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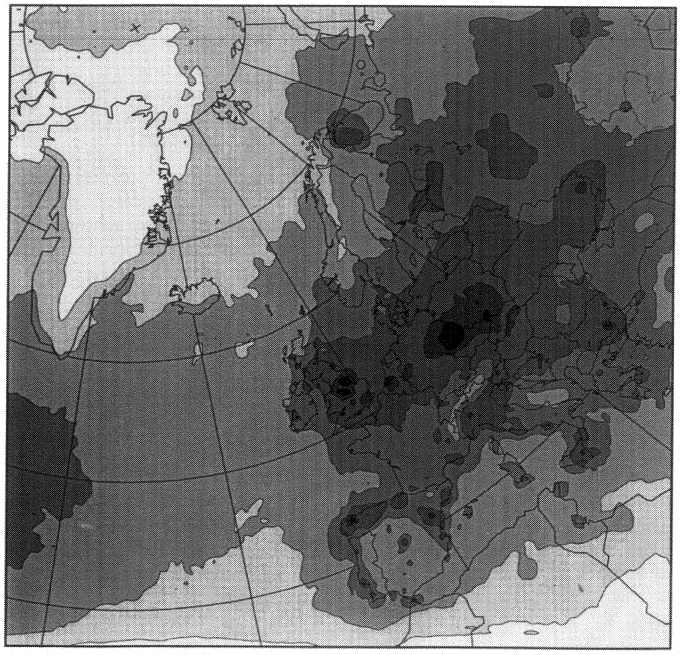
Some preliminary results on transport and deposition of nitrogen components by use of the Multilayer Eulerian Model.



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Some preliminary results on transport and deposition of nitrogen components by use of the Multilayer Eulerian Model.

by

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Preface and Acknowledgements

This note on the inclusion of nitrogen chemistry into the multilayer Eulerian model at MSC-W was prepared for the nineteenth session of the Steering Body of EMEP. The results presented here must be regarded as preliminary and continued development of the model will take place. The present development is a step in the direction of coupled acid rain and photochemical models which are aiming toward the support of future work on multi-pollutant protocols.

The work has largely benefitted from a financial support by the Nordic Council of Ministers to DNMI on the development of coupled acid rain and photochemical models.

The calculations were facilitated by access to the CRAY Y-MP at SINTEF in Trondheim provided by the Norwegian Research Council.

Finally, the authors would like to thank Mr. David Simpson for his assistance during the implementation of the chemical scheme, Dr. Terje Berntsen at the University of Oslo for provision of boundary and background concentrations and Mr. Helge Styve for his continous technical support.

1.0 Introduction

At the Western Meteorological Centre (MSC-W) of EMEP a project on the development of a multilayer Eulerian model is carried out. The background for this project is a need for more detailed information on depositions to the European ecosystem than what has so far been delivered from MSC-W. Additionally, a long term goal for the work under the Convention is to introduce multi-pollutant protocols where both the acidification and the photochemical oxidant problems are coupled. Clouds are key parameters in coupling the acidification to oxidants and multilayer models are needed in order to describe the clouds properly (see Seigneur and Saxena, 1988, Berge, 1993, Jonson and Isaksen, 1993).

In the first phase of this project we have introduced the chemical scheme already applied in the routine Lagrangian model (Hov et al., 1988, Tuovinen et al, 1994). The numerical treatment of the chemistry follows the scheme utilized in the ozone-model (Simpson, 1993, Simpson et al., 1993) in order to be prepared for the inclusion of the photochemistry at a later stage. At this stage we are able to present results for a 10 days period in July 1990, and the first analysis of the model results are important in order to give guidance on the quality of the model at this stage. In the next phase of the development clouds will be included in the model as a natural step toward coupling to the photochemistry.

The present version of the model is so far restricted to a limited number of components by computational constraints. Efforts are therefore for the moment put into implementing numerical schemes that increase the efficiency of the model. Additionally, usage will later be made of the Massive Parallel Cumputing technics described in Skålin et al. (1995) that so far has been applied successfully to the one year sulphur calculations presented in Jakobsen et al. (1995).

2.0 A brief description of the eulerian air pollution model.

The Eulerian air pollution model has already been described elsewhere (Berge, 1993; Jakobsen et al., 1995). Thus, only a brief description is included here. The horizontal domain is defined so that the 50 km grid squares coincide with the original EMEP grid presented by Sandnes (1993). A major part of the model domain can be seen in Figures 1-7. Altogether 20 layers are included in the vertical. To obtain high resolution near the ground, where most of the pollutants are transported 9 layers are placed below about 2 km.

Archived meteorological data are employed every 6 hours. For intermittent timesteps, the meteorological data are interpolated linearly.

The advection is solved using the Bott scheme (Bott, 1989 a and b). In the horizontal a fourth order version of the scheme is applied, whereas in the vertical a second order version is used. Because of the high vertical resolution close to the ground, we are limited to a timestep of 5 minutes only. The vertical diffusivity is derived from the basic meteorological parameters, following the description given by Jakobsen et al. (1995).

2.1 Chemistry

As a reference a model experiment is set up where, unless where otherwise noted, the chemistry formulation follows the parameterization previously applied in the Lagrangian acid deposition model (Hov et al. 1988, and references therein). Altogether 10 components are included. The chemical reactions included in the model are listed in Table 1.

The ratio between NO and NO_2 is to a good approximation determined by reaction 1 and 2. Under clear sky conditions the dissociation rate for NO_2 (reaction 1) is assumed constant in the vertical. Below clouds the dissociation rate is reduced by a factor of 0.5 times the fractional cloud cover. The production of NO_2 (reaction 2) is dependent on the ozone concentration. Ozone is at present not calculated in the model. The concentration field for ozone is described in section 2.4.

PAN (peroxyacetylnitrate) is formed when NO_2 reacts with the peroxyacetyl radical (reaction 4).The peroxyacetyl radical is calculated as described in caption d in Table 1. In addition to dry deposition, PAN is thermally decomposed. The thermal decomposition is highly temperature dependent.

HNO_3, and nitrate, is produced from NO_2 The most important production term (especially in summer) is the reaction with OH (reaction 3), producing HNO_3. OH concentrations are calculated as described in caption c of Table 1. Nitrate is formed through equilibrium reactions (reactions 7-8). As in the Lagrangian acid deposition model, the night time production of nitrate particles (NO_3^-) is assumed to be limited by the reaction $NO_2 + O_3 \rightarrow NO_3 + O_2$. This assumption only holds in the presence of a sufficient number of aerosols, and provided the humidity is above the deliquescence point. (Platt, 1986; Dentener and Crutzen, 1993). The number of particles will usually decrease rapidly with height above the planetary boundary layer. Thus this reaction is assumed to take place in the lowest 8 layers of the model only (below approximately 1500 meters). This reaction is discussed in section 3.

In the gas phase the dominant path oxidising SO_2 to sulphate is the reaction with OH. SO_2 is however also efficiently oxidised to sulphuric acid in liquid clouds. The most important oxidising agents in the aqueous phase are thought to be H_2O_2, O_3 and O_2 (catalysed by metal ions). Reaction 9 in Table 1 represents both oxidation in the gas-phase and in the aqueous phase, and is given by the expression:

$$k_t = 3\times10^{-6} + 2\times10^{-6}\sin\left[2\pi\left(\frac{\tau-\tau_0}{\tau_a}\right)\right] \qquad \text{(EQ 1)}$$

where τ is julian day, τ_0 is 80 and τ_a is 365. With this formulation, k_t is slow in winter, when oxidant concentrations are expected to be low.

The formation of ammonium sulphate is assumed to occur instantaneously, only limited by the availability of NH_4^+ and SO_4^{2-}. Ammonium sulphate may exist in two forms, $(NH_4)_2SO_4$ or NH_4HSO_4. We assume that the concentrations of the two forms are equal.

Table 1: Chemistry

	Reaction	A	$-E_a/R$	note
1	$NO_2+h\nu \rightarrow NO+O$			see caption[a]
2	$NO+O_3 \rightarrow NO_2+O_2$	2.1×10^{-12}	-1450	see caption[b]
3	$NO_2+OH \rightarrow HNO_3$	1.1×10^{-11}		see caption[c]
4	$NO_2+CH_3COO_2 \rightarrow PAN$	3.2×10^{-12}		see caption[d]
5	$PAN \rightarrow NO_2+CH_3COO_2$	7.94×10^{14}	12530	
6	$2NO_2+O_3+H_2O \rightarrow 2NO_3^-+2H^++O_2$	1.2×10^{-13}	2450	see text
7	$HNO_3 \rightarrow NO_3^-$	$10^{-5}\ s^{-1}$		
8	$NO_3^- \rightarrow HNO_3$	$5 \times 10^{-6}\ s^{-1}$		
9	SO_2 + oxidant $\rightarrow SO_4^{2-}$			see text
10	$3NH_4^+ + 2SO_4^{2-} \rightarrow 2\ (NH_4)_{1.5}SO_4^{2-}$			
11	$NH_4^+ + NO_3^- \rightarrow NH_4NO_3$			see text

a. Dissociation rate for NO_2: $J = 0.01 \times \exp(-0.39 \sec\theta)$, where θ is the solar zenith angle.Below clouds the dissociation rate is reduced by a factor of 0.5 times the fractional cloud cover.

b. The ozone concentration field is described in section 2.4

c. $OH = 1\times10^{-5}$ when the sun is below the horizon. In daytime $OH = 1\times10^{-5} + 7\times10^{8} \times J$ Below clouds OH concentrations are reduced by a factor of 0.25 times the fractional cloud cover.(OH in molecules cm^{-3})

d. CH_3COO_2 is calculated as $OH = 1\times10^{-5} + 7\times10^{8} \times J$ Below clouds CH_3COO_2 concentrations are reduced by a factor of 0.25 times the fractional cloud cover.(CH_3COO_2 in molecules cm^{-3})

Provided that NH_4^+ is in excess of sulphate, ammonium nitrate is formed. The formation of ammonium nitrate is dependant on temperature and relative humidity. This process is described in more detail in Hov et al. (1988). We first calculate the equilibrium concentration of NH_3:

$$NH_3eq = \frac{\left(NH_3 - HNO_3\right)}{2} + \sqrt{\frac{\left(NH_3 - HNO_3\right)^2}{4} + k_{eq}} \qquad \text{(EQ 2)}$$

The equilibrium concentration of NH_4NHO_3 is derived from NH_3:

$$NH_4NO_3eq = NH_4NO_3 + (NH_3 - NH_3eq) \qquad \text{(EQ 3)}$$

Provided that the difference between the equilibrium concentration and the former concentration is smaller than the former concentration, the equilibrium concentration becomes the new concentration for ammonium nitrate. Ammonia and nitric oxide are adjusted accordingly. The equilibrium constant k_{eq} is determined as proposed by Stelson and Seinfeld (1982).

2.2 Deposition

The dry deposition processes are treated in the same way as in Jakobsen et al. (1995). Dry deposition velocities at 1 m are from Sandnes (1993) and references therein. For wet scavenging we distinguish between incloud and sub-cloud scavenging. The scavenging rates are listed in table 2. The scavenging rates are based on a scavenging depth of 1000 m, the precipitation within each layer for incloud scavenging, and the total precipitation for sub-cloud scavenging. We do not account for the effect that dissolved material may be released if clouds or rain water evaporate.

Table 2: scavenging rates

	SO_2	sulphate[a]	HNO_3	nitrate[b]	NH_3
incloud	$3 \cdot 10^5 + 1 \times 10^5 \times F$ [c]	7×10^5	$1.4x10^6$	7×10^5	1.4×10^6
sub-cloud	incloud /2	1×10^5	incloud /2	1×10^5	incloud /2

a. Sulphate includes both H_2SO_4 and ammonium sulphate.

b. Nitrate includes both NO_3^- particles and ammonium nitrate.

c. A seasonal variation of F is assumed: $F = \sin\left(2\pi\frac{\tau - \tau_0}{\tau_a}\right)$, where τ is julian day, τ_0 is 80 days, and τ_a is the number of days in a year.

Wet scavenging rates for sulphur components are similar to data utilized by Tarrason (1995, personal comunication) and Hobbs (1993). Nitrate particles are assumed to scavenge with the same efficiency as the sulphate particles. For HNO_3 and NH_3 we have utilized the scavenging ratios that corresponds to the Lagrangian model (Sandnes, 1993) for the in-cloud scavenging. The sub-cloud scavenging for HNO_3 and NH_3 is as for SO_2 assumed to be half the in-cloud value. At this stage we think there is considerable uncertainty particularily in the choice of the scavenging coefficients for HNO_3 and NH_3. The present values must therefore be regarded as preliminary.

2.3 Emissions

Emissions of NO_x, SO_2 and NH_3 are included in the model. Further information on the emission data are found in Berge et al. (1995). The 50 km gridded data are now available for quite a few countries in Europe as seen in Table 3, either through data directly submitted to EMEP or through the CORINAIR90 inventory. The Table 3 is based on the 50 km gridded values for 1990. An empty box in Table 3 means that data are missing for that component. In areas where not information in the 50 km grid is present the 150 km emission numbers are split into 9 equal values. For NO_x and SO_2 a distinction is also made between low level sources (below 100 m), and emissions from tall chimneys (above 100 meters). Whereas low level sources are injected into the lowest model layer (below approximately 90m), the remainder is injected to the 3 model layers immediately above, with 25% of the high emissions injected into layer 2 and 4 (from 90 - 180 and from 300 - 480 m respectively) 50% of the high sources are emitted into layer 3 (180 - 300 m) which is consistent with what is used in other Eulerian Air Pollution models (Hass et al., 1990).

Table 3. Present availability at MSC-W of 50 km gridded data in 1990.

	SO_2	NO_x	NH_3
Austria	X	X	X
Bosnia and Herzegov.	X		
Bulgaria	X	X	X
Croatia	X	X	
Czech Republic	X	X	X
Finland	X	X	X
France	X	X	X
Greece	X	X	X
Ireland	X	X	X
Italy	X	X	X
Luxembourg	X	X	X
Netherlands	X	X	X
Norway	X	X	X
Poland	X	X	X
Portugal	X	X	X
Slovakia	X	X	
Slovenia	X	X	X
Sweden	X	X	
Switzerland	X	X	X
United Kingdom	X	X	X

2.4 Boundary values and initial values.

For some of the components (NO, NO_2,HNO_3, nitrate and to some extent PAN) concentrations in the background atmosphere will increase with height. For these components initial concentrations are specified. For NO we assume an initial mixing ratio of 3 ppt_v up to approximately 3250 m. Then a gradual increase to about 20 ppt_v in 9 km. In the uppermost layer the NO values increase sharply. For NO_2 we assume a constant mixing ratio of 30 ppt_v below 9 km, and a more gradual increase above that. HNO_3 is assumed to have a concentration of 4 times the NO_x ($NO+NO_2$) concentrations. Finally initial PAN levels are a factor of 0.7 times the NO_2 levels. For the remaining components initial concentrations are set to zero. For SO_2 and NH_3 this is justified as they are short-lived, and are mainly controlled by ground sources. Sulphate, ammonium sulphate, nitrate and ammonium nitrate are formed quickly with the former species as precursors.

At the lateral boundaries SO_2 and sulphate levels are obtained from the Hemispheric scale model for 1988 (Tarrason, 1992). For NO_x, PAN and HNO_3 we are using representative values from the 3-D chemical tracer model at the University of Oslo (Berntsen, 1994).

The night time conversion of NO_x to nitrate, and the NO to NO_2 ratio is dependent on the O_3 concentration. Ozone values are prescribed, ranging from between 30 and 35 ppb_v in the boundary layer to 84 ppb_v at around 9 km. Above that there is a rapid increase, and ozone reaches 500 ppb_v at the uppermost model layer.

3.0 Reduced night-time conversion of NO_2 to nitrate.

In the reference model run the conversion of NO_2 to nitrate proceeds through two channels, the first being the reaction with OH (reaction 3), giving HNO_3. The second channel is the night-time conversion of two NO_2 molecules, giving nitrate directly (reaction 6).When comparing model results from the lagrangian acid deposition model to measurements for the years 1985-1993 as given in Tuovinen et al. (1994) it is found that NO_2 in air was underestimated, whereas total nitrate was overestimated. In parts this could be explained by an overestimation of the night time production of nitrate.

The night time production of nitrate is believed to be initiated by the reaction:

$$O_2 + O_3 \rightarrow NO_3 + O_2 \qquad \text{(EQ 4)}$$

An equilibrium between NO_3 and N_2O_5 is then established:

$$NO_3 + NO_2 \leftrightarrow N_2O_5 \qquad \text{(EQ 5)}$$

NO_3 and N_2O_5 are rapidly photolised in daytime. In the absence of sunlight, reactions of N_2O_5

and /or NO_3 on wet aerosol surfaces are likely to result in a rapid conversion to nitrate (Platt, 1984; Mozurkewiech and Calvert, 1988). The mechanism has also been studied by Dentener and Crutzen (1993). Assuming the wetable aerosols to be formed solely from sulphate, they found that the mechanism could be limited by mass transport to the aerosol surface.

In the reference model run it is assumed that this conversion is so rapid that only reaction 6 in Table 1 needs to be considered. This is probably a good assumption. However, in areas with low sulphate concentrations, and/or low humidity, the night-time conversion to nitrate is likely to be overestimated. To compensate for this, the reaction is multiplied by a correction term

$$A = \frac{K}{K + 10^{-3}} \qquad \text{(EQ 6)}$$

Where K is a pseudo first order reaction coefficient for the conversion of N_2O_5 to nitrate, given by the equation:

$$K = V \times \frac{3\alpha v}{4r} \qquad \text{(EQ 7)}$$

where V is the volume fraction of SO_4 and ammonium sulphate, (Dentener,1993), α the sticking coefficient (0.01), v the mean molecular speed of the N_2O_5 molecules and r average aerosol radius in the accumulation mode, (0.3μm). With this formulation the night time conversion is virtually unchanged (A close to 1) if the sulphate concentration is high. (This will be the case in the boundary layer in major parts of Europe. With low sulphate concentrations, the conversion of N_2O_5 to nitrate will be slow (longer than approximately 15 minutes), and A will be smaller than 1. This is more likely to be the case in remote areas, and in the free troposphere.

4.0 Results

In order to compare the first model results with measurements, and with other model simulations, we have selected the 10 first days of july 1990. The reason for chosing this period is that there is already an on-going comparison between the EURAD model (European Regional Acid Deposition model, Hass et al., 1993) and the Lagrangian acid deposition model for these 10 days. Therefore, by selecting this episode we open for the possibility to evaluate the present Eulerian model more thoroughly together with the two other models at a later stage.

At this stage we present our model calculations together with a comparison with the EMEP measurements and results from the latest version of the 150 km Lagrangian model. The formulation for the sulphur components does not differ much from the model version described and evaluated in Jakobsen et al. (1995). We will therefore focus our presentation on the nitrogen components.

The chosen episode is characterized by relatively large amounts of precipitation for this time of the year in conjunction with the passage of several frontal systems over western and central

Europe and southern Scandinavia. A low pressure system dominated over Great Britain, Central Europe and the Nort Sea. In Fig. 1 we present the model accumulated precipitation for the 10 days period which illustrates the rainy weather of the period, and Most of central Europe receive between 10 to 25 mm.

4.1 Results from the Eulerian model

In Figs. 2-5 calculated average ground level values for the 10 days period for total nitrate NO_2 PAN and ammonium are depicted as oxidized nitrogen for NO_2 ,PAN and nitrate, and as reduced nitrogen for ammonia+ammonium. As can be expected the highest concentrations are found in the vicinity of the source areas, and details related to emission pattern are seen for NO_2 (Fig. 3). For the secondary pollutants the gradients are smaller for total nitrate (Fig. 2) and ammonia pluss ammonium (Fig. 5). Rather large variations are seen in the PAN field specially in the Mediterranean area (Fig. 4).

Figures 6 and 7 depicts the accumulated wet deposition of nitrate and ammonia+ammonium, respectively for the 10 days period. The relatively large amount of ammonia+ammonium, and in particular total nitrate deposited over southern Scandinavia reflects the large amounts of precipitation in this area (Figure 1). The accumulated depositions are also high over central Europe, even though the accumulated amounts of precipitation are considerably smaller, and rather reflecting the high concentrations in air.

4.2 Comparisons with measurements and the Lagrangian model.

Only stations with at least 8 days of measurements are included in the comparison. Furthermore, we require that there must be at least 3 days of precipitation in the observational data and in the model results. In addition, some stations, where the quality of the measurements is uncertain, or the station is believed to be unrepresentative for the grid average (i.e. mountain stations), are also omitted. Unfortunately, it was difficult to find one set of stations that could cover all components for the short period. Therefore it is important to bear in mind that the stations may vary some from one component to another when the conclusions are drawn.

In Figs. 8-10 scatter plots are presented, comparing modelled and measured ground level concentrations in air for total nitrate, NO_2 and ammonia+ammonium respectively. All values are averaged over the 10 days period. In Figs. 12 and 13 calculated and measured accumulated deposition of total nitrate and ammonia+ammonium respectively are compared.

From Figure 11 we observe that the calculated accumulated precipitation is underpredicted for most of the stations. This is may be not so surprising since the precipitation is at many places dominated by convective processes which are difficult to represent in a 50 km grid.

For total nitrate a general impression is that the accumulated deposition is underpredicted

(Fig. 12) while the concentration in air is overpredicted (Fig. 8). As an average for all the stations, both precipitation and accumulated deposition of total nitrate is underpredicted by approximately 40% compared to the measured average. As wet deposition is an important loss term for total nitrate in air, the underprediction of the precipitation will certainly contribute to this. However, it must be noted that there are differences in the selection of stations from one component to another which makes the conclusions more uncertain.

For ammonia+ammonium the picture is mixed. Compared to the measurements, the average values for both accumulated deposition (Fig. 13), and for concentration in air (Fig. 10), are close to the observed average. There is however a large scatter in the data, and for the accumulated deposition the correlation is poor.

Compared to the measurements, NO_2 in air is somewhat underpredicted (Fig. 9). The calculated concentration is affected by several factors, as the choice of OH levels and the dissociation rate. The fact that an underprediction of NO_2 is accompanied by an overprediction of total nitrate in air may suggest that the conversion of NO_2 to HNO_3 and nitrate, either through the reaction with OH or through night time reactions on deliquescent aerosols, is to rapid.

As a reference in Figs. 14-19 we present measurements versus calculations by use of the Lagrangian acid deposition. In this case the selceted stations for each component are the same for the two models. Contrary to the Eulerian model, precipitation is based on measurements. For the 10 days period accumulated precipitation is closer to what is observed at the stations than is the case with the Eulerian model (Fig. 17). The Lagrangian model predicts the accumulated deposition of both total nitrate (Fig. 18) and ammonia+ammonium (Fig. 19) better than the Eulerian model. For components in air both models behave quite similar compared with measurements. An exception is ammonia+ammonium in air (Fig. 10 and 16). The eulerian model predicts the overall averaged concentration better than the Lagrangian model compared to measurements, however the scatter is large. On the other hand, the Lagrangian model yields systematically too low values. At the present time of writing this note we are unable to give any good explanation to this and further investigations are clearly needed.

4.3 Slower night-time chemistry

Introducing a reduction in the night time chemistry (see section 3) has little effect on the calculations. NO_2 levels increase by a few percent. The increase in NO_2 is accompanied by a corresponding small increase in total nitrate levels. However, the small effect is not surprising. In summer, OH levels are high, and thus reaction 3 is very efficient in producing HNO_3. At the same time there are only a few hours of darkness for the night time chemistry to have an effect. We expect that a reduction in the night time chemistry will have a much large effect in winter, when OH levels are low, and the sun is below the horizon for much of the time.

5.0 Final remarks.

The results obtained with the Eulerian model are in general comparable to the results from the Lagrangian acid deposition model and this preliminary version of the model gives realistic results. However, 10 days are certainly not enough to draw firm conclusions about the model performance. Some underestimation of the modelled precipitation is evident, which probably also has affected the wet deposition and the concentrations in air. However, an advantage of utilizing modelled precipitation is that concistency with the other meteorological parameters (cloud fractions, cloud water content, etc) is achieved. This will be of large importance when cloud chemistry is included explicitly in the model.

Compared to the measurements the NO_2 levels are underpredicted, whereas total nitrate in air is overpredicted. The overprediction of total nitrate can both be linked to an underprediction of the wet deposition and a too rapid conversion rate of NO_2 to total nitrate. Introducing a reduction in the night time production of nitrate has little effect on the calculations. This parameterization should also be tested for a winter situation with longer dark periods.

Furthermore, it must also be noted that the wet removal is sensitive to the scavenging rates, and that the wet scavenging processes need to be studied further. In the near future we will also pay more attention to a more thorough examination of the present calculations.

Finally, we aim at introducing more efficient calculation methods based on parallel computing techniques. This will be necessary in order to make longer time runs feasible and therby improve the possibilities of evaluating the model.

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FIGURES.

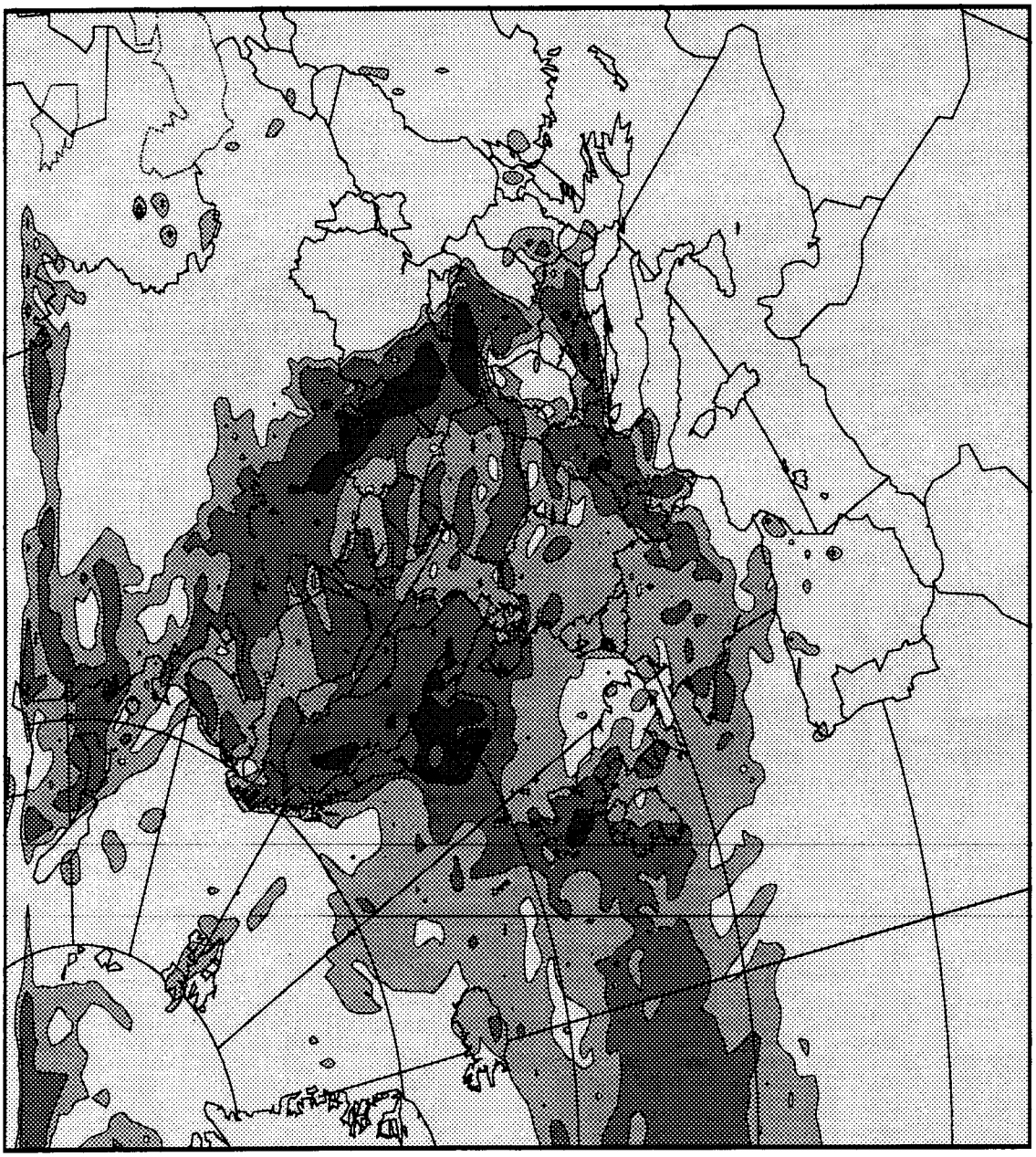

Figure 1 Accumulated precipitation in mm for the 10 first days in july 1990 calculated by the weather prediction model

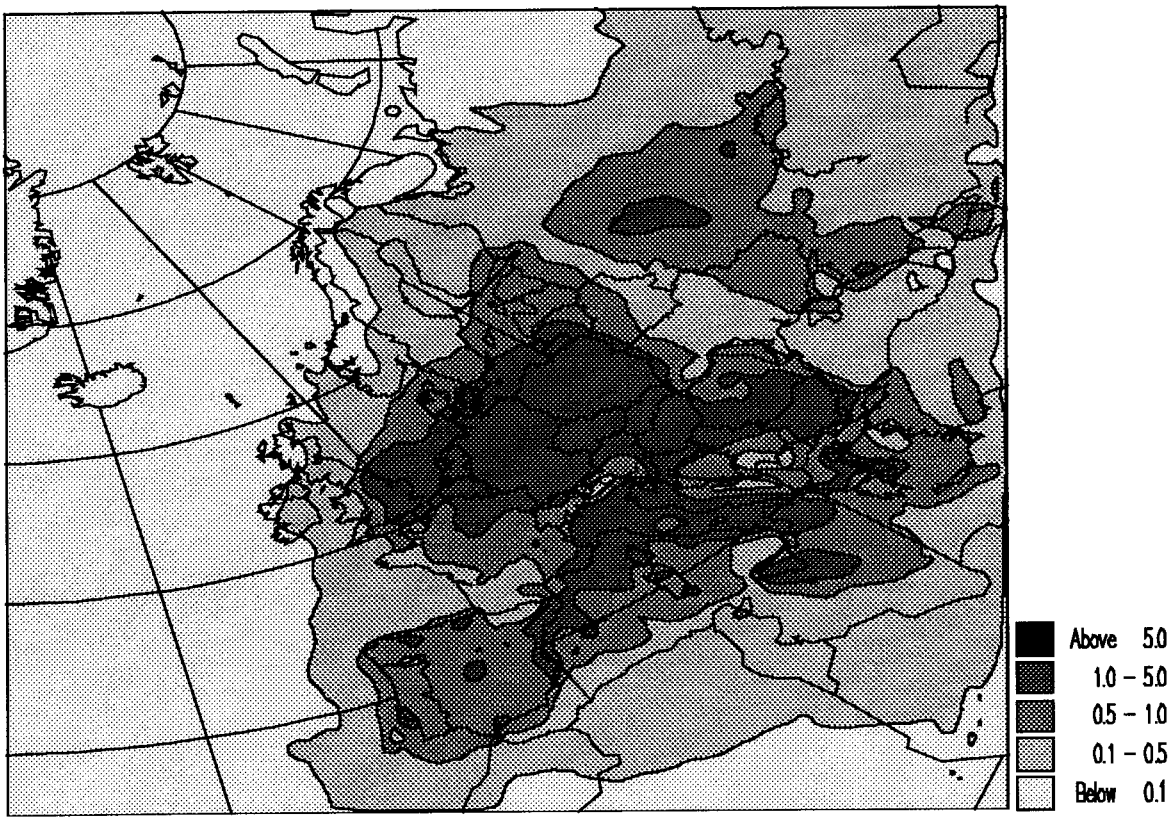

Figure 2 Calculated average ground level concentration ($\mu g\ m^{-3}$) of total nitrate (HNO_3, NO_3^- and ammonium nitrate) for the 10 first days in july 1990.

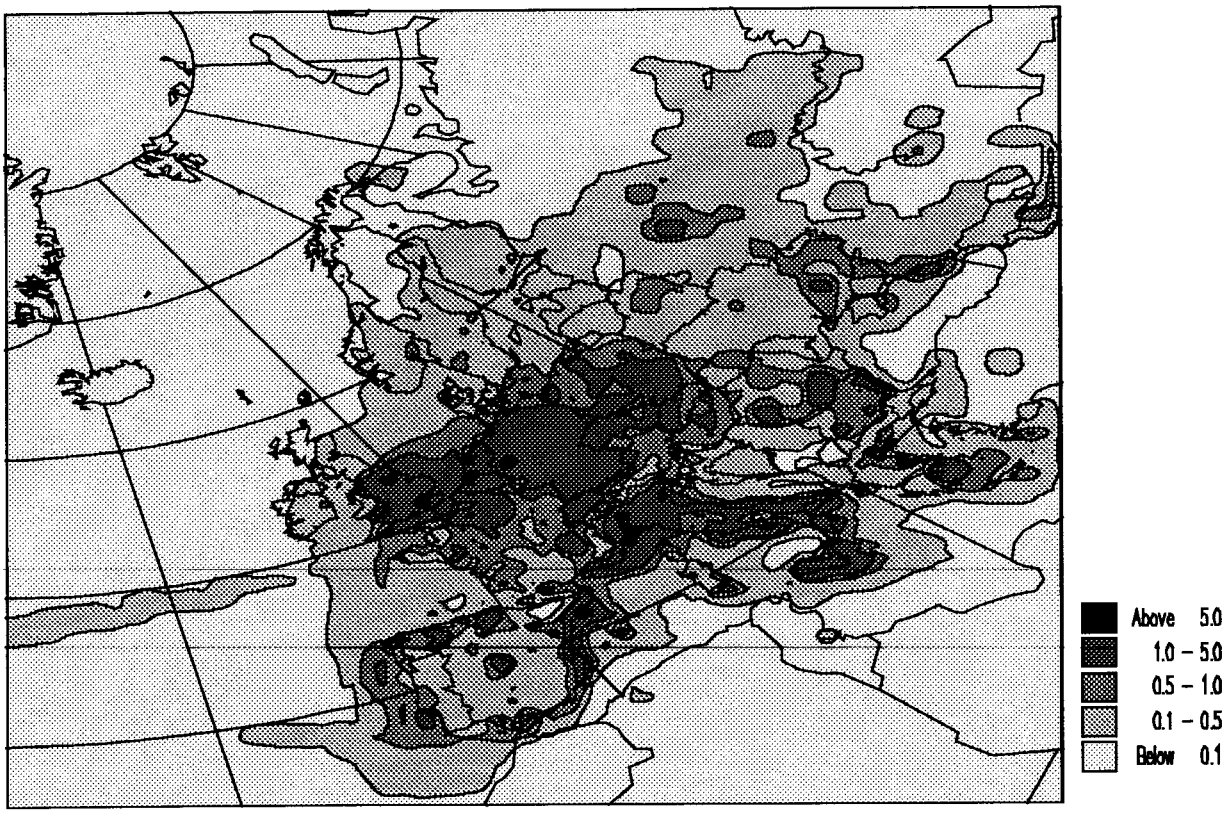

Figure 3 Calculated average ground level concentration ($\mu g\ m^{-3}$) of NO_2 for the 10 first days in july 1990.

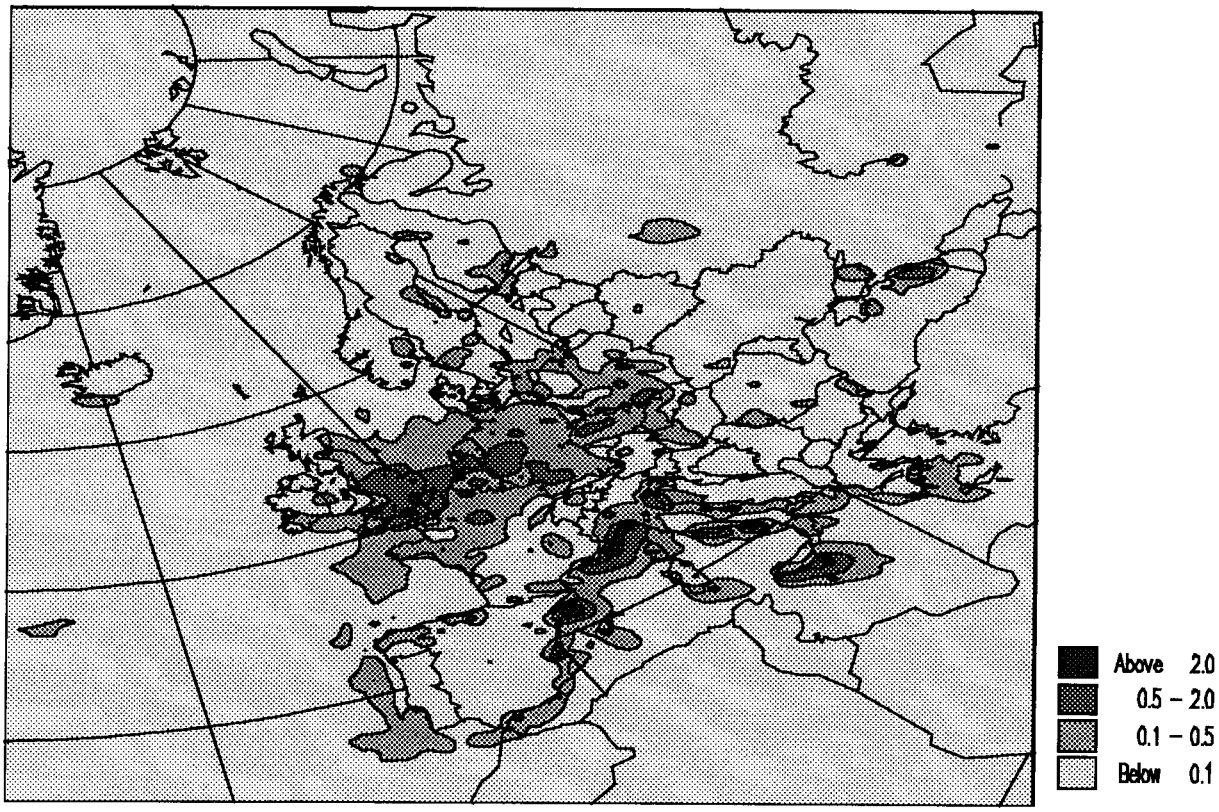

Figure 4 Calculated average ground level concentration of PAN (μg m^{-3}) for the 10 first days in july 1990.

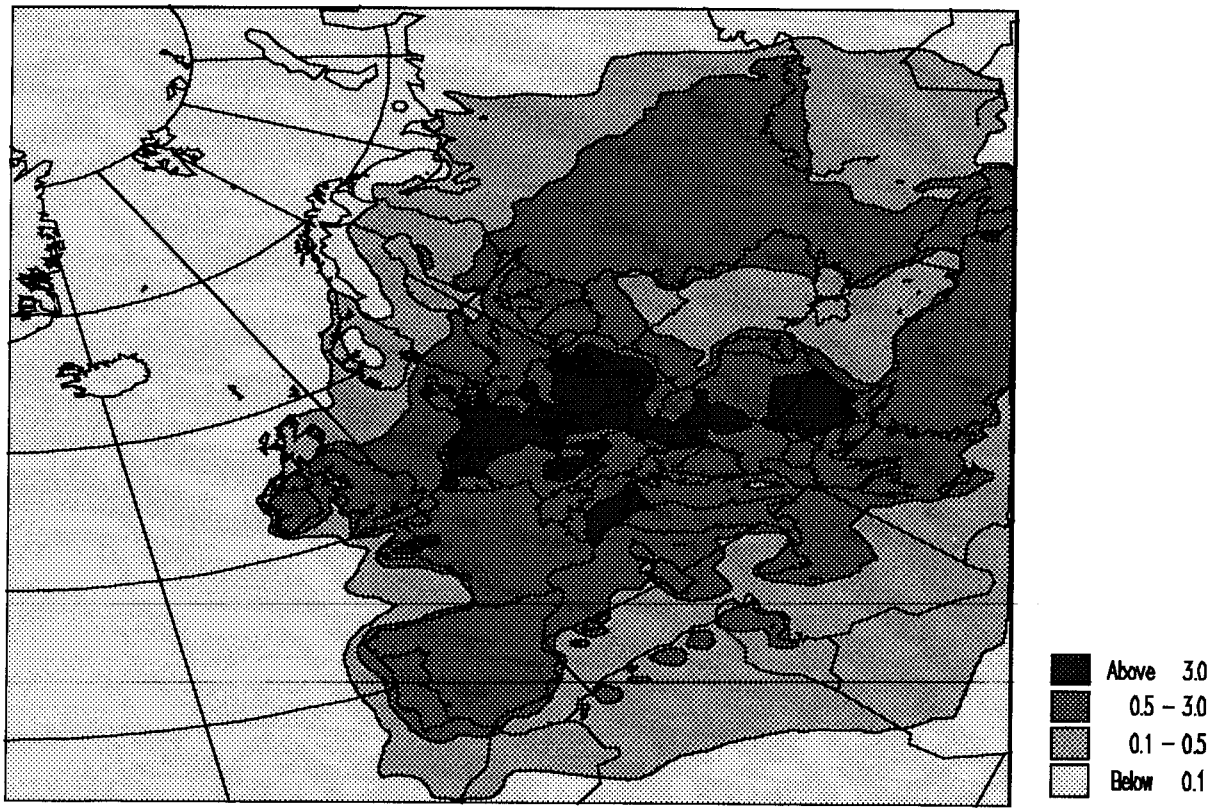

Figure 5 Calculated average ground level concentration of NH_3, ammonium sulphate and ammonium nitrate (μg m^{-3}) for the 10 first days in july 1990.

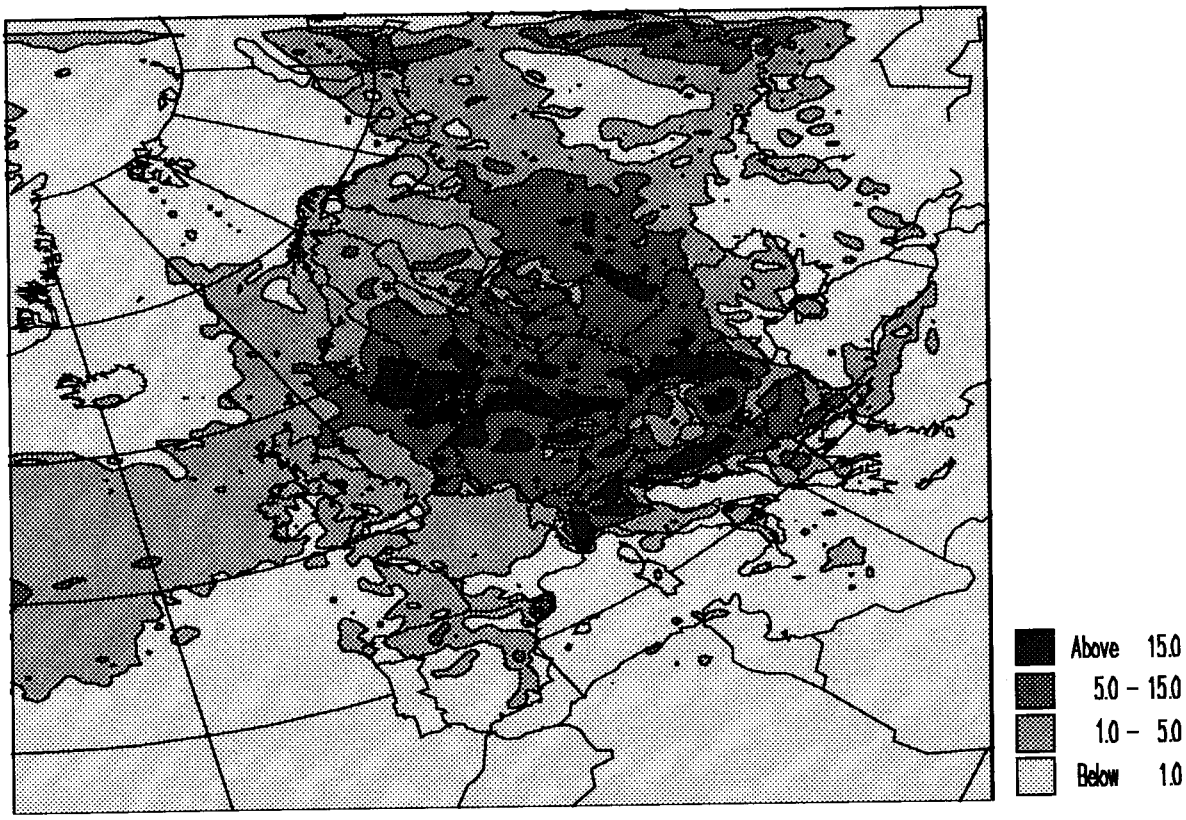

Figure 6 Calculated uccumulated deposition (mg m^{-2}) of total nitrate (HNO_3, NO_3^- and ammonium nitrate) for the 10 first days in july 1990.

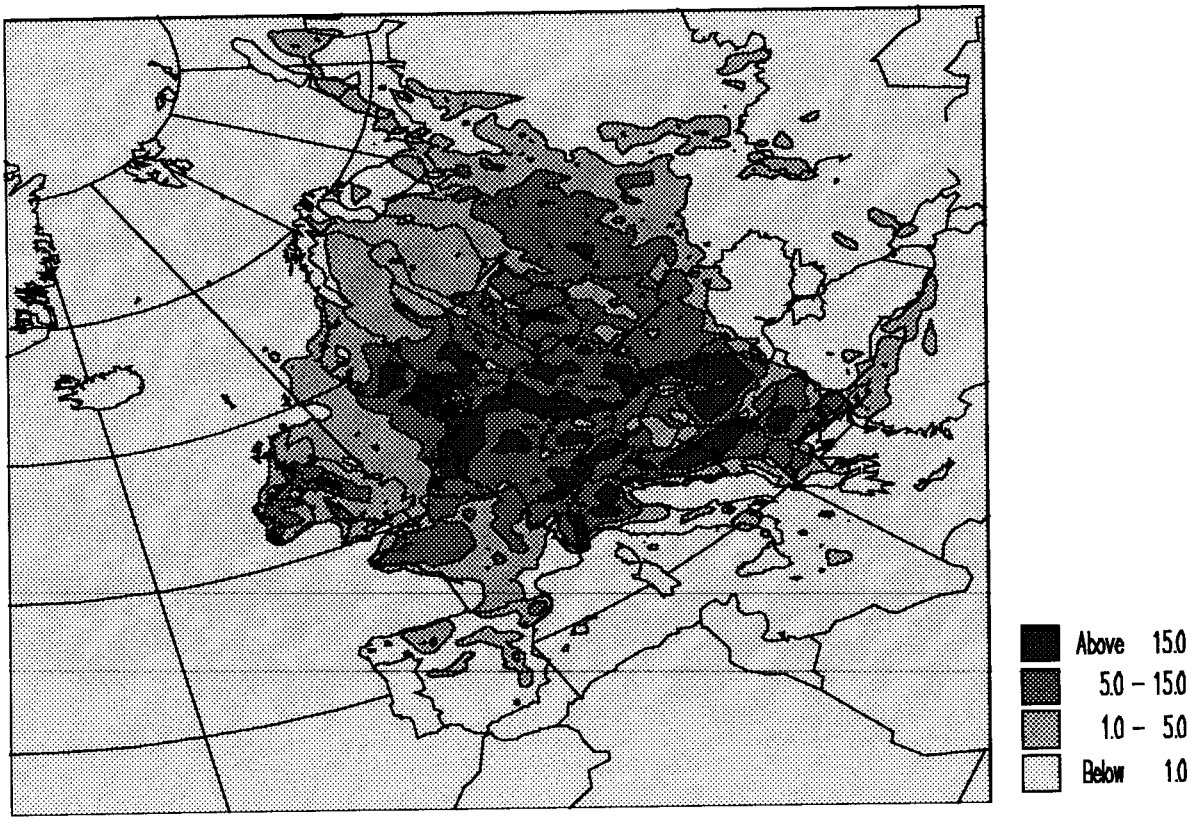

Figure 7 Calculated uccumulated deposition (mg m^{-2}) of NH_4, ammonium sulphate and ammonium nitrate for the 10 first days in july 1990.

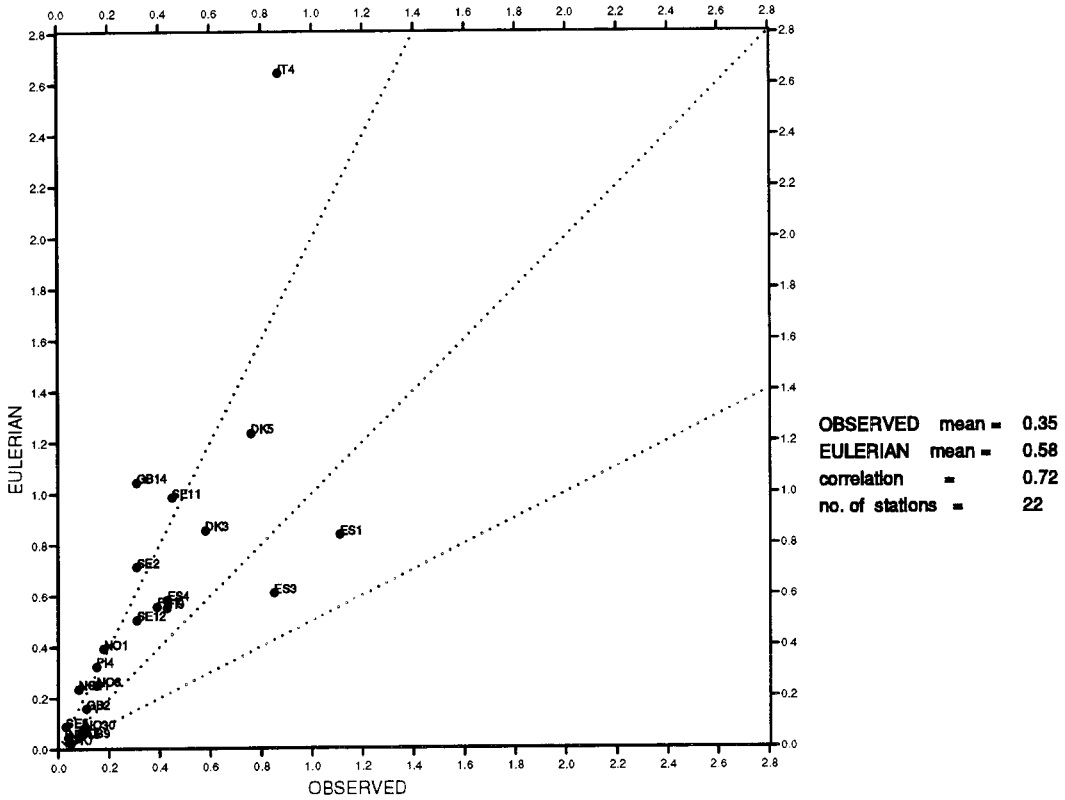

Figure 8 Scatter plot for observed versus calculated total nitrate at ground level (µg m^{-3} as N) average over the 10 first days in july 1990. Stations with less than 8 days of measurements are omitted.

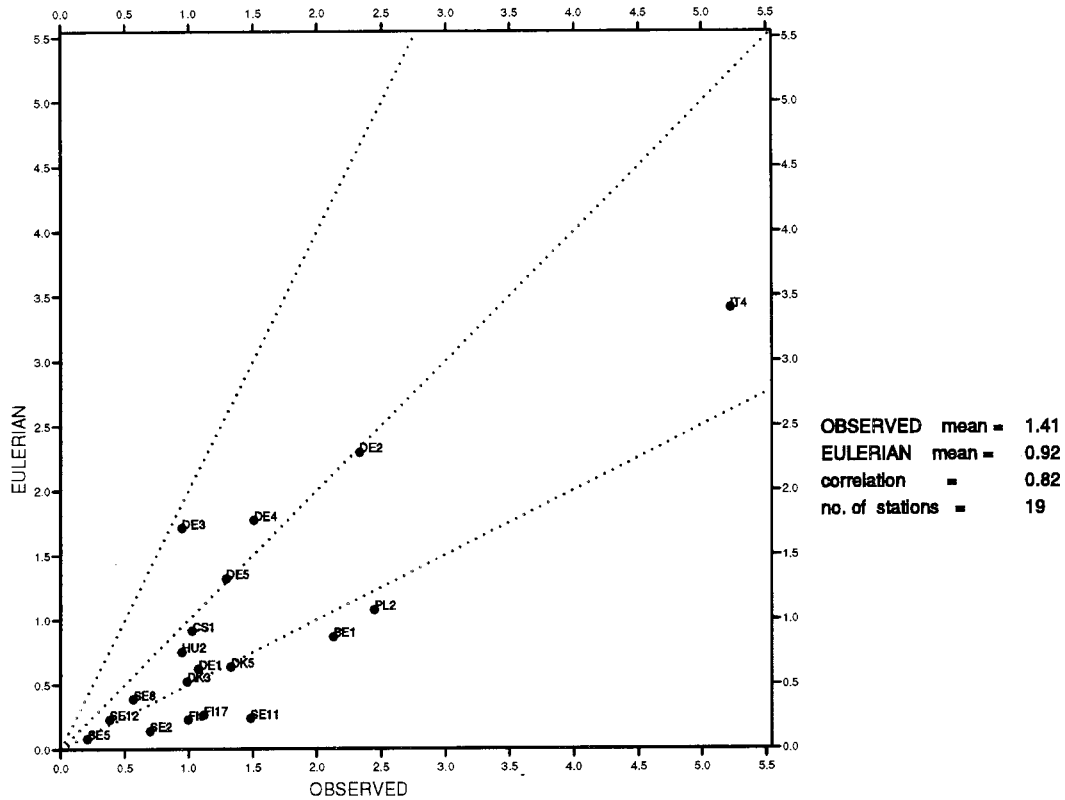

Figure 9 Scatter plot for observed versus calculated NO_2 at ground level (µg m^{-3} as N) averaged over the 10 first days in july 1990. Stations with less than 8 days of measurements are omitted.

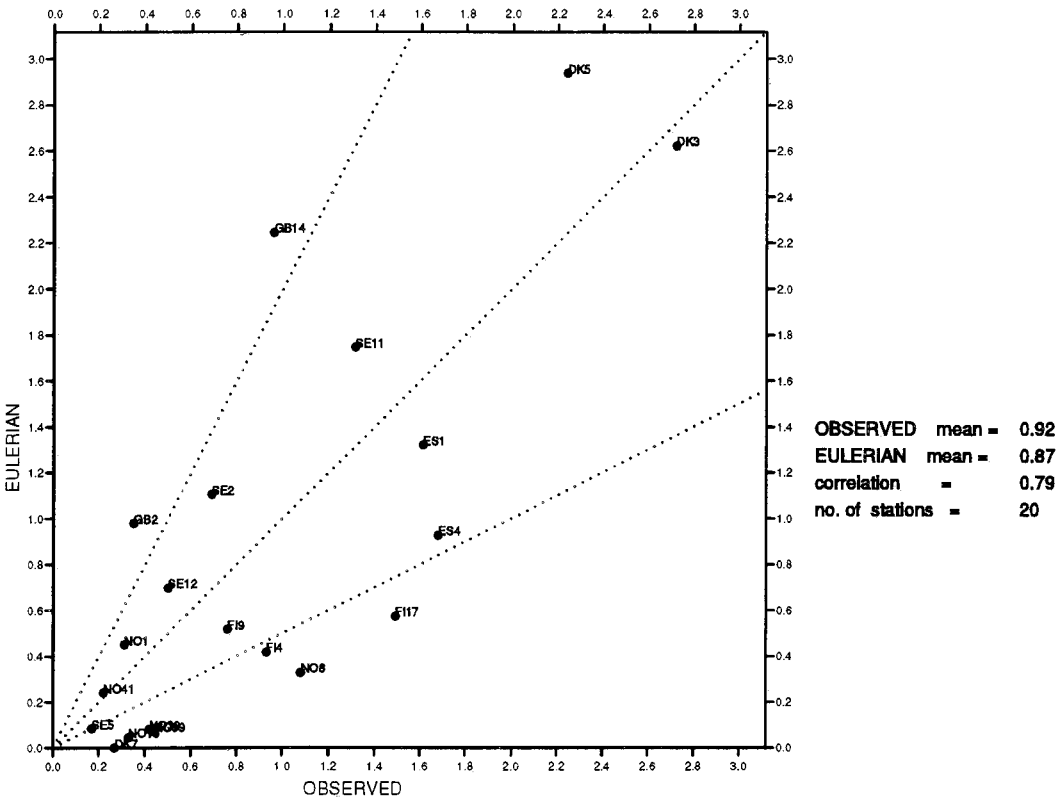

Figure 10 Scatter plot for observed versus calculated ammonia+ammonium at ground level (μgm^{-3} as N) averaged over the 10 first days in july 1990. Stations with less than 8 days of measurements are omitted.

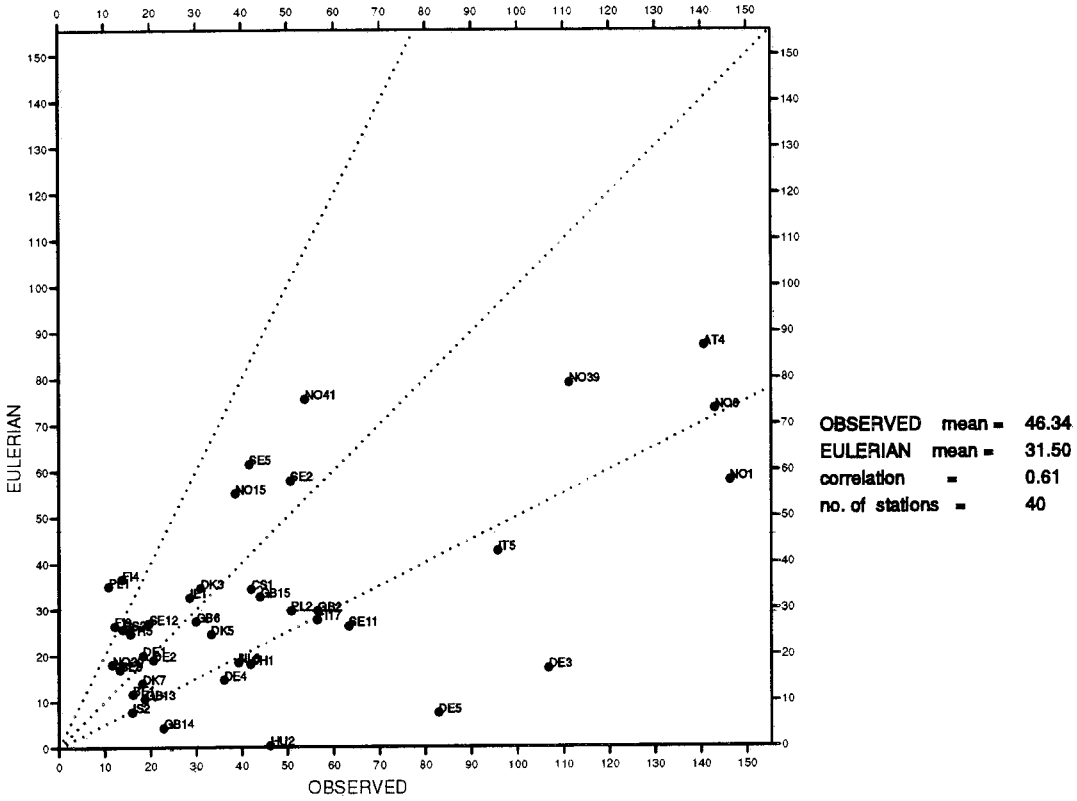

Figure 11 Scatter plot for observed versus pre-calculated accumulated precipitation (mm) for the 10 first days in july 1990. Stations with less than 3 days of measured and calculated precipitation are omitted.

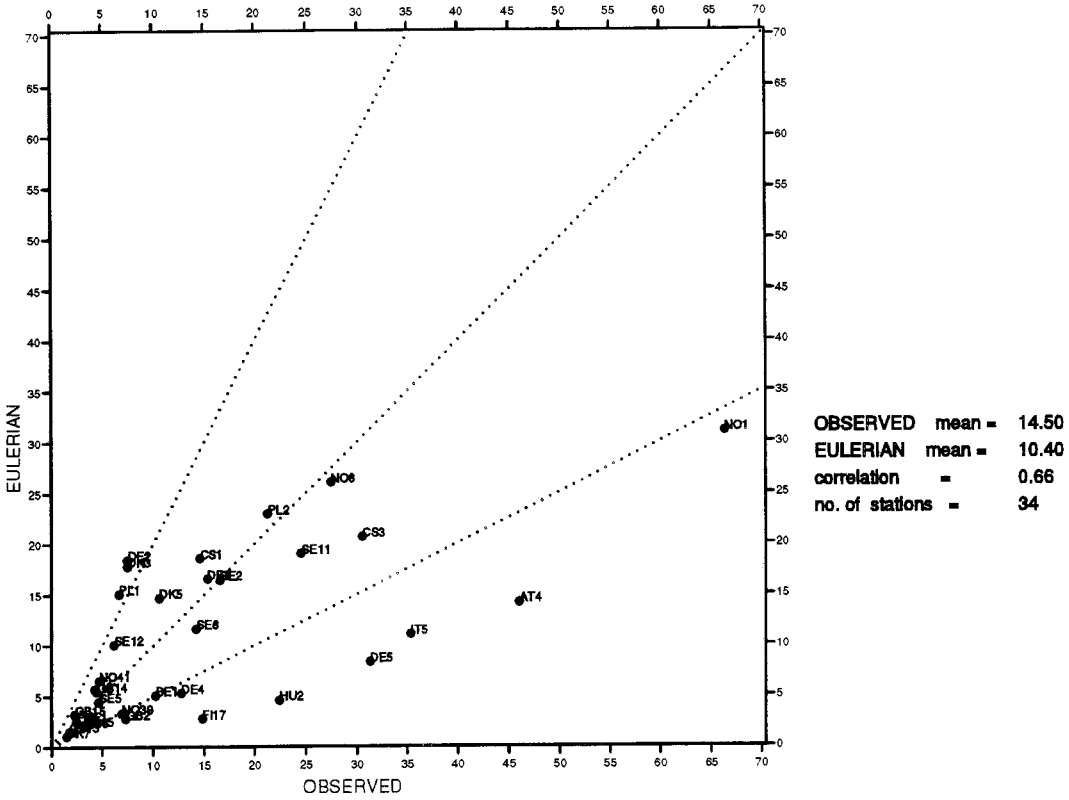

Figure 12 Scatter plot for observed versus calculated accumulated deposition of total nitrate (mgm^{-2} as N) for the first 10 days in july 1990. Stations with less than 3 days of measured and calculated deposition are omitted.

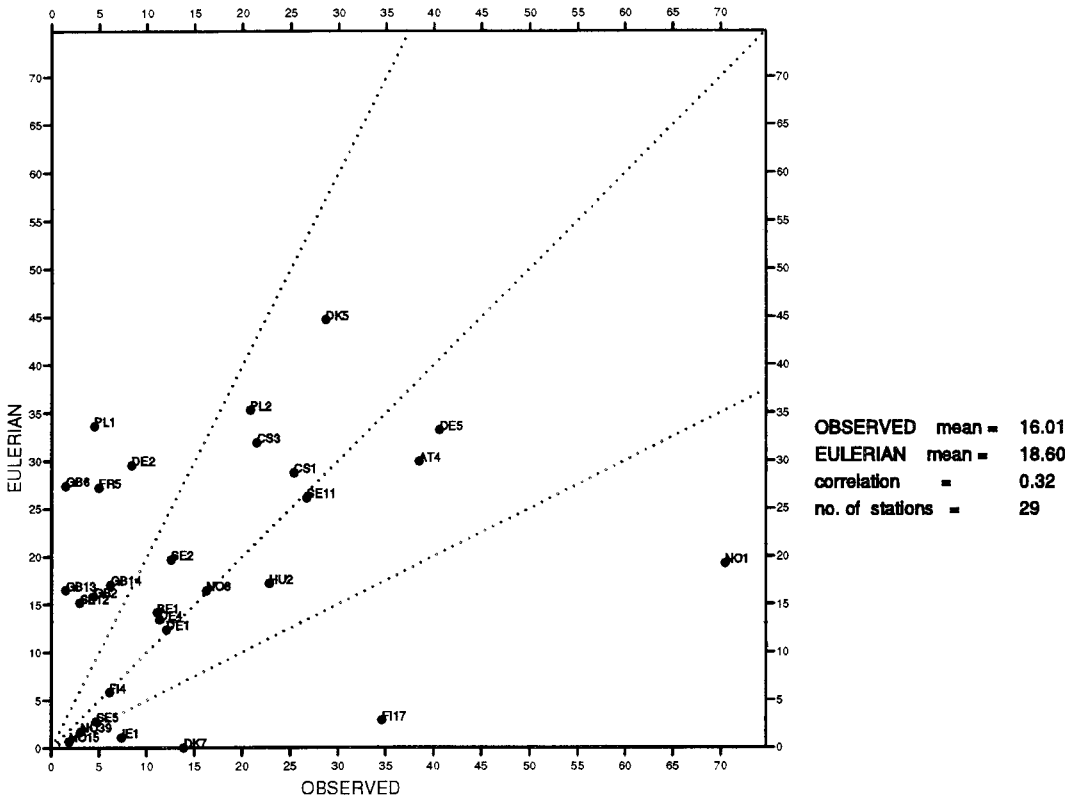

Figure 13 Scatter plot for observed versus calculated accumulated deposition of ammonia+ammonium (mgm^{-2} as N) for the first 10 days in july 1990. Stations with less than 3 days of measured and calculated deposition are omitted.

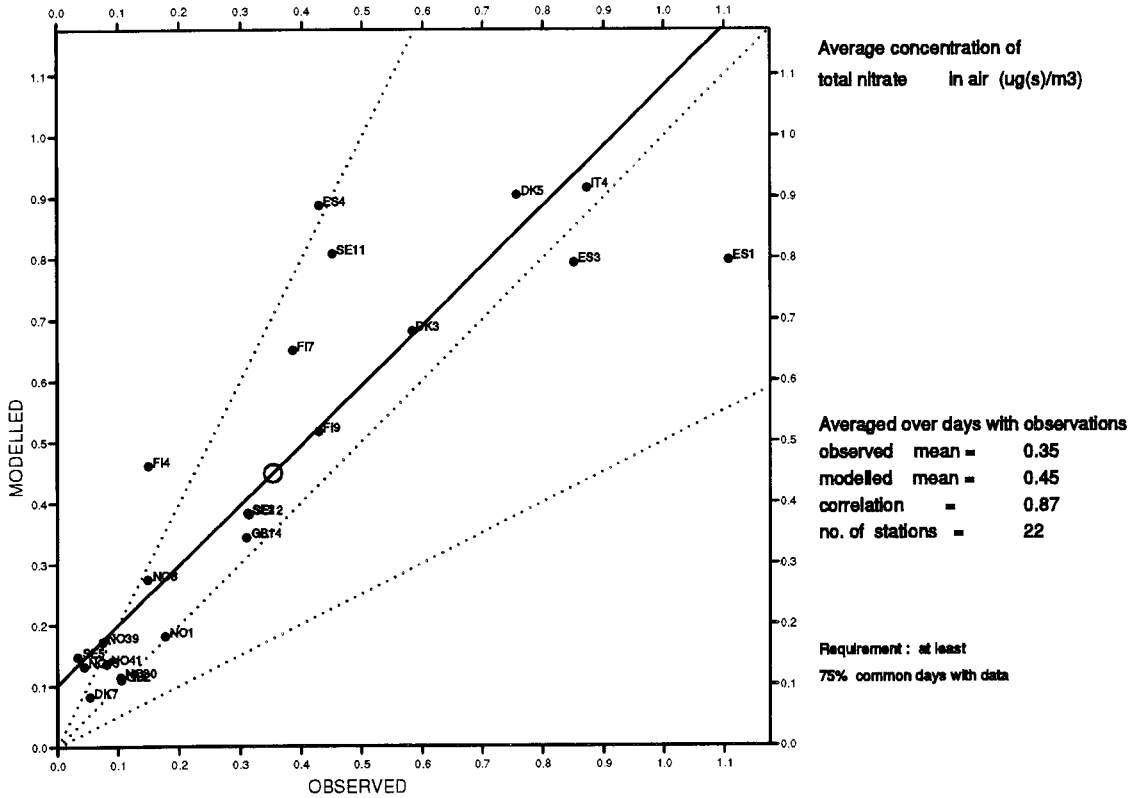

Figure 14 As Figure 8, but with calculations performed with the Lagrangian model.

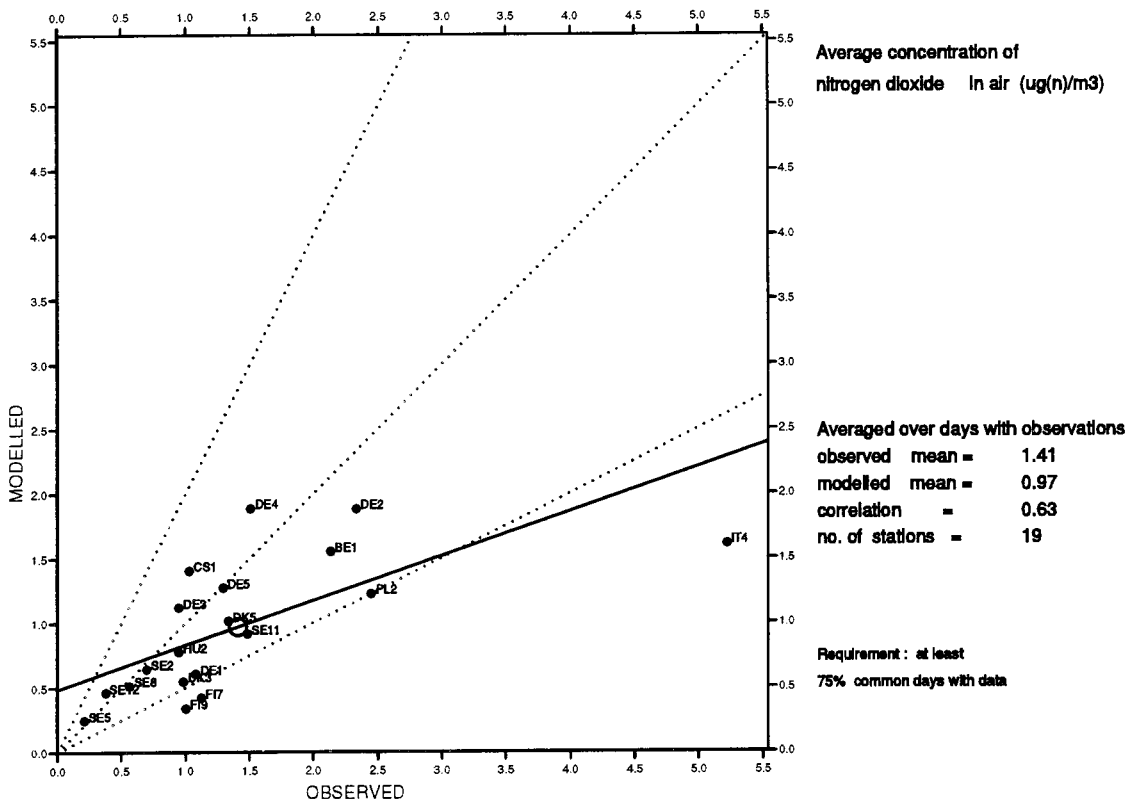

Figure 15 As Figure 9, but with calculations performed with the Lagrangian model.

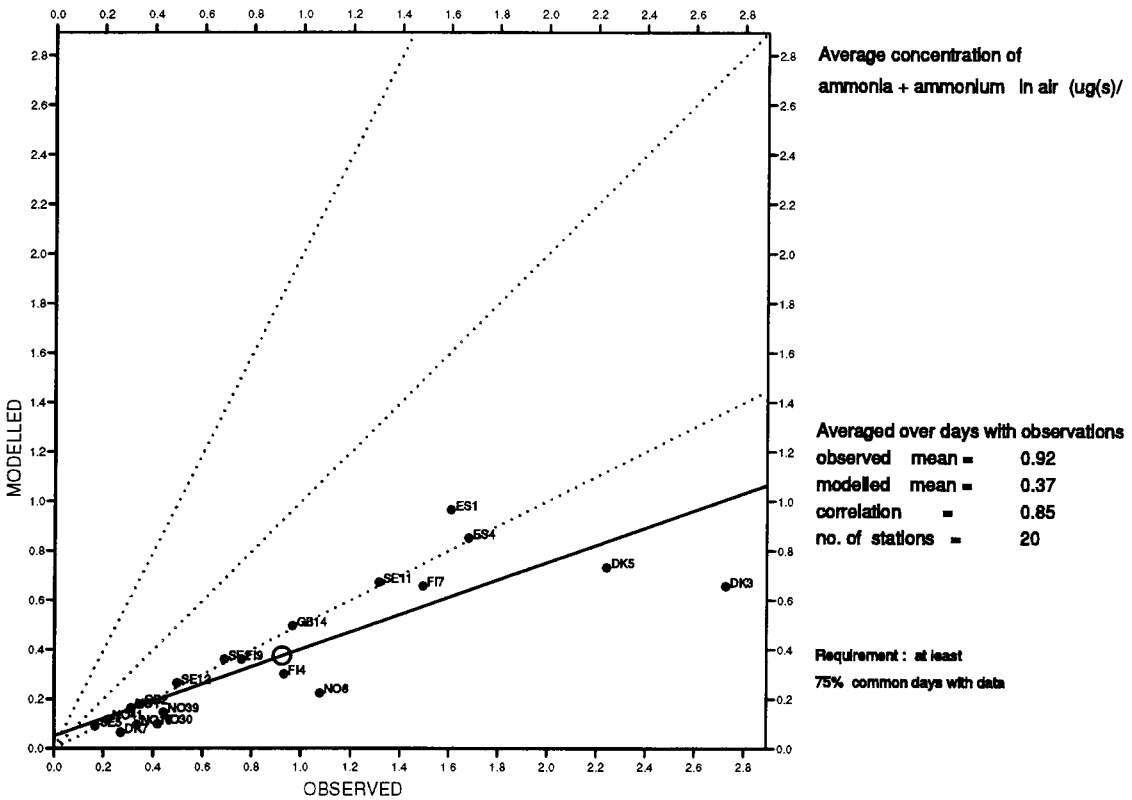

Figure 16 As Figure 10, but with calculations performed with the Lagrangian model.

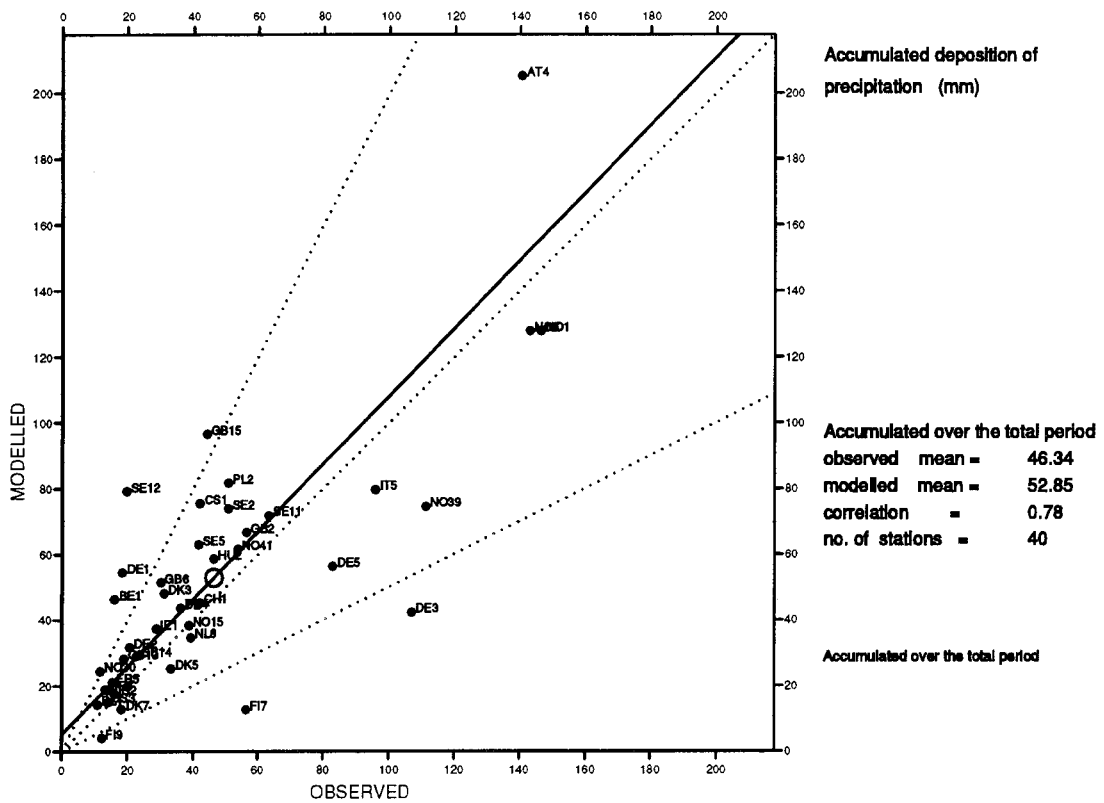

Figure 17 As Figure 11, but with calculations performed with the Lagrangian model.

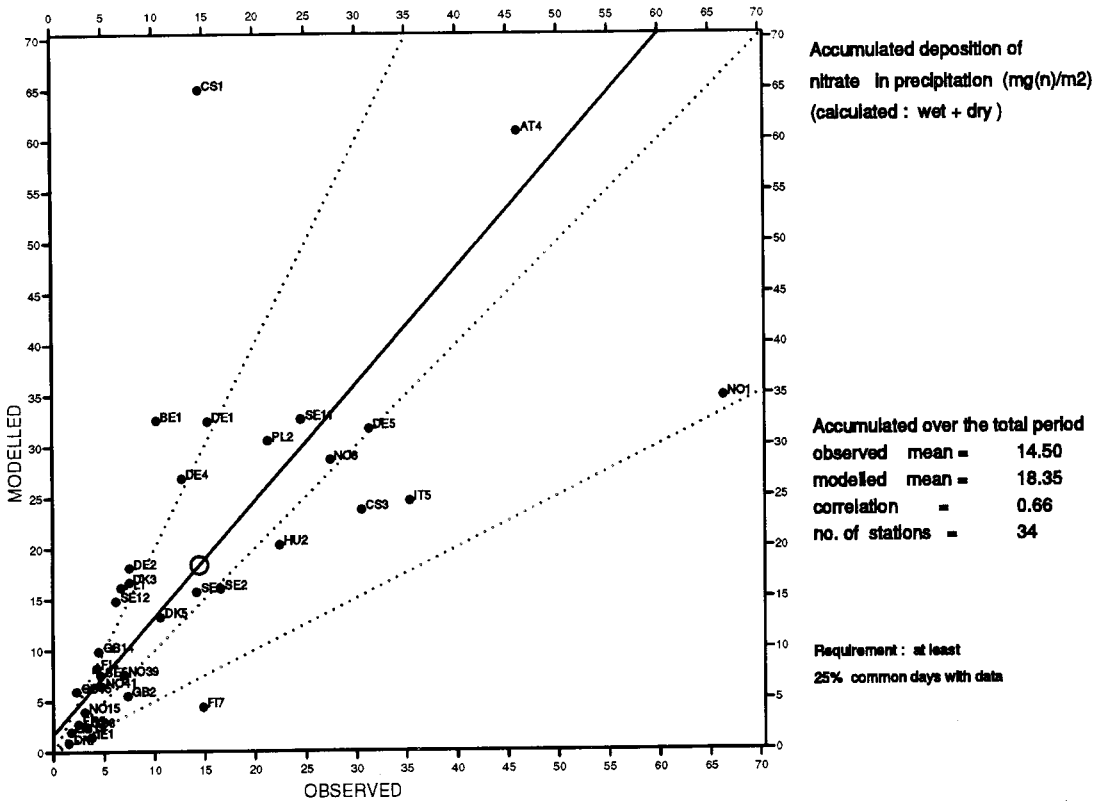

Figure 18 As Figure 12, but with calculations performed with the Lagrangian model.

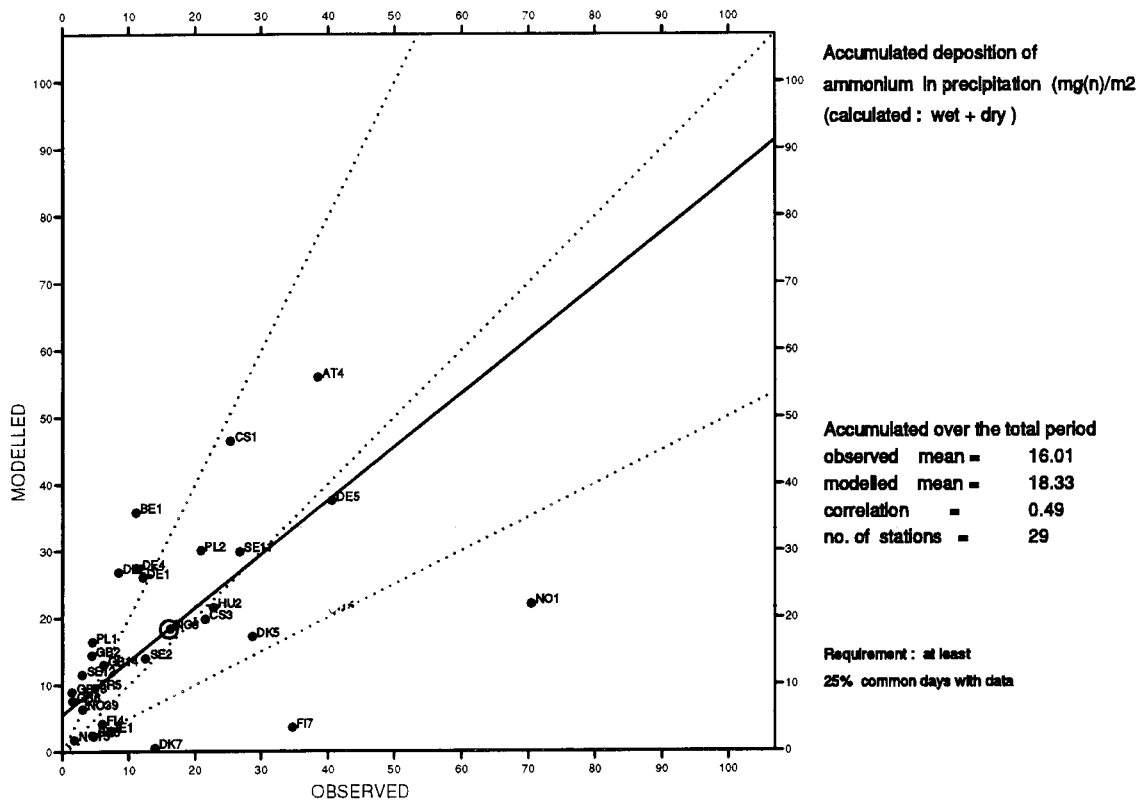

Figure 19 As Figure 13, but with calculations performed with the Lagrangian model.