

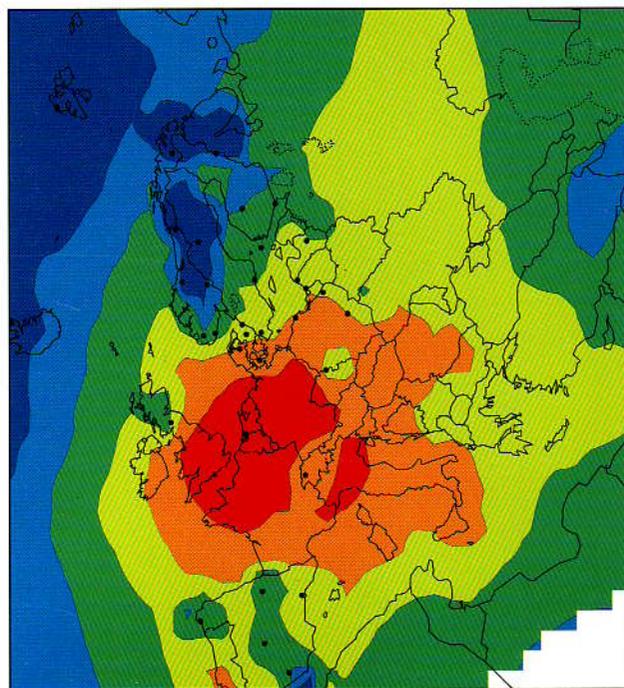
# emep

Co-operative programme for monitoring  
and evaluation of the long range  
transmission of air pollutants in Europe

**Geographical distribution of  
sulphur and nitrogen compounds  
in Europe derived both from  
modelled and observed  
concentrations**

**Leonor Tarrasón, Arne Semb,  
Anne-Gunn Hjellbrekke, Svetlana Tsyro,  
Jan Schaug, Jerzy Bartnicki and Sverre Solberg**

**Total nitrate in air**



# CCC & MSC-W

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Joint EMEP Note  
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## **Preface and acknowledgements**

This note was prepared for the twenty second session of the Steering Body of EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe). It presents a joint effort by the Meteorological Synthesizing Centre-West and the Chemical Coordinating Centre of EMEP to evaluate and qualify our current estimates of concentrations in air and in precipitation of acidifying and eutrophyng compounds. It is concerned with the analysis of systematic differences between model calculations and measurements and presents conclusions on current needs in the monitoring network and model development in view to the increasing demands for assessing compliance with existing protocols.

The authors are grateful to David Simpson for his suggestions and participation in the discussions during the preparation of this note. We would specially like to thank Professor Anton Eliassen and Professor Øystein Hov for initiating the process that lead to elaboration of this note and extend our gratitude to our colleagues at MSC-W and CCC for their contributions at the meeting in Hurdalsjøen where the basic understanding for this project began to take form.

# 1. Introduction

The EMEP programme relies on available information from three different elements: estimates of regional emissions of pollutants, observations from a routinely run monitoring network and results from atmospheric dispersion models. The combination of these three sources of information is fundamental to the assessment of regional concentrations and depositions of air pollutants, the calculation of transboundary fluxes and the evaluation of exceedances to critical loads and levels which form the mandate of EMEP for the Convention on Long-Range Transboundary Air Pollution.

Since its signature in 1979, the LRTAP Convention has adopted six different protocols on reduction or control of emissions of various air pollutants. As different protocols enter into force, EMEP should focus further on the evaluation of international abatement strategies and on the follow-up of the implementation of international commitments for emission reductions. This necessarily demands a thorough evaluation of the quality of the programme results.

The EMEP measurements have been used extensively for comparison with model predictions. Measured air concentrations and precipitation composition have served as an important check on the choice of model parameters and the representation of the physical processes since the start of the programme. Comparisons of modelled and measured concentrations and precipitation quality have been carried out by statistical kriging of the differences between measurements and model estimates (Iversen et al., 1991, Schaug et al., 1993, and Berge et al., 1994). These studies showed that the differences between the model estimates and the measurements were systematic for some components and areas, and that this could be related to properties of the model, the design of the measurement network and/or errors in the emission and monitoring data.

In this joint CCC/MS-CW note, we have chosen to analyse the geographical distribution of acidifying and eutrophying compounds. The atmospheric modelling work has progressed since the last common intercomparison took place, with new and improved parameterisation of dry deposition and sub-grid processes, new treatment of background concentrations and generally updated and more complete emission data. In addition, a new 3-D Eulerian model has become available for comparisons. Focus on quality assurance in the EMEP measurement network has also resulted in improved data quality throughout the network, and more confidence in the measurement data. It is therefore appropriate to make a new comparison of the measurement data with model predictions which qualifies our present estimate of the dispersion of sulphur and nitrogen pollution in Europe.

## 2. Approach

Concentrations in air of sulphur dioxide, particulate sulphate, nitrogen dioxide, total nitrate (the sum of nitric acid and nitrate), ammonia and ammonium have been studied as well as the concentrations of sulphate, nitrate and ammonium in precipitation. The comparison and analysis has been done in four different steps which are summarised below. The same procedure has been followed for all analysed compounds.

a) We consider first the geographical distribution of the compound as calculated by the EMEP Acid Deposition Lagrangian model. Updated descriptions of the EMEP Acid Deposition models can be found in the latest EMEP/MSC-W Status Report (1998).

b) Secondly, we consider annually averaged concentrations measured at the EMEP network and derive a new geographical distribution by using ordinary kriging methods. A short description of the kriging method that has been recently applied by EMEP/CCC can be found in Hjellbrekke et al. (1997).

c) Thirdly, we compare the modelled concentrations for 1996 with observations collected in the stations of the EMEP network. Differences between the measured concentrations and the modelled values in the corresponding gridsquares are calculated for all  $N$  sites and normalized by the sum of observed and modelled values divided by 2. The normalized differences are interpolated spatially using radial basis functions

$$f(x, y) = \sum_{i=1}^N c_i \varphi(d_i(x, y))$$

where  $d_i(x, y)$  is the distance to the measurement point  $(x_i, y_i)$  and  $\varphi(r) = \sqrt{r}$ . This gives a two-dimensional continuous function describing the difference at any point  $(x, y)$  within the modelled grid. At a measurement point  $(x_i, y_i)$ , the use of interpolation ensures that  $f(x_i, y_i)$  equals the normalized difference between observed and modelled values.

d) The last step combines the information gathered from the former analysis. The new maps are derived by weighting the model calculations with the above mentioned interpolated function of the observations. Close to measurements, we give larger weight to observed values whereas in regions where with no observations modelled results are preferred. The actual region of influence of measured values depends on the type of component, in particular, on its characteristic transport distance. For instance,  $\text{SO}_4$  has been given a larger range of influence than  $\text{NO}_2$  because  $\text{NO}_2$  can quickly be exhausted from air due to fast photochemical reactions in the warm season, while  $\text{SO}_4$  is removed by slower deposition processes and transported over longer distances.

Mathematically, the new concentration fields are derived as follows:

$$\begin{aligned}
 N(x, y) &= f(x, y) + mod(x, y) & d \leq 1 \\
 N(x, y) &= f(x, y) \frac{D_{comp} - d}{D_{comp} - 1} + mod(x_i, y_i) & 1 < d \leq D_{comp} \\
 N(x, y) &= mod(x, y) & d > D_{comp}
 \end{aligned}$$

where  $N(x,y)$  are the new optimal fields at coordinate point  $(x,y)$ ,  $mod(x,y)$  are the modelled values and  $f(x,y)$  is an interpolated function of the difference between observed and modelled values;  $d$  is the distance in gridsquares from point  $(x,y)$  to the nearest measurement point  $(x_i,y_i)$ , and  $D_{comp}$  defines the region of influence of measured values.

$D_{comp}$  coincides with the range of the spatial covariance that was used in the kriging in part b). The kriging is based on the spatial covariance between measurements at different distances and the function describing this covariance has been estimated in a conservative way emphasising the best fit in the region surrounding the monitoring site. For nitrogen dioxide, nitrate and ammonium in air the spatial covariance range is set to 2 gridsquares (300km), while for all other components  $D_{comp}$  is set to 5 gridsquares. The fairly short  $D_{comp}$  for  $NO_2$  may be expected from the high reactivity of the substance. However, the estimated range of spatial covariance is also dependent on the number of sites with measurements. Thus the calculated spatial covariance for nitrogen dioxide, nitric acid and nitrate in air, and ammonia and ammonium in air is more difficult to interpret than for other components because of the smaller number of monitoring sites. In particular for nitric acid and nitrate in air, and ammonia and ammonium in air the short  $D_{comp}$  primarily reflects the uncertainty due to lack of measurement sites.

## 2.1 Station selection and site requirements

Not all the stations that were operative in 1996 have been included in the analysis outlined above. In order to secure a consistent set of data for the analysis, the following requirements have been imposed to the measurement sites.

The requirements have been based on results from the annual laboratory intercomparison 15 and 16 from the years 1995 and 1997 (Hanssen and Skjelmoen, 1996; 1997). Data from a laboratory has been included in the analysis if the average deviation from expected values obtained in the two intercomparisons is less than 20%, and the deviation from the expected values in both of the comparisons are less than 25%.

In addition, there are sites within the EMEP network that are not representative for certain components. Precipitation data from Mahon (ES06) and Cubuk (TR01) have been excluded since the sites have low precipitation, and  $NO_2$  from Ispra (IT04) and Montelibretti (IT01) have been excluded due to local source influences.

### 3. Results

Results from the comparison of modelled and measured concentrations distributed over Europe are discussed in the following 8 subsections for each analysed component. In each case, the analysis is documented with four different figures visualizing the four different steps of our comparison procedure. When the information is relevant for the conclusions, results from the EMEP Eulerian model are also presented. In all cases, the year of study is 1996.

#### 3.1 Sulphur dioxide in air

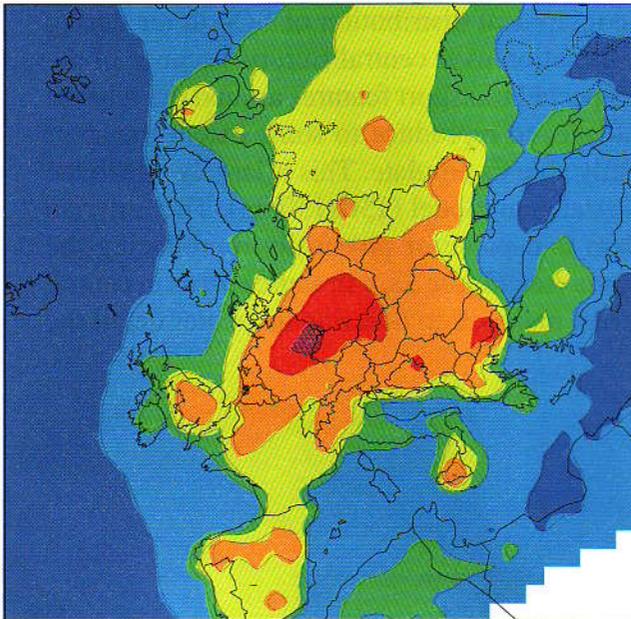
Differences between the observed concentrations of sulphur dioxide in air are related to the fact that SO<sub>2</sub> is a primary pollutant and that the EMEP station network is designed to measure concentrations in rural or background areas. Because of the local character of most SO<sub>2</sub> sources (domestic heating, thermic power plants) we can expect to find sharp gradients in the atmospheric concentrations of sulphur dioxide within relatively short distances. The EMEP Lagrangian model with one vertical layer and coarse horizontal resolution is not able to reproduce these gradients and gives instead averaged values which necessarily overestimate the low concentrations observed away from the source areas and underestimate the concentrations in areas with dense distribution of sources.

In central Europe, the EMEP Lagrangian model overestimates the observed concentration of sulphur dioxide in air. Figure 1c) also shows that the largest differences between observed and calculated values exceed a factor of 2 and occur over the Black Triangle, the region with largest density of SO<sub>2</sub> point sources over Europe (about 80%). This supports the interpretation that the discrepancy between observed and calculated SO<sub>2</sub> in air is enhanced by the design of the EMEP network which selects stations away from source areas. In this sense, an interesting test of this interpretation is to compare model results with observations compiled in a denser network.

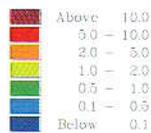
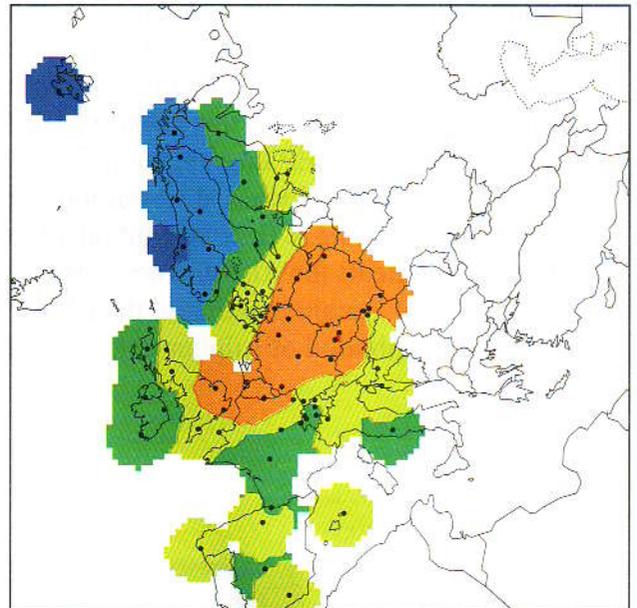
Results from the national network in the Czech Republic from 1995 (Jaroslav Fiala, pers. comm.) consisting of 92 monitors for sulphur dioxide across the country, show that the concentrations in general are higher than those at the two Czech EMEP sites which are background stations in this region. Kriging in a fine grid give large concentrations gradients, and underlines that a measurement average over a 150km x 150 km grid element here, which includes the EMEP sites plus sites from the national network, would give higher grid averages than those given in Figure 1b) and thus in better agreement with the model estimates.

Comparison of Figures 1a) and 1b) also shows that kriged fields derived from observations are not able to resolve long-range transport patterns in sufficient detail. This applies also here despite the fact that the EMEP measuring network for sulphur dioxide covers relatively well the European geographical area.

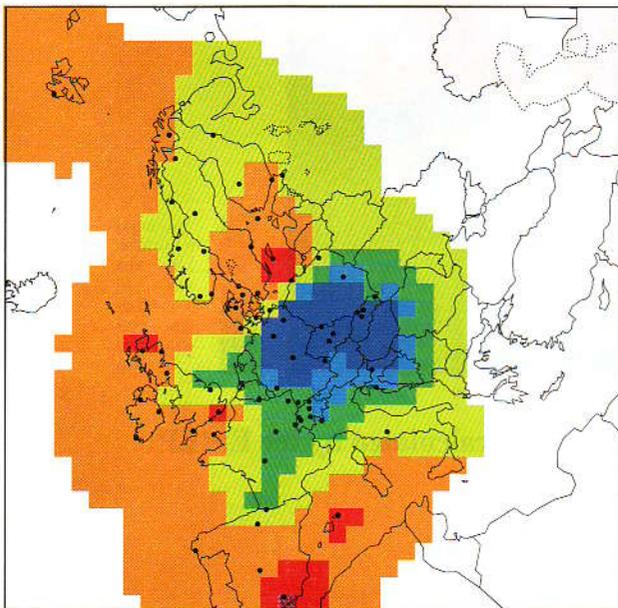
a) Modelled SO<sub>2</sub> in air



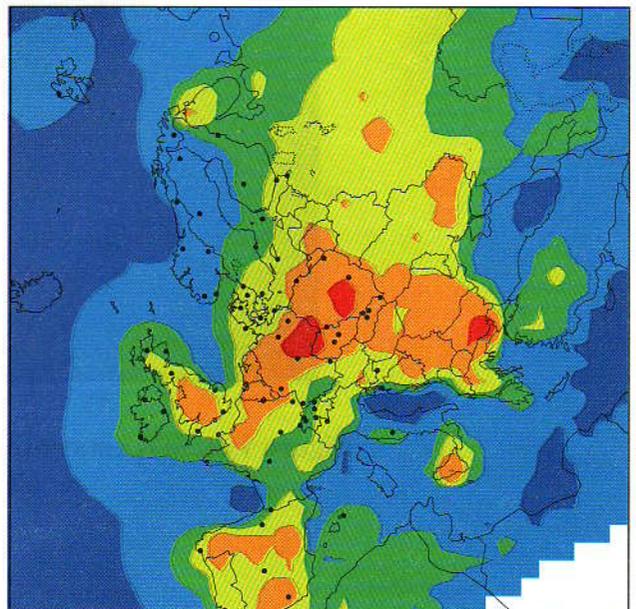
b) SO<sub>2</sub> kriged from measurements



c) Interpolated normalized differences



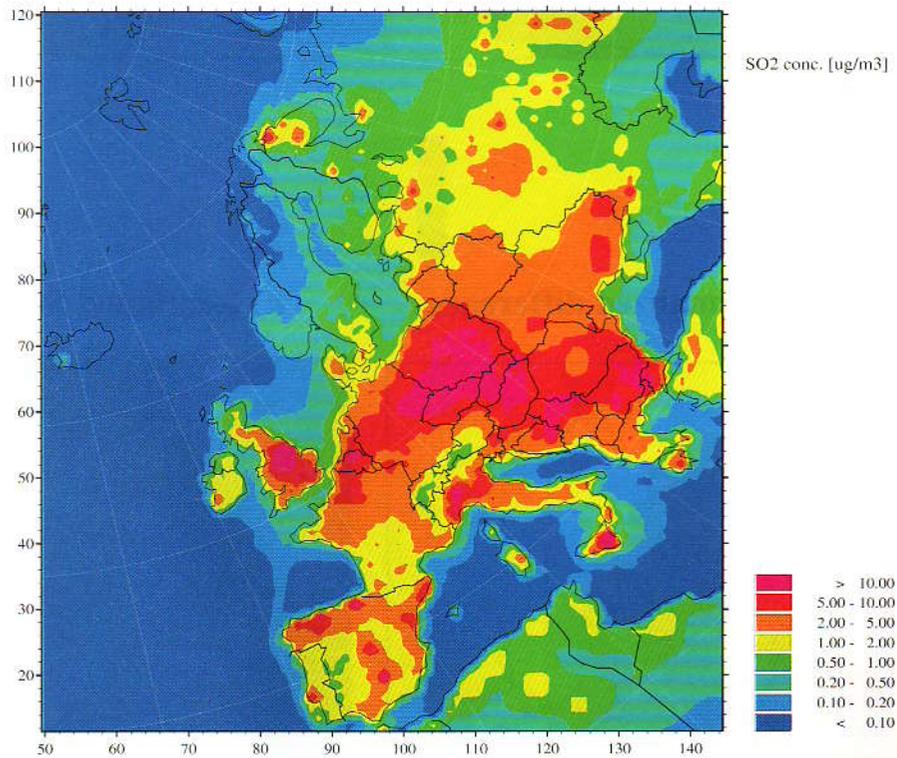
d) Combined SO<sub>2</sub> in air



**Figure 1. a) - d) Analysis of yearly averaged SO<sub>2</sub> concentrations in air. Values for 1996.**

Figures a), b) and d) use the common colour scale given in the figure, units are  $\mu\text{g}(\text{S})/\text{m}^3$ . Interpolated normalized differences between model and observations use a different scale. In figure c) orange, red and purple show where the model underpredicts respectively within a factor of 2, 3 and 4. Light green, green and blue show where the model overestimates observed values respectively within a factor of 2, 3 and 4. Black dots indicate the position of measurement sites.

Figure 1d) represents our new estimate of the geographical distribution of SO<sub>2</sub> in air during 1996. The new estimate reduces the model overestimation over central Europe because of the use of background EMEP stations and traces the expected transport features around the Alps. It is interesting to note that this combined field manages to reproduce to some extent transport features that the EMEP Lagrangian model is not fully able to simulate. This is largely due to the coarse horizontal and vertical resolution of the Lagrangian model (150x150km). The Eulerian EMEP model using a finer resolution of 50x50km is capable of physically reproducing the observed gradients the Alps and northern Scandinavia (see Figure 1e.). In source areas in central Europe, Great Britain and Spain, the EMEP Eulerian manages to describe in greater detail the expected distribution of sulphur dioxide in air.



**Figure 1 e). SO<sub>2</sub> concentrations in air calculated by the EMEP Eulerian model.**

### 3.2 Particulate sulphate in air

The comparison of Figures 2a) and 2b) shows that agreement between model results and observations is generally better for sulphate aerosol than for sulphur dioxide. This result was to be expected since particulate sulphate is a secondary component and less dependent on the model's ability to simulate dispersion in close to the sources. However, the model still overestimates the observed sulphate aerosol at ground level. The interpolated difference field in Figure 2c) shows similar features to those depicted in Figure 1c): slight overestimation over continental Europe and maximum differences over Germany, Poland and the Czech Republic. This indicates again that the model overestimation of observations may be related to processes occurring close to the sources.

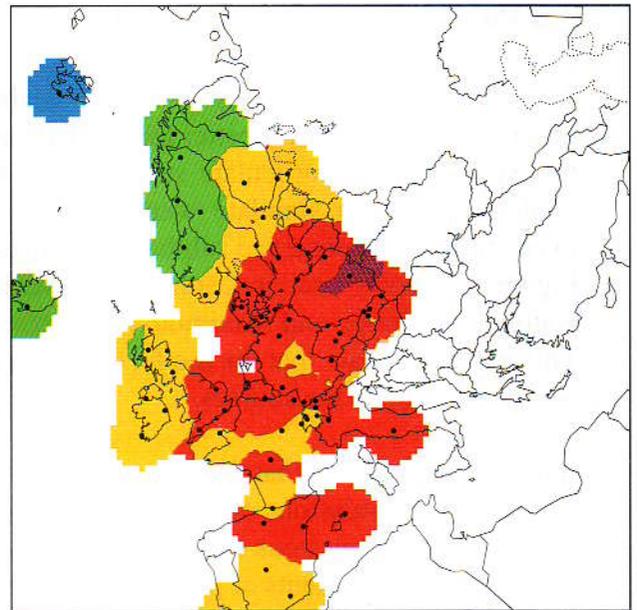
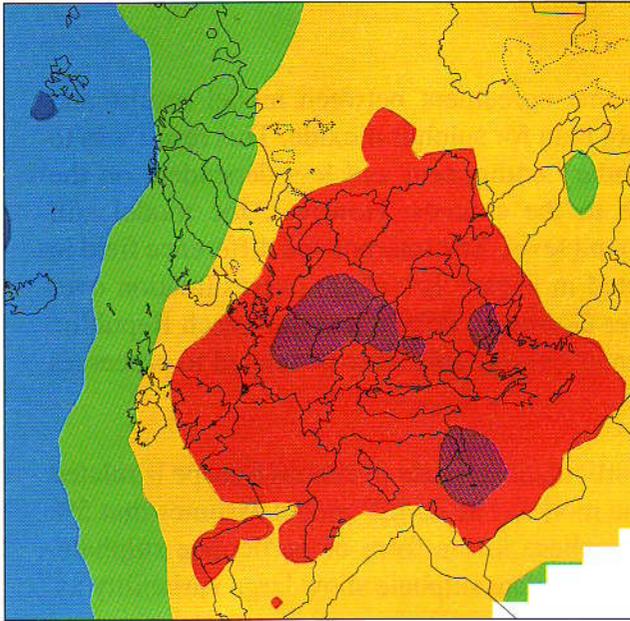
It has been suggested that the overestimation of particulate sulphate in central Europe is related to large direct emissions of sulphate aerosol in the model. The EMEP model assumes that 5% of the sulphur emissions are emitted to the atmosphere in the form of particulate sulphate. Available measurements of primary emissions of particulate sulphate show large variability as indicated below.

USEPA (Shannon et al., 1980)	Fraction of S emissions as sulphate
Coal point sources	1.5%
Residual fuel oil- utilities and industrial	7.0%
Residual fuel oil- commercial and residential	13.4%
Distillate oil	3.0%
Mobile sources	3.0%
Miscellaneous	5.0%

The reason for the large differences in the emitted fraction of sulphate particulates lies among other factors on the OH concentrations during combustion. There are quite high concentrations of OH in the combustion zone of hydrocarbon flames so that the fraction of primary sulphate relative to the total emitted sulphur oxides is generally higher in sources burning oil and petroleum than from coal combustion. On the other hand, the very high fractions of primary sulphate from the commercial and residential sectors may be related to the fact the burning residual oil in small boilers is quite inefficient. Under such conditions, the pyrolysis of large oil droplets will lead to the formation of carbon particulates which may contain significant amounts of soot. Such poor and incomplete combustion processes are expected to occur very seldom in Europe today. Since the sulphur oxide emissions in northern Europe is dominated at present by coal-fired power plants and other stationary sources burning solid fuel, it would seem that the emission fraction of primary sulphates has been reduced since the time the 5% value was determined in the mid 70's and that this fraction is now more likely to be 2-3%.

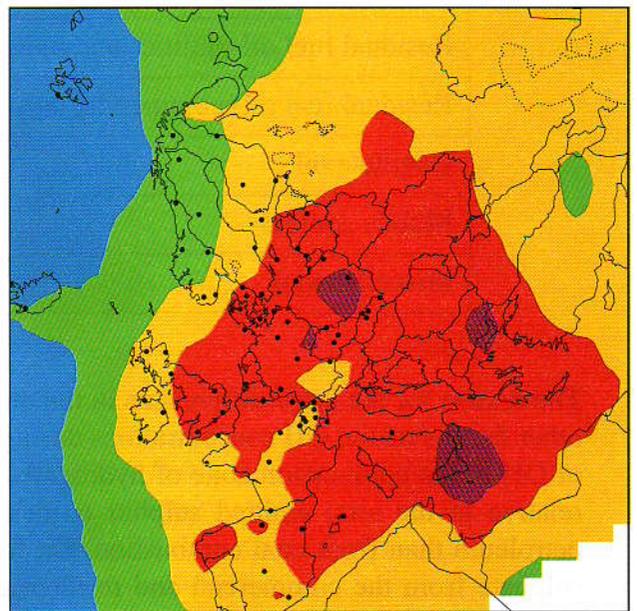
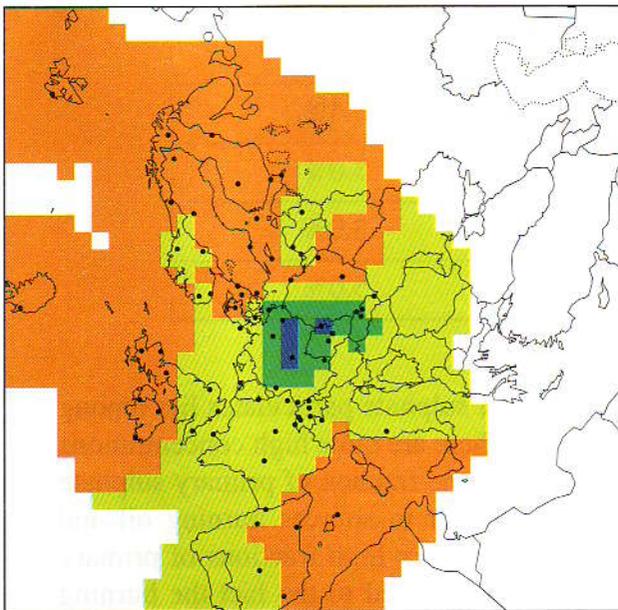
a) Modelled SO<sub>4</sub> in air

b) SO<sub>4</sub> kriged from measurements



c) Interpolated normalized differences

d) Combined SO<sub>4</sub> in air



**Figure 2. a) - d) Analysis of yearly averaged SO<sub>4</sub> concentrations in air. Values for 1996.**

Figures a), b) and d) use the common colour scale given in the figure, units are  $\mu\text{g}(\text{S})/\text{m}^3$ . Interpolated normalized differences between model and observations use a different scale. In figure c) orange, red and purple show where the model underpredicts respectively within a factor of 2, 3 and 4. Light green, green and blue show where the model overestimates observed values respectively within a factor of 2, 3 and 4. Black dots indicate the position of measurement sites.

The question remains open as there are too few estimates of particle emissions in Europe and the data remains inconclusive. Still, differences in the direct emission of aerosol sulphate are rather small to justify the existing overestimations. Another likely factor to account for the observed discrepancies is the parametrisation of dry deposition of sulphate aerosol in the EMEP model.

The distribution of  $\text{SO}_4$  in air depicted in Figure 2d) should be considered as a qualified best guess. For example, Figure 2d) estimates the concentration of particulate sulphate in air over Central France to be 0.9 - 1.2  $\mu\text{g}(\text{S})/\text{m}^3$ , instead of the initial model value of  $\sim 1.5\mu\text{g}(\text{S})/\text{m}^3$  which observations have indicated to be too high. The new interpolated fields should not be used in the calculation of exceedances to critical levels as it will not be possible to allocate the origin of such exceedances. Source allocation requires the fulfilment of mass conservation as formulated in atmospheric dispersion models and therefore, model results should be used for source allocation and compliance purposes.

### 3.3 Nitrogen dioxide in air

NO<sub>2</sub> is chemically very active, specially in summertime when high photodissociation rates imply that the atmospheric lifetime of NO<sub>2</sub> is less than 1 day. This implies that nitrogen dioxide in the atmosphere is usually related to nearby sources. Nitrogen dioxide is primarily emitted from low (traffic) sources and may accumulate inside the nocturnal boundary layer. The EMEP model has difficulties simulating the diurnal variation of the local boundary layer and biases to diurnal mixing. Consequently, the model tends to enhance the mixing of the NO<sub>2</sub> concentrations in the boundary layer and this explains the systematic underestimation of the model results during the summer. In order to analyse systematic differences other than these, we have chosen to study modelled and measured NO<sub>2</sub> values averaged during the cold period (October to March 1996).

A first look to the kriged fields in Figure 3b) reveals the poor station coverage for NO<sub>2</sub> in comparison for example with the previously presented EMEP measurement network for sulphur components. The limitations of the kriging method are more evident in a sparse network due to larger uncertainties during the fitting of covariance functions. Still, the method provides relevant information to the comparison of the spatial distribution of modelled and observed concentrations.

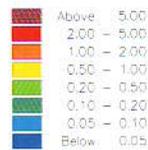
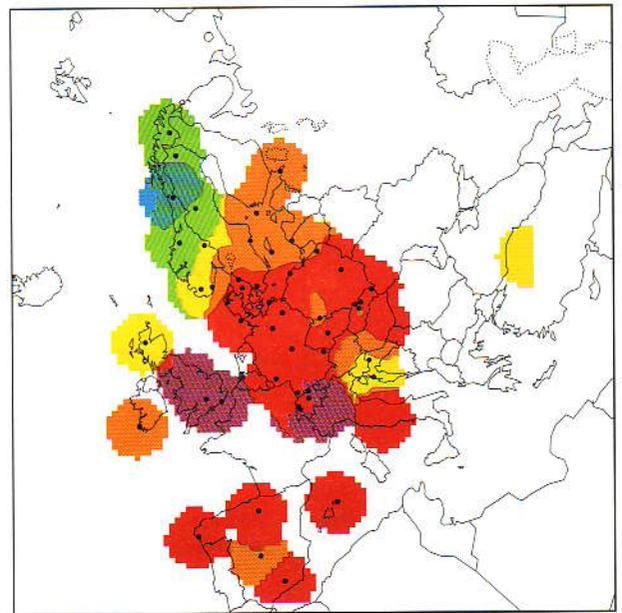
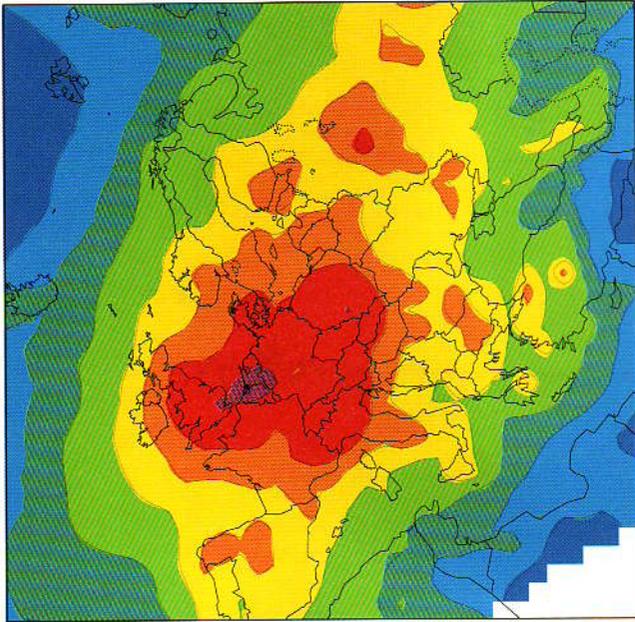
Also during the cold season there is a general underestimation by the model. The reason for this underestimation may again be the diurnal variation of boundary layer as explained above, particularly for observations in west and southern Europe. Over Scandinavia and central Europe, the relative high frequency of winter inversions may be the reason for the averaged better agreement between the model and measurements in these areas. The geographical coverage of the EMEP network for nitrogen dioxide is not sufficient however, to allow conclusive remarks on the chemical parametrisation of the model at the present stage.

The behaviour at Spanish stations deserves a separate comment. Figure 3c) shows the large differences between model and observations in these stations. The actual 1996 measured data is depicted in Figure 3e) and is about a factor of two higher at these three stations than data collected at other European stations. There is no reason to doubt the Spanish data out of their sampling technique or results from intercalibration studies, but it is difficult to explain the high values reported from these stations ever since they were included in the EMEP program in 1988 (see EMEP/MSC-W, Status report, 1998, appendix B).

Because of the reported high values from the Spanish stations included in this analysis, caution is recommended when considering the combined NO<sub>2</sub> air concentrations in Figure 3d). In addition, the lack of measurement data France, Greece and other Mediterranean countries makes it difficult to draw conclusions for NO<sub>2</sub> over Southern Europe.

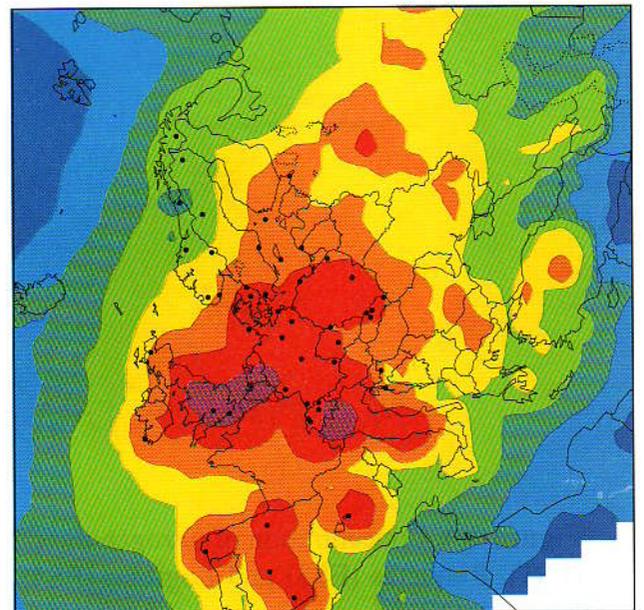
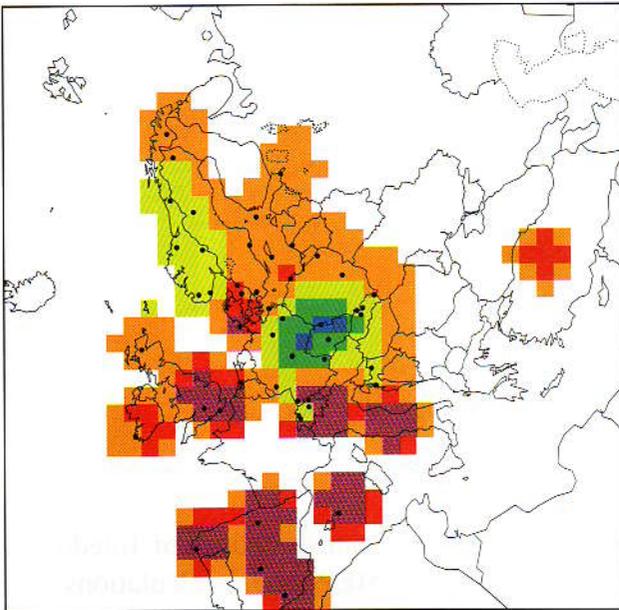
a) Modelled NO<sub>2</sub> in air, cold period

b) NO<sub>2</sub> kriged from measurements

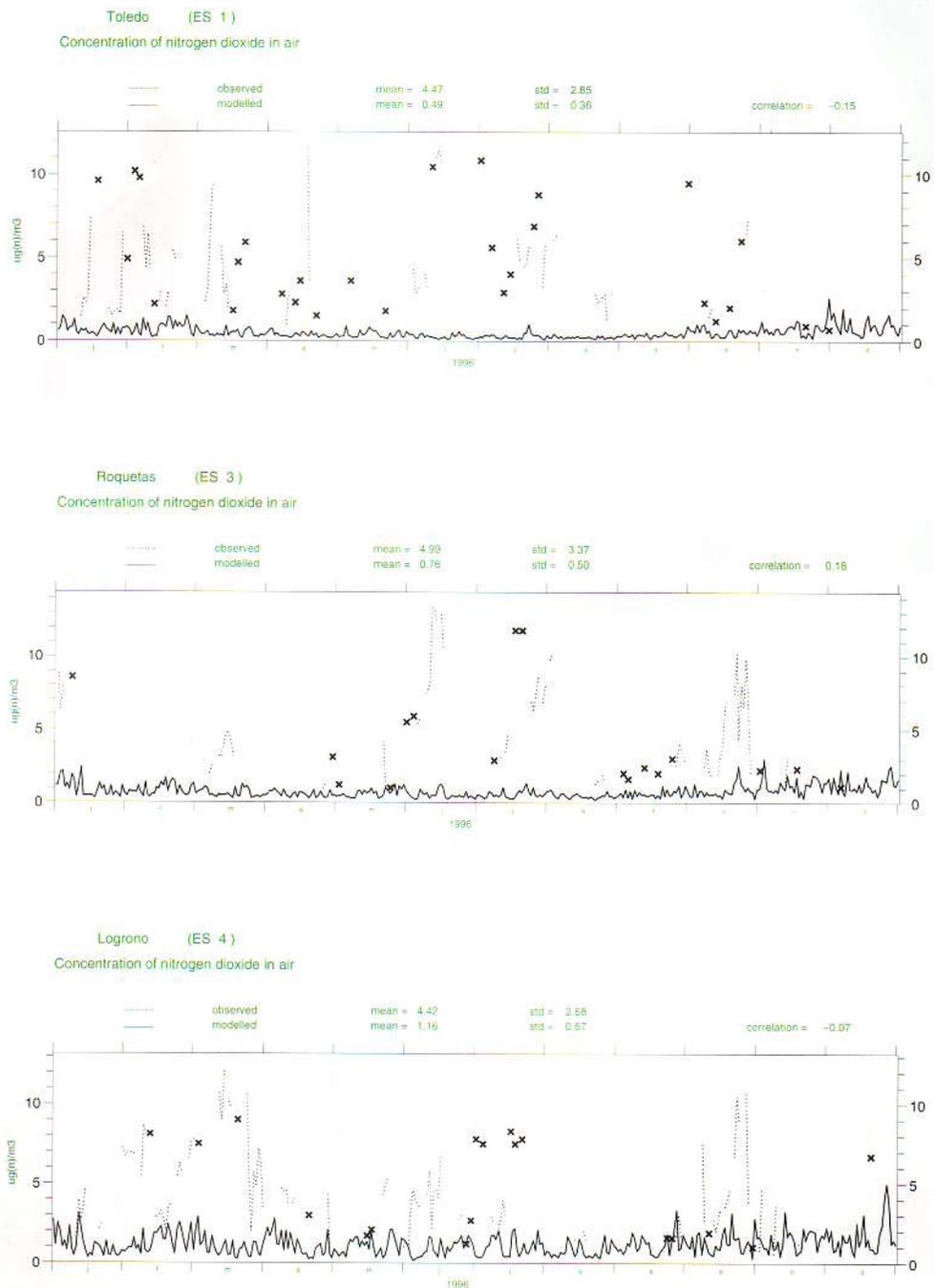


c) Interpolated normalized differences

d) Combined NO<sub>2</sub> in air



**Figure 3. a)-d) Analysis of NO<sub>2</sub> concentrations in air averaged for cold period October-March 1996.** Figures a), b) and d) use the common colour scale given in the figure, units are  $\mu\text{g(N)}/\text{m}^3$ . Interpolated normalized differences between model and observations use a different scale. In figure c) orange, red and purple show where the model underpredicts respectively within a factor of 2, 3 and 4. Light green, green and blue show where the model overestimates observed values respectively within a factor of 2, 3 and 4. Black dots indicate the position of measurement sites.



**Figure 3e).** Concentration of nitrogen dioxide in air collected at the Spanish stations of Toledo (ES1), Roquetas (ES3) and Logroño (ES4) in 1996 compared to EMEP model calculations. Units:  $\mu\text{g(N)}/\text{m}^3$

### 3.4 Total nitrate in air

Total nitrate in air refers to the sum of nitric acid ( $\text{HNO}_3$ ) and particulate nitrate ( $\text{NO}_3$ ). We have chosen to compare total nitrate in order to avoid a discussion on the partitioning between the individual components which is beyond the purpose of this note.

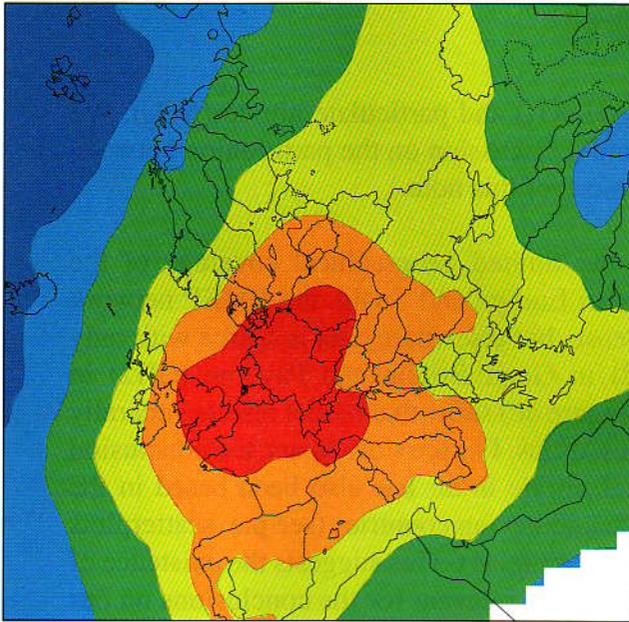
The first feature to note from Figures 4b)-d) is the limited geographical coverage of the monitoring sites for total nitrate in air. Over northern Europe and Spain, the EMEP network reporting total nitrate measurements is relatively dense, but elsewhere data is scarce with only two single reporting stations: Eksdalemuir (GB2) in Great Britain and Payerne (CH2) in Switzerland. The kriged normalized differences in Figure 4c) show that model results generally overestimate the observations collected in the given stations. For previous years, the conclusion that the EMEP model generally overestimates total nitrate in air has also been based in the comparison with observations compiled in mainly Scandinavian countries (see p.e. scatterplots for 1985-96 in EMEP/MSC-W Status Report 1998, appendix B). This suggests the existence of a bias in the spatial coverage of the stations which may be relevant for the conclusions on our ability to simulate total nitrate concentrations in air.

Different explanations have been suggested to understand the overestimation by the EMEP model. Arguments have been primarily concerned with the partitioning of nitric acid and nitrate which affects the dry deposition efficiency of total nitrate because nitric acid has a very large dry deposition velocity (up to 4-5cm/s) while particulate nitrate is dry deposited very slowly. In this discussion little attention has been given before to the acknowledged limitations of the EMEP Lagrangian model to simulate transport in complex areas. However, the present analysis seems to indicate that another possible reason adding to the overestimation of total nitrate by the Lagrangian model may be the coarse resolution of model which limits its ability to simulate the airflow around mountain regions.

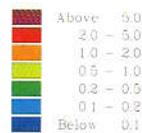
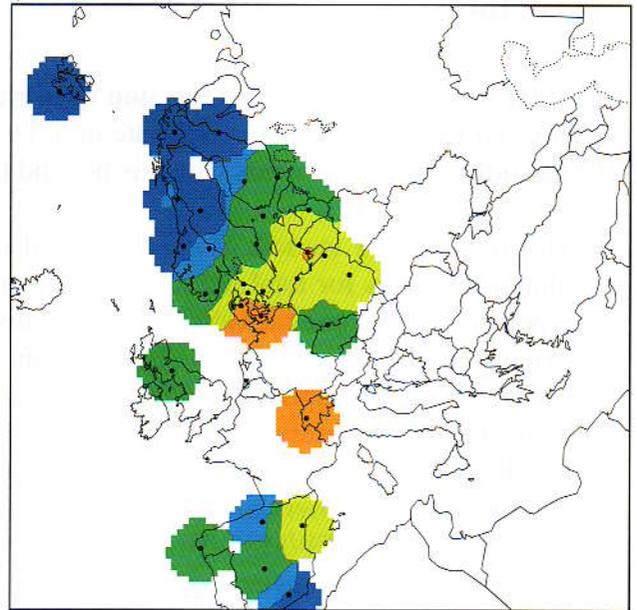
The total nitrate field depicted in Figure 4d) combines the information from the EMEP Lagrangian model with the observations collected in northern Europe, Spain, Switzerland and Great Britain. Differences between 4a) and 4d) closely follow a topographic map of Europe: we can identify the Norwegian mountains, the Alps, the Pyrenees, the Spanish Plateau and Sierra Nevada. These features are so well defined because of the particular location of the reporting EMEP stations.

It could be speculated that a model with better vertical resolution and a similar parametrisation of nitrate chemistry and dry and wet deposition should manage to reproduce the features in Figure 4d). Figure 4e) shows the 1996 distribution of total nitrate as simulated by the Eulerian EMEP model, where not only the Alps and the Pyrenees are well depicted but also the Apennines and the Carpathians. It is also interesting to note the flow of central European nitrate to the north being deflected by the Norwegian mountains and the inflow of less polluted air from the North Atlantic Ocean at Scotland and northern Ireland.

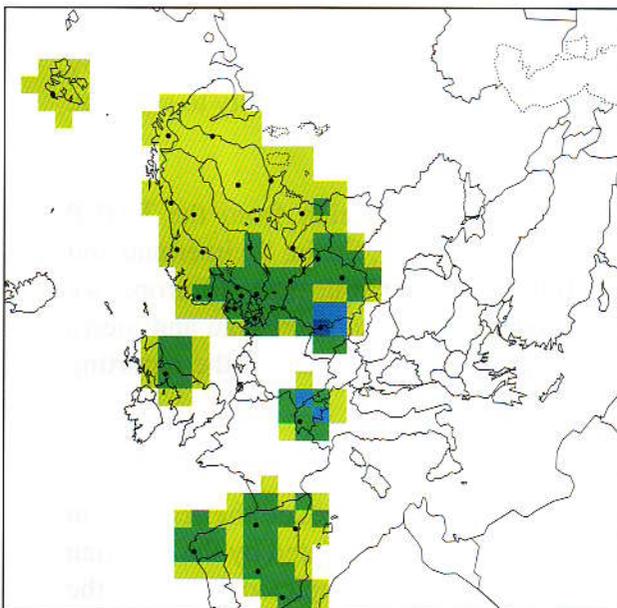
a) Modelled total nitrate in air



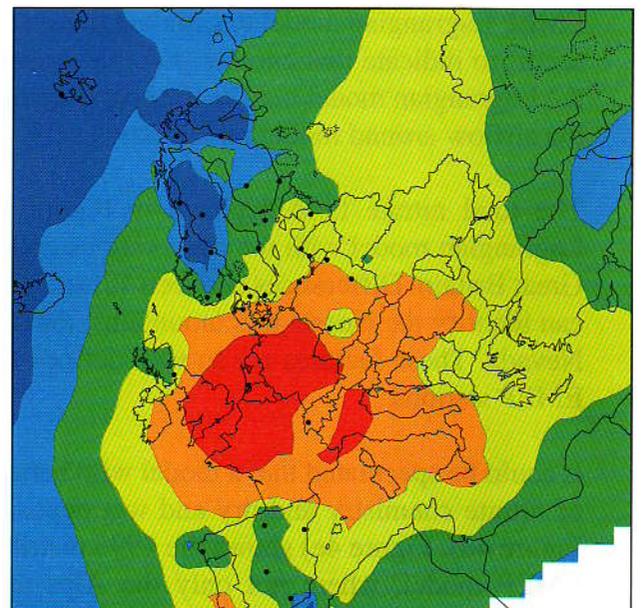
b) Kriged total nitrate in air



c) Interpolated normalized differences



d) Combined total nitrate in air



**Figure 4. a) - d) Analysis of yearly averaged total nitrate concentrations in air. Values for 1996.**

Figures a), b) and d) use the common colour scale given in the figure, units are  $\mu\text{g}(\text{N})/\text{m}^3$ . Interpolated normalized differences between model and observations use a different scale. In figure c) orange, red and purple show where the model underpredicts respectively within a factor of 2, 3 and 4. Light green, green and blue show where the model overestimates observed values respectively within a factor of 2, 3 and 4. Black dots indicate the position of measurement sites.

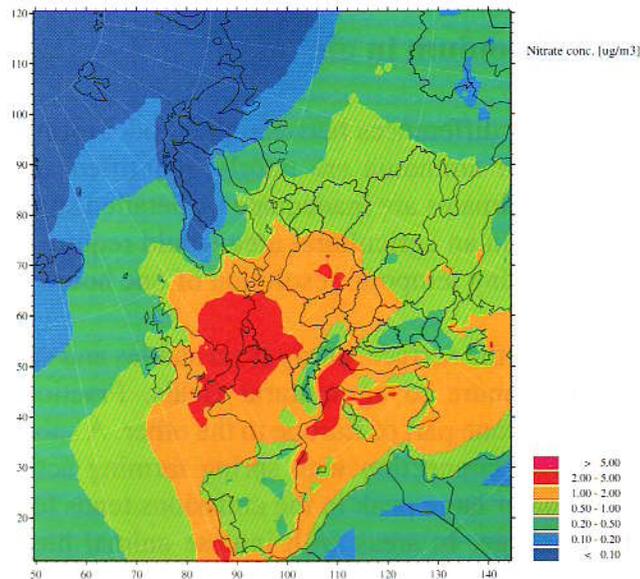


Figure 4e). Total nitrate concentrations in air calculated by the EMEP Eulerian model

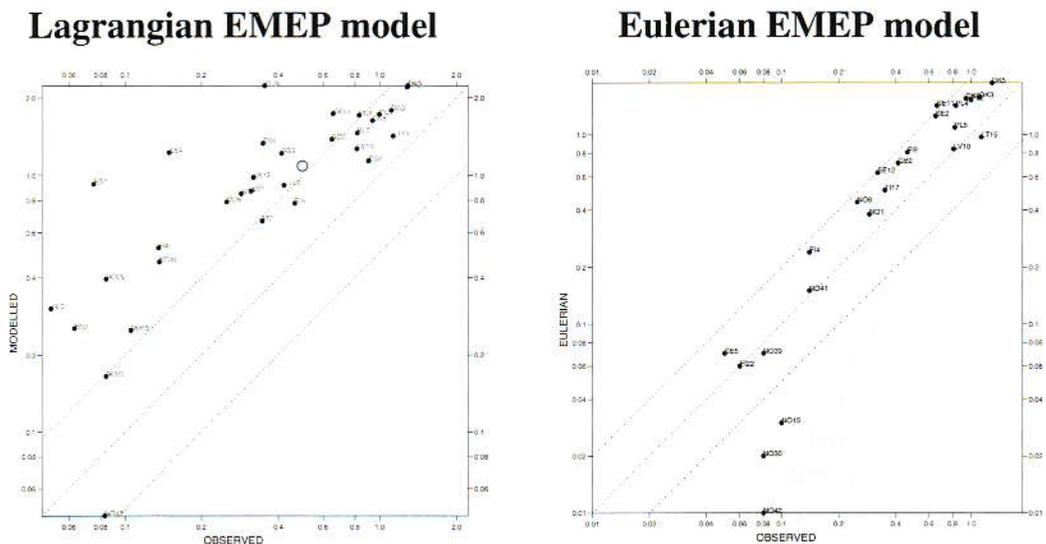


Figure 4 f). Annual scatterplots for comparison of modelled and observed total nitrate in air.

As indicated in Figure 4f) the agreement between modelled and measured total nitrate is considerably improved for the Eulerian EMEP model. There is room for improvement both on the chemical and physical description of total nitrate in the EMEP models, but the testing of our understanding of such processes demands a better geographical coverage of the monitoring network in order to be significant. The present analysis illustrates once more the urgent need for total nitrate monitoring in continental Europe.

### 3.5 Ammonia and ammonium in air

There are several reasons for differences between the model estimates and the measurements. First of all, the emissions of ammonia are poorly quantified and the spatial and temporal resolution of the emission estimates are inadequate. A detailed study of ammonia emission and deposition relationships within an agricultural area would require a spatial resolution of better than 1 km, with a corresponding temporal resolution of one hour.

Ammonia emissions occur at the surface, partly from stables and storage of manure, but mainly from the application of manure to agricultural fields. Practices with respect to manure application vary widely from one part of Europe to the other. A substantial part of the emissions in northern Europe occur in connection with spring farming activities, typically within two weeks in April -May. Another large peak in the emissions tends to be in June, after cutting the first crop of grass for ensilage. In areas with intense animal husbandry and limited storage capacities, manure application and disposal goes on throughout the year.

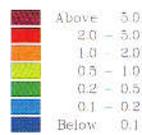
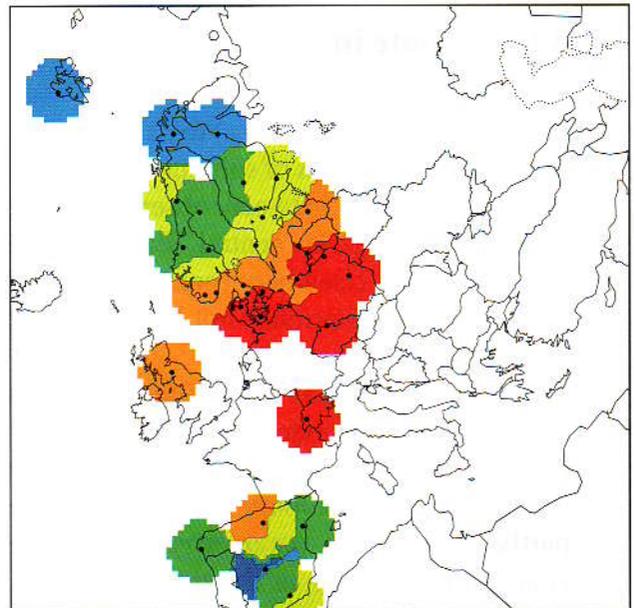
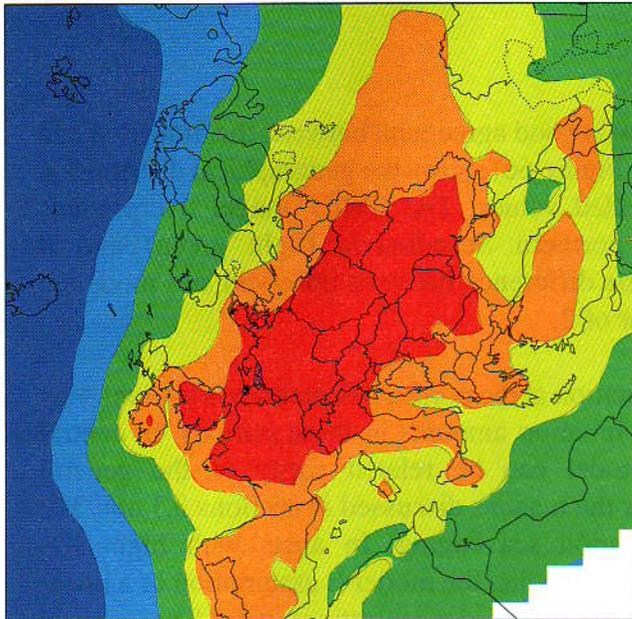
Ammonia emission rates depend not only on the agricultural practices but also on the weather conditions, in particular, on the relative humidity, temperature and wind speed. Precipitation estimates are also relevant as precipitation falls within the first few days after application may prevent emission of any ammonia left in the manure. Differentiated and elaborated ammonia emissions inventories are therefore highly desirable and the emission algorithm should take into account weather conditions.

At present, the EMEP model considers a common seasonal variation of ammonia emissions with maximum emissions in June and minimum in January and no explicit dependence with weather conditions is assumed. Still, it is not easy to see the effect of this simplification in the modelled air concentrations because the seasonal variation of ammonia and ammonium concentrations in air does not depend only on the ammonia emissions and deposition but also on the presence of sulphate and nitrate in air. In general, the EMEP model does not manage to reproduce the seasonal variations of observed reduced nitrogen in air, although for yearly averages, the model generally underpredicts the observed concentrations. Exceptions to this behaviour are found over Spain and are probably related to low emission estimates from the region.

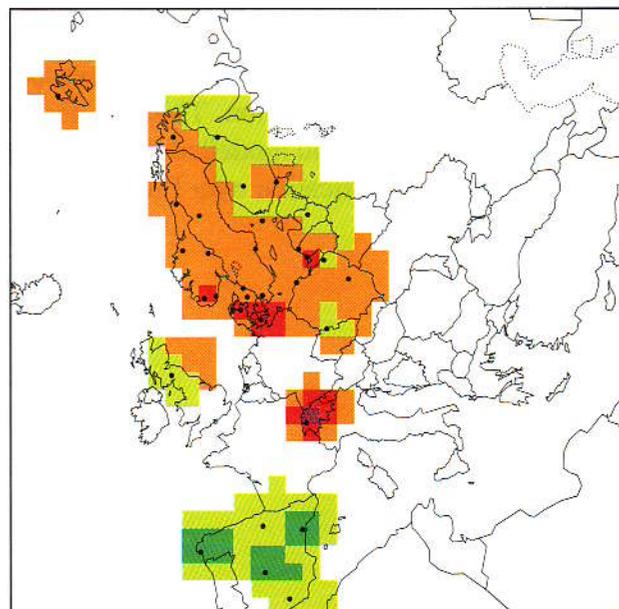
The location EMEP monitoring sites for reduced nitrogen is the same as for total nitrate. However, for reduced nitrogen, the location of these stations does not help to draw conclusions on systematic differences between modelled and observed values, as it did in the case of total nitrate. The geographical distribution of reduced nitrogen in air is determined in equal terms by the concentrations in air of ammonia and ammonium. Ammonium has a longer residence time in the atmosphere but ammonia's residence time is short and its concentration in air is closely related to its sources. Since ammonia emissions are expected to be considerably variable, a denser network is necessary before we can allow ourselves the possibility of combining modelled and monitored results to provide a combined map of our best estimate. We have chosen not to present this type of map for reduced nitrogen. This should be interpreted as our recognition for the need for further improvement in the simulation of ammonia emissions and to stress the need for measurements of reduced nitrogen in continental Europe.

a) Modelled  $\text{NH}_3+\text{NH}_4$  in air

b) Kriged  $\text{NH}_3+\text{NH}_4$  in air



c) Interpolated normalized differences



**Figure 5. a) -c) Analysis of yearly averaged reduced nitrogen concentrations in air. Values for 1996.** Figures a), b) and d) use the common colour scale given in the figure, units are  $\mu\text{g}(\text{N})/\text{m}^3$ . Interpolated normalized differences between model and observations use a different scale. In figure c) orange, red and purple show where the model underpredicts respectively within a factor of 2, 3 and 4. Light green, green and blue show where the model overestimates observed values respectively within a factor of 2, 3 and 4. Black dots indicate the position of measurement sites.

### 3.6 Sulphate in precipitation

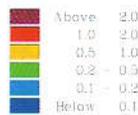
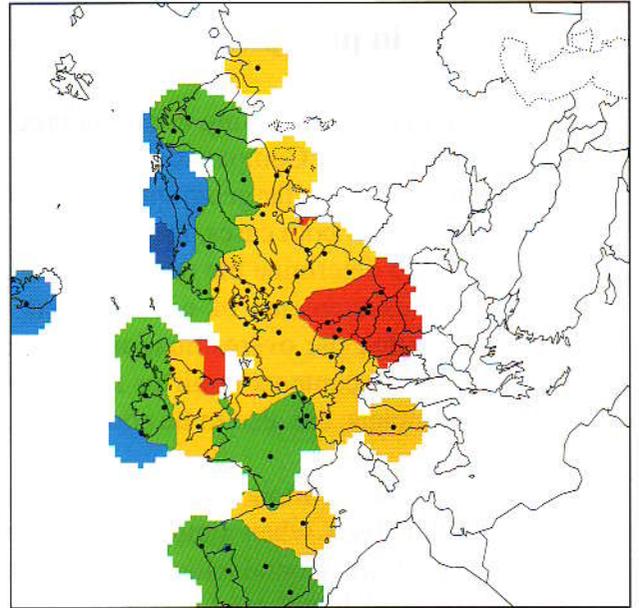
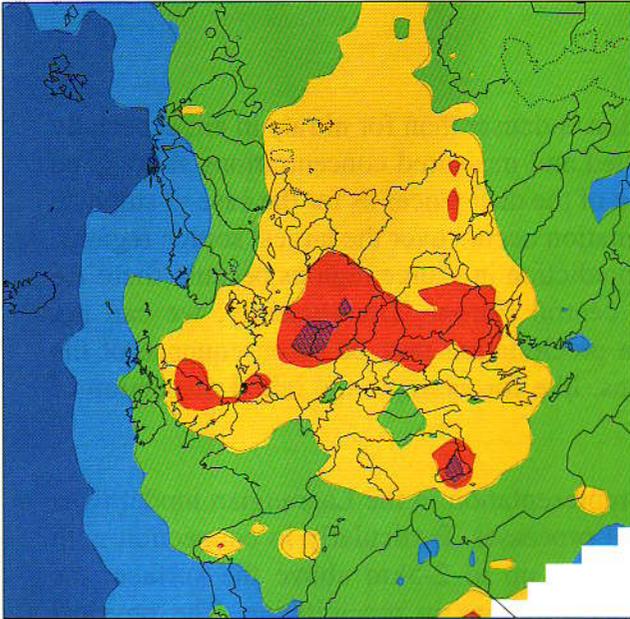
A first glance at Figures 6 a) to d) shows that there is good agreement between the modelled and the observed contents of sulphur in precipitation. Figure 6c) shows the geographical distribution of the difference between observed and modelled values. The EMEP model overpredicts observed values in central Europe and in northern Scandinavia (light green) and it underestimates elsewhere (orange). Generally the difference between observed and modelled sulphur in precipitation is not larger than a factor of 2.

The overestimation of sulphur contents in precipitation at the northern Scandinavia stations may be related to the model underestimation of precipitation amounts in these stations. In central Europe, however, the performance of the model can be related partly to the general overestimation of sulphur in air over the area for the reasons discussed in sections 3.1 and 3.2, partly also to the parametrisation of precipitation scavenging. In areas with high SO<sub>2</sub> concentrations in air, as it is the case in the Czech Republic, the model 's assumption of a linear dependence of wet scavenging with the sulphur dioxide concentrations would necessarily overpredict the contents of sulphur in precipitation.

Former studies on the adjustment of calculated sulphate in precipitation with observations showed larger differences, particularly over the west coast of Europe (Iversen et al., 1991; Schaug et al., 1993). After these first studies with kriged differences, new background concentrations were introduced in the model as well as estimates of emissions from international ship traffic from the North Sea and the North East Atlantic Ocean. International ship traffic emissions represent about 2.6% of the total EMEP sulphur emissions and are estimated to contribute with 10-15% of the total deposition over coastal Europe. Consequently, the introduction of these type of emissions is expected to be a main reason for the better model performance over coastal areas in the present calculation. This is a good example of how the spatial analysis of differences between observed and modelled values has been used to improve our understanding of the sources affecting acidification over Europe.

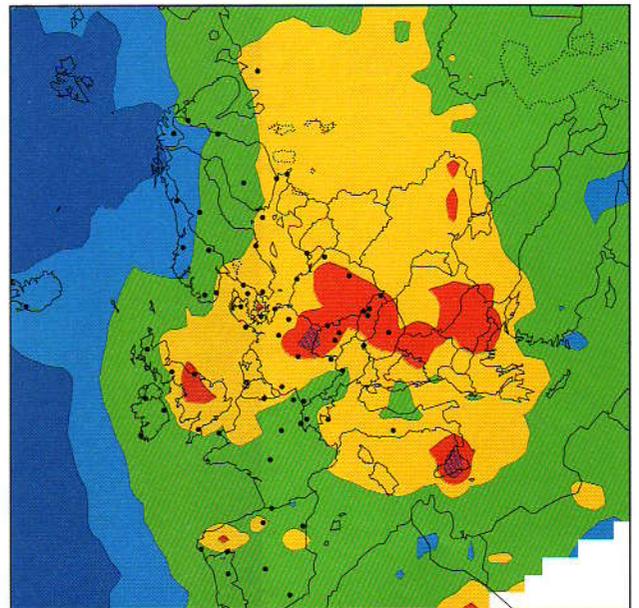
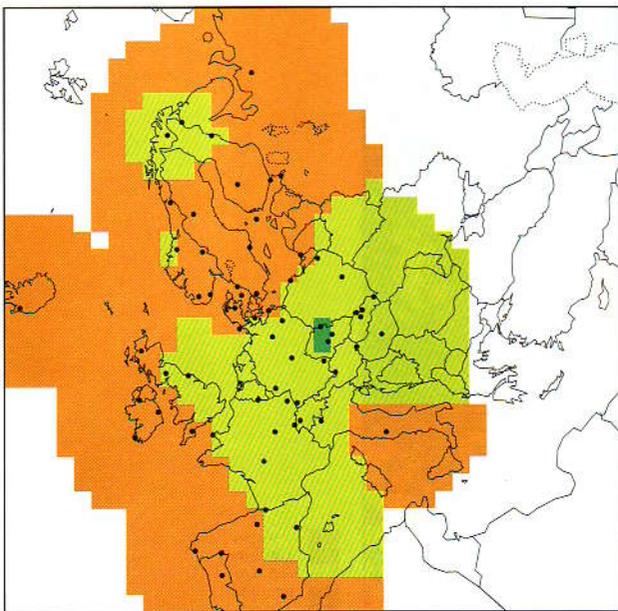
a) Modelled SO<sub>4</sub> in precipitation

b) Kriged SO<sub>4</sub> in precipitation



c) Interpolated normalized differences

d) Combined SO<sub>4</sub> in precipitation



**Figure 6. a) - d) Analysis of yearly averaged sulphate in precipitation. Values for 1996.**

Figures a), b) and d) use the common colour scale given in the figure, units are mg(S)/l. Interpolated normalized differences between model and observations use a different scale. In figure c) orange, red and purple show where the model underpredicts respectively within a factor of 2, 3 and 4. Light green, green and blue show where the model overestimates observed values respectively within a factor of 2, 3 and 4. Black dots indicate the position of measurement sites.

### 3.7 Nitrate in precipitation

The EMEP network reporting nitrate in precipitation is denser than for nitrate in air, especially over central Europe. Comparison between modelled and measured concentrations show good agreement, with a similar geographical distribution of the differences as for the case of sulphate in precipitation. In both cases, the model overestimation occurs over the largest source regions. It is difficult to determine the reason for the overprediction in source regions because there are no EMEP measurements of nitrate in air over central Europe. Consequently, we can not establish whether the overestimation of nitrate in precipitation may be a consequence of the modelled nitrate contents in air or if other reasons, like for example the initial dispersion of primary pollutants, are also to be considered.

It should also be mentioned that the lack of 3-D representation in the Lagrangian model is an important drawback when simulating wet removal processes. Particularly in connection with precipitation from frontal clouds, which may extend up to 2-5km above the surface, the Lagrangian model will tend to underestimate concentrations in precipitation. The physical description of wet removal requires a 3D and has been an important argument for the development of the EMEP Eulerian model. The figure below depicts the estimated concentration of nitrate in precipitation from the EMEP Eulerian model that again are in good agreement with the observations.

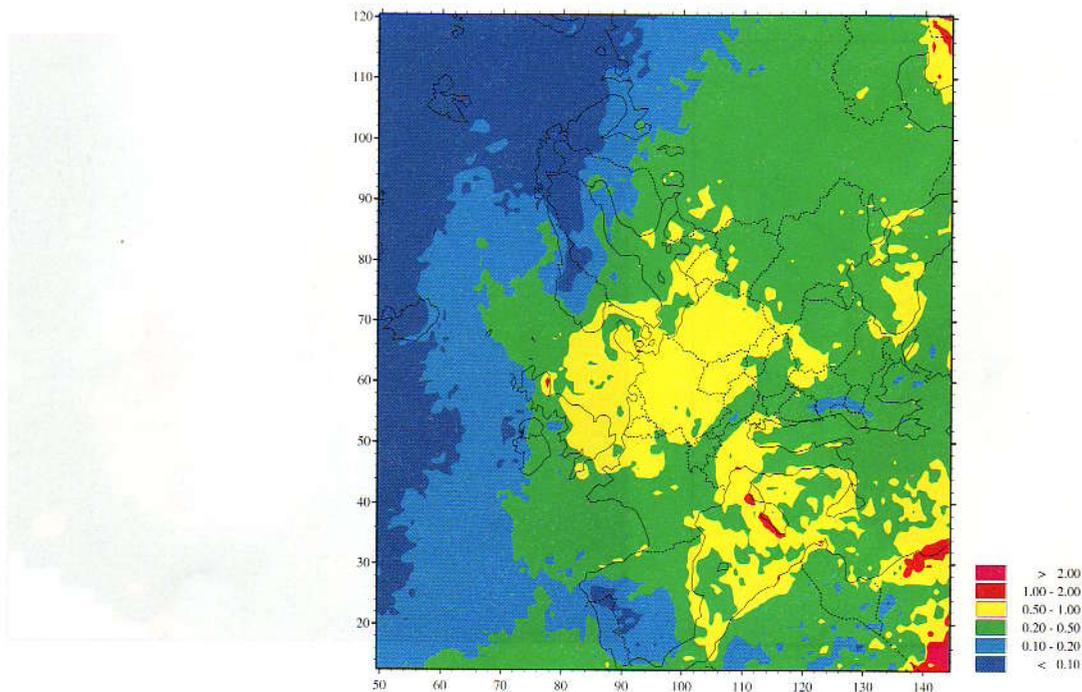
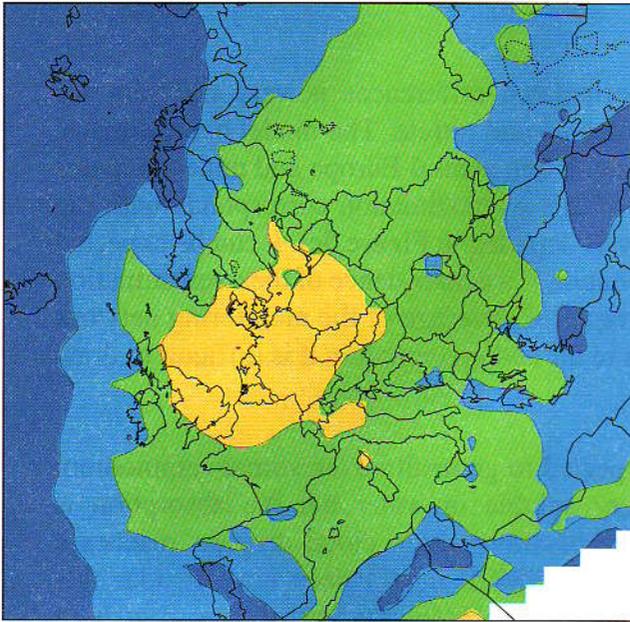
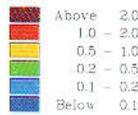
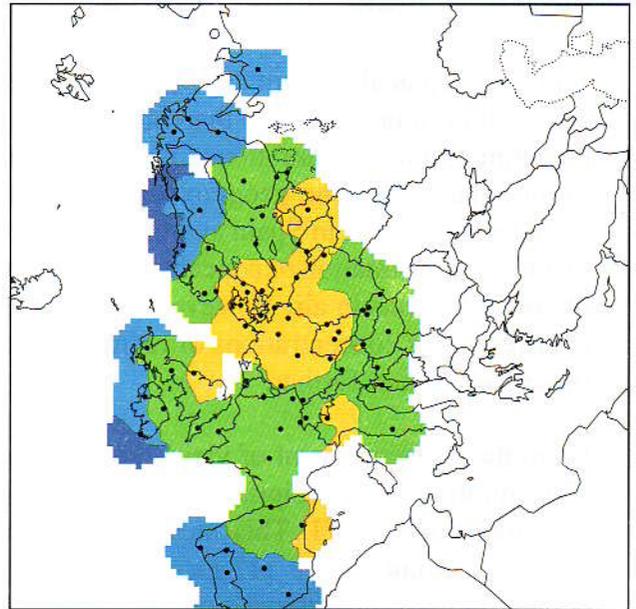


Figure 7e). Nitrate in precipitation as calculated by the EMEP Eulerian model. Units are mg(N)/l.

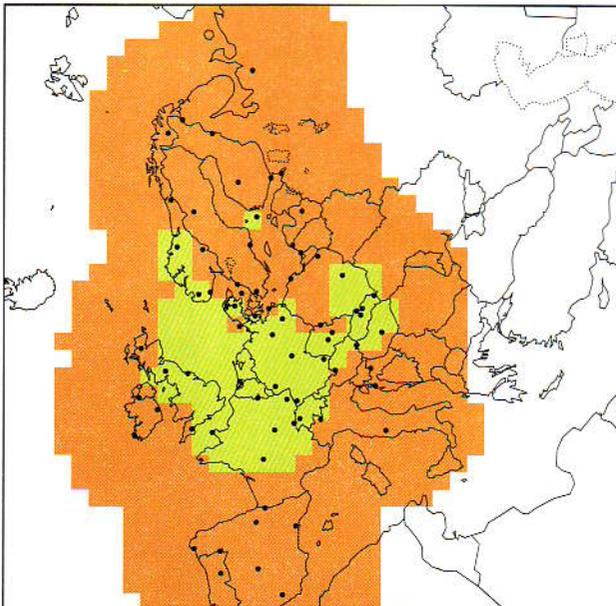
a) Modelled NO<sub>3</sub> in precipitation



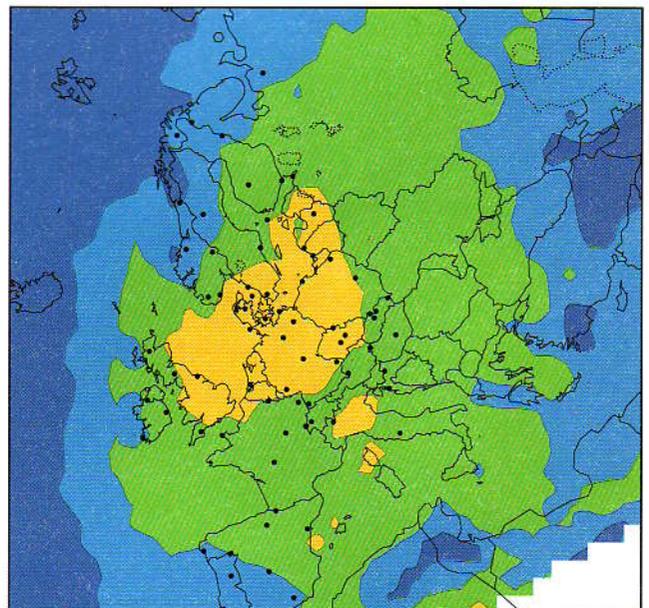
b) Kriged NO<sub>3</sub> in precipitation



c) Interpolated normalized differences



d) Combined NO<sub>3</sub> in precipitation



**Figure 7. a) - d) Analysis of yearly averaged nitrate in precipitation. Values for 1996.**

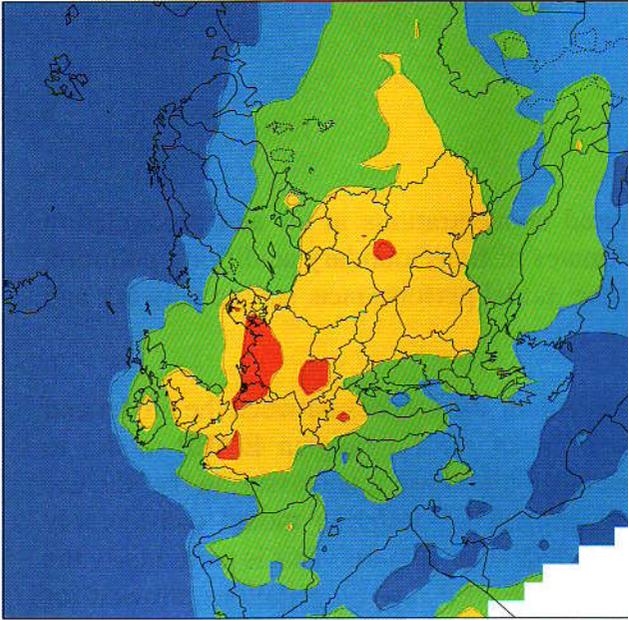
Figures a), b) and d) use the common colour scale given in the figure, units are mg(N)/l. Interpolated normalized differences between model and observations use a different scale. In figure c) orange, red and purple show where the model underpredicts respectively within a factor of 2, 3 and 4. Light green, green and blue show where the model overestimates observed values respectively within a factor of 2, 3 and 4. Black dots indicate the position of measurement sites.

### **3.8 Ammonium in precipitation**

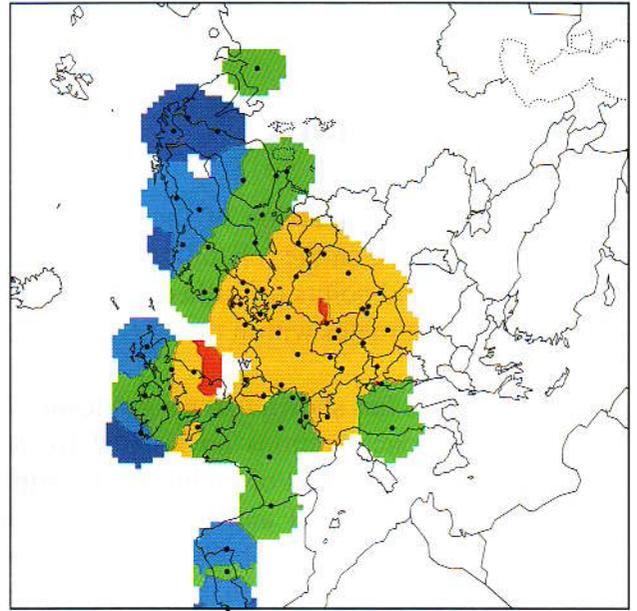
The geographical pattern of the interpolated normalized differences is very different for ammonium in precipitation than in the cases of sulphate and nitrate. The model overestimates the ammonium concentrations in precipitation in south and central Europe and underestimates in the other sites. The geographical distribution of this overestimation corresponds with the model performance in Spain and Great Britain as was depicted in Figure 5c). It can be expected that the overestimation of concentrations in precipitation is a consequence of the overestimation of concentrations in air. However, since the geographical coverage of the monitoring network is different for concentrations of reduced nitrogen in air and precipitation it is difficult to draw these conclusions further.

From the chemical point of view, the model is expected to generally overestimate ammonium concentrations in precipitation. Ammonia is very soluble in water but the absorption is dependent on the pH. This means that the uptake of ammonia in cloud droplets reaches a saturation point as the pH increases. At present the EMEP model does not consider this dependence of wet deposition of ammonium with the pH so the model can give high concentrations in precipitation in areas with surplus of reduced nitrogen.

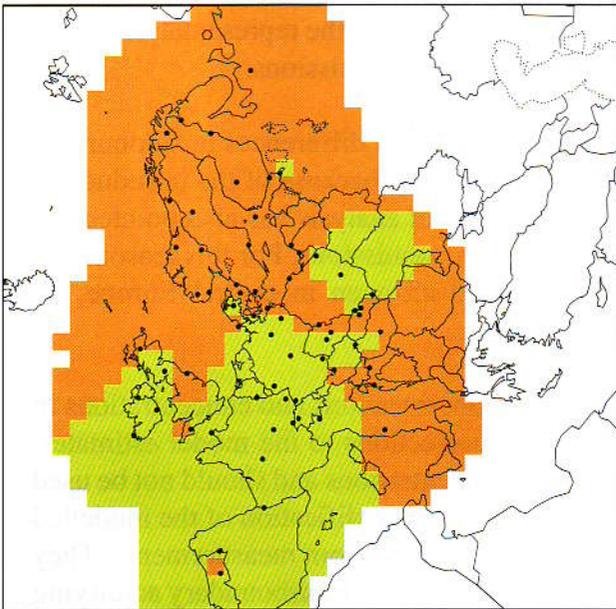
a) Modelled  $\text{NH}_4$  in precipitation



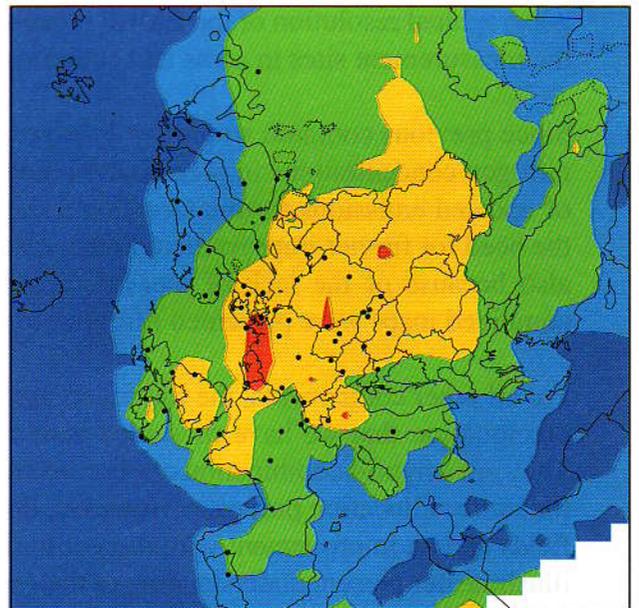
b) Kriged  $\text{NH}_4$  in precipitation



c) Interpolated normalized differences



d) Combined  $\text{NH}_4$  in precipitation



**Figure 8. a) - d) Analysis of yearly averaged ammonium in precipitation. Values for 1996.**

Figures a), b) and d) use the common colour scale given in the figure, units are  $\text{mg(N)/l}$ . Interpolated normalized differences between model and observations use a different scale. In figure c) orange, red and purple show where the model underpredicts respectively within a factor of 2, 3 and 4. Light green, green and blue show where the model overestimates observed values respectively within a factor of 2, 3 and 4. Black dots indicate the position of measurement sites.

## 4. Conclusions

The present comparison of modelled and measured concentrations in air and precipitation shows progress in the reliability of the EMEP estimates of transboundary acidifying pollution in Europe and points to further needs to improve the model performance, station network and emission estimates within the EMEP programme.

The analysis has shown that a significant part of systematic differences between the model and observed concentrations are related to the limitations of the Lagrangian EMEP model to simulate the transport of pollution in complex terrain. In this sense it is reassuring that the use of a finer horizontal and vertical resolution with the EMEP Eulerian model considerably improves the agreement between measurements and model calculations. This is particularly the case for nitrate in air, where the special location of the EMEP reporting stations allowed for discerning plausible causes of the systematic overestimations in the Lagrangian model.

The conclusions from our evaluation are very dependent on the location of the EMEP measurement sites. There is a general need for reporting EMEP measurement sites in central and southern Europe for nitrogen dioxide, nitrate in air and ammonia in air. The geographical coverage of EMEP sites reporting concentrations in precipitation needs to be improved in south-eastern Europe. For sulphur dioxide, the need for a denser measurement site is related to the geographical resolution of the EMEP models and the need to establish the representativeness of the measurement sites in areas and countries with large indigenous emissions.

Since previous common studies with kriged differences, systematic differences in sulphur and nitrogen concentrations in precipitation have been reduced mainly because of the introduction of updated emissions from international ship traffic. The present analysis has also pointed out the need for further improvement in the simulation of ammonia emissions. For this reason, and also because of the lack of measurement sites for reduced nitrogen in central Europe, no combined maps were presented for reduced nitrogen in air.

For all other components, the improved maps of airborne concentrations and concentrations in precipitation that we have presented here can be used as corrections to the model estimates. They are a hybrid combination of observed and modelled concentrations and should not be used for source allocation purposes. However, they provide a valuable qualification of the modelled fields and an improvement with respect to the kriged fields derived from measurements. They illustrate our present understanding of the geographical distribution of transboundary acidifying air pollution in Europe and in this sense they may be useful for the determination of the critical loads and levels to different ecosystems.

## 5. References

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