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THE CHEMISTRY OF THE POLLUTED ATMOSPHERE OVER EUROPE SIMULATIONS AND SENSITIVITY STUDIES WITH A REGIONAL CHEMISTRY-TRANSPORT-MODEL

by

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**The Chemistry of the polluted Atmosphere over Europe:
Simulations and Sensitivity Studies with a regional Chemistry-Transport-
Model**

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Abstract

A model environment has been established, which allows an estimation of the influence of global climate change on the chemistry of the polluted atmosphere over Europe. For this purpose the regional chemistry-transport-model of the EURAD-System has been modified and made adaptable for input data from a regional climate model, which is nested in a global atmospheric circulation model. Thus, the dynamical aspect of a possible global temperature increase as well as enhanced water vapour concentrations and background concentrations of carbon monoxide and methane can be considered. By substituting the meteorological driver model the main problems arise from different vertical grids and physical parameterization schemes. In particular the parameterization of cloud processes has to be checked to avoid inconsistencies between the chemistry-transport-model and its meteorological driver model. As the length of a simulation period is mainly limited by the large amount of computer time spend for the determination of chemical transformation rates, the gas phase chemistry module has been optimized concerning computer time and numerical stability. For validation studies of the new model system two episodic simulations were investigated, one for a summer photo-oxidants period in July 1990, the other one for January 1991.

Key words index: Regional modelling, model evaluation, non-precipitating clouds, sulfur, oxidizing capacity of the atmosphere.

1. Introduction

Acid rain and enhanced surface ozone concentrations during blocking situations in summer are only two examples for the increasing air pollution of the troposphere in highly industrialized areas like Europe and North America. An indication for changes of the atmospheric conditions can be achieved by observations of dynamical variables and chemical constituents of the atmosphere. In an attempt to understand the relationship between emission, transformation, transport, accumulation and deposition of trace gases and particles, three dimensional Eulerian chemistry-transport-models like RADM (Chang et al., 1987) and ADOM (Venkatram et al., 1988) have been designed in the last decade. Besides the processes in the planetary boundary layer, these comprehensive models also include the processes of the free troposphere where clouds play an important role in redistributing and transforming particles and trace gases and in modifying solar radiation and, consequently, photolysis rates.

Although these models are consuming a high amount of computer time, they are suitable, in principle, for a first estimate of the influence of global climate change on the chemistry of the polluted atmosphere over Europe or North America. In this context the self cleaning capacity of the atmosphere is the variable of interest. It depends on the oxidation of trace gases by the hydroxyl radical and the wash-out and rain-out of the water soluble oxidation products. Increasing emissions of methane, carbon monoxide and short lived volatile organic carbon compounds (VOC) seem to reduce hydroxyl radical concentrations, whereas a reduction of the stratospheric ozone column and increasing water vapour concentration due to the greenhouse effect imply an increase of the hydroxyl radical amount (Isaksen, 1988).

To consider the dynamical aspects as well as enhanced water vapour concentrations and background concentrations of carbon monoxide and methane in model studies, the regional chemistry-transport-model (CTM) of the EURAD-System (Hass et al., 1993), the European version of RADM, has been modified and made adaptable for input data from a regional climate model (section 2 and 3). This model, called HIR-HAM is nested in the global atmospheric circulation model ECHAM (DKRZ, 1992)

and thus can provide meteorological data from climate change experiments in sufficient horizontal resolution as input for CTM. Section 4 informs about changes of the gas phase chemistry module which result in an acceleration of the whole model saving more than 50 % of computer time. For validation studies the coupled HIR-HAM-CTM-System was applied for simulations under present climate conditions to compare model results with observations. A summer photo-oxidants period in July 1990 and a winter episode in January 1991 were chosen. Results and discussions of these simulations are presented in section 5. A summary is given in section 6.

2. Model description

The EURAD package is an Eulerian tropospheric model system for the simulation of emission, transport, transformation and deposition of acidifying and photochemical pollutants over Europe. A detailed description is given in Hass (1991) and for the original North American version in Chang et al. (1987). As a so-called 'off-line'-model calculations with a meteorological driver model produce information about the physical conditions of the atmosphere (horizontal wind, temperature, specific moisture, surface pressure and precipitation), which are passed to the CTM. In the European model version as well as in the North American one, the hydrostatic model MM4 (Anthes et al., 1987) is used for this purpose. To avoid interpolation errors both models, MM4 and CTM, employ the same coordinate system: σ as vertical coordinate and a Lambert conformal projection. But the horizontal grid in CTM is a so-called 'Arakawa-C'-grid in contrast to an 'Arakawa-B'-grid in MM4.

The regional climate model HIRHAM was developed from a complete system for short-range numerical weather prediction in operation in the Nordic countries, Ireland and the Netherlands (Kållberg, 1989). It is used to intensify the testing and further development of nested GCM-LAM (General Circulation Model - Limited Area Model) methodology to downscale and regionalize GCM climate simulations. For these studies the physical parameterization package of the GCM ECHAM (DKRZ, 1992) is implemented in HIRHAM. Among a variety of other experiments, the HIRHAM model was applied for simulations of July 1990 and January 1991 with an inte-

gretion area covering Europe, the North Atlantic and parts of North America using ECMWF analysis as boundary fields. The model consists of $k=19$ vertical layers of unequal thickness between the ground and the 10 hPa pressure level. The vertical coordinate system is the terrain following hybrid pressure-sigma system with $\eta=1$ at the surface and $\eta=0$ at model top:

$$\eta(k) = \frac{A(k)}{p_0} + B(k) , \quad (1)$$

where $p_0=1013$ hPa and A and B are given as a function of k (DKRZ, 1992). In comparison to the σ -system of the EURAD-model the η -system is able to smooth out deformations caused by mountains in higher atmospheric layers. The horizontal resolution for the experiments of July 1990 and January 1991 is 0.5° in an artificial spherical coordinate system. This is generated from the normal geographical one by rotating Greenwich longitude 10° east and the equator 57.5° north. The model is formulated for an 'Arakawa-C'-grid.

As already mentioned in connection with the EURAD system, the vertical coordinate and the horizontal coordinates of CTM are determined by the meteorological driver model to guarantee dynamical and mass consistency. Thus, for the coupled HIRHAM-CTM system the transport equation for the 24 prognostic chemical species is

$$\begin{aligned} \frac{\partial}{\partial t} C^* = & - \left\{ \frac{1}{a \cos \varphi} \frac{\partial}{\partial \lambda} (u C^*) + \frac{1}{a \cos \varphi} \frac{\partial}{\partial \varphi} (v C^* \cos \varphi) \right\} \\ & - \frac{\partial}{\partial \eta} (\dot{\eta} C^*) + g^2 \frac{\partial}{\partial \eta} \left(\frac{\rho^2}{p^*} k_z \frac{\partial}{\partial \eta} C^* \right) , \end{aligned} \quad (2)$$

$$\text{where } p^* = \frac{\partial p}{\partial \eta} = \frac{\partial}{\partial \eta} (A + B p_s) = p_0 + (p_s - p_0) \frac{\partial B}{\partial \eta} \quad (3)$$

$$\text{and } C^* = p^* \cdot C . \quad (4)$$

C is the trace species volume mixing ratio, a the earth radius, φ the artificial latitude, λ the artificial longitude, u and v are the components of the horizontal wind velocity in x- and y-direction, $\dot{\eta} = \frac{d\eta}{dt}$ is the vertical wind velocity, g the gravitational accele-

ration, ρ the density of air, k_z the vertical eddy diffusivity and p_s the surface pressure. The vertical velocity $\dot{\eta}$ is derived from the continuity equation

$$\frac{\partial}{\partial \eta} \left(\frac{\partial p}{\partial t} \right) + \nabla \left(v_h \frac{\partial p}{\partial \eta} \right) + \frac{\partial}{\partial \eta} \left(\dot{\eta} \frac{\partial p}{\partial \eta} \right) = 0 \quad (5)$$

by integrating vertical yielding

$$\dot{\eta} p^* = - \int_0^1 \nabla (v_h p^*) d\eta - \frac{\partial p}{\partial t} \quad (6)$$

with v_h as horizontal wind vector. The surface pressure tendency $\frac{\partial p}{\partial t}$ is evaluated by integration of equation (5) from $\eta=0$ to $\eta=1$.

Besides the adaption of the model equations of CTM to the coordinate system of HIRHAM, also emission data, provided on the basis of Memmesheimer et al. (1991), and chemical initial and boundary conditions have to be interpolated to the HIRHAM coordinate system. Only photolysis rates input is identical to that of EURAD-CTM. Clear sky photolysis rates for 21 photolysis reactions are created by a climatological preprocessor model (Madronich, 1987) as a coarse data block as a function of season, daytime, latitude and height. During a simulation the CTM interpolates linearly in space and time to derive clear sky photolysis rates for each grid box. If clouds appear in a grid box photolysis rates are modified based on Chang et al. (1987).

3. Cloud parameterization

The standard cloud module of EURAD-CTM was developed by Walcek and Taylor (1986) and modified by Chang et al. (1987) and Hass et al. (1993). It determines cloud parameters like liquid water content, ice content, cloud cover, cloud top and base and the vertical redistribution of pollutants on the basis of water vapour, temperature and precipitation data provided by MM4. In sensitivity studies with the EURAD-System, Mölders et al. (1994) have illustrated some effects of five different cloud parameterizations of the meteorological driver model MM4 on cloud properties rediagnosed by CTM. If MM4 cloud schemes include the prediction of ice and / or

cloud water and rain water, CTM cannot consider these predicted quantities and the atmosphere in CTM will be dried artificially. One consequence is the underestimation of cloud cover by CTM in comparison to satellite data and an area limited appearance of liquid water (Mölders et al., 1994). A more consistent treatment of clouds in MM4 and CTM was achieved by Mölders (1993) with a new cloud parameterization for CTM. This scheme only determines cloud cover, cloud top and base and the vertical mixing of trace species and receives the information about ice, cloud and rain water as input from MM4.

In a similar way a cloud module was constructed for HIRHAM-CTM. It determines cloud parameters without losing the information of liquid water and cloud cover provided by the meteorological driver model HIRHAM, which considers cloud formation by a combined scheme of cumulus convection (Tiedke, 1989) and stratiform condensation (Sundquist, 1987). A better agreement of modelled cloud cover (Fig. 1b) with observations (Fig. 1c) in comparison to cloud cover as determined by the standard cloud module (Fig. 1a) could be established. An additional diagnosis of fair weather clouds as reported by Mölders (1993) is not included to prevent HIRHAM and CTM from inconsistencies caused by further phase transfer of water vapour to liquid water. As liquid water content is not monitored routinely, a verification of calculated values against observed data was not possible in a straightforward manner. In HIRHAM only one prognostic equation for the liquid water content q_c , the sum of cloud water q_{cl} and ice q_i , is included, assuming that precipitation formation in the mixed phase, i.e. in the temperature range between about 0 °C and -40 °C, can be treated independently for the ice phase and the liquid phase. The amount of cloud water and ice is obtained from an exponential fit (Rockel et al., 1991) to aircraft measurements

$$q_{cl} = q_c (0.0059 + 0.9941 \cdot \exp [-0.003102 (T - 273.15)^2]) \quad (7)$$

with $q_{cl} + q_i = q_c$. The only cloud parameters still unknown in HIRHAM-CTM are cloud top and base and the vertical redistribution of chemical species. Cloud base is

defined as the first layer above the surface containing more than 0.001 g kg^{-1} liquid water, cloud top is the highest level exceeding an amount of 0.001 g kg^{-1} liquid water. Aqueous chemistry processes are calculated with cloud mean values from cloud top to cloud base for fair weather clouds and from cloud top to the surface for raining clouds which produce more than 0.1 mm h^{-1} precipitation. But before these calculations, the subgrid scale vertical redistribution of chemical species due to convective updrafts and downdrafts in clouds is determined by a flux compensating, mass conserving approach based on Mölders (1993). The influence of the two different cloud schemes (standard cloud module and HIRHAM-CTM cloud module) on modelled pollutants concentrations is shown and discussed in section 5.

4. Gas phase chemistry

The determination of the chemical transformation rates of the highly polluted atmosphere consumes the highest amount of computer time in a three dimensional chemistry-transport-model. Several approaches for the simplification of the organic part of photochemical reaction mechanisms have been introduced (Leone and Seinfeld, 1985) as well as numerical integration schemes which reduce the stiffness of the chemical differential equation system and accelerate the solution ensuring numerical stability (Mc Rae et al., 1982).

Here the RADM II chemical mechanism described by Stockwell et al. (1990) is used. The organic chemistry is compressed by a lumped molecule approach with generalized species resulting in a total number of 158 chemical reactions between 63 species. For 19 intermediate products which rapidly transform to their equilibrium values the quasi steady state approximation (QSSA) is applied. Thus it is possible to lower computational cost by solving the chemical differential equation system in a numerically stable way using enlarged timesteps. An additional reduction of the stiffness of the system is achieved by grouping into one another reacting species in a linear combination (Hass, 1991), for example

The resulting differential equation system is solved semi-implicit using a variable time step

$$\Delta t_{chem} = \frac{\epsilon_i \cdot C_i}{P_{chem,i} - L_{chem,i}} \quad (9)$$

with $10^{-3} \text{ min} < \Delta t_{chem} < 5 \text{ min}$ and $P_{chem,i}$ as chemical production rate and $L_{chem,i}$ as chemical loss rate of species i . The scaling factor is $\epsilon_i = 0.02$. Only certain species are allowed to determine Δt_{chem} and only if their concentrations are above a specified lower bound (Hass, 1991).

The main difficulty with the quasi steady state approximation is to identify those species for which the assumption is valid and to determine the time step interval. The characteristic time for decay

$$t_{d,i} = \frac{1}{L_{chem,i}} C_i \quad (10)$$

describes how quickly a species i reaches its equilibrium value (Mc Rae et al., 1982) and is a first measure for the identification of QSSA species. A final check is necessary, however. Since it is assumed for QSSA species that chemical production and loss rates are constant within one timestep, a sufficient chemical independence of all QSSA species is required to exclude numerical instabilities. Looking at the characteristic time for decay of all RADM II species in a zero dimensional box model under varying reaction conditions and taking into account the requirement of chemical independence, nitrogen pentoxide seems to be a potential additional QSSA candidate. Thus, a modified solution approach was established with N_2O_5 as QSSA species considering

$$k = \left(\frac{600}{\exp\left(\frac{RH}{28}\right)^{2.8}} + 5 \right)^{-1} \text{ min}^{-1} \quad (11)$$

with RH as relative humidity in % (Chang et al. 1987) as pseudo first order rate constant for the heterogeneous reaction

The artificial species N_2N_3 was removed from calculation, NO_2 was allowed to determine Δt_{chem} whereas $HCHO$ and N_2O_5 were excluded from Δt_{chem} -determination.

For validation studies concerning numerical stability and computational speed the total number of timesteps and the conservation of total nitrogen concentration were investigated with the zero dimensional box model. It determines the chemical species concentration as a function of initial concentrations according to

$$\frac{dC_i}{dt} = P_{chem,i} - L_{chem,i} \quad ; i=1,2,...,n . \quad (13)$$

The larger the timestep, i.e. the smaller the total number of timesteps, the faster is the solution approach for a given integration time. Using a maximum time step of five minutes, the modified solution approach is already able to lower the total number of timesteps by about 30 % to 50 % in comparison to Hass (1991), a maximum timestep of 10 minutes is even more efficient (Tab. 1). In addition, the total nitrogen concentration as well as the temporal evolution of the other chemical species (Fig. 2) is described in better agreement with the standard algorithm based on Gear (1971).

For a test simulation under realistic conditions the modified solution approach was applied in the three dimensional CTM considering also advection, diffusion, deposition and cloud processes. The modified approach needs an average chemical timestep of $\Delta t_{chem}=51.6$ s in comparison to 21.4 s claimed by Hass (1991) and thus accelerates integration time by more than a factor two. Model simulations described in section 5 were carried out with this optimized solution approach for the gas phase chemistry module.

5. Model simulations

For validation studies of the coupled HIRHAM-CTM-System two episodic simulations have been investigated, one for a summer photo-oxidants period in July 1990

(23.7. - 31.7.) the other one for January 1991 (13.1. - 23.1.). During both episodes the synoptic situation over central Europe was dominated by high surface pressure. Therefore accumulation and large scale transport of pollutants are the main features of the episodes and concentrations at the model boundaries are of minor influence. A control run with the standard cloud module and an additional simulation with the cloud module adapted to HIRHAM were carried out and compared to observations from the European EMEP measuring stations (Schaug et al., 1993).

5.1. Model simulations of a winter episode in January 1991

First the model simulations for the winter episode will be presented, because in winter times biogenic volatile organic carbon (VOC) emissions from forests are negligible (Altshuller, 1983) and anthropogenic emissions, which are more or less included in detail in the EMEP emission data base, are most important.

At the beginning of the episode a mediterranean low pressure system brought rain and snow to the southern parts of Europe while high pressure over the Baltic Sea caused large scale downward motion and thus sunny weather in northern Europe. Continental air masses were transported to central Europe and a stable atmosphere with an inversion layer in 1000 - 1300 m developed. Due to the blocking effect atlantic frontal systems with gentle maritime air and clouds could not influence Europe until the 18th of January. At the end of the episode foggy weather, caused by a calm high pressure situation, dominated.

The weather development during the episode is reflected in the large scale transport of primary and secondary pollutants, which will be described in detail only for sulfur dioxide, the main component of winter smog. Daily averaged surface SO₂ concentrations as model results in the left column of Fig. 3 are compared in space and time to observations on the right hand site. On the 15th of January SO₂ from the main source regions of the former German Democratic Republic were advected by strong easterly winds to the west. The anticyclonic circulation transported polluted air masses in the frontal zone northward. During the following days SO₂ emissions were transported to

northern Germany and Denmark by wind from southern directions. The frontal passage with unpolluted air masses reduced SO_2 concentrations in central Europe, whereas on the 21th of January enhanced SO_2 concentrations were measured and modelled in East Europe. At the end of the episode calm high pressure caused local accumulation of SO_2 .

Based on Umweltbundesamt (1993) the pollutants load in January 1991 was much lower than for example in winter 1984/85 and 1987/88. Gentle weather conditions during January 1991 allowed more SO_2 to be dry deposited than during stronger winters, when the deposition velocity of SO_2 is reduced over dry snow (Valdez et al. 1987). Other reasons for the moderate pollutants level in January 1991 are the breakdown of industry in the former GDR and also emission reduction of power stations in the western parts of Germany.

The spatial and temporal comparison of model predicted surface SO_2 concentration with available observations at EMEP-stations shows that HIRHAM-CTM is able to determine the large scale transport. The temporal shift between simulated and measured concentrations especially on the 17th and 19th is produced by different starting hours for daily sampling at the EMEP measuring sites (Schaug et al., 1993).

A direct comparison of simulated and observed sulfur dioxide at four North European stations is shown in Fig 4., reflecting once again the temporal and spatial weather development in the model domain. SO_2 concentrations are overpredicted with the old cloud scheme as well as with the new cloud module, probably because near source dry deposition is underestimated due to the unrealistic assumption of instantaneous mixing of emissions throughout the emission grid volume. In other models (Langner and Rhode, 1987; Tuovinen et al., 1994) a local deposition factor is included. Additional local deposition in our model calculations would reduce modelled SO_2 concentrations in highly polluted and also in remote areas and may thus correct especially the overprediction far away from sources. A realistic parameterization of near source dry deposition of SO_2 as well as near source conversion of SO_2 to SO_4^{2-} could be

derived from plume model calculations as a function of meteorological conditions, emission height and liquid water content.

The slight improvement of SO_2 prediction by the new cloud scheme (Fig. 4) corresponds with a much better agreement of model predicted sulfate concentrations with observed values (Fig. 5). As shown in sensitivity studies by Karamchandani and Venkatram (1992) an underprediction of non-precipitating clouds and thus of the availability of liquid water mainly limits the aqueous phase conversion of SO_2 to SO_4^{2-} . Also Dennis et al. (1993) demonstrated that a lack in determining non-precipitating clouds is the main reason for SO_4^{2-} underprediction in the North American model system RADM. They could, however, not achieve a correction of SO_4^{2-} concentrations in highly polluted and remote model areas by enhancing primarily emitted SO_4^{2-} . This was proposed by Hass et al. (1993), but their model runs with increased primary sulfate emissions also failed in predicting near source SO_4^{2-} concentrations. Thus our model studies once again emphasise that a realistic determination of clouds and liquid water content is a very crucial part for the correct prediction of sulfate concentrations. The scatter diagrams (Fig. 6) with episodic mean values show the discussed results for sulfur dioxide and sulfate for all available EMEP-stations.

The comparison of modelled and measured surface ozone concentrations (Fig. 6) demonstrate that HIRHAM-CTM is able to determine the oxidizing capacity of the atmosphere during this winter simulation although nitrogen dioxide and nitric acid concentrations are underpredicted (Fig. 6). Considering NH_4NO_3 aerosol formation, transport and deposition may probably further improve model results (Ziegenbein et al., 1994).

5.2. Model simulations of a summer episode in July 1990

At the beginning of the episode the weather situation in Europe was characterized by high surface pressure over the British Isles and a low pressure system in 500 hPa over southern Scandinavia and the Baltic Sea. Over northern Germany, Belgium and the Netherlands a closed stratocumulus layer remained until the 26th of July, whereas it

was sunny in the south of Europe with the exception of some thunderstorms. On the 26th of July the influence of the expanded and eastward drifting high pressure region without clouds dominated over Europe. On the same date a compact frontal cloud system appeared over the Irish Sea and the Bay of Biscay. During the following days it drifted eastward over Ireland, England and France.

In analogy to the described winter simulation in section 5.1, here only the main component of summer smog, surface ozone, will be discussed in detail. To catch the afternoon ozone peak concentration, Figure 7 shows averaged values between 12 and 16 GMT. Air masses containing high ozone and precursor concentrations from middle and northern Europe circulated around the high pressure region, as is already visible on the 24th of July and strengthened two days later. Clearly evident are also background ozone concentrations below 40 ppbv over northern and middle Germany, Belgium and the Netherlands until the 25th of July. These are caused by the closed stratocumulus layer which lowered the photochemical activity (stations St. Denijs and Meinerzhagen in Fig. 8). At alpine stations (for example Ispra in Fig. 8) the European transit traffic across the alpine valleys, inversion weather conditions and mountain-valley wind systems were responsible for the strong diurnal cycle in observed ozone concentrations with peak concentrations exceeding 60 ppbv every afternoon of the episode. The model smoothes away this strong diurnal variability because the horizontal grid size ($\sim 55 \text{ km} \times 55 \text{ km}$) with mean topography is insufficient to resolve mountains and valleys. The frontal passage reduced peak ozone concentrations (stations Mace Head and Yarner Wood in Fig. 8), because unpolluted air masses approached, cloudy conditions lowered the photochemical activity and pollutants were washed out, wet deposited or mixed into higher layers.

Under moderate photochemical activity HIRHAM-CTM can reproduce observed day- and nighttime O_3 , but the model underestimates peak ozone concentrations ($> 40 \text{ ppbv}$) during summer smog conditions systematically with the standard cloud scheme as well as with the cloud module adapted to HIRHAM (see also Fig. 9). This new cloud scheme predicts even lower ozone concentrations, because water vapour in

the model atmosphere is not reduced artificially as with the standard cloud parameterization. That is why slightly higher amounts of O_3 react in the free troposphere according

and, thus, lower the ozone transfer to the planetary boundary layer.

For the same reasons as already discussed in section 5.1, episodic mean SO_2 concentrations (Fig. 9) are overestimated and the prediction of nitrogen containing compounds (NO_2 , HNO_3 , NH_3) may probably be improved.

The results for modelled sulfate during the winter and summer episode are different. For January 1991 a better agreement between observed and predicted SO_4^{2-} concentrations was achieved with the new cloud scheme, whereas during the simulation of July 1990 the underestimation of sulfate is even more pronounced by the new cloud scheme than by the standard cloud parameterization (Fig. 9). A possible explanation is the additional diagnosis of low level fair weather clouds with the standard cloud module creating appropriate reaction conditions for further aqueous phase oxidation of SO_2 to SO_4^{2-} in regions where HIRHAM does not determine clouds. But considering also the underprediction of peak ozone concentrations on photochemically active days, the main problem remains to be the limited oxidizing capacity of the model atmosphere. Without a correction of the reduced oxidizing capability a final validation of the two cloud modules cannot be given, because enhancing OH concentration may force the gaseous phase oxidation of SO_2 and thus compensate the underestimation of sulfate by the cloud module adapted to HIRHAM.

5.3. Sensitivity studies

To investigate the limited oxidizing capacity of the model atmosphere sensitivity stu-

dies with modified emission scenarios and photolysis rates were carried out. The main uncertainties concerning emission data exist for those from East European countries and for volatile organic carbons. Uncertainties in East European emissions are of minor importance during simulations dominated by west wind weather conditions, because most of the observation stations participating in the EMEP program are located in western Europe. But for simulations with a strong anticyclonic circulation over Europe as described here, these uncertainties are not negligible. With the emphasize on analyzing predicted peak ozone concentrations after a one day simulation for July, the 23rd 1990, 12 GMT, emission data sets were modified in the following way:

- (a) doubling of NO_x emissions,
- (b) halving of NO_x emissions,
- (c) doubling of anthropogenic VOC emissions,
- (d) inclusion of biogenic VOC emissions.

The ratio of modelled ozone to observed ozone at all stations shown in Fig. 7 is 0.82 for the control run.

When anthropogenic NO_x emissions are doubled, the limited oxidizing capacity of the model atmosphere within the area of observation stations is even more reduced than in the control run (modelled O_3 / observed O_3 : 0.74). The amount of nitric acid formed via

is most striking. That is why in regions with high NO_x emissions the number of OH-radicals for the oxidation of VOC drops off, leading to smaller H_2O_2 and O_3 concentrations, thus also reducing the formation of sulfate in the aqueous phase as well as in the gas phase. Slightly more ozone is modelled in remote regions with surface $\text{NO}_x < 1$ ppb, because here ozone formation is NO_x limited, as was also shown by other authors (Sillman et al., 1990).

A ratio of $\text{NO}_x / (2 \cdot \text{VOC})$ in the emission data, this means halving NO_x emissions or

doubling anthropogenic VOC emissions, results in increasing O₃, OH and SO₄²⁻ concentrations in those regions of Europe, where high NO_x concentrations are present and oxidation is VOC limited. A slightly enhanced oxidizing capacity of the model atmosphere is achieved: for sensitivity study (b) the ratio of modelled to observed O₃ is 0.86, for (c) 0.89. But only sensitivity study (c) is able to predict ozone concentrations higher than 50 ppbv in better agreement with observations.

In the sensitivity studies (a) to (c) the model was tested with hypothetically changed emissions, whereas biogenic VOC emissions (sensitivity study c) represent a still missing realistic emission source. Including biogenic VOC emissions in model calculations requires a parameterizations of emission rates of the main components, isoprene and monoterpenes, as a function of temperature, irradiance and forest coverage. Here the emission factor algorithm based on Guenther et al. (1991) and (1993) was chosen for two reasons. First, during nighttime no emission of isoprene occurs in agreement with observations. Second, the parameterization is able to describe an exponential increase in isoprene emissions with temperature until the maximum is reached at about 35 ° to 40 ° C. At higher temperatures a fast decrease, as observed, follows. For monoterpenes a temperature dependend emission rate is defined as follows

$$E_M = S_M \cdot \exp (\beta (T - T_s)) \quad (17)$$

with E_M : monoterpene emission rate in nmol (C) m⁻² s⁻¹ for temperature T in K,
 S_M : monoterpene emission rate for standard temperature $T_s = 301$ K, here
 $S_M = 40$ nmol (C) m⁻² s⁻¹,
 $\beta = 0.09$ K⁻¹, empirical coefficient.

Besides the temperature dependence, also the dependence on PAR (photosynthetic active radiation) is considered to describe isoprene emission:

$$E_I = S_I \cdot C_L \cdot C_T \quad (18)$$

with E_I : isoprene emission rate in nmol (C) m⁻² s⁻¹ for temperature T in K and PAR

flux L in $\mu\text{mol m}^{-2} \text{s}^{-1}$,

S_I : isoprene emission rate for standard temperature $T_s = 301 \text{ K}$ and a standard PAR flux of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$, here $S_I = 40 \text{ nmol (C) m}^{-2} \text{s}^{-1}$,

C_L : light correction factor,

C_T : temperature correction factor.

The light dependend correction factor C_L is defined by Guenther et al. (1991) as:

$$C_L = \frac{x - \sqrt{x^2 - 4fIL_1}}{2L_2} \quad (19)$$

with $x = fI + L_1 + L_2$,

$f = 0.385$, fraction of light absorbed by chloroplasts,

I : irradiance in $\mu\text{mol m}^{-2} \text{s}^{-1}$,

$L_1 = 105.6$, empirical coefficient,

$L_2 = 6.12$, empirical coefficient.

Temperature dependence is described by:

$$C_T = \frac{\exp [T_1 (T_B - T_s) / RT_B T_s]}{1 + \exp [T_2 (T_B - T_3) / RT_B T_s]} \quad (20)$$

with T_B : leave temperature in K,

$R = 8.31433 \text{ J K}^{-1} \text{ mol}^{-1}$,

$T_1 = 95100 \text{ J mol}^{-1}$, empirical coefficient,

$T_2 = 231000 \text{ J mol}^{-1}$, empirical coefficient,

$T_3 = 311.83 \text{ K}$, empirical coefficient.

Additionally it is assumed that leaf temperature is identical with surface temperature.

Photosynthetic active radiation is determined as a function of zenith angle Θ to

$$PAR = PAR_0 \cdot \cos \Theta \quad , \quad (21)$$

where $PAR_0 = 410 \text{ W m}^{-2}$ is the integral irradiation intensity between 400 and 700 nm after subtracting ozone absorption, Rayleigh and Mie scattering. Taking into account all simplifications and approximations already introduced to solve equation 18, the astronomic determination of PAR without considering cloud effects is assumed to be sufficient. The information about deciduous and coniferous forest coverage in a single grid box is based on forest coverage data from Lübkert and Schöpp (1989). A total of

744242 km² coniferous forest and 566005 km² deciduous forest is determined for the HIRHAM-CTM area as shown in Fig 4 and 7. It is a common assumption that only isoprene is emitted from deciduous forests and only monoterpenes from coniferous forests. The chemical degradation of isoprene is explicitly included in the gas phase mechanism of Stockwell et al. (1990), whereas the chemistry of monoterpenes is missing. Therefore the emissions of monoterpenes are subdivided to consist to 50 % of alkenes with terminal double bond and to 50 % of alkenes with internal double bond.

The diurnal cycle of biogenic emissions as determined for the 30th of July 1990 by the algorithm of Lübker and Schöpp (1989) and based on Guenther et al. (1991) and (1993) are compared in figure 10 for one grid box in Spain with 1592 km² coniferous forest and 172 km² deciduous forest. Emission rates by Lübker and Schöpp (1989) are about twice as high as those based on Guenther et al. (1991) and (1993).

Sensitivity study (d) results in a ratio of modelled to observed ozone of 0.84. Though biogenic VOC are highly reactive, their contribution to ozone formation might be underestimated due to the chemical mechanism of Stockwell et al. (1990), which does not account for monoterpenes. In comparison to sensitivity study (c) the main difference is obvious in the spatial distribution of sources. But as well as in the sensitivity study (c) measured ozone concentrations in the range of 50 - 100 ppbv are predicted in a more realistic way than in the control run.

Doubling clear sky photolysis rates as determined by the climatological preprocessor model of Madronich (1987) and thus taking into account uncertainties in actinic flux calculations shows the best agreement between modelled and measured ozone (ratio: 0.98). Also sulfate concentrations are enhanced significantly.

A summary with a qualitative valuation of all sensitivity studies is given in table 2. In particular information about anthropogenic and biogenic VOC emission data should be improved to achieve a realistic description of the oxidizing capacity of the atmosphere in the model system. In addition, the determination of photolysis rates should be investigated in detail.

Summary and conclusions

The spatial and temporal comparison of model predicted surface trace gas concentrations with available observations at EMEP-stations shows that HIRHAM-CTM is able to determine the large scale transport and transformation of primary and secondary pollutants. Despite lots of improvements necessary, the model system is stable and sensitive enough to study the influence of global climate change on the chemistry of the polluted atmosphere over Europe.

During the winter study as well as during the summer study the model overpredicts surface SO_2 concentrations revealing an underestimation of near source dry deposition. To parameterize the local deposited fraction of emissions as a function of meteorological conditions, emission height and liquid water content, plume model calculations should be carried out.

In sophisticated three dimensional chemistry-transport-models the oxidation of SO_2 to SO_4^{2-} was often underestimated, because too less liquid water in form of non-precipitating clouds was present in the model atmosphere. The importance of a realistic cloud parameterization for sulfate production can also be stressed for simulations with HIRHAM-CTM. In comparison with satellite data the occurrence of clouds is underpredicted by the standard cloud module. A better agreement of cloud cover determined by HIRHAM with satellite data can be established. During the winter simulation the oxidizing capacity of the model atmosphere is determined in a realistic way and the model prediction for sulfate is improved significantly with the cloud module adapted to HIRHAM. But a final validation of the two cloud schemes cannot be given, because during the summer case the limited oxidizing capacity of the model atmosphere also influences sulfate production. In sensitivity studies peak ozone concentrations could be enhanced by including a parameterization for biogenic VOC emissions from forests, by doubling anthropogenic VOC emissions and by doubling clear sky photolysis rates. These topics should be investigated in future. Research is also required concerning the influence of aerosols on the oxidizing capacity of the atmosphere. Especially HONO formation on aerosol surfaces during night is discussed to be of great importance (Jenkin et al., 1988).

References

- Altshuller A. P. (1983) Review: Natural Volatile Organic Substances and their Effect on Air Quality in the United States. *Atmos. Environ.* **17**, 2131-2165.
- Anthes R. A., Hsieh E.-Y. and Kuo Y. H. (1987) Description of the Penn State / NCAR mesoscale model version4 (MM4). NCAR/TN-282+STR, Boulder, Colorado.
- Chang J. S., Brost R. A., Isaksen I. S. A., Madronich S., Middleton P., Stockwell W. R. and Walcek C. J. (1987) A three-dimensional Eulerian acid deposition model: Physical concepts and formulation. *J. Geophys. Res.* **92**, 14681-14700.
- Dennis R. L., McHenry J. N., Barchet W. R., Binkowski F. S. and Byun D. W. (1993) Correcting RADM's Sulfate Underprediction: Discovery and Correction of Model Errors and Testing the Corrections through Comparison against Field Data. *Atmos. Environ.* **27**, 975-997.
- Deutsches Klimarechenzentrum (DKRZ), Model User Support Group (1992) ECHAM3 - Atmospheric General Circulation Model. DKRZ-Technical Report 6, Hamburg.
- Gear C. W. (1971) The automatic integration of ordinary differential equations. *Commun. ACM* **14**, 176-179.
- Guenther A. B., Monson R. K., and Fall R. (1991) Isoprene and Monoterpene Emission Rate Variability: Observations with Eucalyptus and Emission Rate Algorithm Development. *J. Geophys. Res.* **96**, 10799-10808.
- Guenther A. B., Zimmerman P. R., Harley P. C., Monson R. K. and Fall R. (1993) Isoprene and Monoterpene Emission Rate Variability: Model Evaluations and Sensitivity Analysis. *J. Geophys. Res.* **98**, 12609-12617.
- Hass H. (1991) Description of the EURAD Chemistry-Transport-Model version 2 (CTM2) (edited by Ebel A., Neubauer F. M. and Speth P.). Report 83, Institute of Geophysics and Meteorology, University of Cologne.
- Hass H., Ebel A., Feldmann H., Jakobs H. J. and Memmesheimer M. (1993) Evaluation studies with a regional chemical transport model (EURAD) using air quality data from the EMEP monitoring network. *Atmos. Environ.* **27**, 867-887.
- Isaksen I. S. A. (1988) Is the oxidizing capacity of the atmosphere changing? In Dahlem Workshop Report: The Changing Atmosphere (edited by Rowland F. S. and Isaksen I. S. A.) pp. 141- 157, John Wiley & Sons.

- Jenkin M. E., Cox R. A. and Williams D. J. (1988) Laboratory Studies of the Kinetics of Formation of Nitrous Acid from the thermal Reaction of Nitrogen Dioxide and Water Vapour. *Atmos. Environ.* **22**, 487-498.
- Källberg P. (1990) The HIRLAM forecast model level 1 documentation manual. SMHI, S-60176 Norrköping, Sweden.
- Karamchandani P. and Venkatram A. (1992) The Role of non-precipitating Clouds in producing ambient Sulfate during Summer: Results from Simulations with the Acid Deposition and Oxidant Model (ADOM). *Atmos. Environ.* **26**, 1041-1052.
- Langner, J. and Rhodhe, H. (1991) A Global Three-Dimensional Model of the Tropospheric Sulfur Cycle. *J. Atmos. Chem.* **13**, 225-263.
- Lübker B. and Schöpp W. (1989) A Model to calculate Natural VOC Emissions from Forest in Europe, IIASA Working Paper WP-89-082, Laxenburg, Austria.
- Leone J. A. and Seinfeld J. H. (1985) Comparative analysis of chemical reaction mechanisms for photochemical smog. *Atmos. Environ.* **19**, 437-464.
- Madronich S. (1987) Photodissociation in the atmosphere. I: Actinic flux and the effect of ground reflections and clouds. *J. Geophys. Res.* **92**, 9740-9752.
- McRae G. J., Goodin W. R. and Seinfeld J. H. (1982) Numerical solution of the atmospheric diffusion equation for chemically reacting flows. *J. Comput. Phys.* **45**, 1-42.
- Memmesheimer M., Tippke J., Ebel A., Hass H., Jakobs H. J. and Laube M. (1991) On the use of EMEP emission inventories for European scale air pollution modelling with the EURAD model. In EMEP Workshop on Photooxidant Modelling for long-range Transport in Relation to Abatement Strategies. Berlin, Germany, 16.-19. April 1991, pp. 307-324.
- Mölders N. (1993) Cloud parameterization for a Chemistry-Transport-Model (edited by Ebel A., Neubauer F. M. and Speth P.). Report 88, Institute of Geophysics and Meteorology, University of Cologne (in German).
- Mölders N., Hass H., Jakobs H. J., Laube M. and Ebel A. (1994) Some effects of different cloud parameterizations in a mesoscale model and a chemistry transport model. *J. Appl. Meteor.* **33**, 527-545.
- Rockel B., Raschke E. and Weyres B. (1991) A parameterization of broad band radiative transfer properties of water, ice and mixed clouds. *Beitr. Phys. Atmosph.* **64**, 1-12.

- Schaug J., Pedersen U., Skjelmoen J. E. and Kvalvågnes I. (1993) Data Report 1991, Part 2: Monthly and seasonal summaries. EMEP/CCC-Report 5/93, NILU, Lillestrøm.
- Sillman S., Logan J. A. and Wolfsy S. C. (1990) The Sensitivity of Ozone to Nitrogen Oxides and Hydrocarbons in Regional Ozone Episodes. *J. Geophys. Res.* **95**, 1837-1851.
- Stockwell W. R., Middleton P., Chang J. S. and Tang X. (1990) The second generation regional acid deposition model: Chemical mechanism for regional air quality modelling, *J. Geophys. Res.* **95**, 16343-16367.
- Sundquist H. (1978) A parameterization scheme for non-convective condensation including prediction of cloud water content. *Quart. J. Meteor. Soc.* **104**, 677-690.
- Tiedtke M. (1989) A comprehensive mass flux scheme for cumulus parameterization in large-scale models. *Mon. Wea. Rev.* **117**, 1779-1800.
- Tuovinen J. P., Barrett K. and Styve H. (1994) Transboundary acidifying Pollution in Europe: Calculated Fields and Budgets 1985-93. EMEP/MSC-W Report 1/94, NILU, Lillestrøm.
- Umweltbundesamt (1992) Daten zur Umwelt 1990/91. Erich Schmidt Verlag GmbH & Co, Berlin (in German).
- Valdez M. P., Bales R. C., Stanley D. A. and Dawson G. A. (1987) Gaseous Deposition to Snow, 1. Experimental Study of SO₂ and NO₂ Deposition. *J. Geophys. Res.* **92**, 9779-9787.
- Venkatram A., Karamchandani P. K. and Misra P. K. (1988) Testing a Comprehensive Acid Deposition Model. *Atmos. Environ.* **22**, 737-747.
- Walcek C. J. and Taylor G. R. (1986) A theoretical method for computing vertical distribution of acidity and sulfate production within cumulus clouds. *J. Atmos Sci.* **43**, 339-355.
- Ziegenbein C., Ackermann I. J., Feldmann H., Hass H., Memmesheimer M. and Ebel A. (1994) Aerosol Treatment in the EURAD Model: Recent Developments and First Results. In The Proceedings of EUROTRAC Symposium '94 (edited by P. M. Borrell et al.) pp. 1176-1179, SPB Academic Publishing, The Hague, The Netherlands.

Table 1:

Comparison of the solution approach by Hass (1991) for the gas phase chemistry module with the modified solution approach concerning the total number of timesteps (three days simulation, $T = 298\text{ K}$, $p = 1\text{ atm}$, photolysis rates for 21 June, 40° N).

	$\Delta t_{\text{chem,max}}=5\text{ min}$ solution approach by Hass (1991)	$\Delta t_{\text{chem,max}}=5\text{ min}$ modified solution approach	$\Delta t_{\text{chem,max}}=10\text{ min}$ modified solution approach
clean air	4196	1961	1742
polluted air	9507	6418	6247

Table 2:

Summary of sensitivity studies for predicting $\text{O}_3 > 50\text{ ppbv}$ and qualitative valuation (+: improved prediction, -: worse prediction)

Emissions	2 * $\text{VOC}_{\text{anthropogenic}}$	+
	$\text{VOC}_{\text{biogenic}}$	+
	0.5 * NO_x	-
	2 * NO_x	-
Clear sky photolysis rates * 2		+

Figure 1:

a) Cloud cover as determined by the CTM standard cloud module, b) modelled cloud cover by HIRHAM and c) satellite picture (Meteosat, infrared), all for 0 GMT, 13 January 1991.

Figure 2:

Comparison of the temporal development of species concentrations during a three days simulation as determined by the zero dimensional version of CTM with different solution approaches, full line: standard, dotted line: Hass (1991), broken line: modified solution approach ($T = 298\text{ K}$, $p = 1\text{ atm}$, photolysis rates for 21 June, 40° N , clean air).

Figure 3:

Daily mean surface SO_2 concentrations in ppbv for the winter episode (13 January to 23 January 1991) as simulated with the CTM standard cloud module (left column) and as measured at single EMEP-stations (right column).

Figure 4:

Comparison of modelled and measured daily mean surface SO_2 concentrations at four north European EMEP-stations during the winter episode (note that the units of the y-axes differ significantly). M/O is the ratio of modelled to observed data for the whole episode.

Figure 5:

Same as in Figure 4, but for SO_4^{2-} concentrations.

Figure 6:

Scatter diagrams with winter episodic mean (13 January to 23 January 1991) values of near surface species concentrations. M/O is the ratio of modelled to observed data for the whole episode.

Figure 7:

Daily peak surface O₃ concentrations in ppbv for the summer episode (23 July to 31 July 1990) as simulated with the CTM standard cloud module (left column) and as measured at single EMEP-stations (right column).

Figure 8:

Time series of simulated and measured surface O₃ concentrations (full line: observations, dotted line: standard cloud module, broken line: HIRHAM-CTM cloud scheme), r is the correlation coefficient.

Figure 9:

Scatter diagrams with summer episodic mean (23 July to 31 July 1990) values of near surface species concentrations. For ozone only concentrations between 12 and 16 GMT are considered. M/O is the ratio of modelled to observed data for the whole episode.

Figure 10:

Temporal development of isoprene and monoterpene emissions in g / s for the 30th of July 1990 in a grid element of Spain based on the algorithm of Guenther et al. (1991 and 1993) (G91) and Lübker and Schöpp (1989) (L89).

Figure 1

c)

a)

b)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10