3   AEROSOL SIMULATION WITH RCG

3.1 Introduction

The measurement campaign HoVerT has been accompanied by the Aerosol-Chemistry-Transport-Model RCG simulations. Special attention has been paid to the calculations of secondary inorganic and organic aerosol components and in the improvement of the simulation and thus in the understanding of the formation processes.

An extensive evaluation of the RCG model through the species resolved aerosol measurements during the HoVerT – campaign has been performed with the collected data (Beekmann et al., 2007). This was previous to any further investigations about mass budgets and process analyses executed with the model. Thus, we give a short overview of the model itself and focus on the model performance regarding evaluation with sampled data and process related considerations on seasonal and diurnal time variations. A more comprehensive description of the processes and how they are treated in RCG will be given in chapter 4 when describing the process rate and budget analyses.

3.2 Model description

The REM-CALGRID model is an urban/regional scale model designed to fulfil the requirements of the ambient air quality framework directive 96/62/EC of the European Commission (Stern, 2003). Rather than creating a completely new model, the urban-scale photochemical model CALGRID (Yamartino et al., 1992) and the regional scale model REM3 (Stern, 1994, Hass et al., 1997) were used as the starting point for the new urban/regional scale model, REM-CALGRID (RCG). The premise was to design an Eulerian grid model of medium complexity that can be used on the regional, as well as the urban, scale for short-term and long-term simulations of oxidant and aerosol formation.

The model includes the following features:

1.   A generalized horizontal coordinate systems, including latitude-longitude coordinates;

2.   A vertical transport and diffusion scheme that correctly accounts for atmospheric density variations in space and time, and accounts for all vertical flux components when employing either dynamic or fixed layers;

3.   A new methodology to eliminate errors totally from operator-split transport and ensure correct transport fluxes, mass conservation, and that a constant mixing ratio field remains constant (Yamartino, 2003);

4.   Inclusion of the improved and highly-accurate, monotonic advection scheme developed by Walcek (2000). This fast and accurate scheme has been further modified to exhibit even lower numerical diffusion for short wavelength distributions (Yamartino, 2003);

5.   Updated releases of the SAPRC-93 (Carter, 1996) and CBM-IV (Gery et al., 1989) photochemical reaction schemes;

6.   An equilibrium aerosol module that treats the thermodynamics of inorganic aerosols (ISORROPIA: Nenes et al., 1999);

7.   An equilibrium aerosol module that treats the thermodynamics of organic aerosols (SORGAM: Schell et al., 2001);

8.   Simple modules to treat the emissions of sea salt aerosols and wind blown dust particles;

9.   A wet scavenging module based on precipitation rates;

10.   An emissions data interface for long term applications that enables on-the-fly calculations of hourly anthropogenic and biogenic emissions.

Meteorological data needed by RCG at hourly intervals consist of layer-averaged gridded fields of wind, temperature, humidity and density, plus two-dimensional gridded fields of mixing heights, several boundary layer and surface variables, precipitation rates and cloud cover. All these meteorological data are produced employing a diagnostic meteorological analysis system based on an optimum interpolation procedure on isentropic surfaces. The system utilizes all available synoptic surface and upper air data (Kerschbaumer and Reimer, 2003, Reimer and Scherer, 1992).

The RCG model requires annual emissions of volatile organic carbons (VOC), nitrogen oxides (NOx), CO, SO_2, CH_4, NH_3, PM10, and PM2.5, split into point and gridded area sources.

European-wide annual anthropogenic emission averages for 2000 are taken from the EMEP data base (Vestreng, 2003). Within the Europe domain

Berlin/Brandenburg region has been nested in order to simulate the air pollution in the city and its surrounding areas more accurately. For the nested domain, highly resolved emissions data were obtained from regional administrations (for a description see Cuvelier et al., 2006).

In RCG, different chemical fractions are considered that contribute to PM10:

$$PM10 = PM_{coarse} + PM2.5_{prim} + EC + OC_{prim} + SOA + SO_4^{2-} + NO_3^- + NH_4^+ + Na^+ + Cl^-$$

being PM_{coarse} the mineral coarse particle fraction between 2.5 μm and 10 μm, $PM2.5_{prim}$ the primary aerosol smaller than 2.5 μm, EC the primary elemental carbon, OC_{prim} the primary organic carbon, SOA the secondary organic aerosols, SO_4^{2-} condensed matter sulphate ions, NO_3^- particulate nitrate, NH_4^+, particulate ammonium and Na^+ and Cl^- sea-salt.

A more comprehensive description of the single simulated processes and emission specification is given in section 4.5.

3.3 Model evaluation

RCG has been used in two different horizontal resolutions: one with a grid-spacing of 25 to 30 km covering central Europe, and a second one with a grid spacing of ca. 4 km centred on Berlin.

For secondary inorganic aerosols (SIA = sulphate + nitrate + ammonium), differences between modelled and observed concentrations in the annual averages are below ± 30 % for the majority of HoVerT-sites and always within a factor of two. Results are similar for the nested simulations with 4 km horizontal resolution and for the continental scale simulations with about 25 to 30 km resolution. Apparently, processes within the urban area do not much affect SIA, which is also apparent from the similar concentrations at different sites in the simulations and to a lesser extent in the observations. For sulphate, nested simulations systematically underestimate observations, from -11% to -39%. For nitrate, differences range from -26% to +86%. While for traffic, urban and suburban sites, no systematic tendency appears; simulations show an overestimation for the two rural sites PA and HH. For ammonium, differences range from +8% to +46%, with again a more pronounced overestimation for the rural sites. Thus, especially for the urban sites, there is an

opposite tendency for sulphate and ammonium, i.e. observed aerosols are more acid than simulated ones. On the contrary, the sum of SIA averaged over all sites is very similar in simulations (8.0 µg/m^3) and observations (8.3 µg/m^3).

EC is underestimated at the traffic sites MP174 and BS (by -42 and -25%). This behaviour is expected, because the model with a 4 km horizontal resolution is not designed to resolve local EC emission sources at these sites. On the contrary, at the urban background site MP42 EC is overestimated (by +72%, always with the nested model). For the suburban sites, MP27 and MP77, there is no clear tendency, while for the three rural sites, EC is underestimated (between –45% and –69%). For EC (as for OC), differences between the large scale and the nested simulations can be large: larger values for nested simulations for traffic and urban sites, but smaller values for rural sites.

For OC, a qualitatively similar behaviour as for EC is observed. OC is underestimated at traffic sites (-48 and -58%), overestimated at the urban background site (+29%), and underestimated at town edge and rural sites (between -5% and –69%). This similar behaviour of OC and EC may be explained by the fact that between about 60% (for rural sites) and over 80% (for urban sites) of OC are of primary origin in the simulations and by the fact that primary OC and EC have in common primary emission sources (combustion).

Simulated PM10 is underestimated for most of the HoVerT sites (from -34% to +3%), the strongest underestimation occurring as expected at the traffic site MP174.

For the urban background and town edge sites, there is a slight tendency for underestimation. An underestimation of rural PM10 values is partly expected, because there is still a considerable unknown part in measurements which therefore cannot be modelled.

Model performance depends to a great extent on the quality of the emissions database. This is particularly true for PM10, because the uncertainties in the emissions estimates for particulates are larger than for the gaseous species. These uncertainties stem mainly from the emissions factors and from the differing size distributions of particles emitted from different source groups. There are also particle sources known to exist but difficult to quantify. This includes biogenic sources (pollen, biogenic debris etc.), wind blown dust from agricultural sources, natural surfaces, or from construction work and re-suspension of road dust.

The often unknown spatial representativeness and accuracy of measurements are additional sources of errors that have to be kept in mind during model evaluation. Measurements of PM10 and the chemical constituents of aerosols carried out with various types of monitoring systems can lead to quite different concentration levels (see e.g. Visser et al., 2001).

The modelled seasonal variation for PM10, sulphate, nitrate, ammonium, EC and OC from October 2001 to September 2002 has been analysed in order to evaluate if RCG is able to capture yearly cycles if present. For PM10, a clear seasonal cycle appears neither in observations, nor in simulations, except somewhat lower values in June and July. For sulphate, most of the model underestimation seen in the annual mean is concentrated in the cold season (November to April). For nitrate, much larger levels are observed in the cold season than in the summer season and this seasonal variation is well depicted by the model. The major reason is probably the smaller saturation pressure of NH_4NO_3 for colder winter temperatures. For ammonium, the seasonal variation is similar as for nitrate, but with a smaller amplitude. This seasonal variation is less clearly depicted in the simulations. A similar behaviour in the observed and seasonal variation is also apparent for other HoVerT sites.

For EC at urban sites, the seasonal variation is not very clear, but a minimum appears in both observations and simulations in late spring/ early summer (May to July). Also for rural sites, no clear seasonal variation is observed and simulated. For OC, data are available only between May and September. Both in observations and simulations, OC levels are larger in August and September, which is due (in the simulations) to larger secondary OC values.

In conclusion, when a clear seasonal variation is apparent in observations, as especially for nitrate, it is also depicted by the model. The largest discrepancy in the simulated seasonal variation is the sulphate model underestimation during winter.

The correct representation of day-to-day variability of PM10 and chemical components in RCG is evaluated from inspection of time series and analysis of correlation coefficients between daily values.

The time series of simulated and observed PM10 at the urban background station MP42 show good general agreement. Only few PM10

episodes are missed; however, several ones are overestimated, especially in the cold season. The annual correlation coefficient for this site is 0.63, the values for other HoVerT sites range from 0.46 to 0.73. Correlation coefficients are in general about 0.1 larger during the warm season (taken here between May and September) than during the cold season (between October to April).

For sulphate and ammonium, inspection of time series also shows good agreement. Most of the peaks coincide, but several are also overestimated or missing in simulations. Strong NH_4 peaks (under- and overestimations) are in general linked to similar peaks of either SO_4 or NO_3. Average correlation coefficients of respectively 0.70 and 0.72 for nested simulations (4 km resolution) and 0.72 and 0.74 for the large scale simulations (ca. 30 km resolution) have been calculated. Higher correlation coefficients for the large scale application indicate a regional phenomenon which is captured best with the Europe-wide RCG application. Local scale RCG application brings some more noise in the simulation which lowers the correlation coefficients. For sulphate, correlation coefficients are similar in the warm and cold season; for ammonium on the contrary, they are 0.1 to 0.15 larger in the cold season.

For nitrate, the high annual correlation coefficient is driven by the strong seasonal variation. For the cold season and warm season alone, correlation coefficients are in the range 0.4 to 0.7 and 0.2 to 0.4. This lower correlation than for SO_4 reflects the larger complexity for particulate nitrate formation, in particular the presence of an equilibrium between gaseous and aerosol phase as a function of total nitrate, ammonium and sulphate availability and environmental parameters. Furthermore lower correlation coefficients could also be due to the difficulties in nitrate observations (Schaap et al., 2004).

EC is consistently overestimated at the urban background station, in particular peak values during the cold season. Days with overestimated EC values often correspond to days with overestimated PM10, thus this overestimation probably concerns PM of primary origin in general and may be due either to too large emissions in the urban area or to too small vertical diffusion. As seen before, this overestimation is specific only for the urban background site. The annual average over all correlation coefficients is 0.38 for the 4 x 4 km² resolved model with no particular seasonal tendency.

OC measurements were available at the urban background site only from May on. The correlation (r= 0.5 – 0.6) for the nested version is mainly due

to correlations between simulated secondary OC and observed OC (r = 0.6), while primary OC only poorly correlates with observed OC (r = 0.1 – 0.4). Even if secondary OC only contributes to about 20% to the total simulated one for urban sites and to about 40% for rural sites, its variability is much stronger than that of primary OC (many days with near zero levels, episodic peaks). As noted before, especially the large OC values in the second half of August and first half of September are due to secondary OC formation and largely contribute to the good correlation. This period is also related to enhanced observed and simulated photo-oxidant levels (O_3+NO_2) pointing to an enhanced photochemical activity.

In conclusion, correlation coefficients are satisfying (0.6-0.8) for PM10, SO4, NH_4 and secondary OC, but less good for the other components, NO_3, primary OC and EC.

3.4 Model evaluation: conclusions

For inorganic ions (sulphate, nitrate and ammonium), simulated annual averages agree to observations within ± 30% for more than half of the sites and ions, and always within a factor of two. Averaged over all HoVerT sites, the model shows a tendency for a too large nitrate to sulphate ratio, but the sum of sulphate, nitrate and ammonium agrees within 5% to observations. These results are satisfying; they are in the order of previous comparison exercises. The seasonal variations, when present, are in general well depicted, with the exception of a SO_4^{2-} deficiency in winter/spring time simulations. Correlation coefficients are larger for SO_4^{2-} and NH_4^+ (> 0.7) than in previous model evaluation studies. This is ascribed to a good model representation of the transport patterns into the Berlin Brandenburg, leading to large transport values from the south-east sector, and lower values from the Western sector. It may also reflect progress in the parameterization of the SO_2 to SO_4^{2-} conversion, although model uncertainties are still large, especially in regard of the estimation of cloud water content from relative humidity and the removal processes. For nitrate, correlation is lower, which is ascribed to additional uncertainty in the thermodynamic equilibrium calculation between NH_4NO_3 and its gaseous precursors.

It makes evident a probable overestimation of EC emissions in the Berlin area and a possible underestimation of EC at rural sites. Too fast EC removal and/or a positive bias in observations may be among the reasons for the rural underestimations.

OC shows a similar picture as EC, with a probable urban emission overestimation, and an underestimation at rural sites. Scaling of OC with EC shows that there is no significant bias in the combination of three error sources: OC/EC emission ratios, secondary organic aerosol formation during VOC oxidation, and measurement errors in the OC/EC ratio. Although error compensation cannot be excluded, these results give some credit to the crude description of OC/EC emission ratios in the model and to the correctness of the SORGAM SOA formation scheme. Also the correlation coefficients around 0.6 between SOA and measured OC indicate that the model depicts part of the variability in SOA formation.

The overestimation of urban EC and OC and the rural underestimation together may lead to a "local" bias of the model in the Berlin area, i.e. differences between urban and regional background levels are overestimated by the model. This local bias may have an effect also on PM10 levels: for days with a significant EC overestimation at the urban background site, also PM10 is strongly overestimated. These considerations are important to be taken in mind when using the model for budget studies.

As an overall conclusion, the evaluation study has helped to gain increasing confidence in simulations of chemical constituents of particulate matter with the RCG model. It also has made evident some model (including input data) deficiencies: sulphate underestimation during winter/spring time, nitrate overestimation at rural sites, probable EC, OC emission overestimation in the Berlin area and underestimation at rural sites. Nevertheless, the main processes are reproduced in a satisfactory manner and are worth analysing more deeply in process rates inspection and mass budget considerations.