Regional modelling of particulate matter with MADE

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Abstract
Describes the development and application of an aerosol model for regional air quality simulations. The aerosol model MADE is based on a modal concept and describes the chemical composition and the size distribution of atmospheric particulate matter. Primary as well as secondary aerosol components are considered in the model, which is fully integrated into the photo-chemical transport model EURAD. The model system has been applied to a European domain with different resolutions, using a one-way nesting procedure. Simulations show the potential import-ance of secondary organics of anthropogenic and biogenic origin for the tropospheric particle load-ing. In addition it is shown that a reduction in precursor emissions for the inorganic ion fraction of PM (sulphate, nitrate and ammonium) does not necessarily lead to an equivalent reduction in PM2.5 mass concentrations, as for example a reduction in sulphate aerosol caused by reduced SO_2 emissions might be compensated by enhanced formation of nitrate aerosols in certain regions.

1. Introduction

In order to fulfil their scientific tasks' state-of-the-art air quality models should be capable of predicting particulate matter in addition to the gas-phase concentrations. A suitable aerosol model for the application in complex regional transport models has to provide sufficient information on the chemical com-position as well as on the size distribution of the particles. Furthermore, it has to be integrated to a photochemical model in order to be able to represent the interactions between the gas phase and the particle phase.

The Modal Aerosol Dynamics Model for Europe (MADE) has been developed as such an aerosol model. It is based on the Regional Particulate Model (RPM) (Binkowski and Shankar, 1995), and has successfully been implemented into the EURAD model system to the simulation of tropospheric aerosols over Europe (Ackermann *et al.*, 1998). How-ever, the first model version was limited to submicron particles consisting of inorganic ions and water.

This paper describes the further develop-ment of the model, among others, the exten-sion to include the coarse particle size range and a more complete fine particle chemistry. These modifications have been performed by the incorporation of the aerosol portion of the EPA's Models3 (Binkowski, 1998). Also a first three-dimensional application of the extended system is briefly illustrated and the sensitivity of predicted PM2.5 mass concen-trations to SO_2 emissions is investigated.

2. Model description

A detailed description of the MADE model can be found in Ackermann *et al.* (1998) and Binkowski and Shankar (1995), therefore we

will focus here on the major modifications made on that. The aerosol dynamics model MADE is coupled to the chemistry transport model CTM2 of the EURAD model system which is described in Hass *et al.* (1995) and is called at every transport time step of the gas phase model.

MADE solves the following conservation equations that are formulated in terms of integral moments M_k, defined as

$$M_k = \int_{-\infty}^{\infty} d_p^k n(lnd_p)d(lnd_p), \qquad (1)$$

of three particle modes:

$$\frac{\partial}{\partial t} M_{k_i}^* = -\nabla \cdot (\vec{v} M_{k_i}^*) - \frac{\partial}{\partial \sigma}(\dot{\sigma} M_{k_i}^*) + \left(\frac{\partial M_{k_i}^*}{\partial t}\right)_{dif}$$

$$+ coag_{kii} + coag_{kij} + cond_{ki} + nuc_{ki} + e_{ki}$$

$$\frac{\partial}{\partial t} M_{k_j}^* = -\nabla \cdot (\vec{v} M_{k_j}^*) - \frac{\partial}{\partial \sigma}(\dot{\sigma} M_{k_j}^*) + \left(\frac{\partial M_{k_j}^*}{\partial t}\right)_{dif}$$

$$+ coag_{kjj} + coag_{kji} + cond_{kj} + e_{kj}$$

$$\frac{\partial}{\partial t} M_{k_c}^* = -\nabla \cdot (\vec{v} M_{k_c}^*) - \frac{\partial}{\partial \sigma}(\dot{\sigma} M_{k_c}^*) + \left(\frac{\partial M_{k_j}^*}{\partial t}\right)_{dif}$$

$$- \frac{\partial}{\partial \sigma}\left((V_{k_c}^*)_{Sed} M_{k_c}^*\right) + e_{kc}, (2)$$

where the index i represents the Aitken mode, j the accumulation mode, c the coarse mode and $\vec{v}$ the horizontal wind vector. The equations are formulated in a σ-coordinate system defined as

$$\sigma = \frac{p - p_{top}}{p_{surf} - p_{top}}, \qquad (3)$$

with p the pressure at layer height and p_{surf} and p_{top} the pressure at the lower and upper model boundary respectively. Within each mode a lognormal size distribution

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$$n(lnd_p) = \frac{N}{\sqrt{2\pi}ln\sigma_g}exp\left[-\frac{1}{2}\frac{(lnd_p - lnd_{p_g})^2}{ln^2\sigma_g}\right]$$

(4)

is assumed, where N is the number concentration, d_p the particle diameter and d_{p_g} the median diameter and σ_g the standard deviation of the distribution. The time rate of change of a given moment M_k is therefore given by the transport terms of horizontal and vertical advection and vertical diffusion (additionally horizontal diffusion can be activated if required), the aerosol dynamics terms for coagulation ($coag_k$) within and between the modes, condensation ($cond_k$) and nucleation (nuc_k) for the Aitken and accumulation mode and sedimentation for the coarse mode as well as primary particle emissions (e_k). Size dependent dry deposition is treated as lower boundary condition for vertical diffusion.

Equation 2 are solved for $k = 0$ (i.e. the total number concentration per mode) and for $k = 3$ (which is proportional to the aerosol volume concentration in the mode). In contrast to the formulation given in Ackermann *et al.* (1998), the standard deviations σ_g of the modes are assumed to be constant. Consequently the prediction of two moments is sufficient to define the size distribution functions.

The equations for the third moment are further subdivided into the submoments of the substances contributing to the chemical composition of the aerosol particles M_3^n:

$$M_{3_l} = \sum_{n=1}^{n=spec} M_{3_l}^n = \sum_{n=1}^{n=spec} \frac{m_l^n}{\frac{\pi}{6}\rho_l^n} l = i, j, c$$

(5)

where m_l^n is the mass concentration of species n and ρ_l^n the bulk density of the species in mode l (currently $spec = 3$ for the coarse mode and $spec = 8$ for each of the two fine particle modes, water is not transported but locally equilibrated, moment index k is neglected here). This results in a total of 22 prognostic variables in the aerosol model.

A description of the process parametrizations and the derivation of the according terms of equation (2) can be found in Binkowski and Shankar (1995) and Ackermann *et al.* (1998). In addition to the nucleation scheme described in Binkowski and Shankar (1995) and Ackermann *et al.* (1998) an optional nucleation treatment has been implemented into the model (Youngblood and Kreidenweiss, 1994). Sedimentation is treated as a vertical advection process using the implemented advection schemes of the model. This requires interpolation of the

sedimentation velocities to the layer boundaries and a subsequent unit conversion according to

$$\left(V_{k_c}^*\right)_{Sed} = (V_{k_c})_{Sed} * \rho_{air} * g/(p_{surf} - p_{top})$$

(6)

where ρ denotes the air density and g the mean gravitational acceleration. The sedimentation velocities $(V_k)_{Sed}$ are calculated by solving

$$V_{Sed} = \left[\frac{g}{18\nu}\left(\frac{\rho_p}{\rho_{air}}\right)d_p^2\right]C_C$$

(7)

where ν is the kinematic viscosity, ρ_p the particle density, d_p the particle diameter and C_C the Cunningham correction factor, in the appropriate form for the moments of a lognormal distribution.

Figure 1 shows a schematic representation of the chemical composition of the fine particle modes together with gas-phase precursors. Secondary inorganic ions are represented by sulphate, nitrate and ammonium.

Emissions of sulphate that are given from the emission inventory are no longer treated as particle emissions – as in the original model formulation – but assigned to the gas-phase species H_2SO_4-vapor which has been added to the RADM2 formulation. This vapor is then – depending on the actual conditions – either condensing on existing particles or nucleating to form new particles, subsequently reacting with ammonia to become partly or fully neutralised. Excess ammonia is used for the neutralisation of nitrate aerosol to ammonium-nitrate. Precursor concentrations of ammonia, nitric acid vapor and sulfuric acid vapor are treated by the gas-phase model.

Three groups of primary aerosol particles have been added to the fine particle composition: elemental carbon (EC), primary organics and PM2.5, which is a lumped class of other primary particles.

In the troposphere reactive organic gases (ROG) are mainly oxidised by the OH radical, the nitrate radical NO_3 and O_3. Some of the oxidation products have low volatility products and might condense on available particles forming secondary organic aerosol (SOA).

Following the approach of Pandis *et al.* (1992) these reaction products accumulate in the gas phase. If the saturation concentration is exceeded, they condense on the available aerosol surface, establishing a thermodynamic equilibrium between the gas phase and the aerosol phase. Therefore a condensable reaction product G_i, which is the product from the oxidation of an ROG by,

for example, the OH radical, is partitioned between the gas and the aerosol phase:

$$[G_i]_{tot} = [G_i]_{gas} + [G_i]_{aer}. \tag{8}$$

The measured quantity available is the aerosol mass yield

$$Y_i = [G_i]_{aer}/\Delta ROG \tag{9}$$

where ΔROG represents the reacted precursor concentration. The aerosol yields Y_i in $[\mu g/m^3/ppb]$ are adapted from Pandis *et al.* (1992) for use with RADM2 classes of lumped organic species given in Figure 1. A more detailed description of the scheme and an outline of future developments is given in Schell *et al.* (1998a).

The gas phase chemical mechanism RADM2 was extended to include a more detailed treatment of biogenic compounds. Hence the biogenic model species API and LIM and their reactions were adapted from the new RACM mechanism (Stockwell *et al.*, 1997). API represents α-pinene and other cyclic terpenes with one double bond, LIM stands for d-limonene and other cyclic diene terpenes. In the aerosol phase SOA is distinguished between those of biogenic and those of anthropogenic origin.

The coarse mode particles currently are segregated into three contributions, which are soil-derived particles, particles of marine origin and anthropogenic coarse mode particles. However, for the fine mode primary particles, the number of contributors and type of segregation can be adjusted to the emission inventory available.

Figure 1
Schematical representation of the fine particle (Aitken and accumulation mode) chemical composition with gas-phase precursors in MADE
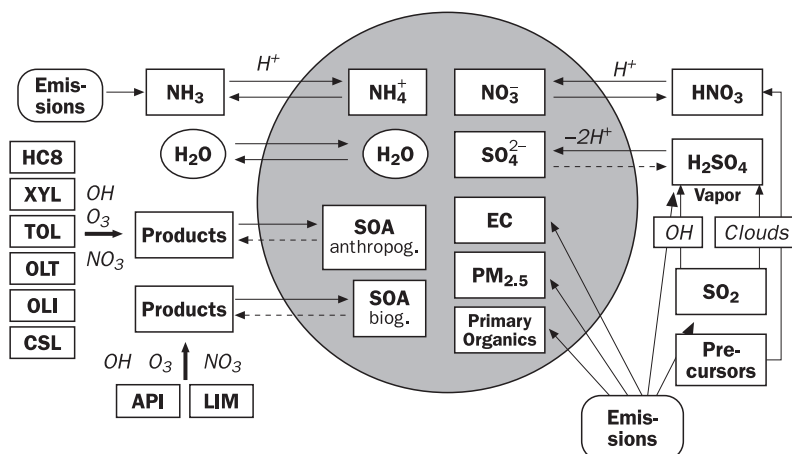
3. Model application

3.1 Nesting results
Figure 2 shows the model domains and the nesting technique used for the simulations with the coupled system of the CTM and MADE. Three subdomains are nested with a one-way nesting scheme into the mother domain that covers Central Europe, whereas the highest resolution grid covers the greater Cologne area in Germany with a resolution of 1km. Nesting is realized by using output from the higher level domain for the initial values at the beginning of the simulation and the boundary values throughout the period for the nested domain. This is done for both the gas phase as well as the aerosol fields.

A ten-day episode in July 1994 has been simulated in order to test the model system. Figure 3 shows the calculated number concentration of Aitken mode particles for the 9km grid (bottom) and the according subdomain of the 27km (top) simulation as an example of model results. Although the general features – with a dominating inflow from the eastern boundary – as well as the maximum and minimum concentrations in the domain are similar between the two simulations, the results from the finer resolution show greater horizontal gradients, e.g. in Belgium and along the coast of The Netherlands. Another significant difference is the location of the central minimum which is shifted to the south-west in the case of the simulation with finer resolution.

In the case of nucleation events number concentrations in the Aitken mode reach up to values of several 10^{11} $1/m^3$. However, these high number concentrations are rather rapidly reduced by efficient coagulation processes.

Figure 2
Model domains and different nest levels used for the aerosol model in a one-way nesting mode
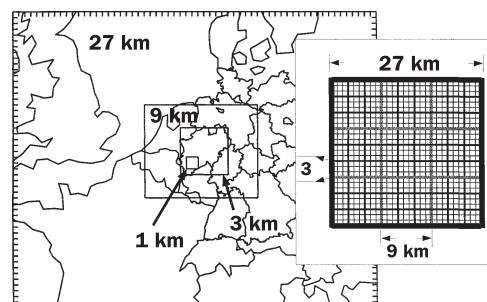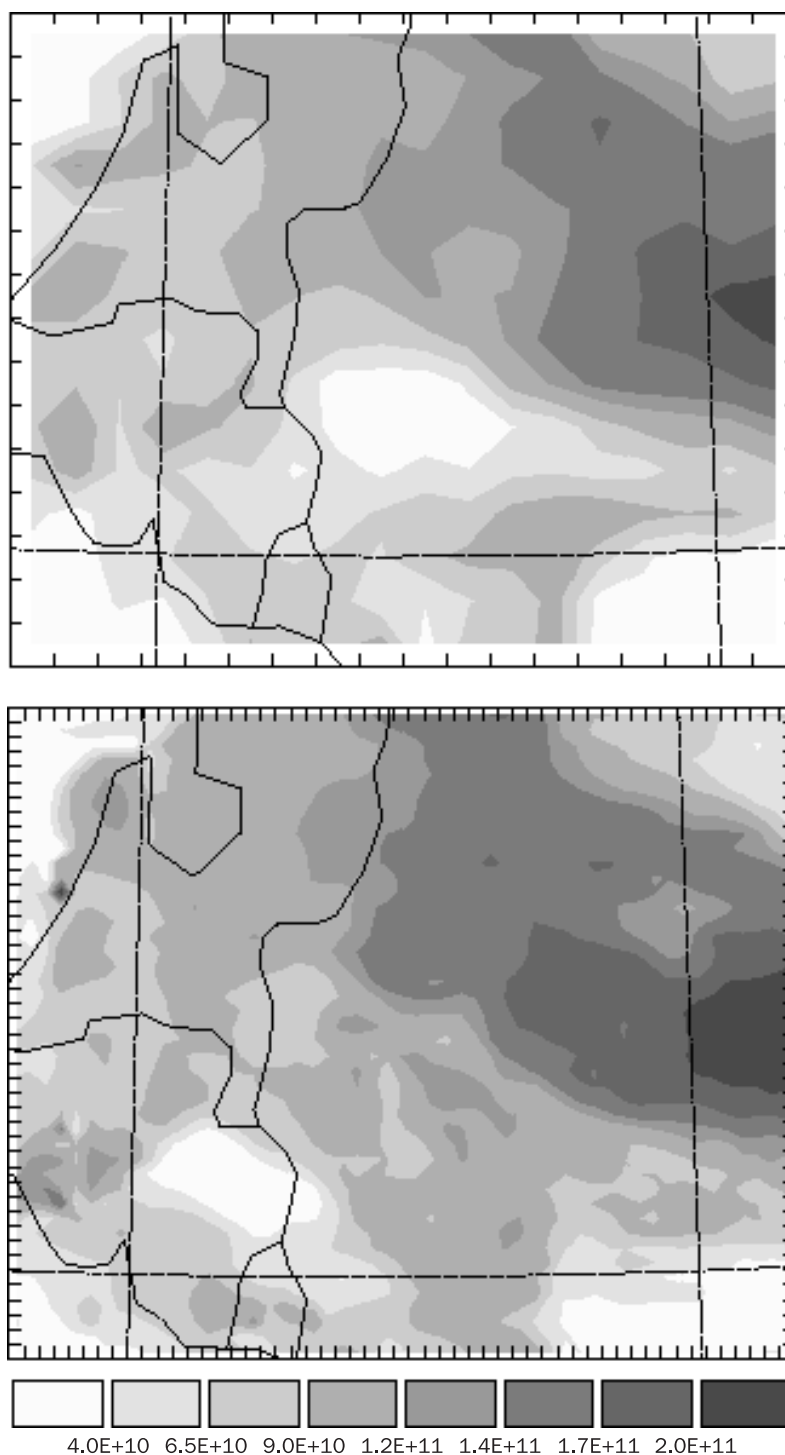
Figure 3

Number concentration in the Aitken mode for 24 July 1994, 12 noon GMT [$1/m^3$] at the surface layer for a simulation with 9km resolution (bottom) and for a subdomain of the simulation with 27km resolution (top)

4.0E+10 6.5E+10 9.0E+10 1.2E+11 1.4E+11 1.7E+11 2.0E+11

3.2 Secondary organics

In Figure 4, concentrations of secondary organic aerosols resulting from anthropogenic (top) and biogenic (bottom) sources are given at the same point of time for the coarse level domain. In this case, both source categories contribute about equally to the total SOA load, whereas the spatial distribution shows some differences. Simulations over the ten-day period show that the spatial distribution of SOA is highly variable and that the maximum concentration can be

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Figure 4

Mass concentration of secondary organic aerosol in the accumulation mode for 24 July 1994, 12.00 GMT in $\mu g/m^3$ at the surface layer from anthropogenic (top) and biogenic (bottom) origin
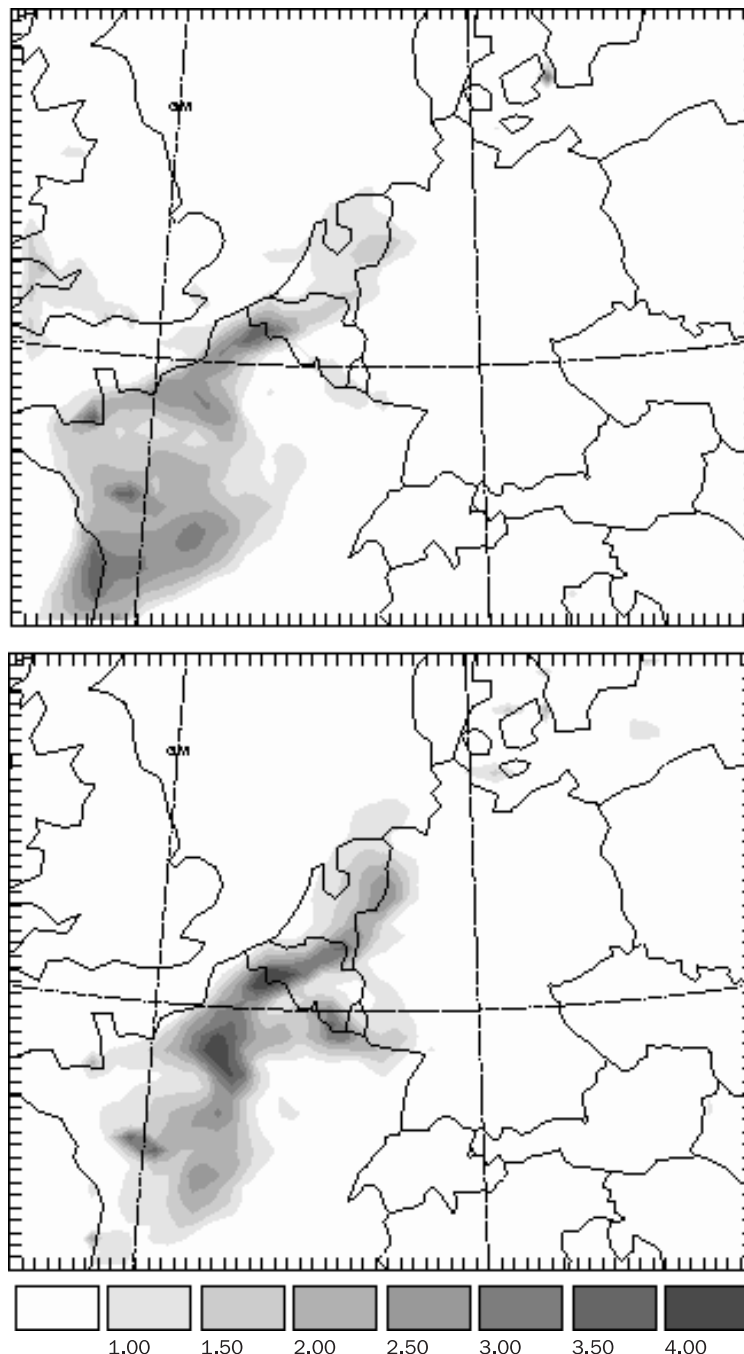
dominated by anthropogenic as well as biogenic precursors, depending on the actual conditions (meteorology, time and temperature dependence of the emissions, etc.) over the domain. Concentration ranges up to about $10\mu g/m^3$, thus providing a significant contribution to the total PM2.5 mass.

3.3 Emission sensitivity inorganic ions

Inorganic ions comprise a major fraction of tropospheric PM2.5 (e.g. about 42 per cent for urban average fine particle mass loadings (Heintzenberg, 1989)). These particles are formed in the atmosphere from the gas-phase precursors, sulphuric acid, ammonia and nitric acid. Whereas ammonia is not

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formed by chemical reactions but only directly emitted, the other two precursors are secondary components formed by gas-phase and in-cloud oxidation of sulphur and nitrogen compounds. Therefore, one can expect a linear response of NH_3 concentrations to changes in NH_3 emissions, whereas for example a reduction in the emission of NO and NO_2 does not necessarily lead to a linear response in HNO_3 and subsequently ammonium-nitrate aerosol concentrations.

The response of PM2.5 to inorganic precursor concentration changes is investigated in Ansari and Pandis (1998). In a simple ammonium-sulphate system, the response of PM2.5 to changes in sulphur concentrations is expected to be linear with different slopes depending on the degree of neutralisation. The additional introduction of nitrate, however, leads to non-linearity that is caused by the formation process of ammonium-nitrate which is strongly dependent on temperature, relative humidity, sulphate and gas phase ammonia concentrations. Under certain conditions, the addition of sulphate into this system might lead to a decrease in PM2.5 concentrations and vice versa, because the

additional sulphate will be neutralised by ammonia, which is then no longer available for ammonium-nitrate formation. If the ammonium-nitrate formation is ammonia limited, one mole of ammonia used for sulphate neutralisation will cause a reduction of two moles in ammonium-nitrate concentration, resulting in an overall mass decrease of PM2.5.

Figure 5 shows that this effect also is visible in the 3D model simulations. The difference in inorganic PM2.5 concentrations resulting from a 50 per cent reduction in SO_2 emissions is shown. Whereas the PM2.5 concentrations are significantly reduced by up to 50 per cent in some regions, other regions show only a slight decrease or even a small increase in PM2.5 concentrations. Sulphate aerosol concentrations are reduced by at least 40 per cent over the whole model domain (not shown in picture) but this effect is compensated by additional ammonium-nitrate formation, in particular in the Western part of the model domain.

This is further illustrated in Figure 6, showing the concentration changes in $\mu g/\mathrm{m}^3$ for sulphate and nitrate aerosol in the accumulation mode caused by the reduction in SO_2 emissions. The replacement of sulphate by nitrate aerosol, which is obvious from this Figure, is not restricted to the point of time shown in the Figures but can be found as a general feature, although with varying extents. Another difference that is introduced by the SO_2 reduction is a reduction in nucleation events, leading to slightly larger particle sizes. Therefore the reduction alters not only the chemical composition but also the size distribution of the particle population. PM2.5 mass is additionally increased in the regions of increased aerosol nitrate concentrations by an enhanced uptake of water into the particles. Also, moving from an ammonia limited to a nitrate limited regime might alter the diurnal variation of the concentrations.

Figure 5

Response of secondary inorganic PM2.5 concentrations to a 50 per cent reduction in SO_2 emissions. Values are given as differences between reduction simulation and base simulation in percentage in the model surface layer at 23 July 1994, 00.00 GMT
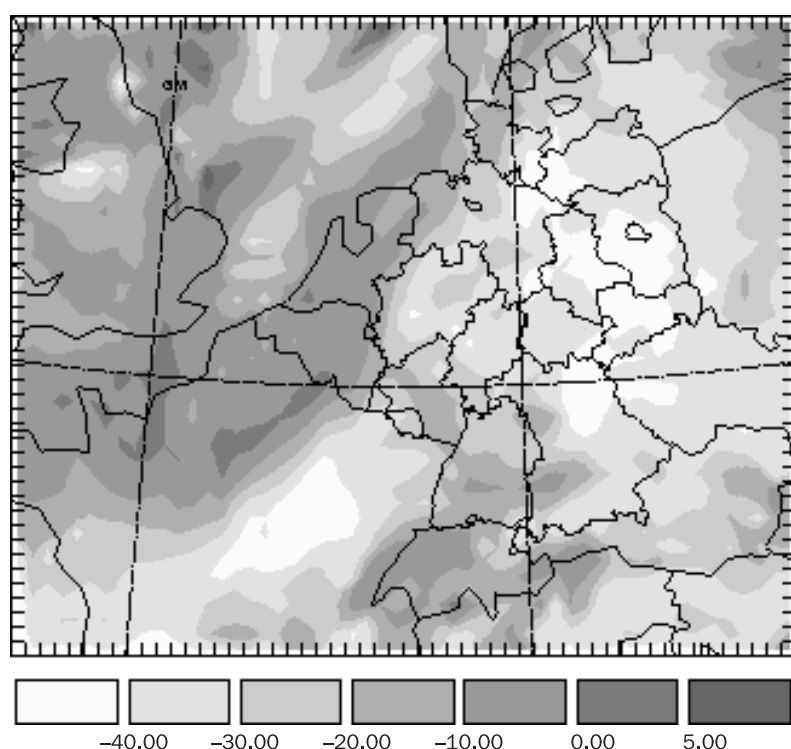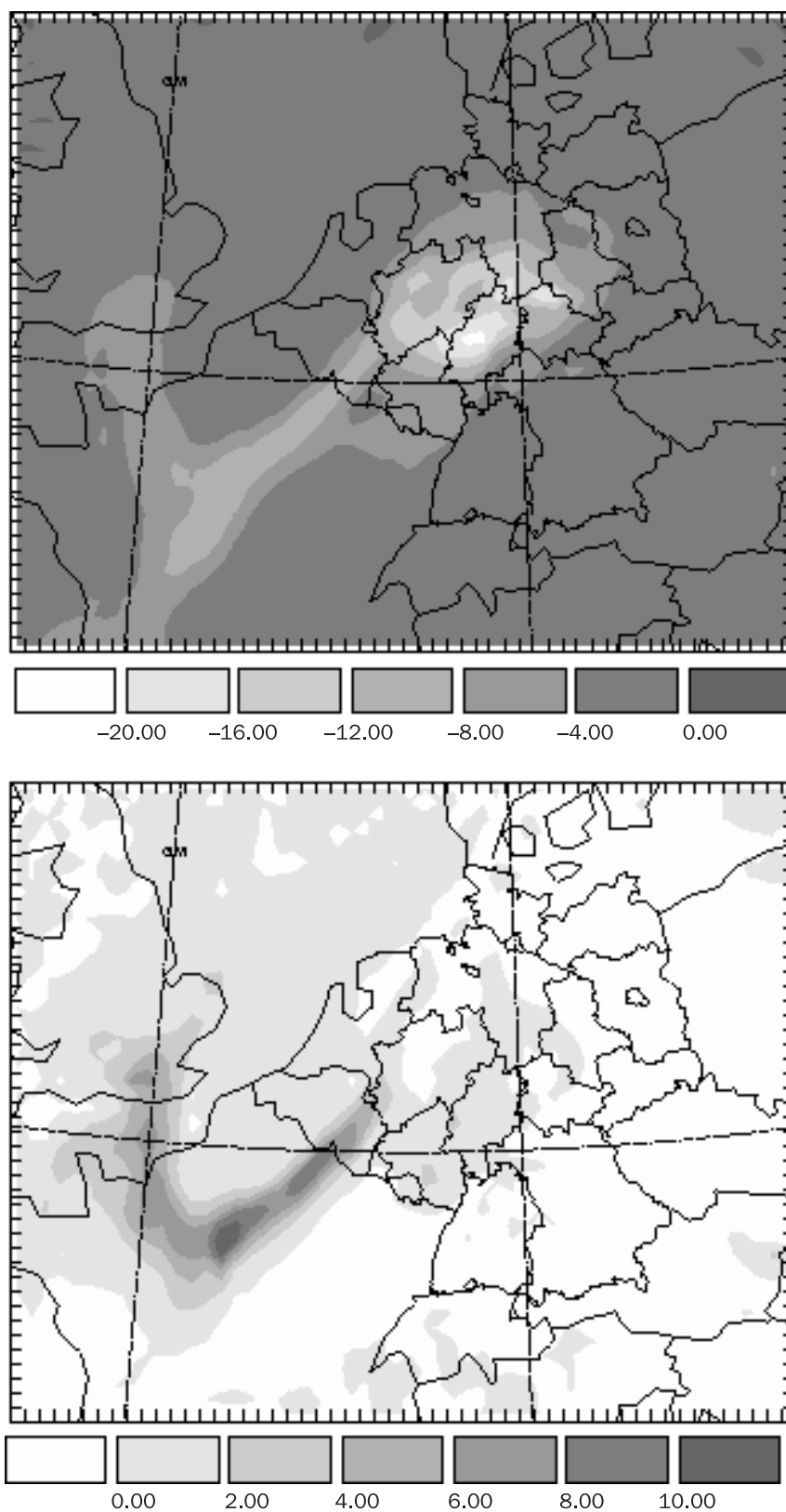

4. Summary and outlook

An extended aerosol model system which is integrated into a sophisticated gas-phase chemistry model has been developed and applied to test simulations over Europe with variable horizontal resolutions. The nesting capability of the model system provides the opportunity to study the importance of aerosol effects on different horizontal scales, as well as the impact of horizontal resolution on the results of the process parametrisations.

It has been shown that secondary organics provide a potentially significant aerosol

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Figure 6

Response of accumulation mode sulphate aerosol (top) and accumulation mode nitrate aerosol (bottom) concentrations to a 50 per cent reduction in SO_2 emissions. Values are given as differences between reduction simulation and base simulation in $\mu g/m^3$ in the model surface layer at 23 July 1994, 00.00 GMT

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source over Europe, which has to be considered in atmospheric models, although knowledge on the formation processes and ambient measurements is still limited.

Owing to the complex interactions in gas-phase chemistry and aerosol formation, the PM2.5 response to emission reduction of gas-phase precursor species is not necessarily linear. In particular, it has been shown that the reduction in sulphate aerosol caused by reduced sulphur emissions can be compensated by enhanced formation of ammonium-nitrate aerosol in some regions over Europe, leading to a modified chemical composition but not a significant mass reduction of PM2.5.

Since particulate matter in the troposphere is a primary, as well as a secondary, pollutant, the successful application of the model system is crucially dependent on the availability of sophisticated PM emission inventories.

Future developments of the model will – among others – include parametrisations of aerosol-cloud interactions (Meyer *et al.*, 1998) and an updated formation mechanism for SOA (Schell *et al.*, 1998b). Field measurements of the relevant aerosol parameters are required to evaluate the aerosol model.

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