4   MASS BUDGET ANALYSIS BY MEANS OF THE CHEMICAL TRANSPORT MODEL – METHOD

The model mass budget analysis is a process oriented model inspection. Thus, a process rate analysis can be used in order to perform a detailed investigation how pollutants are accumulated and removed from the air. The mass budget in this work is intended as the sum of changes in time of pollutants mass in a fixed volume of the simulation domain due to physical or chemical processes. That means simulated process rates are summed. The simulation domain has been chosen within the RCG-Berlin-Brandenburg-domain: thus, the resolution is 4 x 4 km in the horizontal and variable in the vertical. The extent of the sub-domain, within the mass budget is calculated, is 12 cells times 12 cells (horizontal) times 5 cells (vertical). It is centred over Berlin urbanised area. RCG is organised in process modules: that means, individual processes (like emission injection, transport, chemistry and deposition) are calculated one after the other and can thus be traced separately. This mass budget study sums the mass change in the 144 cells and in the 5 horizontal layers separately for different time periods ranging from hours to a whole year. The mass budget is therefore the sum of the relative contribution from the individual physical and chemical processes to the concentration field in the analysed volume. There are three different approaches in the summation of mass change explained by the individual processes:

1. gross contribution,
2. net contribution and
3. contribution by transport processes only:
   a. gross contribution analysed for the horizontal inflow and outflow separately and
   b. net contribution analysed for the horizontal flux through the lateral boundaries

Gross contributions differentiate positive (accumulation) parts from negative (loss) parts.

Net contribution indicates the sum of positive and negative parts together giving one contribution to the total mass.

Transported mass via advection and diffusion in the horizontal is considered separately and here, too, the gross (inflow and outflow separately)

and net (sum of inflow and outflow) has been considered. A distinction where the inflow and where the outflow took place has be done in the gross contribution consideration.

4.1 PROCESS ANALYSIS - GENERAL

Process analysis techniques can be used in Eulerian photochemical models such as RCG to obtain information that provides insights into how model predictions are obtained. This is particularly useful in modelling non-linear systems as atmospheric heterogeneous chemistry. Contributions from individual processes are integrated over a time interval, an area or a volume. The integrated process rate analysis can be used to determine the relative contributions of individual physical and chemical processes to the simulated concentration field.

Eulerian air pollution models predict the spatial and temporal distributions of ambient air pollutants solving systems of partial differential equations. These equations define the time-rate of change in species concentrations due to a series of physical and chemical processes such as emissions, chemical reactions, horizontal advection and diffusion and wet and dry deposition. Normally, the output of grid-models is the concentration field which is the cumulative effect of all processes. At the end, information about the impact of individual processes is not available because the contributions of the individual processes are not stored.

Jeffries and Tonnesen (1994) and Jang et al. (1995a, 1995b) started to give more attention to the importance of single processes to the overall concentration field introducing special code in chemistry transport models in order to provide descriptions of how the air pollution predictions are obtained. The same approach has been followed in the CTM RCG. Output has been recoded in order to store the mass change during the defined integration time step and the defined area of interest.

Process analysis is useful in assessing a model's performance. Quantifying the contribution of individual processes to model predictions provide a fundamental explanation of the reasons for a model's predictions and shows the relative importance of each process. This information is also useful in identifying potential sources of error in the model formulation or its inputs.

The inclusion of process analysis in a model application is generally carried out in two steps. First, the model itself has to be changed introducing some additional code to produce supplemental outputs about the contributions of the individual processes. These data are then, in a second step, used with the concentration fields in postprocessing operations to provide quantitative explanations of the factors affecting a model's predictions.

Integrated process rate analysis deals with the effects of all the physical processes and with the net effect of chemistry on model predictions. The distinction in net and gross contribution to the concentrations forecast is in the time interval integration. Chemistry is integrated with a higher time step than all the other simulated physical process, thus only a net budget of the chemical reactions can be given after the defined output time step.

The governing equation for Eulerian models is the species continuity equation. If this equation is applied to a group of chemically reactive species a system of partial differential equations is produced that gives the time-rate of change in species concentration as a function of the rates of change due to various chemical and physical processes. The solution of this partial differential equations system is the ambient species concentrations. The concentration fields reveal only the net effect of all processes.

RCG utilizes the technique of operator splitting. As a result, it is relatively easy to obtain quantitative information about the contribution of individual processes to total concentrations. In operation splitting, solutions to the system of partial differential equations are obtained by separating the continuity equation for each species into several simpler partial differential equations or ordinary differential equations. The simpler equation systems represent the impact of only one process. These equations are then solved separately to arrive at the final concentration.

Consider the simple case of two-dimensional horizontal advection of a single species in the absence of any other processes. Then the governing equation can be expressed as follows:

$$\frac{\partial c}{\partial t} + \frac{\partial (uc)}{\partial x} + \frac{\partial (vc)}{\partial y} = 0,$$

where c is the species concentration, u and v are the x- and y-components of the wind velocity vector, respectively. This is split into two 1- dimensional operators, one for each direction:

$$\frac{\partial c}{\partial t} + \frac{\partial (uc)}{\partial x} = 0$$

$$\frac{\partial c}{\partial t} + \frac{\partial (vc)}{\partial y} = 0$$

These two equations are then solved sequentially, with the solution to the first being used as the initial condition for the second. The solution to the second equation then represents the final solution and gives the net effect of 2-dimensional advection.

The final solution for the example can also be represented as follows:

$$c(t + \Delta t) = c(t) + (\Delta c)_x + (\Delta c)_y$$

where $c(t + \Delta t)$ is the final solution, c(t) is the initial condition for the 2-dimensional problem, and $(\Delta c)_x$ and $(\Delta c)_y$ are the changes in concentration produced by each of the 1-dimensional operators.

$(\Delta c)_x$ and $(\Delta c)_y$ give the impact of each operator in moving from the initial to the final concentration and are equivalent to the results obtained by integrating the process rates individually. Hence the term "integrated process rates" is used to describe them. These process rates are the difference between the final and initial concentrations for each operator. Thus, it is only necessary to save the $(\Delta c)_n$ to obtain process budget analysis capabilities.

The concentration at the end of a time step can be expressed as follows:

$$c(t + \Delta t) = c(t) + \sum_{n=1}^{N} (\Delta c)_n$$

where the model is assumed to have N operators.

It should be noted that most integrated process rates can be either positive or negative since most processes can cause concentrations to either

increase or decrease. Further, it should also be evident that integrated process rates are additive. Thus, the process rates for horizontal advection and vertical advection can be summed to give one integrated process rate that represents the net impact of the two advection processes.

The operators themselves are most often non-linear and therefore, the magnitude of the integrated process rates for most processes would change if the order of the model's operators was altered or even if only one of the operators was changed. Thus, the additive property for integrated process rates holds only for a particular application of the model. Nevertheless, the mutual dependence of the individual processes and the relative strength of the process's contribution to the final simulated concentration's field hold for a wider range of applications. That is, the model analysis via process analysis shows how the model simulates the individual species concentrations.

4.2   PROCESS RATE ANALYSIS – RCG SPECIFIC

Figure 13 gives a schematic overview over the mass budget method applied in this work. Emissions (P_E) in the analysed volume and the turbulent transport into the region ($P_{ADV}+P_{TRB}$) from near sources as well as from distant areas through lateral as well as upper boundaries contribute to a local increase of the analysed species. A reduction of the species' mass, at the other hand, is due to deposition (L_D) in the region and to advective and turbulent transport ($L_{ADV}+L_{TRB}$) form the control volume toward the surrounding areas. Chemical processes contribute to a local production (P_{CH}) as well as to a local loss (L_{CH}) of the species mass.
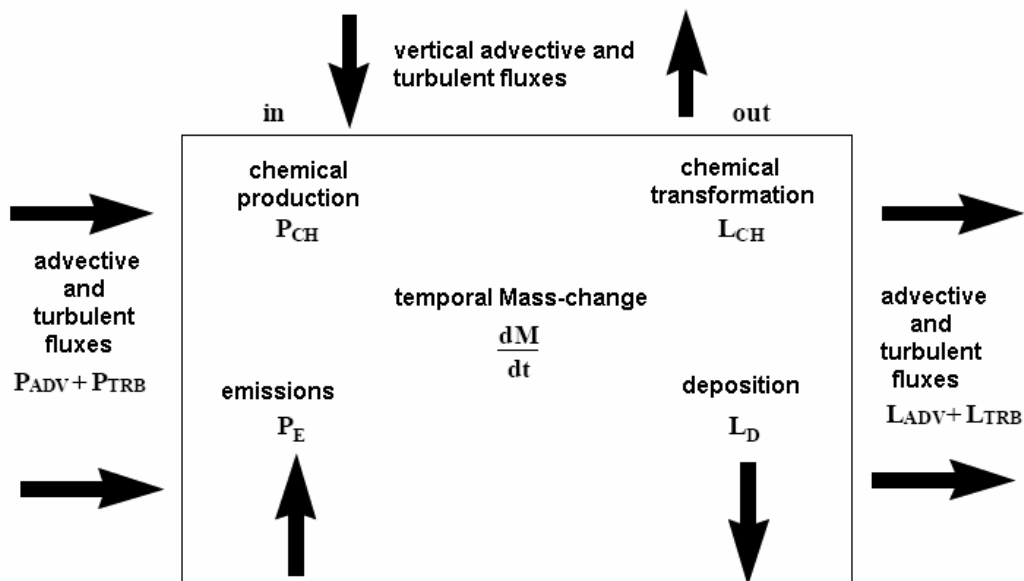
$$\frac{dM}{dt} = (P_{ADV} + P_{TRB} + P_E + P_{CH}) - (L_{ADV} + L_{TRB} + L_D + L_{CH})$$

Figure 13 Schematic Mass Budget Analysis Method in a predefined control volume.

RCG is a multi-scale Eulerian 3D grid transport and chemistry model which simulates mean hourly concentrations (C_i) of atmospheric pollutants solving the following differential equation for every single simulated species:

$$\frac{\partial \overline{C}_i}{\partial t} = -\nabla\left(\vec{u}\,\overline{C}_i\right) + \nabla\left(\hat{k}\nabla\overline{C}_i\right) + \overline{P}_i - \overline{L}_i + \overline{Q}_i$$

The first term on the left hand side indicates the temporal change of the concentration of the i-th species, the first and the second terms on the right hand side indicate advective and turbulent transports including deposition, respectively, P_i and L_i indicate chemical production and loss, respectively, and Q_i indicates direct emission.

The lower boundary condition is given by the deposition flux equation:

$$F = v_{D,i}\overline{C}_{r,i} = \left(\hat{k}\nabla\overline{C}_i\right)\vec{n}_h$$

where $\vec{n}_h$ is the unit vector perpendicular to the ground, $v_{D,i}$ is the dry deposition velocity of the i-th species and $\overline{C}_{r,i}$ is the mean concentration on the reference height r.

The modelling system is configured to include detailed treatment of horizontal and vertical advection, turbulent diffusion based on K-theory (Yamartino, 2003), gas-phase chemical transformations using a modified version of the CBM-IV chemical mechanism (Gery et al., 1989, Stern, 2003), bulk solid-phase aerosol building mechanism for inorganic and organic aerosols (Nenes et al., 1998, Schell et al., 2001), anthropogenic and natural emissions comprising wind blown dust, dry and wet depositions, and attenuation of photolysis rates due to the presence of clouds.

Every single physical or chemical process is calculated explicitly and thus mass budget analysis can be done considering the following relationship and using the Gauss' theorem:

$$\frac{\partial \overline{M}}{\partial t} = \frac{\partial}{\partial t}\int \overline{C}_i dV = \oint_F \left(\vec{u}\,\overline{C}_i\right)d\vec{f} + \oint_F \left(\hat{k}\nabla\overline{C}_i\right)df + \int_V \left(\overline{P}_i - \overline{L}_i\right)dV + \int_V \overline{Q}dV$$

The first and second term on the right hand side of the equation describe the advective and the turbulent flux through the integration volume including deposition processes, whereas the third term depicts the net contribution of the chemical reactions, while the forth term is the contribution of emissions to the temporal change of the total mass M.

The total mass change in the chosen volume is given by the sum of the following masses produced in the individual simulated processes:

- Advective and turbulent fluxes through the lateral and top boundaries,
- Chemical production and transformation in the volume,
- Direct emissions and
- Wet and dry deposition.

Similarly, the net flux through the volume's surfaces is equal to the non-transport specific mass accumulation and removal processes inside the chosen volume.

The control volume has been chosen within the nested 4 km horizontal resolution RCG application comprising Berlin urbanised area. The domain extensions are about 42 km (West-East-Direction) x 36 km (South-North-Direction) around Berlin area (13.125°E – 13.75°E, 52.34375°N – 52.65625°N) on a horizontal plane and 3000 m height. The whole volume is thus approx. $4.4*10^{12}$ m^3.

Since our primary objective was to understand the contemporarily mutual importance of the single building and removing aerosol processes, we used the modularity of RCG in order to consider the process contributions to the total pollutant's concentration. In RCG each of the physical and chemical processes is cast into modules following the operator-time-splitting approach. Each process module operates on a common concentration field, making it possible to analyse budgets of modelled species by examining the contribution from each modelled process. On an hourly basis, contributions to the total concentration fields of the processes have been taken into account considering the mass difference in the control volume at the end and at the beginning of every hour. We summarised the results on different temporal intervals, considering the yearly mass changes and seasonal differences. Equally, mass fluxes through the lateral boundaries of the control volume around Berlin have been memorized on an hourly basis in order to be able to give indications on preferred directions of pollutants transport. We distinguished primary coarse and primary fine particles considering them non participant at any further physical or chemical transformation, originating mainly from direct injection into the atmosphere by anthropogenic emissions and by dust dispersion due to wind. Primary elemental carbon and primary organic carbon constitute separate classes, not coinciding with the class of "primary fine particles". This distinction has been made in order to evaluate separately the contribution of primary elemental and organic carbon to the overall aerosol mass budget in the

region of Berlin. Secondary inorganic and organic aerosol components undergo chemical transformation. The class of "Secondary inorganic aerosols" comprises sulphate-, nitrate-, ammonium-, chloride- and sodium-ions, while secondary organic aerosols comprise build-up species containing organic carbons.

4.3 DOMAIN SELECTION

We simulated the PM10 concentrations on two different scales, one covering approximately political Europe (EU25) from -10°W to 30°E, and 35°N to 66°N, with a resolution of 0.25° in latitude and 0.5° in longitude and the second covering the Berlin Brandenburg area (12°E - 15°E, 53.5°N – 55.5°N, i.e. approx. 300 km x 300 km) with a 4 km horizontal resolution (Figure 14). Vertical levels are dynamic, i.e. their position follows the planetary boundary layer height, except the terrain following surface layer which extents up to 20 m height and the top layer height which is 3000 m.
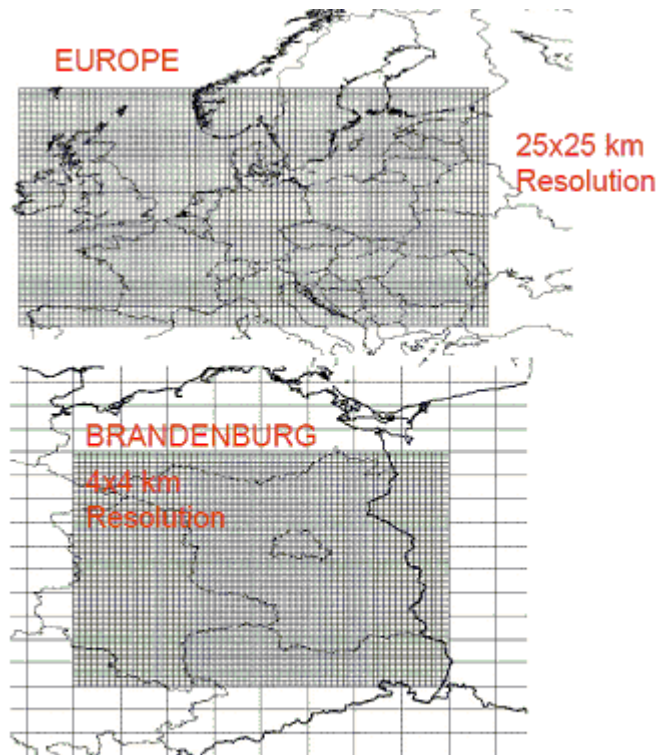
Figure 14 Simulation domains within the HoVerT-campaign-programme. The 4x4 km resolved domain is nested in the Europe-domain. Boundary conditions of the nested domain are provided by the Europe-domain.

The lateral boundary conditions of the nested 4x4 km resolved RCG application derive from the large scale run.

Within the nested domain a sub-region (Figure 15) has been chosen in order to obtain a representative area to calculate mass changes concerning a highly populated area and to establish a source receptor relationship between locally produced and remotely risen and advectively transported toward the city area. The domain extensions are about 42 km (West-East-Direction) x 36 km (South-North-Direction) around Berlin area (13.125°E – 13.75°E, 52.34375°N – 52.65625°N) on a horizontal plane and 3000 m height. The whole volume is thus approx. $4.4*10^{12}$ m^3. One of the most prominent characteristics of this volume is the net difference between highly urbanised inner area and the mostly rural surrounding landscape.
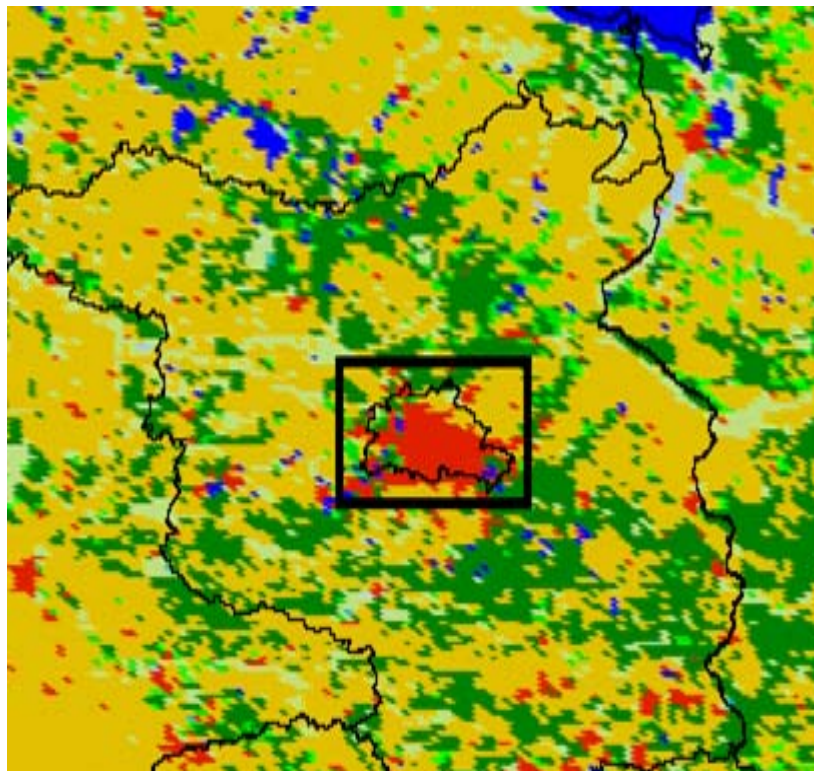
Figure 15 Land-use classes in the Berlin-Brandenburg-Region with the black rectangle indicating the control volume around Berlin. Red indicates urbanisation, green forests, yellow agriculture and blue water.

4.4 ORGANISATION OF SIMULATIONS

On an hourly basis, contributions to the total concentration fields of the processes have been taken into account considering the mass difference in the control volume at the end and at the beginning of every hour. We summarised the results on different temporal intervals, considering the yearly mass changes and seasonal differences.

On the other hand, mass fluxes through the lateral boundaries of the control volume around Berlin have been stored on an hourly basis in order to be able to give indications on preferred directions of pollutants transport.

4.5 PROCESS DESCRIPTION

4.5.1 Meteorology

The meteorological fields – wind, temperature, moisture, and density as 3D variables, Monin-Obukhov-Length, friction velocity, mixing layer height, cloud cover, precipitation and surface temperature and winds - are computed following an optimum interpolation scheme between observations on the large scale as well as on the small scale around Berlin (Kerschbaumer and Reimer, 2003). Special attention has been paid to simulate the planetary boundary layer using a bulk approach and the exchanges between the mixing layer and the above free troposphere. The meteorological 3D fields are computed on isentropic surfaces to allow a better description of large scale phenomena also on a local domain (Reimer and Scherer, 1992). The vertical extend of the transport model is 3000 m above ground in a surface following co-ordinate system with its layer depths depending on the mixing layer height. This model set-up makes it possible to analyse the height dependent budget contributions and the different importance of single processes in different heights.

Routine measurements from the WMO network (SYNOP) and additional local meteorological observations are interpolated on the surface and on isentropic levels. Time resolution is 6 hours from the data from the SYNOP-network and 3 hours from the additional information obtained mainly by local

measurement networks. Upper air measurements are transmitted every 12 hours. Thus, this inhomogeneous temporal resolution has also to be interpolated on a defined one hour time scale.

The meteorological analysis is done by an optimum interpolation approach, starting from a first-guess field, which is obtained by first order interpolation or likewise by global numerical weather prediction outputs. Starting from observations, a Cressman-interpolation (Cressman, 1959) is applied using a quadratic weighing factoring. Applying more than once the Cressman interpolation, undesired wave lengths are filtered out giving an appropriate first guess field for the following meteorological variables:

- pressure,
- humidity,
- wind-components,
- stability,
- Montgomery-potential and
- wind-shear

on 24 isentropic levels. The further statistical approach is based on auto-correlation functions and on a spatial synoptic error analysis. All observations are treated in a homogeneous way, except land-sea-representative measurements. These are differentiated by anisotropic weighing. The vertical resolution in the lower troposphere is 1 Kelvin. The representation on isentropic surfaces allows a better description of synoptic thermal structures like inversion zones and local stability regions. Vertical homogeneity is forced by mass-conservative constrains

The meteorological fields represented on the coarse grid serve as first-guess-fields for any further increase of the grid resolution. The vertical isentropic representation is interpolated on terrain-following height coordinates.

The representation of the planetary boundary layer (PBL) is one of the most important features in the meteorological driver for the chemistry-transport model. The approach proposed by van Ulden and Holtslag (1985) and Hanna and Paine (1989) is applied. The PBL Model over land is based on predictive equations for wind components, potential temperature and water vapour mixing ratio. It solves the surface energy budget as well as the surface radiation budget estimating the surface fluxes from routine weather data. Incoming solar radiation, reflected solar radiation from the surface, incoming longwave

radiation from the atmosphere, outgoing longwave radiation from the surface (Holtslag, 1987) as well as sensible heat flux, latent heat flux and soil heat flux are taken into account in the budget approach. The PBL Model over water is based on a profile method.

The overland boundary layer is calculated solving

$$Q_* + Q_f = Q_H + Q_e + Q_g$$

where Q_x is the net radiation[W/m²], Q_f is the anthropogenic heat flux [W/m²], Q_H is the sensible heat flux [W/m²], Q_e is the latent heat flux [W/m²] and Q_g is the ground heat flux [W/m²]. Seasonal land use dependent

parameterisations are given for the Bowen ratio $B = \dfrac{Q_H}{Q_e}$ and range from 0.1

over water to >1.0 over deserts. The soil heat flux Q_g is parameterised during

daytime with the net radiation $Q_g = c_g Q_*$ where c_g depends on the surface

properties and ranges from 0.05-0.25 for rural areas to 0.25-0.30 for urban areas (Oke, 1982). Larger values over cities reflect higher thermal conductivity and heat capacity of buildings. The anthropogenic heat flux is a function of population density. It is small compared to the other flux terms and will be neglected.

At the other side the net radiation Q_x is the residual of incoming and outgoing radiation and can be expressed as:

$$Q_* = Q_{sw}(1 - A) + Q_{lw-d} - Q_{lw-u}$$

where Q_{sw} indicates direct solar and diffuse short wave radiation [W/m²], A is the surface albedo, Q_{lw-d} and Q_{lw-u} represent incoming long-wave and outgoing, emitted by the surface long-wave radiation [W/m²], respectively.

Holtslag and van Ulden (1983) estimated the net radiation by air temperature, cloud cover and solar elevation angle during the day. The daytime sensible heat is a function of the parameterised Bowen ratio, the net radiation and surface properties. The Monin-Obukhov length and the surface friction velocities are computed iteratively departing from the sensible heat flux. A

detailed description is given in Holtslag (1987). Stable conditions and night time u_* is estimated following Venkatram (1980) and depend on wind speed, drag coefficient and land use type. The heat flux is related to u_* and θ_* by

$$Q_H = -\rho c_p u_* \vartheta_*$$

and Monin-Obukhov can be computed in the same manner as during daytime

$$L = \frac{-\rho c_p T u_*^3}{kgQ_H}$$

where T is the temperature, c_p is the specific heat of air, ρ is the air density and g is the acceleration due to gravity.

The daytime convective mixing height over land is computed iteratively starting from the hourly variation in the surface heat flux and the vertical temperature profile. The neutral mechanical boundary layer height is a function of the friction velocity and the Brunt-Väisälä frequency (Venkatram, 1980) and in the stable boundary layer, mechanical turbulence production determines the vertical extent of dispersion and is again a function of the friction velocity (Venkatram, 1980).

Parameterisations are different over land and sea. Over water, the aerodynamic and thermal properties of the surface determine a much smaller sensible heat flux driven by solar radiation. Air – sea temperature differences and overwater wind speeds allow a good description of the marine boundary layer. The neutral momentum drag coefficient is expressed in terms of the 10 m wind (Garratt, 1977) and the u_* is determined as a function of the wind speed and the drag coefficient. Monin-Obukhov length is calculated using the virtual potential temperature which takes into account the latent heat (Hanna et al., 1985). The overwater mixing height is computed as a function of the friction velocity, again.

All mixing heights are limited by the height of the base of the clouds.

4.5.2 Advection – Diffusion

Within the Aerosol-Chemistry-Transport model, the horizontal advection is simulated using a mass conserving, monotonic in mixing ratios, non diffusive transport algorithm based on Walcek (2000) while the vertical transport is simulated using a Crank-Nicolson-Method considering the vertical velocity and diffusion. (Yamartino, 2003). The vertical transport and diffusion scheme accounts for atmospheric density variations in space and time, and for all vertical flux components when employing either dynamic or fixed layers.

The horizontal advection scheme eliminates errors from velocity-shear-induced operator-splitting transport and ensures correct transport fluxes, mass conservation, and that a constant mixing ratio field remains constant.

The RCG model horizontal diffusion methodology is explicit and forward-in-time, which is appropriate given the small size of the horizontal non-dimensional diffusivities on spatial scales of a few km or more. The concentration gradients estimated for use in RCG model's diffusion module are first-order accurate in space, as they simply involve the differences of grid-point concentrations. In order to account for diffusion due to distortion or stress in the horizontal wind field it has been emphasised the importance of capturing as much as possible of the wind field shear in the advective portion of the transport flux vector (Hanna, 1994)

4.5.3 Emissions

The RCG model requires annual emissions of VOC, NOx, CO, SO_2, CH_4, NH_3, PM10, and PM2.5, split into point and gridded area sources. Mass-based, source group dependent VOC profiles are used to break down the total VOC into the different species classes of the chemical mechanisms. Hourly emissions are derived during the model run using sector-dependent, month, day-of-week and hourly emissions factors.

European-wide annual anthropogenic emission averages for 2000 for CO, NOx, VOC, Sulphur Oxides (SOx), NH3 and PM10 on a 50 km x 50 km grid are taken from the EMEP data base (Vestreng, 2003) and were transformed into the geographical RCG-grid. For the nested region Berlin/Brandenburg, highly resolved emissions data were obtained from regional administrations

(Table 4). To ensure consistency between the urban-scale and the continental-scale emissions, the Berlin/Brandenburg data were scaled sector-by-sector to the level of the EMEP data.

PM10 emissions were split into a PM2.5 and a coarse PM (PM10 – PM2.5) part, the PM2.5 part was further split into mineral dust, EC and primary OC. EC fractions in PM2.5 emissions for different sectors given in Table 5 were taken from (Builtjes, 2003). For primary OC, no such factors exist to our knowledge for Europe. Thus the following crude method was applied to estimate these emissions in a preliminary way: An average primary OC to EC emission ratio for all sectors of about two was set (Seinfeld and Pandis, 1998) except if the sum of the two factors would have been larger than unity. In this case ($f_{EC} > 0.33$), f_{OC} was set as: $f_{OC} = 1 - f_{EC}$. This allocation is crude as it relates the spatial distribution of primary OC to that of PM2.5 without taking into account specific patterns of OC emissions. Nevertheless, it should be able to give rough estimations for primary OC emissions at least for urban regions, were traffic related sources are dominant (Table 5).

Table 4 Berlin Emission totals [tons/year] (Stern et al., 2004)

	CO	NH3	NMVOC	NOX	SO2	PM25	PMCO	PM10
Power generation	20080	0	2760	14566	20937	1268	2549	3817
Resid., comm. other comb.	3441	0	33581	670	419	1682	952	2634
Industrial combustion	8984	0	128	3778	13	45	66	111
Industrial processes	0	0	0	0	0	0	0	0
Extr. distr. fossil fuels	0	0	0	0	0	0	0	0
Solvent use	0	0	0	0	0	0	0	0
Road transport gasoline	61912	0	8899	12602	383	1514	374	1888
Road transport diesel	0	0	0	0	0	0	0	0
Road transport evap.	0	0	0	0	0	0	0	0
Other mobile sources	4988	0	1420	5085	113	1350	189	1539
Waste treatment & disposal	0	0	0	0	0	0	0	0
Agriculture	0	310	0	0	0	0	0	0
sum	99405	310	46789	36702	21864	5859	4130	9989

Table 5 EC emission ratios of PM2.5 emissions for different sectors from (Builtjes, 2003)

Sector	EC fraction of PM2.5-Emissions (f_{EC})
Power generation	0.12
Residential, commercial and other combustion	0.2
Industrial combustion	0.13
Industrial processes	0
Extraction, distribution fossil fuels	0.79
Road transport	0.47
Other mobile sources	0.49
Waste treatment and disposal	0.004

Biogenic VOC-emissions are derived using emissions factors for isoprene and OVOC (Other VOCs) as described in Simpson et al. (1995). These biogenic calculations are based on the land-use data for deciduous, coniferous, mixed forests and crops. Light intensity and temperature dependencies are also considered. Soil NO emissions are calculated as a function of fertilizer input and temperature following Simpson et al. (1999).

4.5.4 Chemistry

The lumped chemistry scheme CBM-4 (Gery et al., 1989), including Carter's 1-Product Isoprene scheme (Carter, 1996), was used for simulations. Homogeneous and heterogeneous conversion of NO_2 to HNO_3 is added. In addition to gaseous phase, also simple aqueous phase conversion of SO_2 to H_2SO_4 by H_2O_2 and ozone has been incorporated. Equilibrium concentrations for SO_2, H_2O_2 and ozone are calculated using Henry constants from Seinfeld and Pandis (1998) and assuming progressive cloud cover for relative humidity above 80%. Effective rate constants for the gas phase reactions $SO_2 + H_2O_2$ and $SO_2 + O_3$ have been calculated for an average pH of 5 using acid / base equilibrium and kinetic data from Seinfeld and Pandis (1998). The pH of 5 is close to annual averages in rain samples. Due to uncertainties in cloud liquid water content, pH, and gas phase H_2O_2 levels, aqueous phase SO_2 to SO_4 conversion rates are relatively uncertain, but this is a common feature for air quality models.

For numerical solution of the chemistry differential equations system, the quasi-steady-state-algorithm (QSSA) chemistry solver with a variable time step control is used.

Aerosol treatment

In RCG, different chemical fractions are considered to contribute to PM10, i.e. particulate matter with a dynamical diameter up to 10 μm:

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

For efficiency reasons, a bulk approach is used, i.e. the major PM constituents are treated as a single model species with a given log-normal size distribution. For the majority of species, its geometrical average is set to 0.48 μm corresponding to the accumulation mode. For PM_{coarse} (mineral coarse particles between 2.5 and 10 μm in diameter) and for sodium and chloride (sea salt) the maximum diameter is set to 4-5 μm, corresponding to the coarse mode.

The equilibrium between solid, aqueous phase and gas phase concentrations for inorganic ions as a function of temperature and humidity is calculated on-line with the ISORROPIA thermodynamic module, which is optimised for urban and regional pollution conditions (Nenes et al., 1999). Production of secondary organic aerosol is treated with the SORGAM module (Schell et al., 2001) which calculates the partitioning of semi-volatile organic compounds produced during VOC oxidation between the gas and the aerosol phase. This module was adapted to be used with CBM-4. Terpenes (α-pinene and limonene) were added to the chemical scheme, but only for the purpose of SOA formation.

The aerosol scheme also includes resuspension of mineral aerosol as a function of friction velocity and the nature of soil; both the direct entrainment of small particles (Loosmore and Hunt, 2000, Gillette and Passi, 1988) and saltation, i.e. the indirect entrainment due to large particles which fall back to the soil and entrain smaller particles (Claiborn et al., 1998) is taken into account. The sea-salt aerosol emissions (Na+, Cl-) are parameterized according to Gong et al. (1997) as a function of size and wind speed

4.5.5 Deposition

Dry deposition for gaseous species and particles is calculated using the resistance analogy. Turbulent or viscous sub-layer resistance are calculated following Prado (1993) from surface roughness, Monin-Obukhov length, friction velocity, molecular diffusivity. Surface resistance is computed following Erisman and van Pul (1994) for different surfaces (leaves, soils etc) taking into account species dependent (Henry constant, oxidation power) micro-meteorological (leave temperature, radiation) and land-use (agricultural land, grass land, forest) information. For particles, surface resistance is zero. The atmospheric resistances are large for particles in the accumulation mode (0.1 μm < Ø < 1 μm), because neither Brownian motion, nor sedimentation are effective pathways; they are calculated for the different species, divided in particles smaller and bigger than 2.5 μm. Wet deposition due to in and below cloud scavenging is parameterized as a function of the species dependent Henry constant and the precipitation rate.