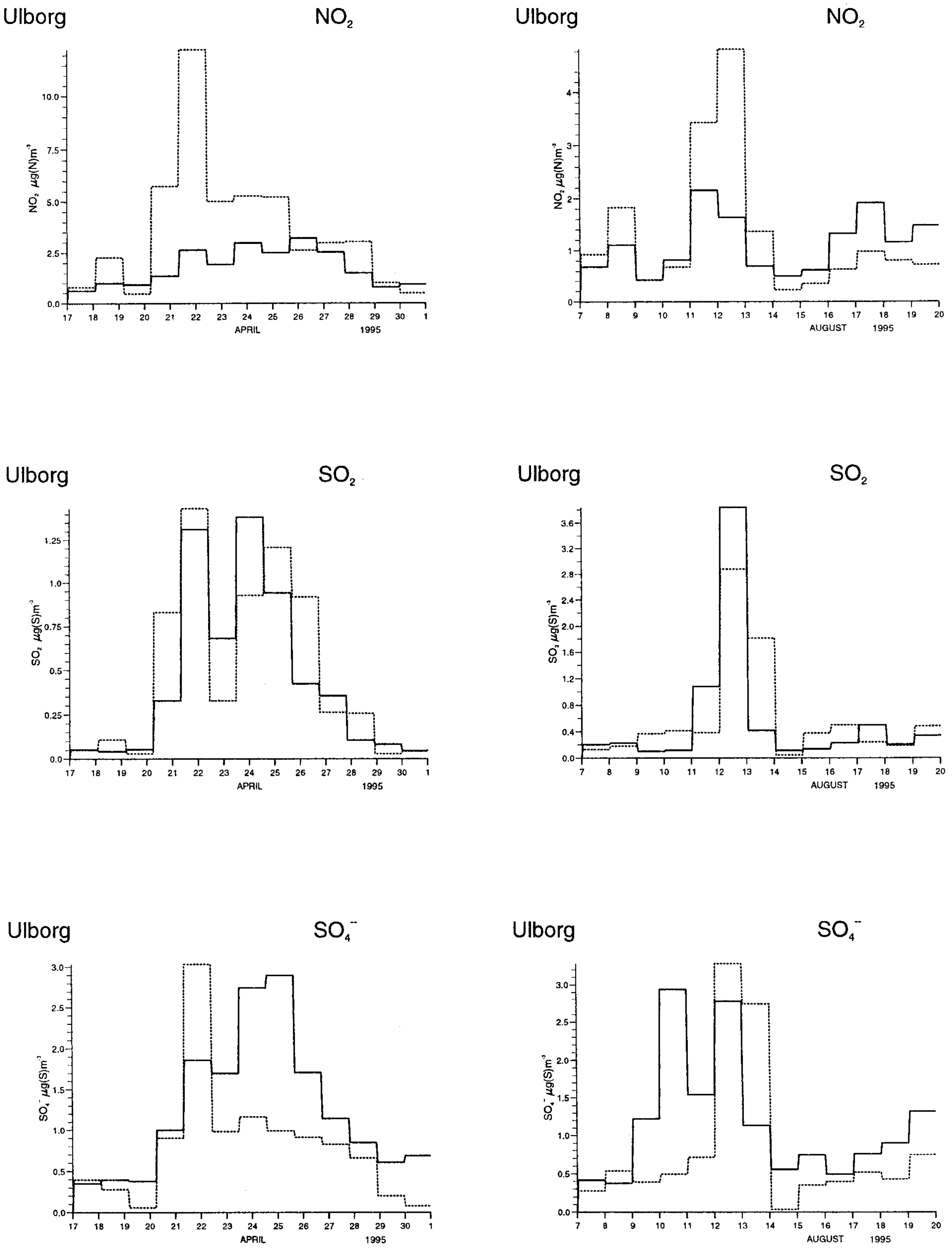

Figure 6.2 Continued.

Comparison for the Ulborg site

In the present report only the comparison for the Ulborg station is presented. The results are given in figure 6.2. In Skov et al. (1996) an extensive examination of the ACDEP-model have been made for these and other three EMEP (European Monitoring and Evaluation Programme) stations for the entire period 1989 to 1995 using EMEP meteorological data. The results from these comparisons showed that the ACDEP-model in general reproduced the observed aerosol phase NH_4^+, SO_4^- and total nitrate concentrations fairly well. The agreement was less good for the wet depositions, probably due to uncertainties in the precipitation amounts.

NO_2

Earlier comparisons have shown that the model has a tendency to underestimate NO_2 levels during summer (Hertel et al., 1995), which probably is due to a too rapid conversion of NO_2 to HNO_3. In the present comparison the model reproduces reasonably well the NO_2 levels, except for the second half of the august period, where a considerable underestimation is seen. No explanation for this underestimation has been found.

NH_3

For the NH_3 concentrations, the local emissions govern the levels. Since that data for the NH_3 emissions are subject to large uncertainties this is also reflected in an, in some cases rather poor, agreement between observed and computed concentrations. However, in the present case the model does not perform considerably worse for NH_3 than for the other compounds.

NH_4^+

Earlier comparisons have shown that the ACDEP- model in general reproduces NH_4^+ concentrations reasonably well, especially when monthly mean values are concerned. When shorter averaging time is used, an uncertainty in a single trajectory may lead to a substantial error. This uncertainty should to some degree have been eliminated by the present procedure with 10 different trajectories being used (see section 3.2). However, the present comparison shows that the NH_4^+ concentrations are generally underestimated in the current calculations, by typically a factor 2.

Estimates of the uncertainties in model calculations

In Skov et al. (1996) the uncertainties in the model calculations for the yearly nitrogen deposition was estimated to about 40 % for open sea and to about 60 % for the coastal waters, with the largest uncertainties associated with the wet depositions concerning both regions. The results in Skov et al. (1996) were presented as monthly mean values for which the uncertainties were even higher. The present sites are certainly coastal waters and the total computation periods are two weeks each presented as 24 hour mean values. Therefore the uncertainties of the present results are considerably larger than in Skov et al. (1996). Based on the presented comparison the uncertainty in the computed nitrogen depositions is estimated to be in the order of a factor 2 given on 24 h mean values.

7 Calculated nitrogen deposition to Løgstør Bredning

In the present chapter the results of the model calculations are summarised. These results cover deposition of the primary pollutants ammonia (NH_3) and nitrogen oxides ($NO_x = NO + NO_2$) and the reaction products of these compounds in the atmosphere (so-called secondary pollutants); aerosol phase NH_4^+ (bound to nitrate or sulphate aerosols) and NO_z (e.g. HNO_3, N_2O_5, NO_3, HNO_2, HNO_4 etc. in gas phase and NO_3^- in aerosol phase).

Tables 7.1 and 7.2 show the deposition of NH_3, NO_x, NO_z and NH_4^+ for the April and August campaigns respectively. The main difference between these two periods lies in the amount of precipitation, which is considerably higher in April. It also appears from the table that NO_x is not contributing to neither dry nor wet deposition to water surfaces (NO_2 is only dry deposited to land surfaces covered by vegetation).

Figures 7.1 and 7.2 show the distribution of the nitrogen deposition during the two campaigns; Figure 7.1 the distribution between dry and wet deposition (again reflecting the difference in precipitation during the two periods) and Figure 7.2 the distribution on compounds, that in accordance with table 7.1 and 7.2 shows a large contribution from locally emitted NH_3.

Table 7.1 Mean calculated deposition in kg nitrogen per km^2 per day for the April campaign.

	NH_3	NO_x	NO_z	NH_4^+	Total
Dry	0.68	0.00	0.05	0.06	0.79
Wet	9.86	0.00	2.79	1.23	13.87
Total	10.54	0.00	2.84	1.28	14.66

Table 7.2 Mean calculated deposition in kg nitrogen per km^2 per day for the August campaign.

	NH_3	NO_x	NO_z	NH_4^+	Total
Dry	0.66	0.00	0.04	0.05	0.75
Wet	1.64	0.00	0.18	0.15	1.97
Total	2.31	0.00	0.22	0.20	2.73

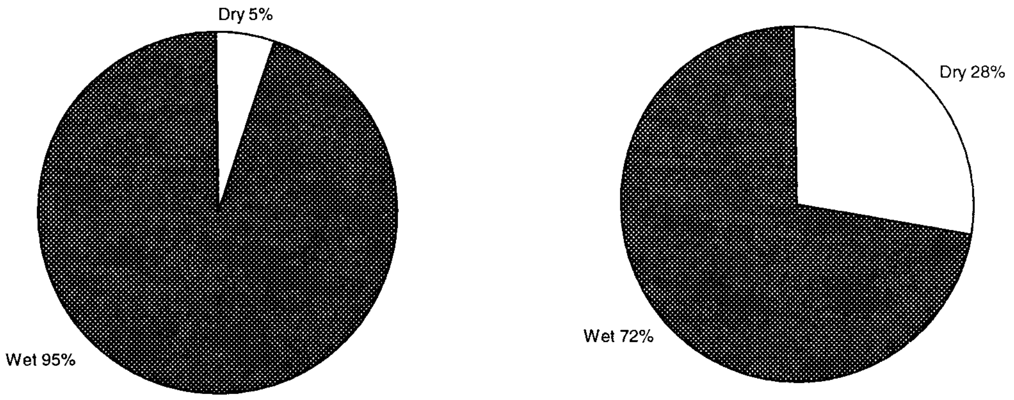

Figure 7.1 The calculated distribution on dry and wet -N deposition for the April campaign (to the left) and the August campaign (to the right).

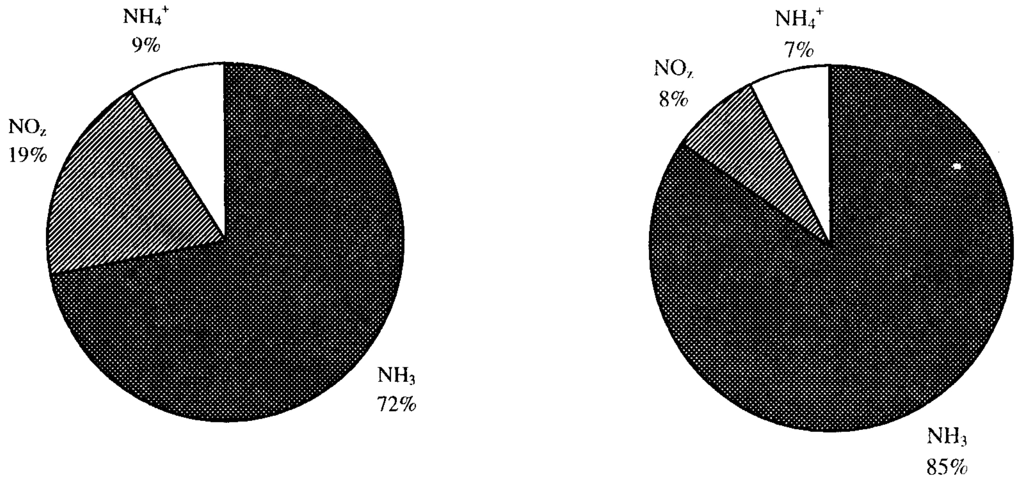

Figure 7.2 The distribution on different deposited compounds for the April campaign (to the left) and the August campaign (to the right).

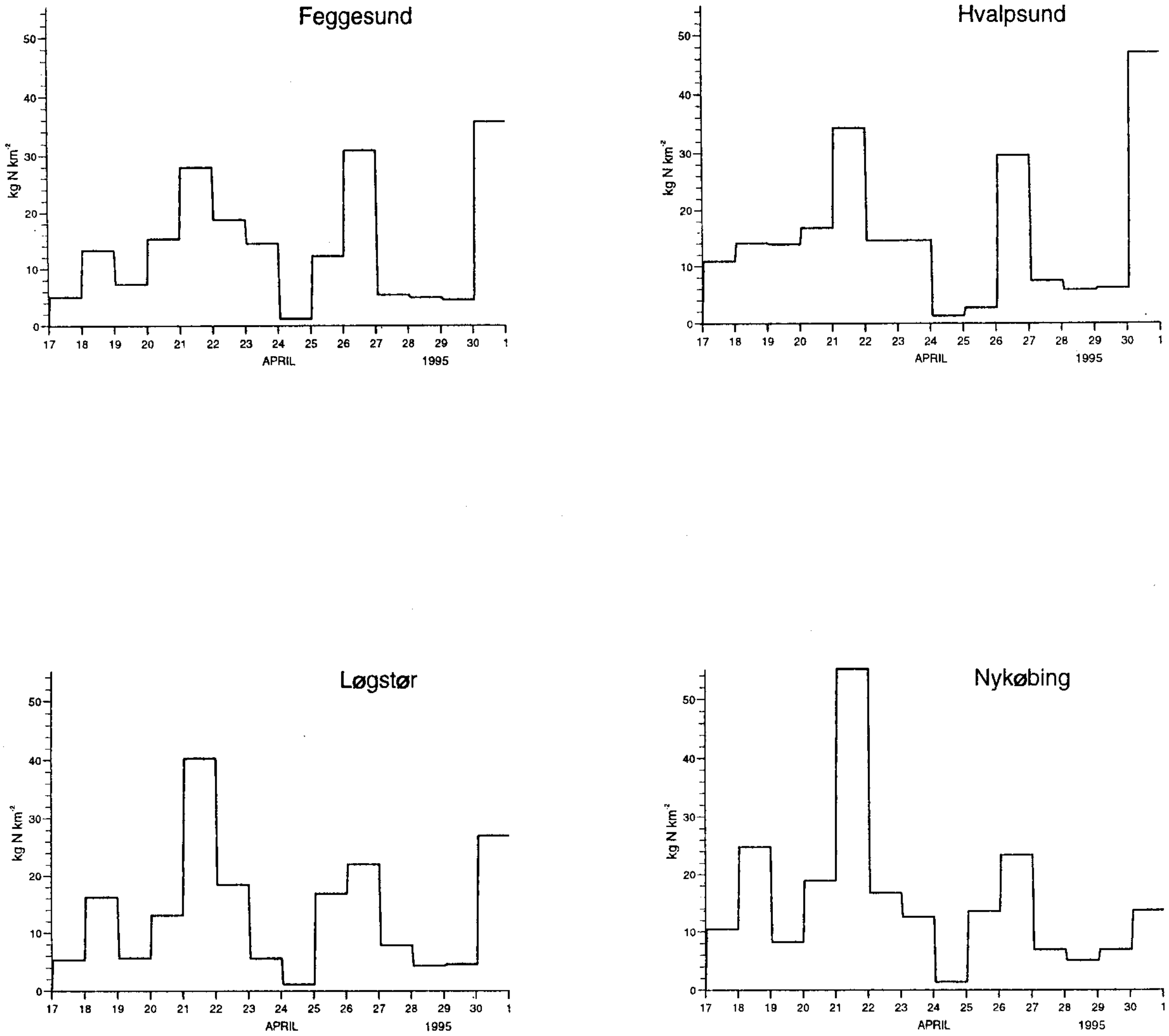

Figure 7.3 Nitrogen deposition in kg -N per km^2 calculated by ACDEP for the campaign in April.

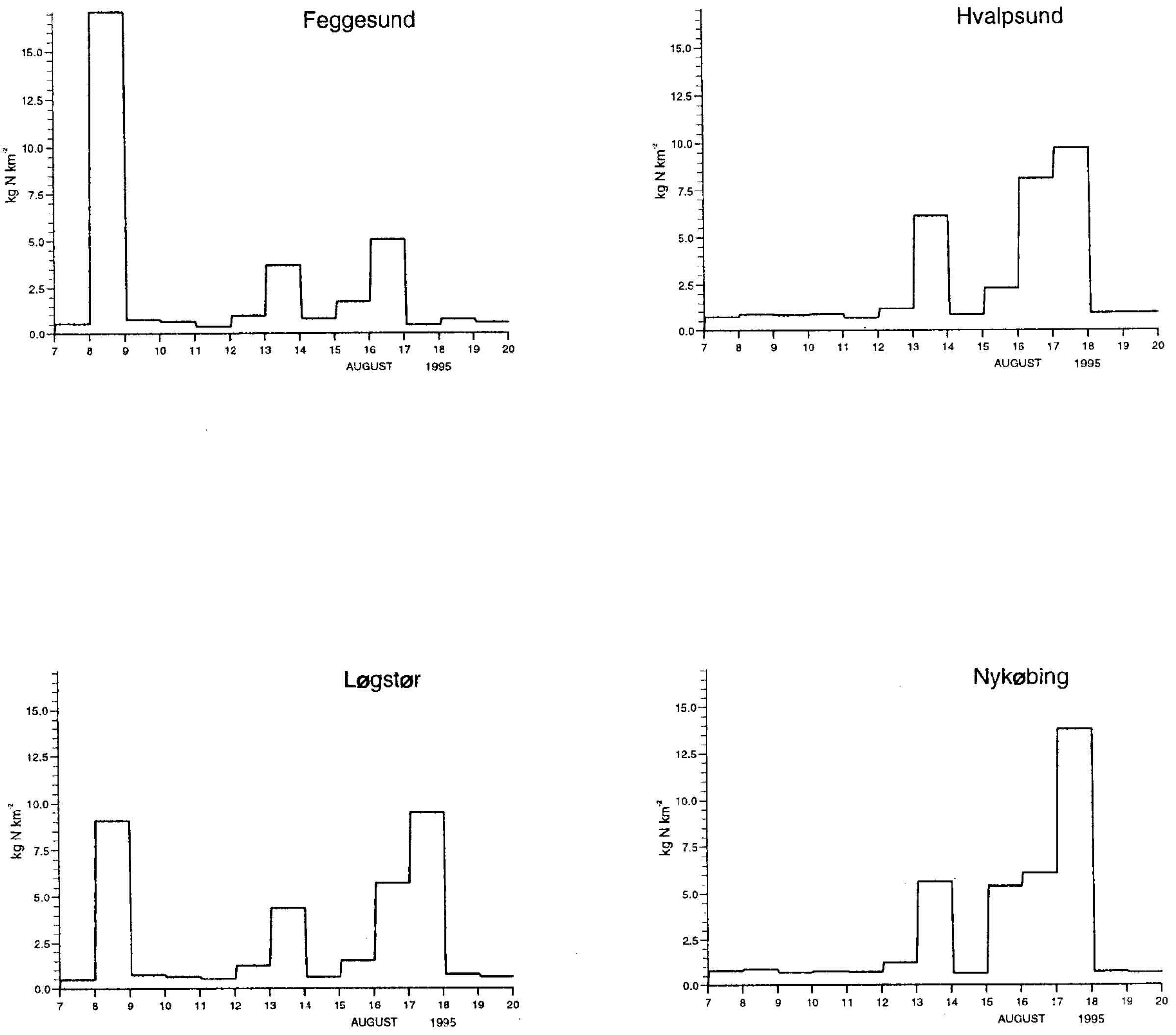

Figure 7.4 Nitrogen deposition in kg -N per km^2 calculated in the present work with ACDEP for the campaign in August.

Figure 7.3 and 7.4 show the calculated time evolution in nitrogen deposition to Løgstør Bredning for the two campaign periods in April and August respectively. It is seen that the deposition was considerably higher during April than during August due to differences in precipitation. On the average the deposition was approximately 15 kg N per day in April and approximately 3 kg N per day in August.

The difference in precipitation was reflected also in previous calculations (Skov et al., 1996) as shown in the ratio in contributions from respectively dry and wet deposition, see Figure 7.5. The contribution from dry deposition is dominated by deposition of locally emitted NH_3. Note that these calculations are performed using EMEP meteorological data

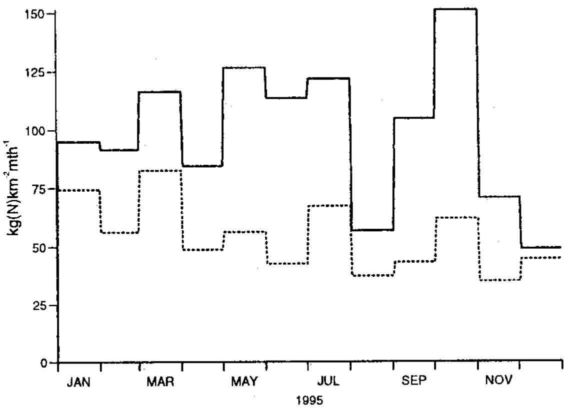

Figure 7.5 Calculated monthly mean nitrogen deposition to the four receptor points in Løgstør Bredning. Full line is total deposition, broken line is dry deposition. The calculations are taken from the results obtained in the Nation Wide Background Monitoring Programme (see Skov et al., 1996)

The yearly nitrogen load to the total Limfjord system has been calculated to vary between 1.4 and 2.2 tonnes N per km^2 per year in the period 1989 to 1995 with no systematic trend over the years (Skov et al., 1996). The year to year variations were here found mainly to be due to variations in the amount of precipitation. Similarly to the year to year variation, no systematic seasonal variation could be detected. Again this was due to the considerable contribution from wet deposition of mainly aerosol bound nitrogen compounds. Figure 7.5 shows the seasonal variation in monthly mean nitrogen deposition to the four receptor points in Løgstør Bredning taken from calculations performed under the framework of the Danish Monitoring Programme. The results show a minimum in August and again in November - December, but otherwise a rather constant load of 100 to 150 kg N per km^2 per month.

A similar calculation performed without Danish pollution sources (not shown here) shows 30 to 40 % lower loads, mainly due to the contribution from dry deposition of locally emitted NH$_3$.

8 Discussion and conclusions

A new modelling system, for calculating nitrogen deposition to Danish fjord systems, has been established partly in the present project. This system is a combination of DMI's 3-D trajectory model together with a program for selecting meteorological parameters from the HIRLAM model and NERI's transport - chemistry model ACDEP.

An evaluation of the new model system - trajectory model/HIRLAM/ACDEP - was performed by comparing model results to measurements from monitoring data. Unfortunately the calculation periods were too short for a proper analysis of the model performance. Earlier estimates of the uncertainties of ACDEP calculations performed on meteorological input from EMEP is in the order of 60 % for the yearly mean nitrogen depositions to the fjord systems. Based on these estimates and the comparisons for the two 14 day periods the uncertainties in the present calculations of nitrogen deposition to Løgstør Bredning has been estimated to be about a factor 2.

Model calculations of nitrogen deposition to Løgstør Bredning during the two campaign periods have been performed for 4 receptor points in the fjord system. These calculations show a total deposition of 166 kg per km^2 during the campaign in April and 33 kg per km^2 during the campaign in August.

Further calculations performed under the Danish Background Monitoring Programme for the whole year 1995 has been presented in order to evaluate the seasonal variation and yearly nitrogen load to the Løgstør Bredning. These results show an atmospheric nitrogen load in the order 60 to 180 kg N per km^2 per month and a total atmospheric load in 1995 of 1.4 ton N per km^2 per year.

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Addresses:

URL: http://www.dmu.dk

National Environmental Research Institute
Frederiksborgvej 399
PO Box 358
DK-4000 Roskilde
Denmark
Tel: +45 46 30 12 00
Fax: +45 46 30 11 14

Management
Personnel and Economy Secretariat
Research and Development Secretariat
Department of Atmospheric Environment
Department of Environmental Chemistry
Department of Policy Analysis
Department of Marine Ecology and Microbiology

National Environmental Research Institute
Vejlsøvej 25
PO Box 413
DK-8600 Silkeborg
Denmark
Tel: +45 89 20 14 00
Fax: +45 89 20 14 14

Department of Lake and Estuarine Ecology
Department of Terrestrial Ecology
Department of Streams and Riparian areas

National Environmental Research Institute
Grenåvej 12, Kalø
DK-8410 Rønde
Denmark
Tel: +45 89 20 17 00
Fax: +45 89 20 15 14

Department of Landscape Ecology
Department of Coastal Zone Ecology

National Environmental Research Institute
Tagensvej 135, 4
DK-2200 København N
Denmark
Tel: +45 35 82 14 15
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Nr. 177: Ferske vandområder. Vandløb og kilder. Vandmiljøplanens Overvågningsprogram 1995. Af Windolf, J. (red.). 228 s., 125,00 kr.
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