

Hilatar, a limited area simulation model of acid contaminants

Part I Model description and verification

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Abstract

The three-dimensional model Hilatar, designed to study and predict the physico-chemical transport, transformation and deposition of various trace constituents over Europe and its subparts is shortly described. The performance of individual algorithms and comparison with parameterisation with other models are discussed. In comparison with measurements at the EMEP network stations both the modelled concentrations and deposition were rather close to the observations. NO₂ was somewhat underestimated while NO₃+HNO₃ was over-estimated indicating that there are missing chemical sinks of nitrogen compounds. The reasons for the model-measurement deviations at individual stations are discussed.

Key word index: Eulerian model, atmospheric concentrations, deposition, sulphur, nitrogen

INTRODUCTION

The Hilatar model has been constructed for estimating the air pollution load in Finnish background areas, and for studying the meteorological and other processes influencing the deposition and transport specially over the Baltic Sea domain. A detailed report on this model (referred as the NMR-Hilatar, Hongisto, 1998) can be found on the www-pages of the Finnish Meteorological Institute (FMI) (http://www.fmi.fi/research_air/air_25.html). In order to achieve an operational capability and get an on-line estimate of the long-range transported (LRT) pollutant contribution the model has been extended to cover the whole of Europe (the EUR-Hilatar). This paper introduces the main features of the Hilatar model together with verification in the Baltic Sea domain. Long-term simulations and verification over the European domain are presented in the companion Part II of the paper.

Hilatar is an extension of the Finnish regional dispersion model for oxidised nitrogen FINOX (Hongisto, 1992a, 1993), applied for estimating the nitrogen load in the 1980's and for generating source-receptor matrices for the Finnish integrated assessment model (Syri et. al., 1998).

Model structure

The NMR-Hilatar covers the Baltic Sea region with a horizontal resolution of 0.25°, around 26 km (since 1999 0.2°), while the European model has a 0.5°, since 1999 0.4° resolution. Additionally a zooming model of 0.1° for Finland and its close surroundings has been constructed. It uses the grid of the FMI operational weather prediction model HIRLAM (HIGH Resolution Limited Area model), which is horizontally a rotated spherical grid and vertically a terrain-following hybrid grid. The lowest 10 layers are below 3 km. Above this height 3 additional layers between 3 and 10 km are used since 1995.

The concentrations $c(\bar{x}, t)$ at time t and place $\bar{x} = x, y, z$ are calculated by numerically solving the transport-transformation equation

$$\frac{\partial}{\partial t} c(\bar{x}, t) + [\bar{V}(\bar{x}, t) \cdot \nabla c(\bar{x}, t)] = \nabla \cdot [\bar{K}(\bar{x}, t) \cdot \nabla c(\bar{x}, t)] + S(\bar{x}, t) \quad (1)$$

where $V(\bar{x}, t)$ is the wind velocity, K is the eddy diffusivity and $S(\bar{x}, t)$ includes emissions, chemical source and sink terms and deposition. The equation is decomposed into one-dimensional diffusion, advection and chemistry sub-problems which are solved successively by an algorithm suitable to each one (the time-splitting method). The concentrations are required to be known along all borders. The dry deposition flux defines the lowest boundary condition for vertical turbulence. Vertical diffusion is solved using the gradient transport theory: turbulent fluxes are assumed to be proportional to local mean concentration gradients.

The 1 to 6-hour weather predictions of the FMI HIRLAM are used. A meteorological database, provided also for other environmental researchers, has been maintained since 1991. Up to November 1999 the resolution of meteorological fields was 0.5° , since then 0.2° and 0.4° . The vertical fluxes are calculated as surface-coverage-weighted averages of sea and land values. Before 1999, over land areas, the FMI meteorological pre-processor used in local dispersion model studies with vertical data from the sounding stations had been adapted to use HIRLAM profiles of wind $u(z)$ and moist potential temperature $\theta(z)$. During unstable situations the mixing height h_{mix} is evaluated from the $\theta(z)$ profile by searching for the first inversion level. In stable and near-neutral situations an analytical form is used. Since 1999, the h_{mix} is directly available from HIRLAM, and the friction velocity and other scaling parameters are solved analytically from the surface fluxes. Over sea areas, where the diabatic effect of the moisture flux on buoyancy and the interaction between the surface roughness and the wind are important, the iterative method of Lindfors et al. (1993) is used.

In all model versions the vertical velocity is calculated from the horizontal wind fields and the eddy diffusion coefficient parameterisation is based on the scaling regimes (Holtslag & Nieuwstadt, 1986) as presented in Hass (1991). Weak mixing across the boundary layer top was allowed, and above it a constant K_z value was used. The fractional cloud cover is parameterised in terms of relative humidity according to HIRLAM (1996). The liquid water content of the clouds depends on cloud type, temperature, convectivity and the possibility of cold advection over sea areas.

The surface characteristics are extracted from the forecast model or from the Grid Arendal on-line GIS Baltic Sea Drainage Basin database (<http://www.grida.no/baltic/>). Over Finland a Landsat TM image inventory with over 50 land-use categories has additionally been applied.

For estimates of the long-range transported pollutants, daily average concentrations, obtained for 1993-1995 from the EMEP MSC-W centre (Iversen et al., 1989) or from the European Hilatar, are added to the air flowing through the NMR-model boundaries. The emissions, meteorological parameters and dry and wet deposition sink terms vary every hour during the simulations.

Chemistry and numerical methods

Gaseous and particle concentrations are calculated for the following substances: $\text{NO}_x(\text{g})$, $\text{HNO}_3(\text{g})$, $\text{NO}_3(\text{p})$, $\text{PAN}(\text{g})$, $\text{NH}_4\text{NO}_3(\text{p})$, $\text{NH}_3(\text{g})$, $\text{SO}_2(\text{g})$, $\text{SO}_4(\text{p})$ and $(\text{NH}_4)_{1.5}\text{SO}_4(\text{p})$ or selected heavy metals or multi-size dust particles. The temporal value of NO can be calculated if the ozone and peroxy radical concentrations are known. The chemistry module is the EMEP-MSW-W code (Iversen et al., 1989) with updated rate coefficients and modifications that are connected to the model structure and sink terms. The emitted SO_2 is assumed to be a

non-scavengable variable which is linearly transformed into scavengable SO₂. No local deposition corrections are used.

The aqueous phase sulphate conversion rate $k_{\text{SO}_2\text{aq}}$ was estimated by studying SO₄ production with a specific 1-D cloud model. A first-order rate, that provided best compatibility at 60° N latitude, when oxidant concentrations, temperature, pH, emissions, cloudiness and liquid water content were varied, was selected. The rate $k_{\text{SO}_2\text{aq}}$ varies between $(1.5-4) \cdot 10^{-5} \text{ s}^{-1}$ in daytime and $(0.2-1.2) \cdot 10^{-5} \text{ s}^{-1}$ at night, during winter and summer, respectively. These rates are higher than in the EMEP-MSC-W model ($0.11 \cdot 10^{-7}$ in winter and $5 \cdot 10^{-6}$ during summer), but comparable to the rates of Möller (1980) and modest in comparison with the aqueous phase rates of Benkovitz et al. (1994).

The advection problem is solved by the Bott (1989) algorithm, the chemistry equations by the QSSA (quasi steady-state approximation) method (Hesstvedt et al., 1978), and vertical diffusion by the Crank-Nicholson algorithm with a staggered grid (Tuovinen, 1992).

Dry deposition

The dry deposition velocity v_d is calculated using the resistance analogy, with the aerodynamic and molecular resistances of Voldner et al. (1986). The surface resistance r_c for gases depends on radiation, temperature, relative humidity, amount of rain, dew or fog, pollutant exposure time and canopy height and density. Separate resistances for the gas transfer into plants through different paths and surfaces are parameterised following Wesely (1989). In winter, the snow resistance of Erisman (1994) is used. A minimum value of $r_c = 0.1 \text{ s cm}^{-1}$ for all gases is assumed.

Over water, the method of Joffre (1988) and Lindfors et al. (1993) is used. The aerodynamic resistance was calculated using the diabatic correction function for moisture. The surface resistance was assumed to be zero for soluble gases like HNO₃, NH₃ and SO₂ and also over a frozen sea. For NO₂, the surface resistances of Voldner et al. (1986) were used. The dry deposition of marine particles follows the schemes of Slinn et al. (1978) and Williams (1982).

The average v_d of soluble gases increase towards the open sea in winter. As an example, Fig. 1 illustrates the summer and winter distribution of the 1993-98 average HNO₃ v_d fields. The other compounds follow a similar seasonal variability. The v_d of SO₂ was higher in summer over forested areas in Sweden and Finland than in the southern parts of the domain. Over the open Baltic Sea $v_d(\text{SO}_2)$ was slightly lower than $v_d(\text{HNO}_3)$, exceeding 1 cm s^{-1} in January and being typically half of this value during summer. Over land, the wintertime grid average v_d of sulphate particles was $0.05-0.2 \text{ cm s}^{-1}$, exceeding 0.3 cm s^{-1} in summer, while the monthly average over water was smaller throughout the year. The average of $v_d(\text{NO}_2)$ over land was $\leq 0.02 \text{ cm s}^{-1}$ in winter, and $\leq 0.2 \text{ cm s}^{-1}$ in summer.

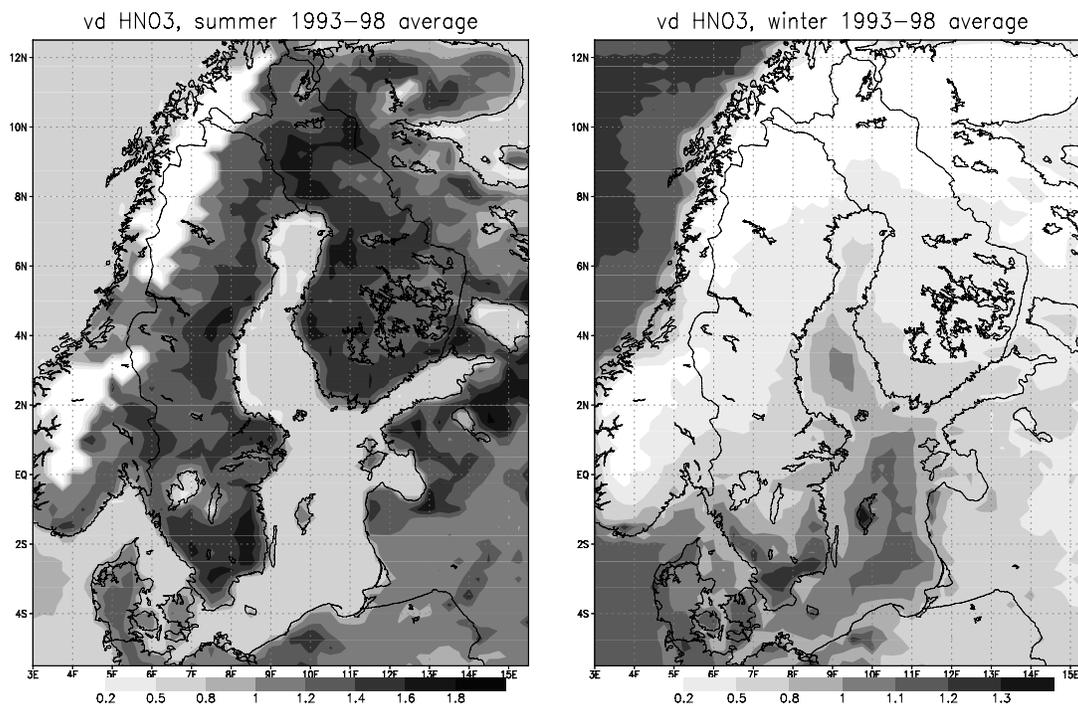


Fig. 1. HNO_3 dry deposition velocity, cm s^{-1} , winter and summer averages over 1993-1998.

The monthly average $v_d(\text{NO}_x)$ was clearly lower than $v_d(\text{NO}_2)$ in the EMEP model (Seland et al. 1995) both in summer and winter. For other compounds the gradients are sharper, especially in summer, and v_d is clearly lower over the Scandinavian mountains in the Hilatar model. In summertime and in winter near Denmark and on the shores of the Baltic Sea $v_d(\text{NH}_3)$ is around the same in both models, however, $v_d(\text{NH}_3)$ in Hilatar is higher over sea and lower over the land areas than in the EMEP model. Our $v_d(\text{SO}_2)$ is slightly higher over water, slightly smaller over land areas than the respective v_d -values in EMEP.

Wet deposition

In determining scavenging rates for the Hilatar model, formulas of the nitrogen compounds have been used as a base, and similar expressions are derived for sulphur compounds either directly from the literature or by using relative scavenging efficiencies of compound in other models.

For HNO_3 the scavenging rate L_c of Chang (1984,1986) is used. Its in-cloud scavenging equals the cloud droplet removal rate by falling raindrops and the below-cloud scavenging by snow is more efficient than by rain. During snowfall, the values of Chang (1986) were used for nitrate and sulphate particles. For rain, those formulae do not give similar relative L_c rates as does the EMEP model (Jonsen & Berge, 1995). Thus, a slightly faster rate, $L_c = 4.0 \cdot 10^{-4} R^{0.74}$ for particles in-cloud, and $L_c = 3 \cdot 10^{-4} R^{0.78}$ below cloud, which are closer to the Scott (1982) rates, are used. Scavenging rate of NH_3 follows the parameterisation of Asman & Janssen (1987). In-cloud scavenging of NH_3 will proceed at about the same rate as that of SO_4^{2-} aerosols. The scavenging rates of SO_2 were estimated using the ratio of the respective EMEP efficiencies, following the annual variation of the HNO_3 scavenging rate.

Several experiments (e.g. Jylhä, 1995) beneath the plumes of large power plants have shown that SO_2 is not immediately scavenged out from the flue gases. The emitted SO_2 is assumed to be non-scavengable near the sources. Precipitation is assumed to occur as rain with a gradual transition to snow when temperature decreases from 270 to 260 K. The inter-annual variation

of vertical precipitation $R(z)$ is from Chang (1986): $R(z)$ at a height of 3 km is 22-58 % of the surface value in winter and summer, respectively.

The EMEP vs. Hilatar scavenging coefficients are compared in Hongisto (1992a). The removal rates using different scavenging parameterisations depend on mixing height and precipitation. Generally, the Chang (1986) removal rate of HNO_3 is slower in summer than the rate of Jonsen & Berge (1995), but faster in winter. The below-cloud NH_3 scavenging rate of Asman is only 38 % of the EMEP value (if h_{mix} is 800 m and the rain intensity 1 mm hr^{-1}), but faster in cloud. When the mixing height is low, the EMEP removal rate of HNO_3 is clearly faster than that of Chang, especially with higher precipitation amounts. With a 1 mm hr^{-1} rain, the SO_2 concentration drops by 50 % in 0.9-3.5 hours in summer and 1.7-7.7 hours in winter, depending on the cloudiness. With 3 mm hr^{-1} rain, the corresponding times are 1.3-3.5 h in winter and <10 min - 3.2 h in summer. Precipitation scavenging is more efficient in the early part of the rainfall.

MODEL VERIFICATION

The correctness of the used schemes was checked for each individual algorithm using mass conservation tests. Detailed numerical tests of all algorithms are performed in Hongisto (1993, 1998). Similar mass tests have been performed for all model versions with various differing grids and domains (fixed 30 km Polar Stereographic grid and rotated spherical grids of 0.1° , 0.2° , 0.25° , 0.4° and 0.5°).

Advection

The performance of the advection algorithm was tested by rotating a frozen initial distribution around an axis of symmetry. The mass and distribution of the transported quantity were compared with the initial values after 12.5 days circulation. In two dimensions the test equation is

$$\frac{\partial c}{\partial t} - \omega y \frac{\partial c}{\partial x} + \omega x \frac{\partial c}{\partial y} = 0 \quad (2)$$

where $\omega = 2\pi / T_{\text{rot}}$ and T_{rot} is the period of rotation.

The tests were made with two different initial shapes, a rectangular and a conical one, over the European Hilatar model domain (a 76×80 horizontal grid of 0.5° resolution). Because the model height varies with pressure, temperature and humidity, the vertically-integrated mass of each layer is used as the conserved quantity. A 300 hr period was simulated with circular wind velocities of $u = -\omega \cdot (x - x_0)$ and $v = \omega \cdot (y - y_0)$. The circulation started from the grid position (20,20), with as initial distributions:

$c(x, y, z, t = 0) = 100 \text{ BC}$, if $18 \leq x \leq 22$, $18 \leq y \leq 22$ for the rectangular block,

$c(x, y, z, t = 0) = 100 \text{ BC} (1 - r/4)$, if $r \leq 4.5$ for the cone, and

$c(x, y, z, t = 0) = \text{BC}$ otherwise,

where $r = \sqrt{(i - 20)^2 + (j - 20)^2}$ $i = 1, 76$, $j = 1, 80$.

and the background concentration, BC, is 10^{12} molecules m^{-3} . The evolution of the peak maximum and mass M during the rotation (Fig. 2) shows that the maximum error, $M(t)/M(t=0)$, was $\pm 0.15 \%$ of the initial mass. The error depends on the location of the initial distribution and on the ratio of the mass of the peak to the background mass, which was here 36.2 % for the cone-shaped, and 41.1 % for the rectangular block. $M(t)/M(t=0)$ is related to

the truncation error when the concentrations are represented in the algorithm by polynomials. The simulation time, 12.5 days, is so long that this numerical error is insignificant.

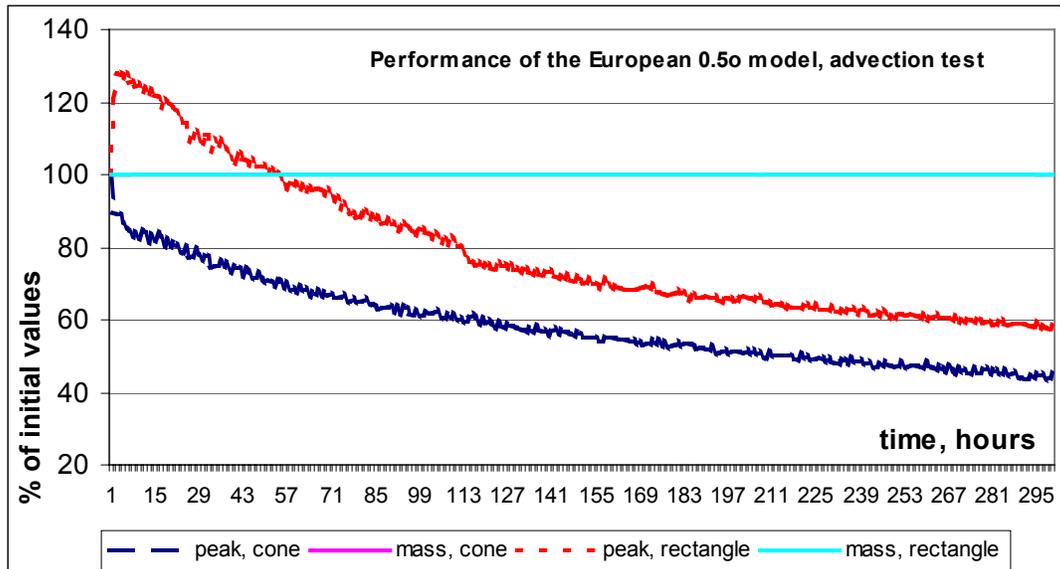


Fig. 2. Mass test, 0.5° European model, advection. Peak and mass conservation. Rectangular and cone-shaped distributions.

The performance of the peak maximum is related to the error caused by the splitting up method during advection in a diagonal direction. This is much higher and depends on the grid dimensions. The worst case is discussed in Hongisto (1998): the maximum concentration of a delta puff drops to 25 % within 5 hours circulation. After that time the shape started to resemble a cone and the decrease was much slower, as well as in the case of constant emission.

Vertical diffusion and chemistry

The performance of the vertical diffusion algorithm is compared to an analytical solution in Tuovinen (1992). Pure mass conservation tests of the algorithm in the Hilatar grid did not show any mass loss when the upper boundary was closed. Examples of the mass transfer rate across the inversion layer can be found in Hongisto (1998). Under efficient mixing conditions, the time required to achieve a uniform mass profile is less than 2 hours for a typical daytime K_z -profile with a maximum of $50 \text{ m}^2 \text{ s}^{-1}$ below the mixing height, and less than one hour if K_z is increased to $100 \text{ m}^2 \text{ s}^{-1}$. The mixing efficiency depends on the initial concentration profile and the structure of the grid.

The chemistry algorithm QSSA does not conserve mass exactly. There are three reasons for this: firstly a relatively long time step, 225 s, during which the concentrations are assumed to keep their previous time-step values, even though they are actually consumed or produced during the process. Secondly: the sink and source terms are independent of each other, described by an exponential or linear decay, depending on the strength of the sink. Finally, the requirement of a minimum background concentration level in the numerical algorithms also increases the mass slightly.

COMPARISON BETWEEN MODEL RESULTS AND MEASUREMENTS

The daily concentrations of SO_2 , NO_2 , NH_3 , $\text{SO}_4^{=}$, NO_3^- , NH_4^+ , $\text{HNO}_3+\text{NO}_3^-$ and $\text{NH}_3+\text{NH}_4^+$ in air, and monthly mean wet depositions of $\text{SO}_4^{=}$, NO_3^- and NH_4^+ over the NMR-model domain were compared with the 29 EMEP station measurements (www.emep.int) over the period 1996-1998. The station codes and locations are presented in Table 1. The European 0.5° model grid averages are compared with measurements at around 90 European EMEP-station over the same period in part II of this article.

Furthermore, comparison of measured and modelled Pb, Cd and Zn and various nitrogen concentrations in air and in precipitation, during the BASYS winter- and summer field campaigns at four coastal stations and at two research vessels, are presented in Schulz (1998), Schulz et al. (1999), Schneider et al. (1999), Sofiev et al. (2001) and Plate (2000). Inter-comparison with other Scandinavian models and with measurements for the 1997 reference period are presented in Zlatev et al. (2001), and with the EMEP model and measurements in Hongisto, (1992a, 1998). Model-measurement comparison during episodes are presented in Hongisto (1992b, 1998), Tervahattu et al. (2002), and Hongisto & Joffre (1994).

Concentrations in air 1996-1998

The model-measurement comparison of annual and monthly average concentrations of SO_2 (Fig's 3 and 7) shows a general good agreement. SO_2 is slightly overestimated at the southern stations, but underestimated at specific marine stations (Hoburg, SE-8, Utö, FI-9) influenced by ship emissions and in Lapland at stations (RU-1, NO30, SE13 and FI22) influenced by the Kola emissions.

The high concentration events are smoothed to the neighbouring cells. For instance Aspvreten (SE12), close to Stockholm, suffers from the time-splitting error: in advection part of the pollutants are transported into the neighbouring grids. The transfer of emissions from the EMEP to the HIRLAM grid possibly also smoothes the emissions between several grids.

The 1996-1998 average correlations of the daily SO_2 values were 0.55-0.63 at the German and Danish stations, slightly less at the Nordic stations (FI, NO and SE) and poor in Russian and other eastern European countries. When the concentrations were over-estimated, the difference was larger in summer than in winter. One explanation is the too low mixing height in HIRLAM and its time-integration. Meteorological input are read at 6 hr time intervals, but hmix has its maximum late in the afternoon. Thus, it is higher between 12 and 18 UTC than the time interpolation can estimate.

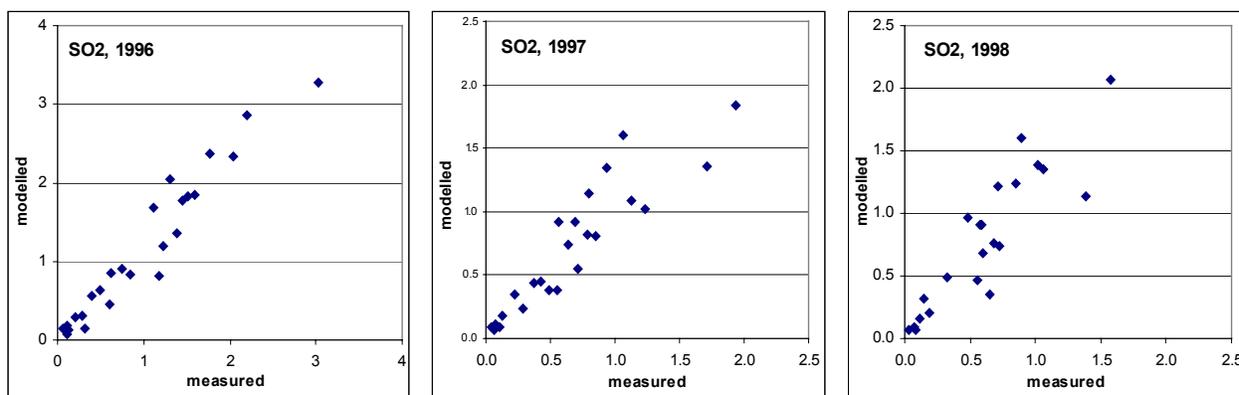


Fig. 3. Comparison of the modelled and measured annual average SO_2 concentrations at the EMEP stations. NMR-area model

NO_2 is underestimated everywhere in 1997 and at most of the stations in 1996 and 1998 (Figs 4 and 7). The underestimation is the highest at the coastal station of Preila, LT15, indicating either

too low marine or road traffic emissions. This underestimation in fact occurs at all coastal stations, and is the largest in spring. Some land measurements also suffer from local traffic pollution. In summer and spring 1998, however NO₂ was overestimated by around 20 % at SE11, SE2, SE12 and in 1996 slightly at some southern Swedish and Norwegian stations. The reasons are the same as for the SO₂: too low a mixing height in HIRLAM, smoothing in transferring of the emissions from the EMEP to the HIRLAM grid, high and clean mountainous measurement place or splitting up method in advection. Correlation of daily values was lower than that for SO₂, being around 0.6 only at DE-1, DK-8 and NO-1, > 0.4 at other southern stations, < 0.3 or poor at marine or northern or eastern stations.

At the coastal stations, model underestimation can also be caused by stability differences between land and sea during cold months. If the sea is open and cold air advects over it, mathematical averaging makes the partly frozen shores too unstable, and the modelled pollutants are mixed through too high a layer.

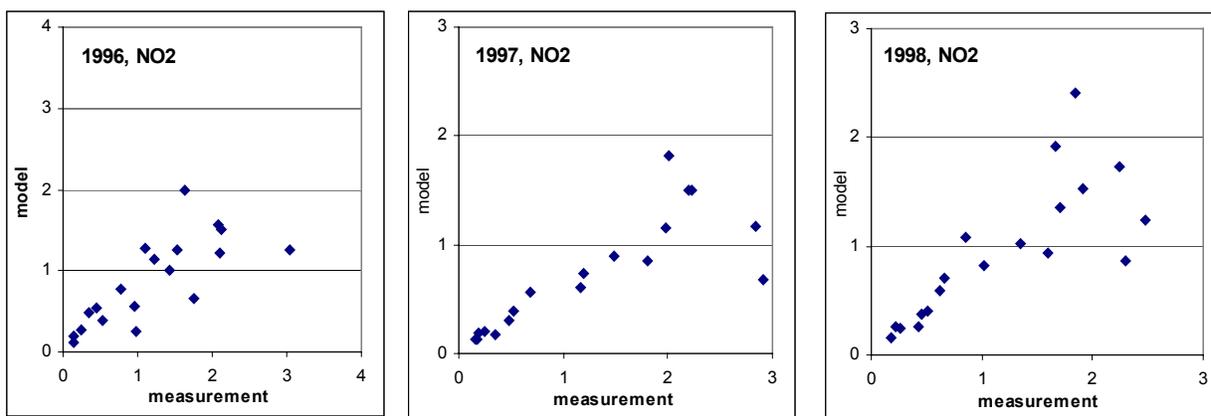


Fig. 4. Comparison of the modelled and measured annual average NO₂ concentrations at the EMEP stations, NMR-area model

NH₃ was measured only at Rucava (LV10) in 1997 and at Jäniskoski (RU_1) in 1996. In LV10 it was strongly underestimated especially in summer, but the correspondence was better at the northern station. The sum of nitrate and HNO₃ is overestimated everywhere else than in Lithuania, in summer 1996 in Latvia and winter 1998 in DK-3 (Fig's 5 and 7).

Sulphate in air is underestimated in 1993 as well as in 1996-1998 at all stations, on average by 44 % in 1996 and 64-61 % in 1997-98 (Fig. 6). Ammonium in air is measured only at four stations and underestimated as well (Fig. 8). Sulphate particles are transported over longer distances, so more non-European and natural contribution can be expected than for nitrate. According to the EMEP calculations, the geographically highly variable inattributable contribution is three times larger for sulphate than for oxidized nitrogen deposition (Barrett and Berge, 1996). The chemistry module might produce too much nitrate, or there are unknown sinks, e.g., dry deposition (at least to the sea surface) might be too slow. Nitrate scavenging coefficients cannot be increased, because wet deposition is rather well predicted.

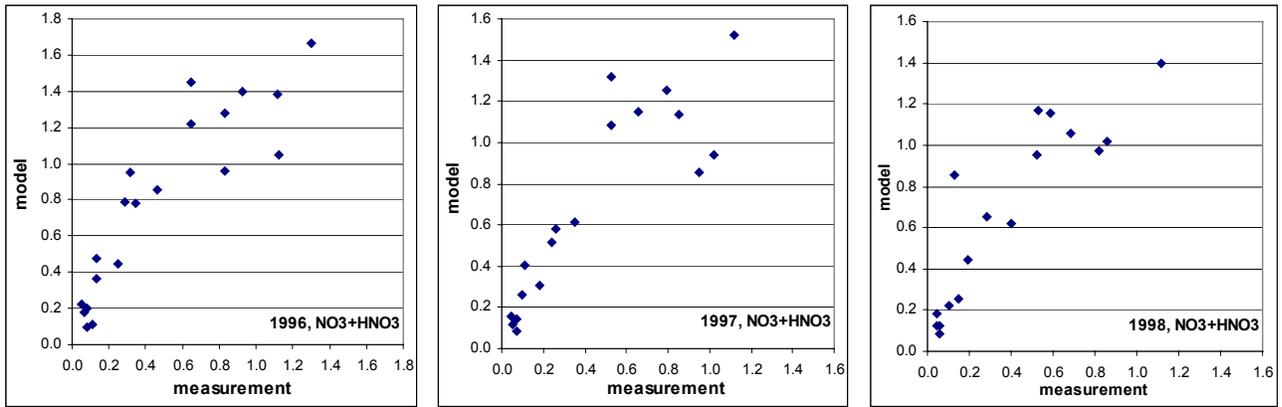


Fig. 5. Comparison of the modelled and measured annual average $\text{NO}_3 + \text{HNO}_3$ in air, 1996-1998, NMR-area model.

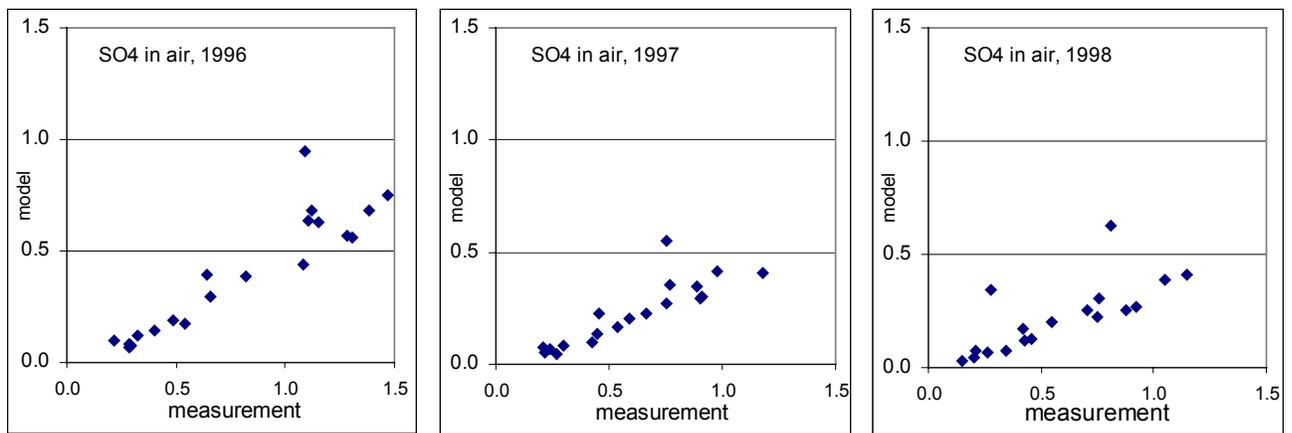


Fig. 6. Comparison of the modelled and measured annual average SO_4 in air, 1996-1998, NMR-area model.

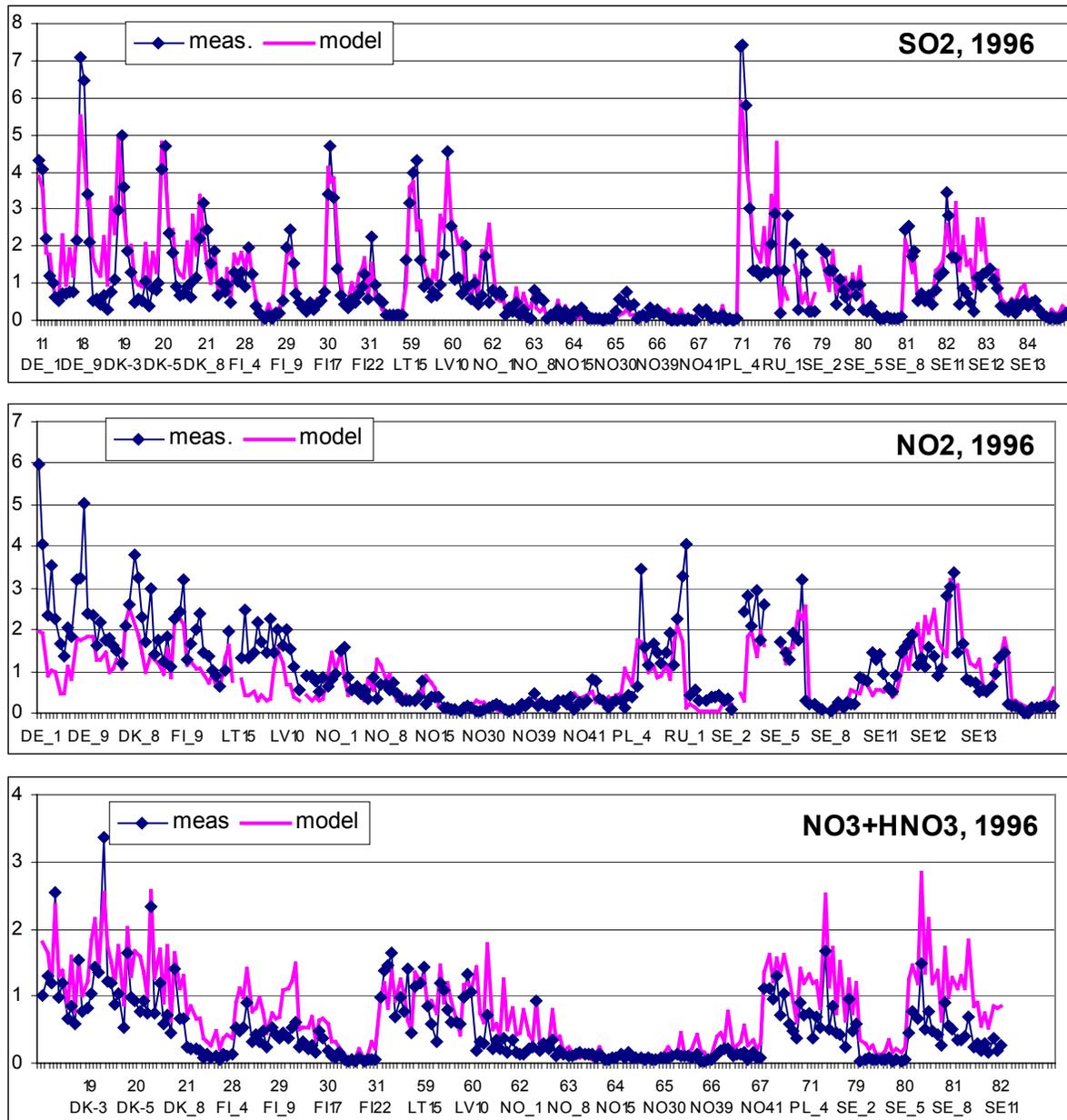


Fig. 7. Concentrations of SO₂ $\mu\text{g (S) m}^{-3}$, NO₂ and sum of NO₃ + HNO₃ $\mu\text{g (N) m}^{-3}$ in air, 1996.

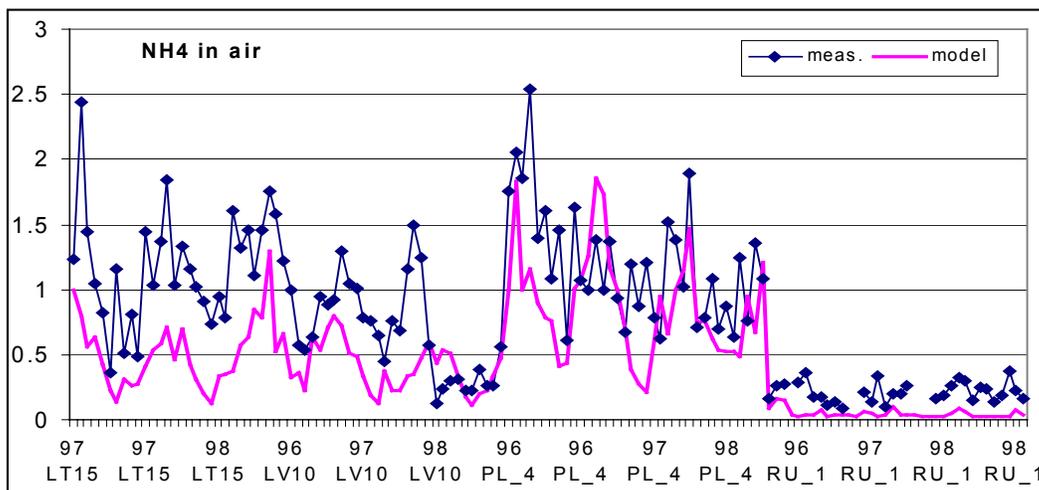


Fig. 8. NH_4 in air, monthly averages at the NMR-domain stations, 0.25° model

Precipitation

Precipitation from HIRLAM is considerably underestimated in Southern Norway, during January-April 1993 with a maximum of $230 \text{ mm month}^{-1}$. The difference decreased northwards. Elsewhere, HIRLAM overestimated the wintertime rain. During spring and some summer months, precipitation was generally slightly underestimated. In Central Norway the forecasts strongly exceeded the local measurements in summer. During the autumn and early winter, the modelled precipitation was generally an underestimate.

Although it is difficult to achieve compatibility in model-measurement comparisons if one does not use measured rain, modelled values have to be used. Over open sea areas no measurements exist, and over land measured precipitation is strongly affected by local topography.

Wet deposition

The modelled wet deposition of oxidised nitrogen is under-predicted in Southern Norway and Sweden, and also in Northern Norway, however slightly over-predicted elsewhere (Fig. 9). The overestimation was the strongest in the wet year 1998, while 1996 was rather well predicted as well as 1993. In the southern parts either precipitation amounts or the scavenging rates for light rain might be too efficient, and the transport distance becomes too short in the model. The ammonium deposition was mainly under-predicted (Fig. 9), except near Denmark in 1997 and 1998 indicating that the scavenging efficiencies might be too low.

Wet deposition of sulphur in mg m^{-2} was overestimated in 1996-1998 at the Finnish north-eastern border, in Preila, LT15, and in some years at DK-5 (Fig. 9). Overestimation of wet deposition of sulphur occurred mainly in winter. The summertime deposition should in fact be slightly underestimated while during rainy periods dry deposition is included into the measured values. Sulphur wet deposition was under-predicted at all Norwegian stations, at the coastal site of Utö and at most of Southern Swedish stations. The absolute deviation was the highest in Norway where also the HIRLAM rain was under-predicted at the same stations. In 1996 the deviation was $\pm 60\%$ at all stations and $\pm 30\%$ at the majority (60%) of the stations. In 1997 and 1998 the average deviation was larger. The underestimation at the Atlantic coast is partly due to missing non-European contribution and incomplete ship emission inventory.

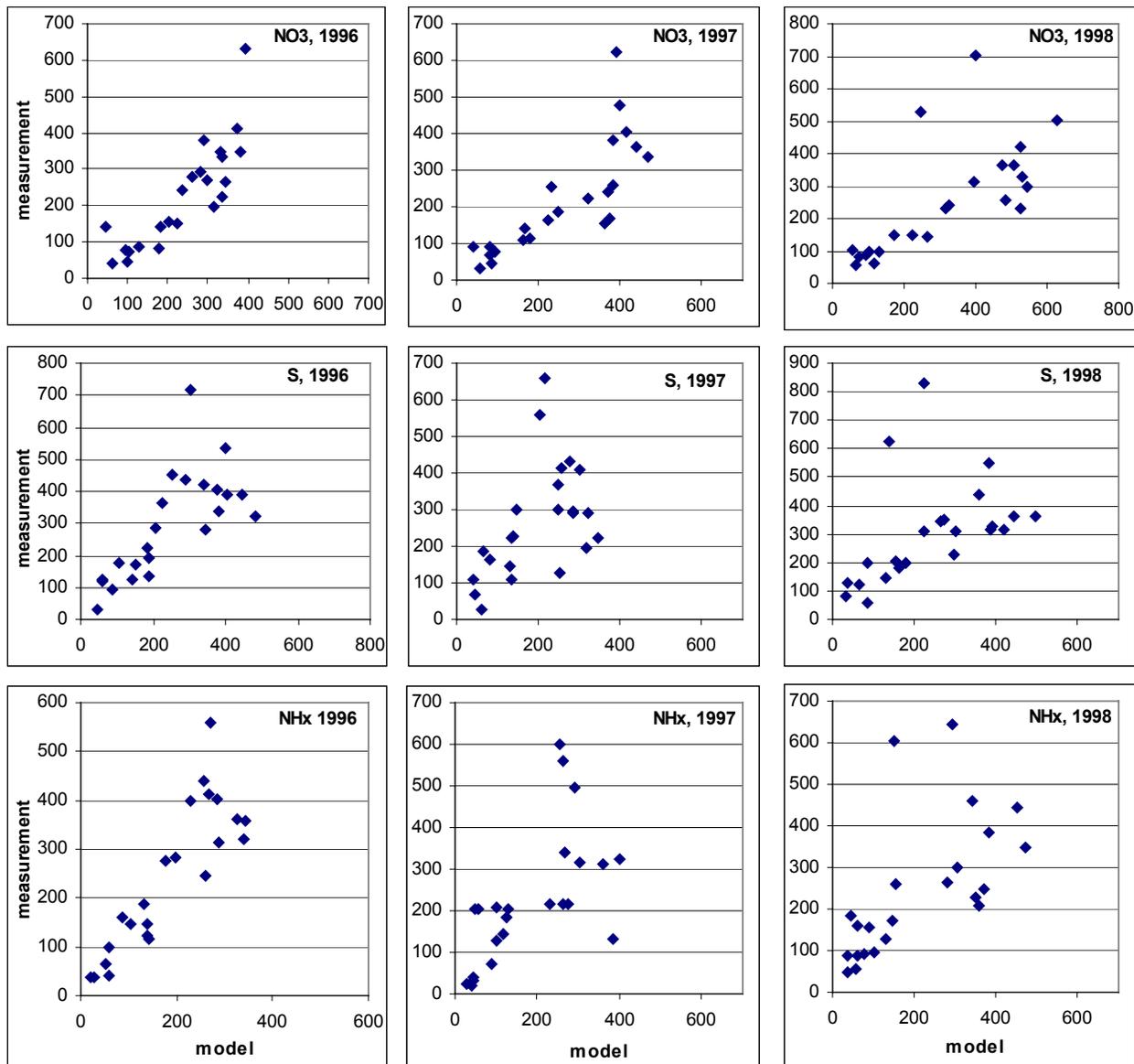


Fig. 9. Comparison of wet deposition NO_3 , S and NH_4 , mg m^{-2} , 1996-1998 annual averages at the Nordic EMEP Stations.

Modelled values in relation to accuracy of the measurement methods

Since the EMEP monitoring program is based on different sampling and analytical methods, (Hjellbrecke et al., 1995, Schaug et al., 1997), intercalibration exercises are regularly undertaken. In the 1993 intercalibration study (Hanssen & Skjelmoen, 1997), measured SO_2 in air was 0.74-1.39, NO_2 0.84-1.24 and SO_4^{2-} 0.83-1.31 times the test sample value, respectively. Because 88/58/64 % of the modelled SO_2 values and 95/78/84 % of the modelled NO_2 values were within ± 50 % of the measured ones in 1996/97/98, respectively, the uncertainty can be due to measurements or model. However, SO_4 and NH_4 concentrations in air are clearly underestimated and the sum $\text{NO}_3 + \text{HNO}_3$ is clearly overestimated.

The measured SO_4^{2-} , NO_3^- and NH_4^+ concentrations in precipitation were 0.71-1.47 times the test concentration, with a relative standard deviation of 3.2-9.9 % if the clearly contaminated or

otherwise irrelevant results are disregarded. Bearing in mind the differences in the modelled and measured accumulated precipitation, which easily can be ± 50 % in a month at any station, we can conclude that by changing any model parameters it is difficult to get values which are closer to the measurements.

Instruments generally have more difficulties in measuring either high or low concentrations; precision is better in the normal concentration range. The lower detection limit of the worst devices can exceed $1 \mu\text{g m}^{-3}$ (N or S) for NO_2 , the sum of NH_3+NH_4 , SO_2 or sulphate. In the NMR-area in 1996-1998, at 44-47 % (52-82 %) of the stations the annual average of NO_2 (SO_2) was below $1 \mu\text{g (N/S) m}^{-3}$. Because the concentrations are very episodic, the background station devices should be of the best quality and frequently inter-calibrated. Otherwise they can work below the detection limit, especially in summer.

A field intercomparison between national and EMEP reference sampling equipment has been carried out at four EMEP stations (Schaug et al. 1997). For SO_2 the 4-month average reference concentration was 55-103 %, for SO_4 93-111 %, for HNO_3+NO_3 112 % and for NO_2 25-78 %, of the national measurement. During episodes the difference could be as high as 600 % for SO_2 . For sulphate the reference method gave even twice as much or only 30-40 % of the routine analysis. The comparison of one-hour concentrations at 6 Finnish stations (Hongisto, 1998) yielded as big relative instantaneous differences. Only a slight change in the wind direction keeps the modelled plume just in close vicinity of the station at the time, when elevated concentrations are actually detected. The model did anyway catch most of the peaks, but generally with a lower intensity.

The laboratory precision for contaminants in water was at least 5 %, and the detection limit generally high (Schaug et al., 1997). The collection efficiency of rain gauges, which at some stations is corrected, contains much higher source of inaccuracy. In northernmost Finland the corrected meteorological precipitation has been 40-60 % larger than that measured, while the difference is generally 15-20 % in places where the proportion of precipitation as snow is not as high (Klim, 1987). The collection efficiency of the wet deposition gauges is lower than that of the meteorological precipitation gauges, the difference being in Finland most pronounced at windy coastal stations. In 1993 at Utö, only during 63 % of the rainy days the air quality gauge collected enough water for identification of the deposition (Leinonen, 1994).

At stations reporting very low monthly and annual precipitation, such as DE-9, different precipitation rates for the daily deposition values are found in the EMEP-CCC data base. Thus, the sum of daily values gives much higher deposition than the official monthly or annual values. It is not clear when the rain amount of the meteorological precipitation gauge or that of the air quality gauge is used. E.g. at the Finnish EMEP stations the official precipitation is used for daily samples, in calculating the monthly deposition while for weekly samples (heavy metals), the precipitation amount of the air quality gauge is used in order to estimate the effect of evaporation. Since the official rain amount can be twice the rain collected in the air quality gauge (e.g. at FI-9 in 1996-1998 or almost that at DE-9 in 1998), this leads to rather high uncertainty in the measured annual deposition.

CONCLUSIONS

The 3D transport-chemistry model for N and S compounds is described. The test of the algorithms show, that numerical errors are insignificant in comparison with the errors connected with the grid size, initial dilution and time-splitting parameterisations. The inaccuracies in input data, model parameterisation and resolution are difficult to determine quantitatively, but comparison between the model results and observations show a rather good agreement in general.

During selected episodes, although some situations are well simulated, the model could not explain all the measured fluctuations. With the current resolution, the model has difficulties in explaining concentrations in mountainous areas, during stable situations near high sources if no correct stack information is available, and near coastal areas. For the coastal zone, the reasons lie in the 1990 ship emission inventory and in grid-averaging of marine and continental ABL parameters. Since the model results are grid averages, whereas measurements are influenced by local and sub-grid phenomena and they also embed a lot of uncertainty, the results can be considered very satisfying.

Regarding shortcomings in the model chemistry, missing compounds and natural emissions may affect the model-measurement comparison. Field studies have showed that the vertical fluxes of NO, NO₂ and NH₃ are bidirectional (in agricultural areas as well as in estuaries with significant riverine nitrogen discharges, if the gas-phase concentrations are low). Interactions with sea salt may also change the marine deposition. Even the most detailed dry deposition module can never describe the capacity of real living vegetation to respond to the influence of air pollution.

The Monin-Obukhov theory cannot satisfactorily describe all meteorological situations, e.g. over water, where the moving waves either increase or decrease the surface momentum flux (Smedman et al., 1999). The grid average roughness is also quite a theoretical concept.

The agreement for concentrations in precipitation can be improved by re-estimating the time variation of the scavenging intensity - however, this affects the air concentrations and the transport distance. The winter deposition of SO₄ in rain is overestimated as well as the first-level sulphate concentration, but SO₂ concentrations lie within normally-accepted deviations, so that diminishing the scavenging would make the error to appear somewhere else. Alternatively, we have to allow the pollutants to be mixed to higher levels either by re-estimating the winter boundary-layer height or the initial vertical mixing profiles of the areal emissions (which were constant throughout the year). For areas with a detailed stack-emission inventory, where the effective emission height was evaluated for each meteorological situation, the correlation with the measurements was much better.

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Table 1 Station codes and locations

Station	Country	No	code	Location		Height m	Station	Country	No	code	Location		Height m
				Lat	Lon						Lat	Lon	
Westerlanc	Germany	11	DE_1	54.55	8.18	12	Krvatn	Norway	66	NO39	62.5	8.53	210
Zingst	Germany	18	DE_9	54.26	12.44	1	Osen	Norway	67	NO41	61.2	11.5	440
Tange	Denmark	19	DK_3	56.21	9.36	13	Spitzberge	Norway	68	NO42	78.5	11.5	474
Keldsnor	Denmark	20	DK_5	54.44	10.44	9	Jarczew	Poland	69	PL_2	51.2	21.6	180
Anholt	Denmark	21	DK_8	56.43	11.31	40	Leba	Poland	71	PL_4	54.5	17.3	2
Ahtari	Finland	28	FI_4	62.33	24.13	162	Janiskoski	Russia	76	RU_1	68.6	28.5	118
Virolahti II	Finland	29	FI_9	60.31	27.41	4	Pinega	Russia	77	RU13	64.4	43.2	28
Uto	Finland	30	FI17	59.47	21.23	7	Roervik	Sweden	79	SE_2	57.3	11.6	10
Oulanka	Finland	31	FI22	66.19	29.24	310	Bredkaeler	Sweden	80	SE_5	63.5	15.2	404
Preila	Lithuania	59	LT15	55.21	21.04	5	Hoburg	Sweden	81	SE_8	56.6	18.1	58
Rucava	Latvia	60	LV10	56.13	21.13	18	Vavihill	Sweden	82	SE11	56	13.1	172
Birkenes	Norway	62	NO_1	58.23	8.15	190	Aspvreten	Sweden	83	SE12	58.5	17.2	20
Skreaadale	Norway	63	NO_8	58.49	6.43	475	Esrang	Sweden	84	SE13	67.5	21	475
Tustervatn	Norway	64	NO15	65.5	13.55	439	Karasjok	Norway	182	NO55	69.3	25.1	333
Jergul	Norway	65	NO30	69.24	24.36	255	Ähtäri II	Finland	177	FI37	62.4	24.1	180