5 SIMULATED MASS BUDGETS - RESULTS

We considered accumulation and removal of aerosols in a defined volume comprising Berlin city. We distinguished primary coarse and primary fine particles considering them non participant at any further physical or chemical transformation, released 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. The class of “Organic Matter” is made up of the sum of “Secondary organic aerosols” and “Primary Organic Carbon”.

We distinguished the net and the gross contribution to the mass budget in Berlin. Net contribution indicates the sum of positive and negative parts giving the total mass budget, while gross contributions differentiate positive (accumulation) parts from negative (loss) parts. Percentages sum up to 100% distinctively for accumulating and removing processes.

Case studies for one day during winter and one day during summer will explain the mass budget method in detail. The episode consideration takes into account the whole control volume for one day. The temporal integration step was the RCG-output time-step, i.e. one hour.

Aggregation has been done on different temporal and spatial scales as well as for lumped species like secondary inorganic and organic aerosol components.

Minimal temporal interval has been one hour. Based on that time step and on the maximum net budget consideration, integration over seasons and over the whole year has been performed.

Minimal spatial integration step was the defined surface over Berlin and the vertical extent of the RCG Model. The first layer is fixed and is 20 m high, thus the minimal spatial volume was 36 km x 42 km x 20 m. The maximum spatial integration volume was the whole control box over Berlin with an extension $4.4*10^{12}$ m^3.

The mass flux through the lateral boundaries has been considered individually by inflow and outflow directions over the 4 borders taking into account also the height of the flux. Integration has been performed summing over the vertical levels and over inflow and outflow directions.

5.1 CASE STUDIES

A method has been developed by which detailed process analysis can be performed. Two short periods of one day in winter (15th January, 2002) and one day in summer (28th July, 2002) have been investigated profoundly in order to become confident with the mass budget analysis and to explain in detail all relevant processes contributing to PM10 concentrations

Observations on those days at the urban background station MP42 show during the winter day higher PM10 concentrations than at the neighbouring days. The winter day is characterised by high contributions of secondary inorganic components to the total daily mean aerosol concentration (52%). The primary elemental carbon contribution at the urban background station is also slightly higher than during the days before (ca. 10% EC). Measured organic matter is not showing any extraordinary behaviour (5% of total PM10). The non analysed part at that day is 33% of the total PM10 mass concentration. The meteorological situation showed a cold clear winter day with temperatures not exceeding 0° Celsius (-6°C to -1°C) with light winds (3 – 5 m/s) from south-east during the night veering to south during noon going back to south-eastern directions during the evening again. The mixing heights did not reach more then 900 metres at 3:00 pm and there where inversion layers throughout the whole day stronger during the night, but also present during the day hours.

The summer day was characterised by high temperatures (16°C at 3:00 a.m. and 29°C at 3:00 p.m.) with no clouds during the whole day. Wind speeds ranged from 2 to 4 m/s and came from south-east to east. Mixing heights ranged from 70 m over Berlin during the night and 2500 m at 3:00 p.m. There were very light inversions during the night hours between ground and 300 m.

The observed PM10 concentrations were the highest measured during summer 2002 at MP42 (June – August). The daily mean concentration was 52 µg/m³ with 18% sulphate ions, 15% organic matter, 8% elemental carbon, 7% ammonium ions and only 1% nitrate ions. The non analysed part was 51%.

Figure 16 to Figure 28 show the hourly mass changes inside the control volume expressed in kg/hour for all relevant processes, i.e. processes contributing zero mass changes have been left out; also, some processes have been grouped into lumped processes, like “TOPGAIN” stands for inflow (positive) and outflow (negative) due to vertical advection and vertical diffusion through the upper boundary layer. As both days were without rainfall, deposition comprises only dry deposition and is therefore rather small for all considered species. Every plotted box indicates a mass change at the specified hour of the day.

5.1.1 Winter

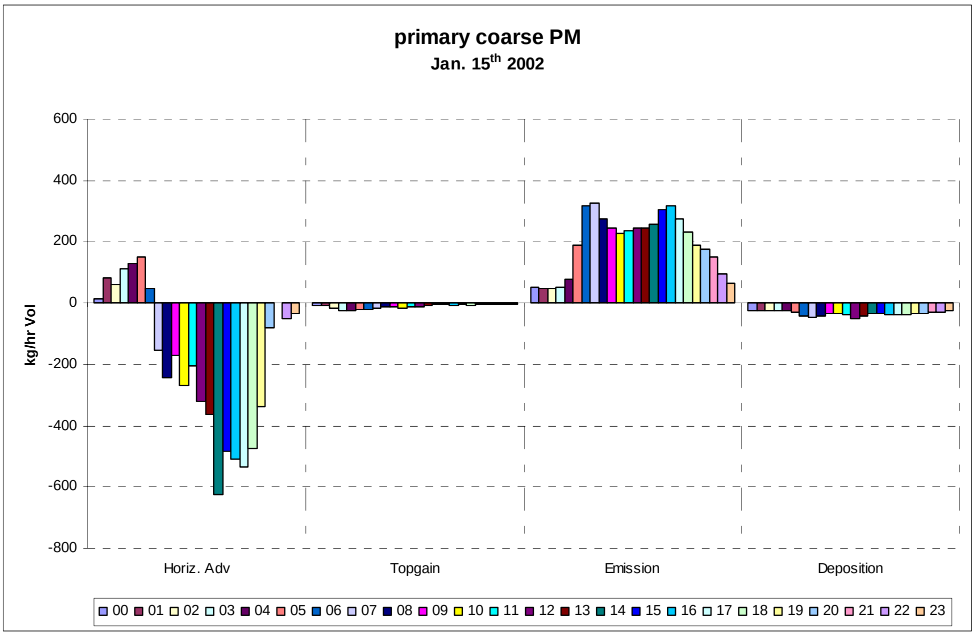

Figure 16 Hourly mass change rate due to net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), Emission and deposition of primary coarse mode aerosols during January, 15th 2002

Primary coarse mode particles as also fine mode primary aerosols show in the winter case a distinct traffic related emission pattern (Figure 16). Highest injections into the air over Berlin are registered during the morning and late afternoon hours. Until 6:00 a.m. of the 15th January 2002, there are also net positive contributions of primary coarse mode particles coming through the lateral boundaries.

This situation changes afterwards, when wind transports more coarse mode material from the city toward the Brandenburg region. It has to be stressed that horizontal advection is considered in a net way, that is the contribution of advection to the hourly mass change in the control volume is summed over all inflow and outflow vertical borders. Nevertheless, the fact that advective processes lead to a net removal of primary coarse mode aerosols is only explainable in case the inflowing mass will be enhanced by local material due to emissions. Dry deposition is the only exclusively local removal process and is rather small compared to the emissions. Again, the winter day was without rain. Fine mode primary particles (not shown) show even much less mass removal due to deposition. The loss into the "free atmosphere" through the upper boundary is small, but in the same order of magnitude of the deposition of coarse mode particles during night and early morning.

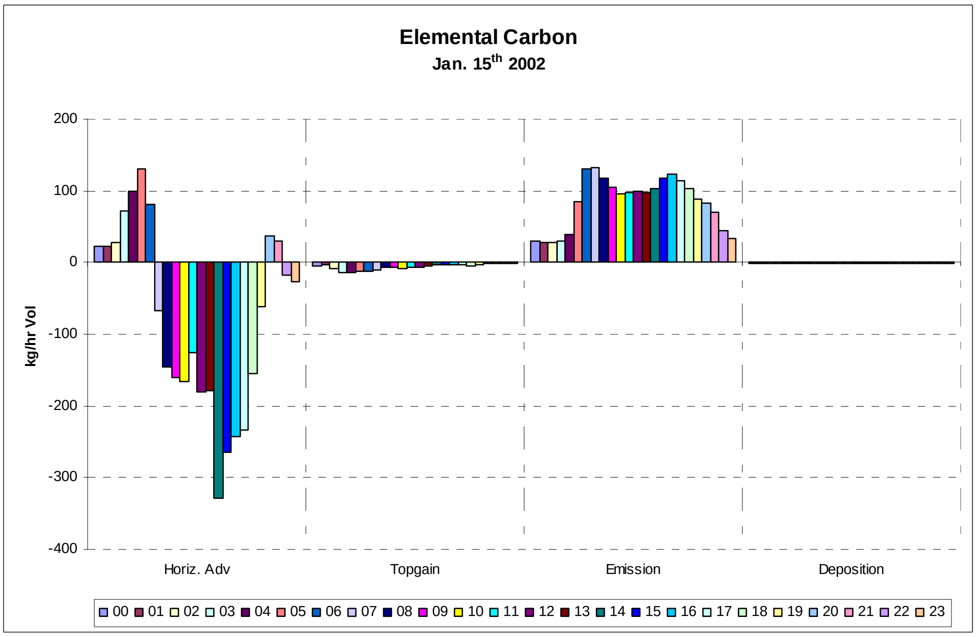

Figure 17 Hourly mass change rate due to net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), Emission and deposition of elemental carbons during January, 15th 2002

Elemental carbons (Figure 17) show again the traffic related emission daily cycle during January, 15th. The accumulation until 6:00 a.m. is enhanced by horizontal advective processes and is balanced due to that process afterwards. During early afternoon hours, the mass budget at that specific day is even negative for the city of Berlin; that means, during that day Berlin exports more elemental carbon than it imports. Again, the local emissions are transported outside because of the wind. Primary organic carbon is treated like EC in RCG and thus shows the same diurnal behaviour.

Sulphate ions (Figure 18) are built form gaseous precursors. There is a net contribution to this particular day budget from chemistry during the central day hours. There is also a net accumulation due to direct emissions of sulphate in Berlin during all winter day hours and there is net contribution to the accumulation of sulphate ions during the early morning and late night hours due to horizontal advection. These contributions due to windborne processes are by far more intensive than the contributions due to direct emissions and due to local chemistry at that winter day. The contribution to the loss of sulphate ions is again because of the wind.

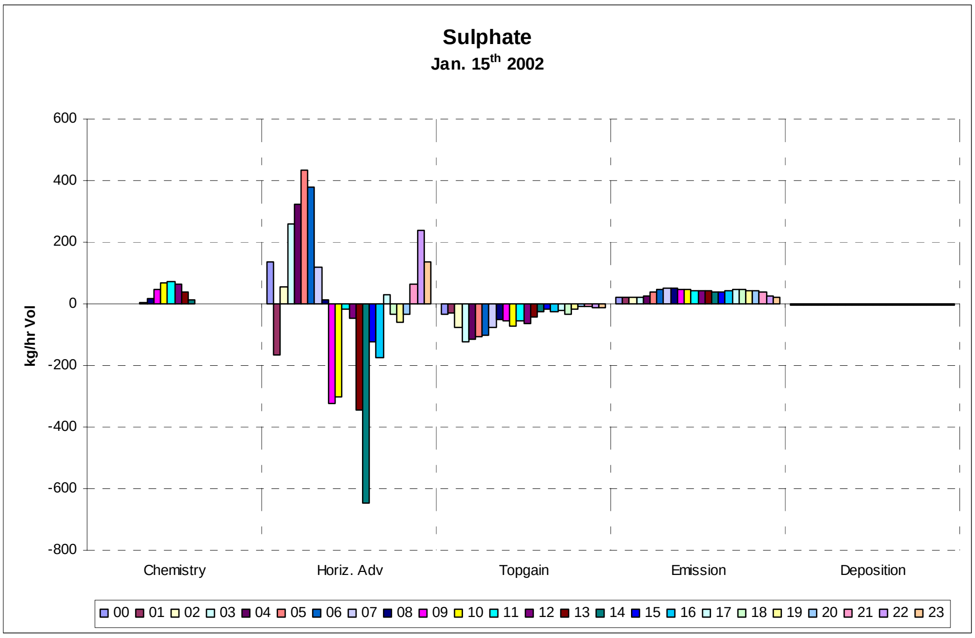

Figure 18 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), Emission and deposition of secondary sulphate aerosols during January, 15th 2002

During the central hours of the winter day high amounts of sulphate particles are removed from the control volume. Very interestingly, also considerable amounts of sulphate is lost into the free atmosphere (above 3000 m) through the upper boundary. This loss is more intensive during morning hours. Integrated over the whole day, the loss through the upper boundary is the same order of magnitude as the accumulation due to direct emissions. This behaviour is explainable considering the fact that SO_4 shows almost no vertical gradient compared to the strong vertical gradient of EC or OC.

Figure 19 shows the hourly nitrate mass changes during the winter day. The most striking feature is the order of magnitude of accumulation due to chemistry which at 10:00 a.m. reaches more than 1000 kg/hour in the whole volume. Compared to the sulphate chemical production this is almost 2 orders of magnitudes higher at that clear winter day.

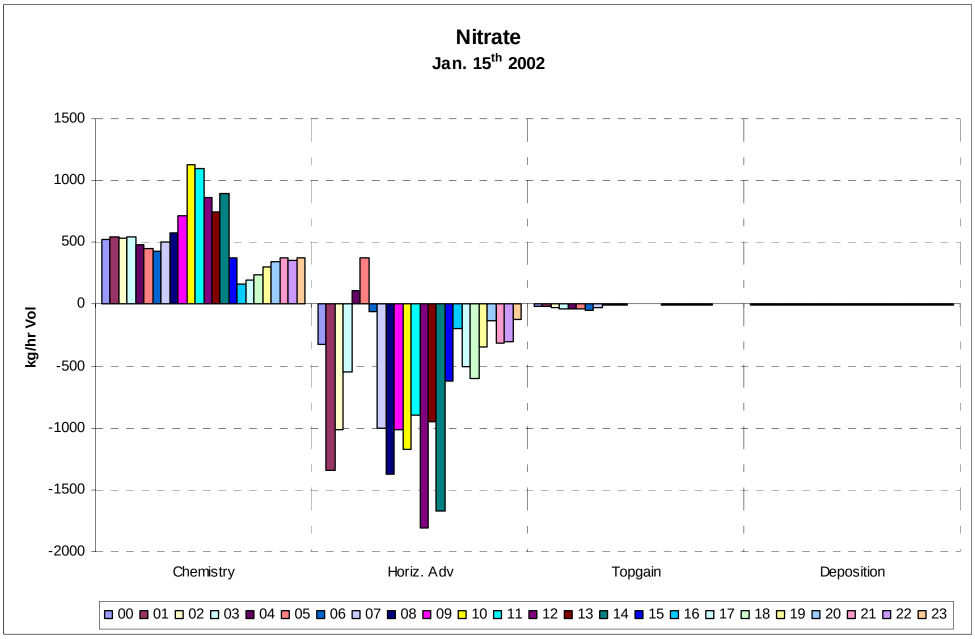

Figure 19 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), and deposition of secondary nitrate aerosols during January, 15th 2002

Also compared to the ammonium production during the winter day (Figure 21) the nitrate chemical production is double. There are some losses through the upper boundary in the nitrate as well as in the ammonium budget, the counter-balance for both inorganic ions is horizontal advection, anyway.

Looking with more detail into the mass budget of nitrate in the city of Berlin we analysed the nitrogen containing gaseous precursors. Berlin metropolitan area emits high amounts of NO due to the heavy traffic in the city. This gaseous species reaches an emission strength of about 3000 kg/hour in the whole volume at 10:00 a.m. NO is rapidly oxidised by O3 into NO_2. Horizontal export due to advection is for both species lower than local emission and chemical production, respectively. HNO_3 (Figure 20) was produced in Berlin at that winter day due to gas-phase chemistry with a maximum strength of ca. 1000 kg/hour in the whole control volume at 11:00 a.m. Aerosol conversion was more intensive during daylight and less effective during night. Again, horizontal advection of HNO_3 is high, but not enough to export all HNO_3. The low temperatures and the availability of ammonium ions favoured the stability of the aerosol phase nitrate and led to the high amount of local production and thus accumulation.

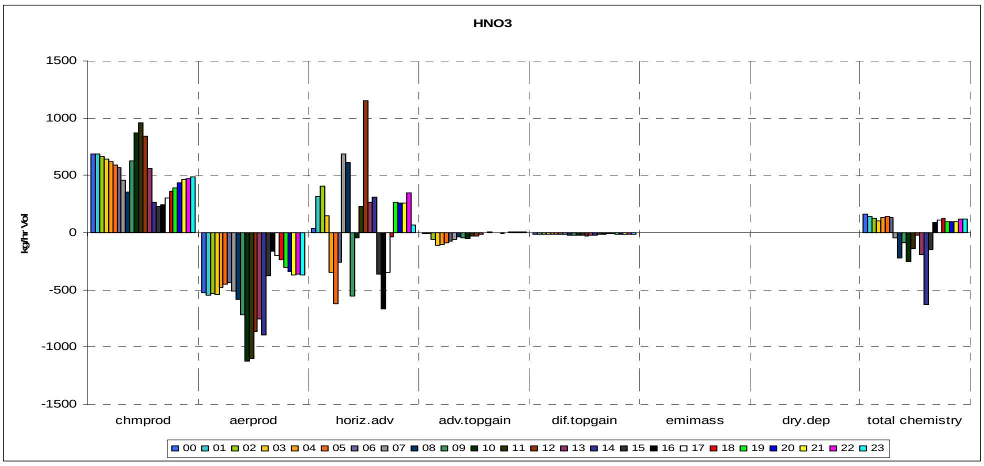

Figure 20 Hourly mass change rates for HNO_3: gas phase chemistry (chemprod), aerosol chemistry (aerprod), horizontal advection (horiz.adv), advection through the upper boundary (adv.topgain), diffusion through upper boundary (diff.topgain), emission (emimass), dry deposition (dry.dep) and net total chemistry (total.chemistry), January, 15th 2002

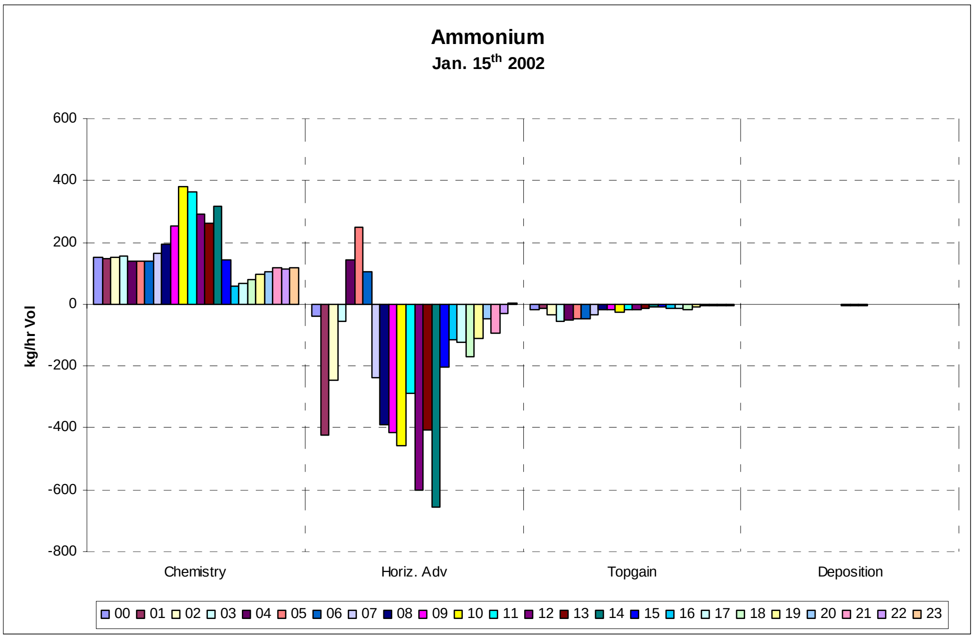

Figure 21 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), and deposition of secondary ammonium aerosols during January, 15th 2002

Ammonium ions (Figure 21) were built more during day light and less during night. The net transport shows a surplus of out-flowing mass during almost all hours of the winter day chosen. As there are only very few local NH_3-emissions in Berlin because of the very limited agricultural activities inside the chosen control volume and the small NH3-emissions due to traffic, the net loss, besides deposition of NH_3, of ammonium nitrate due to advection is explainable only through the conversion of NH_3 into NH_4 due to chemistry in the presence of high amounts of HNO_3. Inflowing NH_3 is removed from the atmosphere by transformation into NH_4. This species, then, is net-exported to the outskirts. The reaction with OH is relatively slow and is thus negligible in the NH_3-NH_4 budget consideration over Berlin.

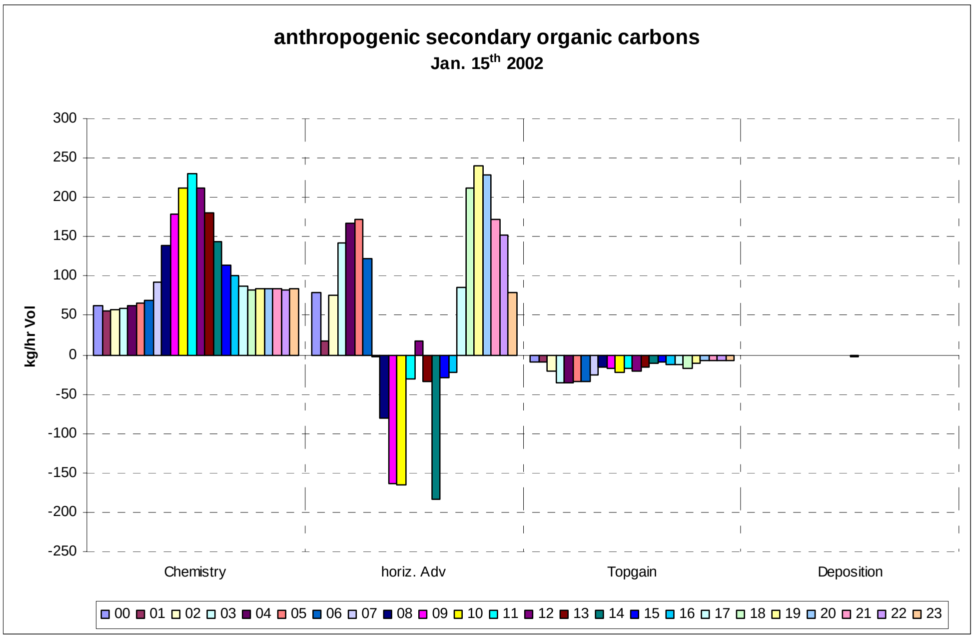

Figure 22 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), and deposition of anthropogenic secondary organic aerosols during January, 15th 2002

Anthropogenic secondary organic carbons (Figure 22) are accumulated mainly during day light because of chemical transformation from gaseous precursors. At the considered winter-day, the net export was during the central hours of the day, the overall contribution of the accumulation, though, was positive because of net –inflow during night. Comparing this behaviour with the sulphate aerosol and EC components, it seems evident that anthropogenic secondary organics reside longer time in the atmosphere than primary components showing the same flow pattern as sulphate ions.

Secondary organics stemming from biogenic precursors show a net daily cycle in their chemical production but are at least a factor of 2 less intense than there anthropogenic counterparts during the winter day (Figure 23).

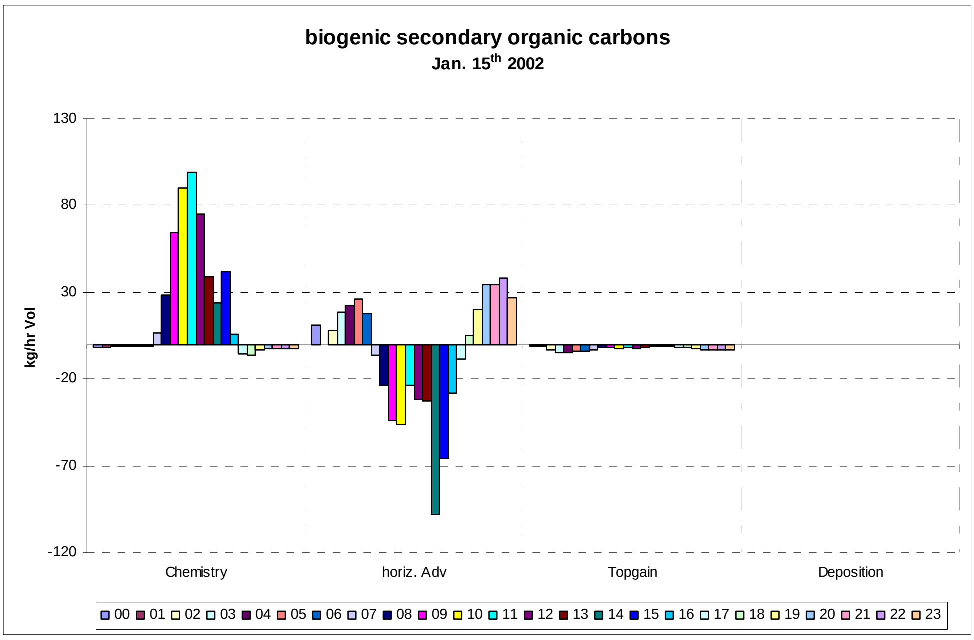

Figure 23 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), and deposition of biogenic secondary organic aerosols during January, 15th 2002

5.1.2 Summer

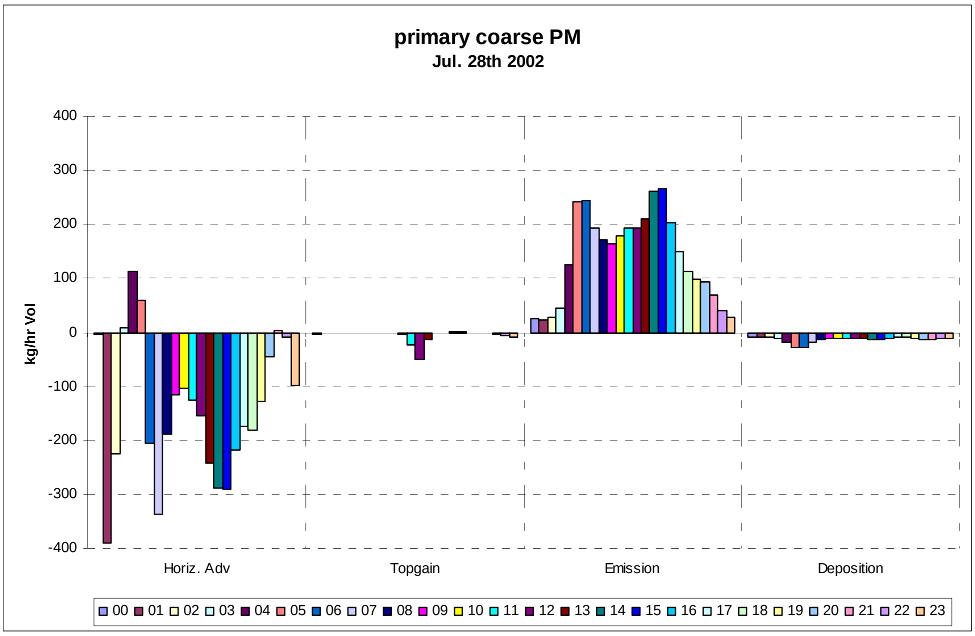

Figure 24 Hourly mass change rate due to net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), Emission and deposition of primary coarse mode aerosols during July, 28th 2002

Primary coarse mode aerosols (Figure 24) show no net difference between the winter-day and the summer-day in all considered processes. Again, human activity conform emission patterns are evident. The horizontal advection is the counter-force in removing the accumulated mass in the atmosphere over Berlin.

The same holds for elemental carbon (Figure 25). Seasonal differences in the primary components budget seem to be more related to human differentiation in their emission behaviour, i.e. use of traffic or working cycles than to other factors. Transport, as being the most effective counterbalance in the mass budget, is related to wind fields and these are subjected to seasonal patterns. They, at the other hand, are not as strong as for other meteorological variables like temperature and thus mixing heights.

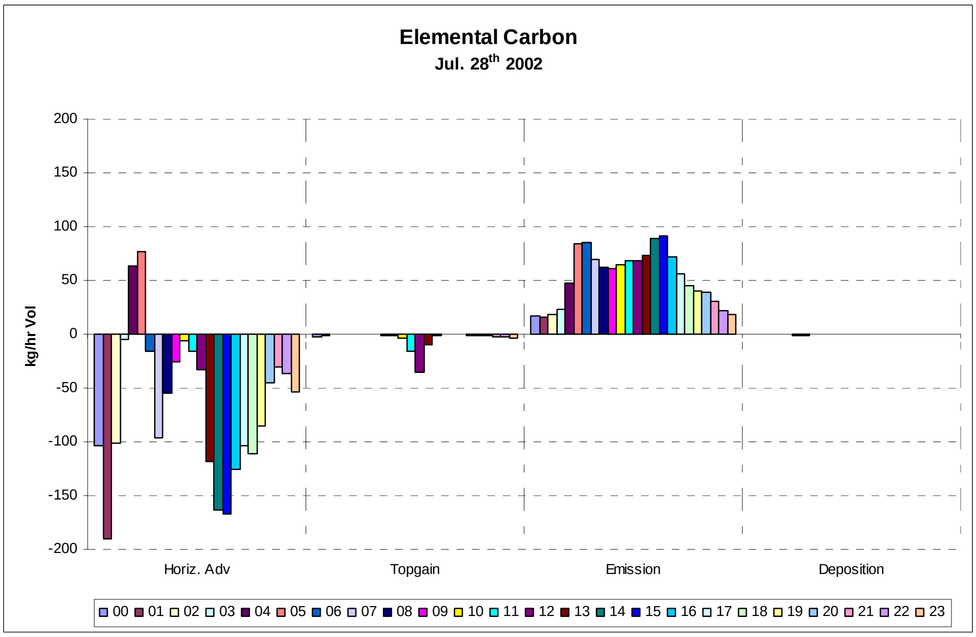

Figure 25 Hourly mass change rate due to net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), Emission and deposition of elemental carbons during July, 28th 2002

Considering the fact that during the summer episode there was some more loss of EC through the upper boundary than during the winter day can be attributed to that meteorological phenomenon of higher mixing layers.

Sulphate ions (Figure 26) are built chemically much more effective during summer than during winter. While the clear sky winter day showed a maximum chemical production rate of ca. 75 kg/hr the clear sky summer day had a maximum of almost 200 kg/hr at 14:00 hours. This is because of the temperature and therefore OH-availability related oxidation rate of SO_2 into SO_4 and thus because of the higher H_2O_2 and O_3 availability during summer. At the other hand, the transport accumulation and loss rates during the whole day were much higher in summer than in winter. This is a strong indication of a mostly flow-through behaviour of sulphate ions in Berlin. Higher production of SO_4 occurs everywhere during summer and flow-paths are stronger during summer than during winter. This is explainable through the relatively long life-time of sulphate aerosols.

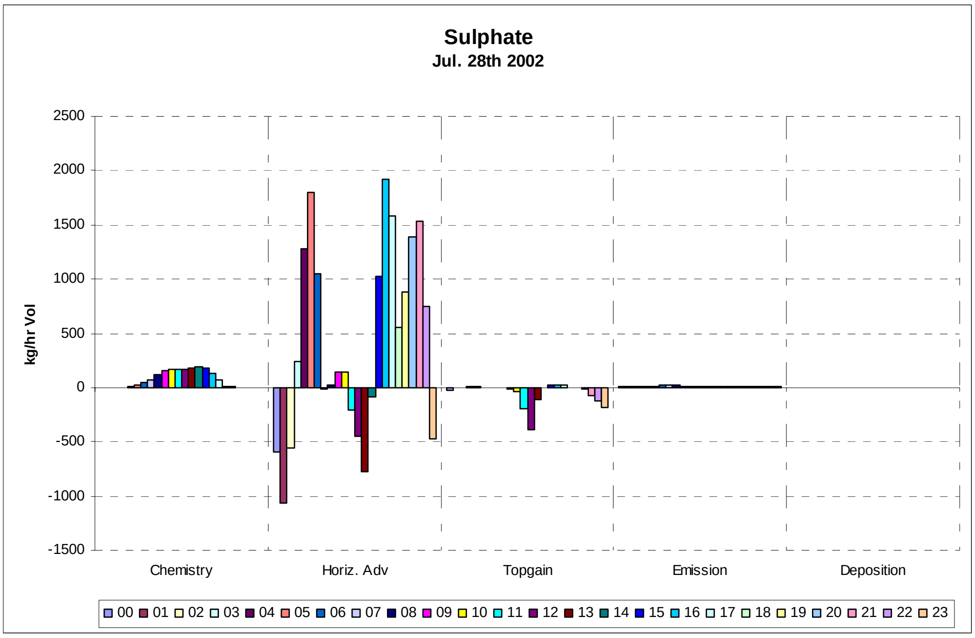

Figure 26 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), Emission and deposition of secondary sulphate aerosols during July, 28th 2002

When sulphate production rate is much more intense during summer, the opposite holds for nitrate (Figure 27). This aerosol component becomes almost negligible during the summer day episode. RCG simulates a strong accumulation rate due to advection at 15:00 hours and a very strong loss of nitrate due to chemistry at 16:00 hours. We did not investigate further the detail of this behaviour. Short life-time and fast exchange of nitrate ions may be a first explanation of the abrupt high inflow of NO_3. Consequently, the chemistry module re-converted this abnormal amount of nitrate into the gas-phase because of the high temperatures and the consequently high volatility of nitrate.

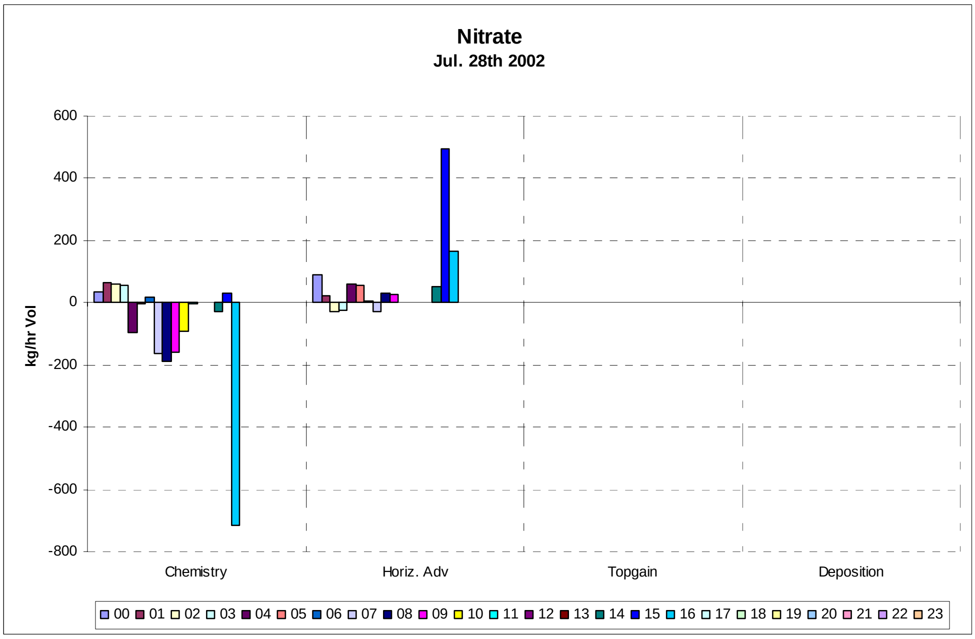

Figure 27 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), and deposition of secondary nitrate aerosols during July, 28th 2002

Also the chemical production rate of ammonium (Figure 28) becomes almost negligible during the summer day episode, especially when compared to the winter day. At the other hand, looking at the horizontal advective production and loss rate, ammonium shows the same behaviour as sulphate. The flow pattern with its high variability in inflowing and out-flowing mass to and from the city of Berlin is most probably due to the flow-through behaviour of ammonium during summer.

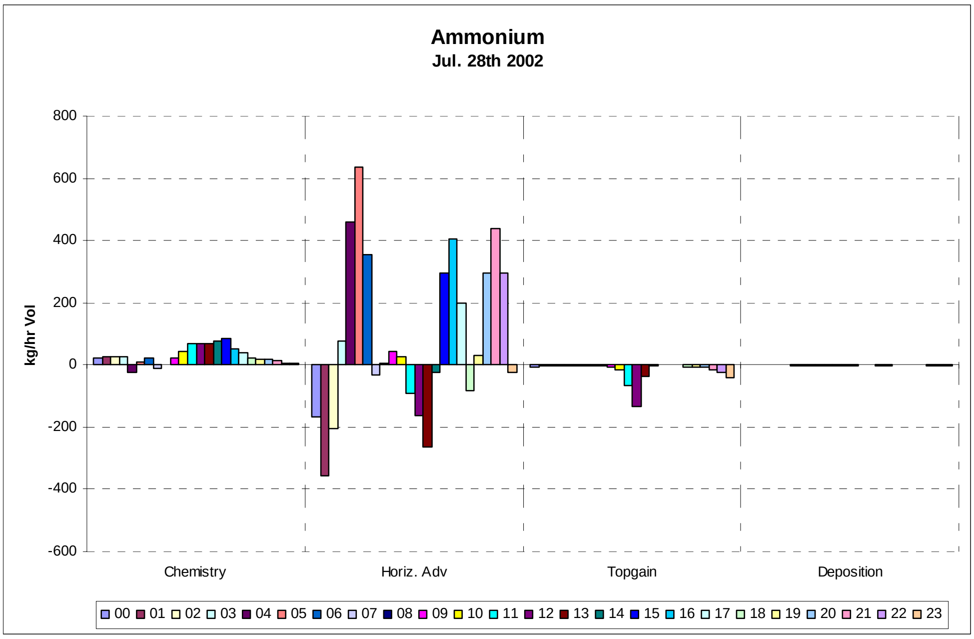

Figure 28 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), and deposition of secondary ammonium aerosols during July, 28th 2002

Anthropogenic secondary organic aerosol (Figure 29) production rate is at least a factor of 4 higher during the clear sky summer day than during the clear sky winter day. While the January day showed a clear day-light-related chemical production rate pattern, this is not true for the July-day. It must be reminded that the mass budget considerations comprise all processes contemporaneously, i.e. if there is not less mass due to transport related export form the control volume, the consecutive hour may have less availability for the chemistry process to build mass. This is clearly shown in the secondary organic aerosol pattern. While the winter-case was divided in inflowing mass during the night and out-flowing mass during the day, this regularity does not hold any more for the summer case. For instance, at 14:00 hours there is a strong removal of mass due to advection. The following hour (15:00) shows a weaker chemical production than the hours later. As said, this is not due to the less efficient chemical production but is due to the less available mass in the control volume.

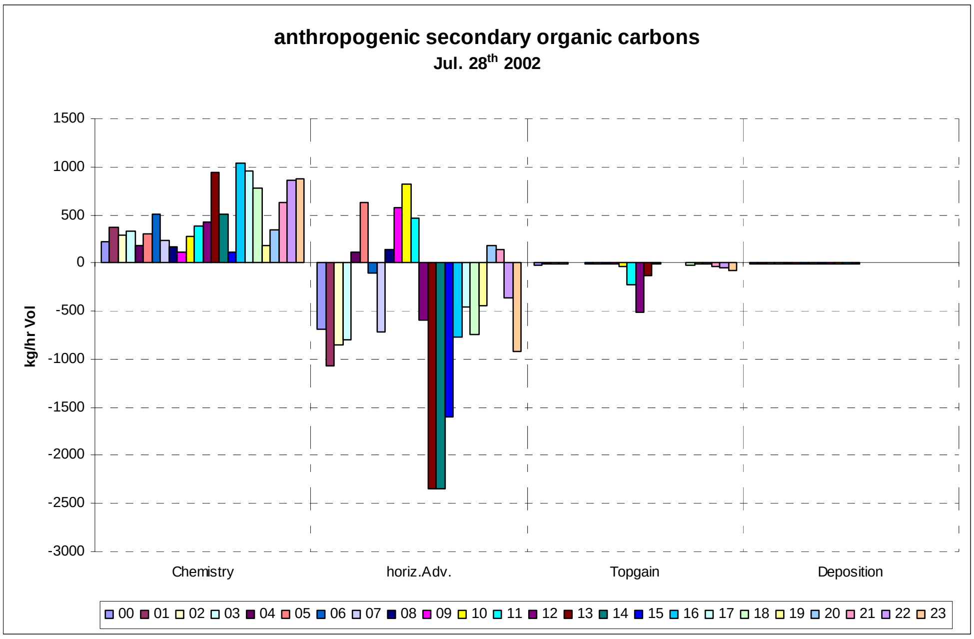

Figure 29 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), and deposition of anthropogenic secondary organic aerosols during July, 28th 2002

Considering the July-case it becomes evident that all city-related secondary organic aerosol production gets distributed efficiently to the non-urban environment. That means that anthropogenic secondary organic carbons are produced in Berlin and exported to the Brandenburg neighbourhoods. The over-regional character of the secondary aerosol components becomes evident when considering the fact that a considerable part is injected into the "free troposphere" above the modelled domain.

Also biogenic secondary organic aerosol components (Figure 30) show the regional character exhibiting a strong variability in the inflowing and out-flowing mass changes due to horizontal transport. There, again, is a net injection of secondary biogenic carbons into the atmosphere above 3000 m. Comparing, at the other side, the winter case with the summer case, the chemistry production rate strength is more or less the same in both periods. This behaviour is at least strange, also considering the high differences in winter and summer chemistries for sulphate or for anthropogenic secondary organic carbons, for instance. One reason is certainly in the very few local biogenic gaseous volatile organic carbons in the city of Berlin. Nevertheless, it might be worth to re-consider the biogenic emission data-base also for the greater Berlin area which consists also of considerable forest areas.

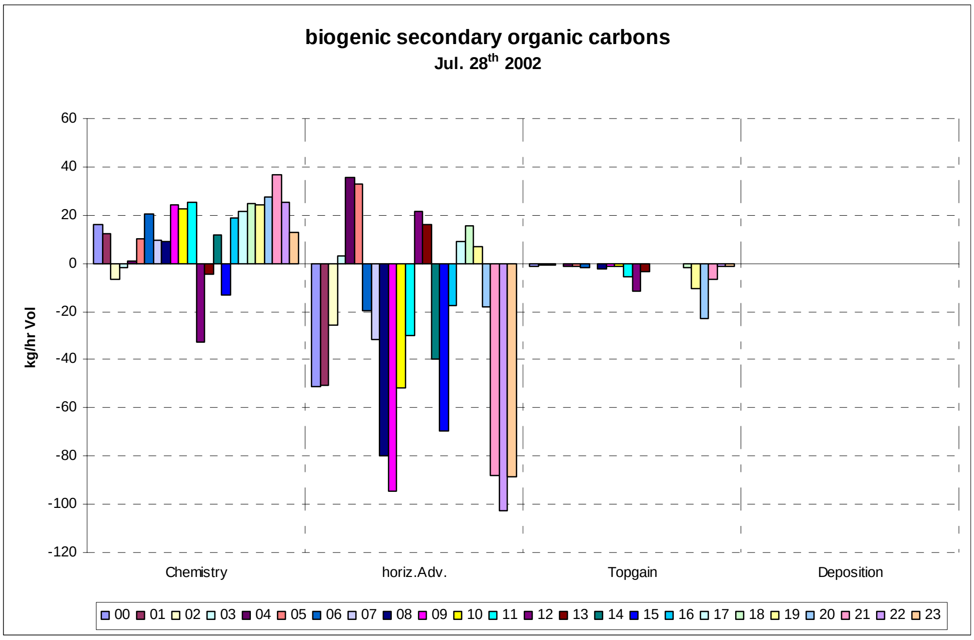

Figure 30 Hourly mass change rate due to chemical production (Chemistry), net horizontal advection (Horiz.Adv.), flow through the upper boundary (Topgain), and deposition of biogenic secondary organic aerosols during July, 28th 2002

5.2 THE HoVerT-PERIOD – ANNUAL BUDGET

Changes in pollutant concentrations over the whole HoVerT time period are integrated by linking the variation of pollutant concentrations in the control volume over time to physical-chemical processes that increase (production processes) or reduce (loss processes) the concentration of a chemical compound in the atmosphere. The yearly sums of the processes related contributions to the accumulation (positive) and reduction (negative) to the final concentrations are shown in Figure 31. The sums have been executed for primary mineral coarse and fine particles, for elemental carbons and for secondary inorganic and organic carbon compounds.

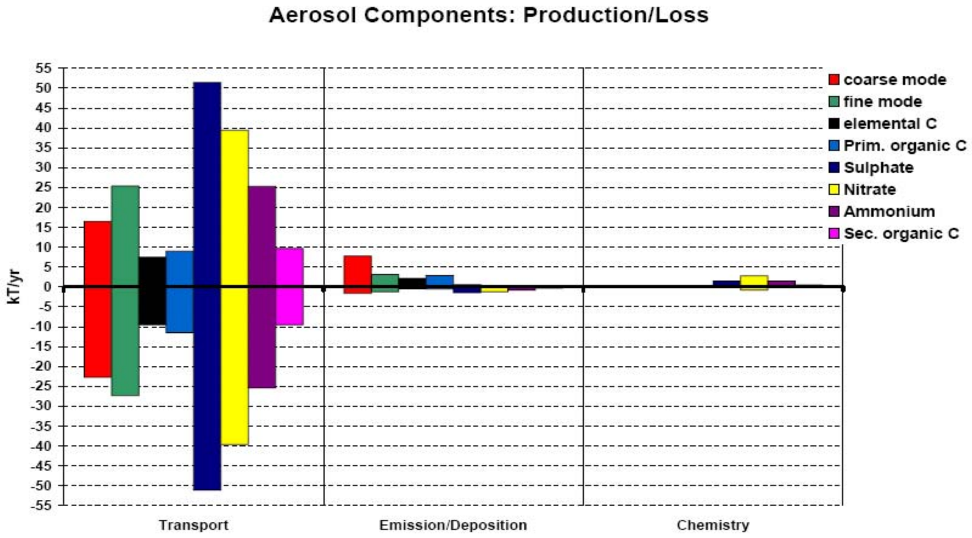

Figure 31 Annual accumulation (positive) and removal (negative) mass change due to transport, emission/deposition and chemistry, simulated for PM10 constituents.

The total sum of aerosol accumulating and removal processes has shown the predominant influence of advective and diffusive processes. Figure 31 displays the accumulation (positive) and loss (negative) terms of the considered PM10 components for the whole HoVerT-campaign-year. Compared to the transport processes emission, deposition and chemistry seems negligible. This is understandable by considering the importance of advection in the transport model. Wind fields cross the boundaries importing and exporting mass constantly. This means that the aerosol mass flux through the four fictive walls around Berlin is integrated over the whole year. The imported mass from outside the city and the exported mass from the city toward the surrounding area are considered separately. Nevertheless, the contribution form the city is intelligible only considering the difference between entering and leaving mass. This would be the difference of the positive and negative contribution of all fluxes through the walls. Since we are more interested in the flux characteristics of the polluted mass we decided to analyse the transported mass coming in and going out of the control volume.

The plot (Figure 31) gives a first impression which processes are important. However, the simple integration does not help in understanding the contribution of individual processes to the concentrations fields, since the integration itself inhibits a distinct apportionment. Considering, for instance, only the difference of emission and deposition, the fact that pollution is also arriving form other sources than local emissions is not contemplated any more. The same holds for the flux consideration. An integrated analysis must be performed and will be explained in the following sections.

Gross accumulation terms are intended to be the sum of positive contributions coming from individual processes to the final mass, while gross removal terms are the sum of the negative contributions to the final mass. Net accumulation is the total contribution to the final mass, i.e. the sum of the positive and the negative contributions.

5.2.1 Primary Aerosols

Table 6 summarises numerically the PM10 gross accumulation and gross loss in the control volume over Berlin, integrated over the whole year, depicted in Figure 31. The mass transport of modelled primary aerosols through the lateral boundaries around Berlin gives a gross 58.4 kT/yr positive contribution from the surrounding area toward the city of Berlin and a gross 71.0 kT/yr contribution of the city of Berlin toward the outskirts and to the free troposphere. Primary fine mineral particles form the biggest part of the transported material. 43.5% of the imported and 38.5% of exported mass is fine mode mineral particles. The total mass change due to emission of aerosols accounts for 15.92 kT/yr, having its main part in the emission of coarse mode mineral aerosols (almost 50%). This aerosol mode is also the preferred deposited PM component. The wet part in removing primary aerosols from the atmosphere is for coarse particles ca. 70% and only 30% is due to dry deposition. Almost 100% of the deposition of fine mineral particles, elemental carbon and organic primary carbons is removed due to scavenging effects.

Table 6 Numerical accumulation and removal values in kilo-Tons per year [kT/yr] due to transport, emission/deposition and chemistry in the control volume over Berlin.

	Accumulation in Berlin			**Loss from Berlin**		
	Transport	**Emission**	**Chemistry**	**Transport**	**Deposition**	**Chemistry**
Primary PM	**58.40**	**15.92**	**0.00**	**71.00**	**3.68**	**0.00**
coarse mode	16.50	7.79	0.00	22.70	1.60	0.00
fine mode	25.40	3.16	0.00	27.30	1.17	0.00
elemental C	7.50	2.14	0.00	9.50	0.41	0.00
organic C	9.00	2.83	0.00	11.50	0.50	0.00
Secondary PM	**125.80**	**0.56**	**6.31**	**125.63**	**3.72**	**0.92**
Sulphate	51.40	0.56	1.50	51.10	1.43	0.00
Nitrate	39.40	0.00	2.82	39.60	1.19	0.79
Ammonium	25.30	0.00	1.49	25.40	0.80	0.06
organic C	9.70	0.00	0.50	9.53	0.30	0.07
Biogenic C	*7.08*	*0.00*	*0.31*	*6.79*	*0.10*	*0.01*
Anthropogenic C	*2.62*	*0.00*	*0.19*	*2.74*	*0.21*	*0.06*

Primary particulate matter is gross-accumulated in the city of Berlin due to transport processes for almost 80% and due to local emissions for 20%. The coarse mineral fraction shows a greater contribution from emission (almost 40%), while the fine mode mineral particles exhibit a more consistent part from advective processes. In fact, almost 90% of fine mode primary aerosol gross accumulation is due to transport processes. Remember that coarse and fine PM in RCG is intended to be minerals and constitute separate classes from carbons. Elemental carbon and organic primary carbon are accumulated in Berlin due to local production for about 30%. Wind-blown dust is one reason for the high contribution of primary fine particles coming from the surrounding areas to the city of Berlin. The fact that the control volume does not make any difference between Berlin Centre and Berlin suburbs makes the rather low city contribution of primary aerosol components explainable. Considering also wind-blown dust, coarse mode PM is the fraction of primary aerosol which is emitted most, followed by fine mode PM. This components in RCG are modelled to be emitted by resuspension, wind-blown-dust, constructing activities and non-combustion processes. EC and OC are related directly to anthropogenic processes like motor-vehicle combustion, heating and industrial emissions. Combustion processes like wood-firing and forest fires and biogenic emissions due to pollen, biogenic leaf-debris as well as emissions coming from forests are not considered in RCG until now.

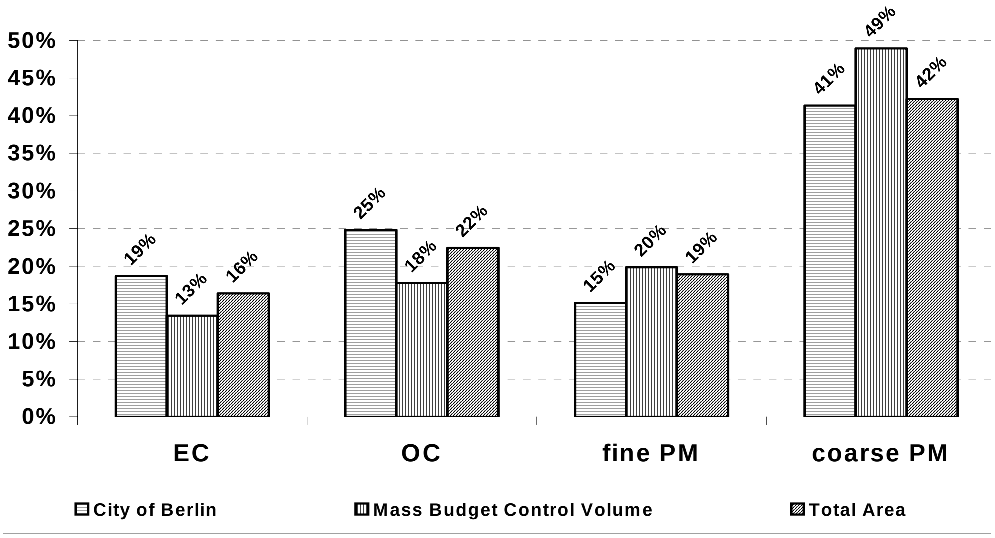

Figure 32 Relative composition of the PM10 emissions in the city of Berlin, in the control volume used in the mass budget study and in the total Berlin-Brandenburg simulation domain.

The urbanised area is thought to produce high quantities of non-combustion aerosols, and less elemental and organic carbons. The original emission data for the city of Berlin attribute the biggest primary PM10 contribution to the coarse fraction (coarse mode minerals) (41% i.e. 4.1 kT/yr) followed by OC with almost 25% (2.5 kT/yr), EC with 19% (1.9 kT/yr) and fine mode primary PM (fine mode minerals) with 15% (1.5 kT/yr) (Figure 32).

The high percentages of OC and EC are consequence of their emission-parameterisation based on the available full PM loads smaller than 2.5 µm. In fact, about 50% of the traffic-related PM2.5-emissions are attributed to OC and EC. On the other hand, the considered control volume not only comprises the City of Berlin, but also some 30% of rural areas. The mass budget analysis takes into account the global gross emission change from one hour to the next, i.e. the emission mass difference integration does not differentiate between different origins of fine and coarse mode particles. Within RCG a simulation of wind-blown-dust is done. This fraction contributes to the fine-mode particles up to a threshold friction velocity and to the coarse mode particle emission from that threshold on. This threshold and the emission strength depend on the land-use class of the grid-cell. Urban grid-cells contribute to wind-blown-dust emissions in RCG. In these cells the roughness is higher and thus the friction velocity assumes higher values. Therefore, urban cells often contribute more to mineral emissions than grid-cells with a dominant agricultural land use. This might give an indication of the highly uncertain emission data bases in use.

Lenschow et al. (2001) estimate that traffic induced particle resuspension accounts for ca. 50% of vehicle PM10 emissions in Berlin. These figures are included in the emission inventory only as a percentage of the exhaust emissions. No figures can be given concerning wind-blown dust in the city. However, particles lying on the streets and on other surfaces are brought to the air by wind-shear and moving traffic and must be modelled. Until now, these traffic-related anthropogenic emissions are part of the RCG vehicle emissions input. They contribute most to the traffic related coarse PM emissions in the model domain.

The RCG aerosol scheme 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) 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 following relation has been proposed based on observations of small particles:

$$F_d = 3.6\,(u_*)^3$$

with F_d being the emission flux in µg/(m^2 s) and u_* the friction velocity.

The indirectly induced saltation due to large particles' ability to free smaller minerals dropping on the surface is parameterised by the following equation:

$$F_d = 12000\,(u_*)^3\,(u_* - u_{*thr})$$

where u_{*thr} is the threshold friction velocity when resuspension starts. The threshold friction velocity is dependent on the soil and its land-use and lies between 0.4 m/s (dry soils) and 1.6 m/s (pasture). The indirect resuspension gives thereby higher emission fluxes than the direct wind-induced particle flux when the threshold value is exceeded. Thus, its determination is of paramount importance in simulating well the emission intensity due to wind. However, data which describe the soil characteristics as moisture and texture in detail are not available. Therefore, the u_{*thr} – classification has been performed only on the type of dominant land-usage. Moreover, the traffic induced resuspension because of turbulences due to driving vehicles can not be modelled by the approach described above.

Figure 33 summarises the relative importance of the gross accumulation processes with respect to the primary PM10 composition. Transport is double as important for fine mode primary aerosol as for coarse mode primary particles. Elemental carbon and organic primary matter constitute only about 30% of the total advected primary aerosol. The opposite holds for the relative accumulation due to direct emissions: coarse mode primary particles constitute half of the total PM10 emission, fine mode PM and organic carbon constitute same parts and elemental carbon is the smallest fraction in the emission accumulation process.

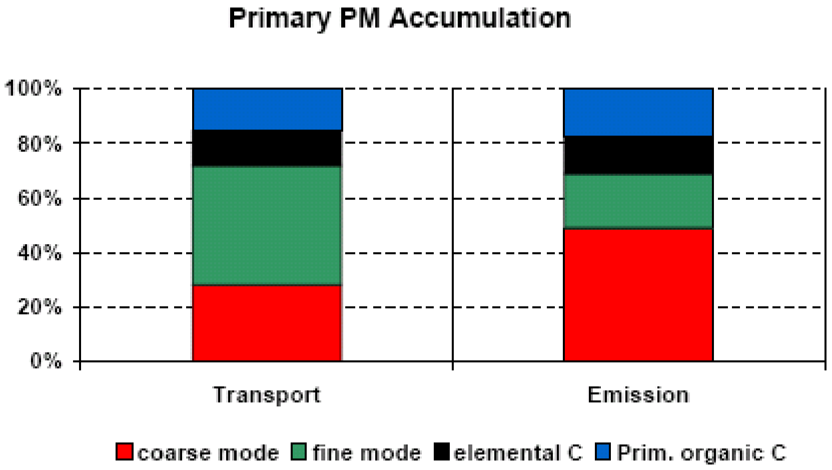

Figure 33 Relative annual gross accumulation of primary PM components due to transport and to emissions in the control volume over Berlin.

The most prominent process in removing primarily emitted mass from the city of Berlin is advection which accounts for more the 90% of the loss-terms in the removal budget (compare Table 6). Considering the fact that 58.4 kT/yr of primary aerosols are imported to Berlin and that 71 kT/yr leave the urban area, Berlin exports ca. 12.6 kT/yr of aerosols to the surrounding areas, which are due to Berlin specific emissions cleared by deposited mass. Again, the fine fraction of the primarily emitted PM mass is transported more easily from the city of Berlin toward the surrounding area (see Figure 34). Deposition processes are the only local removal process for primary aerosol pollutants as they do not undergo any chemical transformation. This process is most effective as wet scavenging for all fine mode particles. In fact, this mechanism accounts for more than 90% of the deposited mass in Berlin for fine mode PM, for EC and for OC. Only coarse mode PM is deposited also via dry deposition for some 30%. This is due to the settlement deposition velocity parameterised in this way inside RCG. According to the locally emitted primary aerosol constituents, also the relative contributions of these species to the deposited mass are higher for coarse mode PM, followed by the fine mode fraction, OC and EC. Transport processes contribute less to the locally deposited primary mass than to the flow-through.

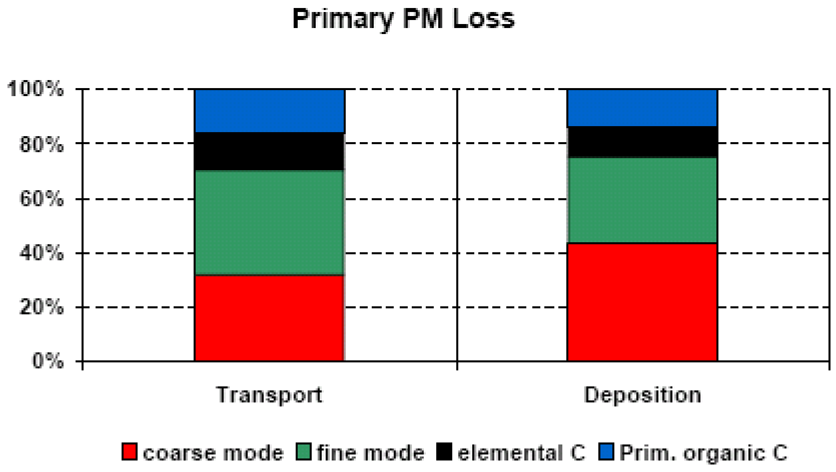

Figure 34 Relative annual gross removal of primary PM components due to transport and to deposition from the control volume over Berlin.

5.2.2 Secondary Aerosols

125.8 kT/yr of secondary inorganic and organic aerosol components are transported towards Berlin, while 125.63 kT/yr leave the domain of Berlin. Considering a gross direct contribution of 0.56 kT/yr sulphate emissions and a 6.31 kT/yr chemical production on the accumulation side, and a gross 3.72 kT/yr deposition and 0.92 kT/yr of chemical loss on the removal side, there is an overall net secondary aerosol accumulation of 2.39 kT/yr in Berlin. Relative contributions to gross accumulation and gross removal due to relevant processes are shown in Figure 35 and Figure 36, respectively.

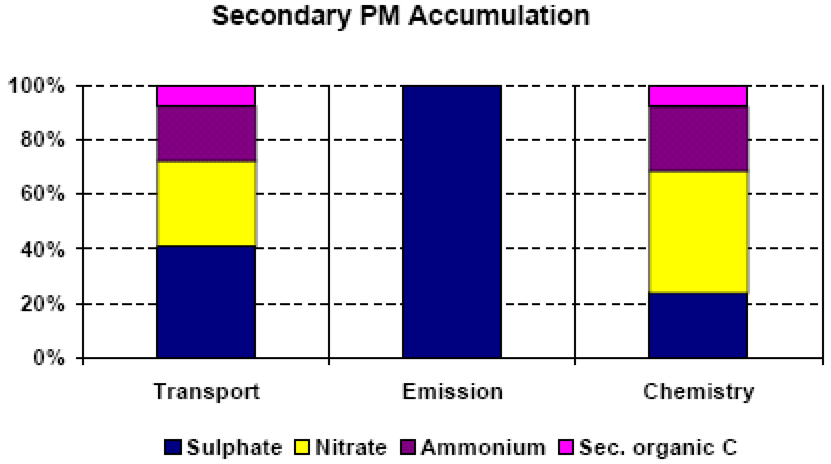

Figure 35 Relative annual gross accumulation of secondary PM components due to transport, emissions and chemistry in the control volume over Berlin.

Considering only the gross transport there is the same amount of imported mass as exported mass. The gross accumulation due to chemistry, at the other side, is much higher than the gross removal due to chemistry. In the building process of secondary inorganic aerosols, nitrate is the most reactive part. Whether the high percentage of chemical contribution to the gross accumulation of SIA is due to city-related precursors or due to the fast chemical production, is not deducible univocally from the process-related analysis. A sensitivity study without Berlin emissions could give insight in this feature.

However, there is some 5% of gross SIA accumulation in Berlin due to chemistry not counterbalanced by gross chemical destruction.

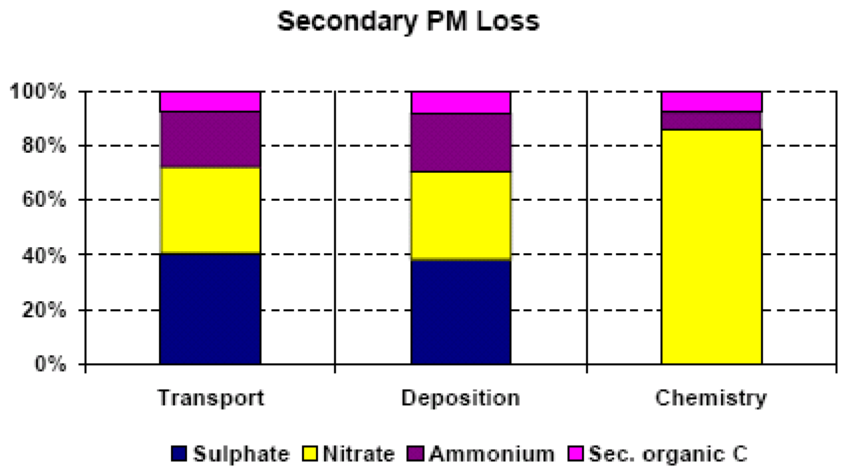

Figure 36 Relative annual gross removal of secondary PM components due to transport, deposition and chemistry from the control volume over Berlin.

The transported, incoming as well as outgoing, mass in Berlin is with almost 95% the most important process in the local mass budget. The chemical transformation rate within the urban boundaries is about 5% in accumulating mass and only about 1% in removing mass. Reducing secondary aerosols from Berlin is due to wet deposition only by ca. 3%. This strongly indicates a fundamental pass-through of secondary aerosol components. Considering the components of the secondary aerosols, sulphate is with more than 40% the species which undergoes the strongest mass exchange via advection. Nitrate with 30% and ammonium with 20% contribute to the incoming as well as outgoing mass transports. The remaining 8% are due to secondary organic carbon transported toward and from Berlin, where the biogenic part is 70% and the anthropogenic part only about 30% of the advective contribution to the mass budget in Berlin. Considering the chemical transformation, nitrate is with 45% in the production process and with more the 85% in the destruction process the species which contributes most to mass changes in the secondary aerosol budget. Sulphate and ammonium contribute both ca. 23% to the accumulating mass budget, while in the destruction process, sulphate plays almost no role and ammonium contributes about 7% to the mass budget loss. In the overall secondary aerosol chemistry budget, the organic carbon accumulation as well as loss contributes with about 7.5% to the mass budget. Within this process, the biogenic secondary organic aerosol production rate is more than double than the anthropogenic part, while in the chemical removal process the anthropogenic part is about 90%. The city of Berlin is responsible for the anthropogenic aerosol building processes, while the fundamentally rural surrounding areas of Berlin contribute to a biogenic aerosol accumulation in Berlin.

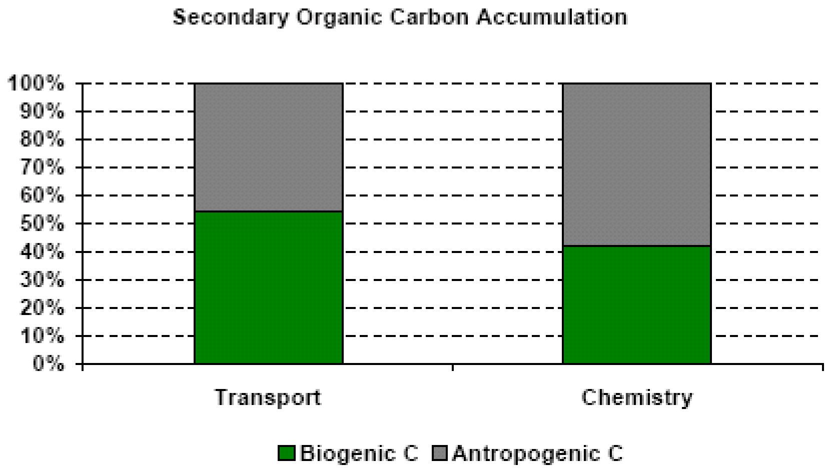

Figure 37 Relative annual accumulation of biogenic and anthropogenic secondary organic matter due to transport and to chemistry in the control volume over Berlin.

Figure 37 shows the relative contribution to accumulation of biogenic and anthropogenic aerosols due to advective and turbulent transport and due to chemistry. The biogenic carbons are advected slightly more (52%) than the anthropogenic carbons (48%). The chemical production of anthropogenic secondary organic carbons is higher (59%) than the chemical production of the biogenic carbons in the urbanised area of Berlin.

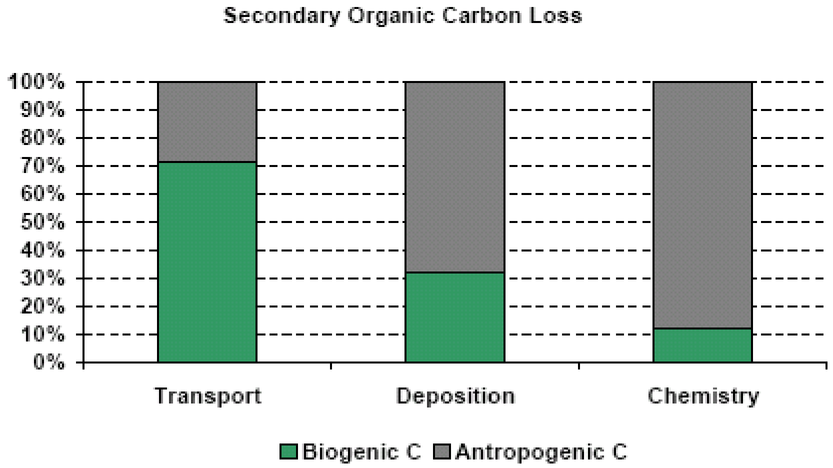

Figure 38 Relative annual removal of biogenic and anthropogenic secondary organic matter due to transport, deposition and to chemistry from the control volume over Berlin

Figure 38 shows the relative contribution to removal of biogenic and anthropogenic aerosols due to advective and turbulent transport, due to deposition and due to chemistry. The biogenic carbons are removed more (70%) than the anthropogenic part (30%) form the Berlin agglomeration. Contemporaneously, the anthropogenic part is more deposited locally (70%) than the biogenic part. Also the chemical destruction is more efficient with anthropogenic precursors (90%) than with biogenic precursors (10%).

Figure 39 and Figure 40 show the relative importance of the advective, chemical and depositional processes in accumulating and removing secondary organic biogenic and anthropogenic carbons. Secondary organic carbons, as already seen with the inorganic fraction, are built, transported and deposited on longer time scales than primary aerosol components. This becomes also very evident considering the relative contribution of advection compared to the other relevant processes. Essentially, these PM10 components are blown through Berlin. The anthropogenic part shows as slightly higher contribution from chemistry in the accumulation as well as in the removal process than the biogenic part. This is due to the higher local anthropogenic precursors.

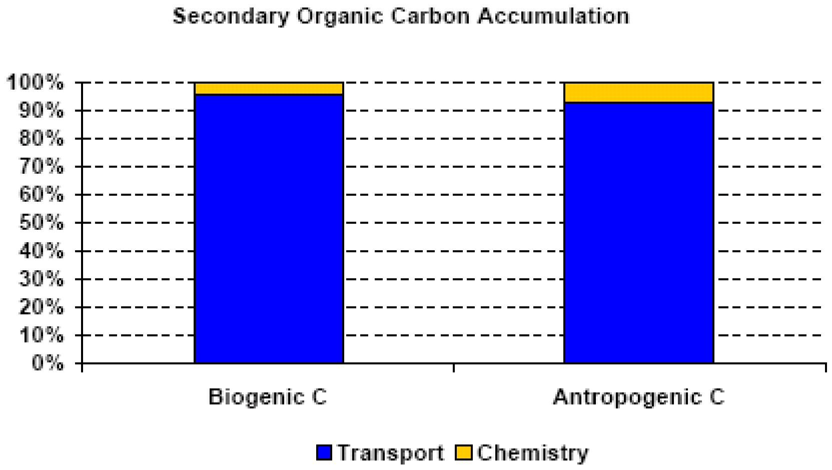

Figure 39 Accumulative Transport vs. Chemistry Production for biogenic and anthropogenic secondary organic aerosols. (Whole Year)

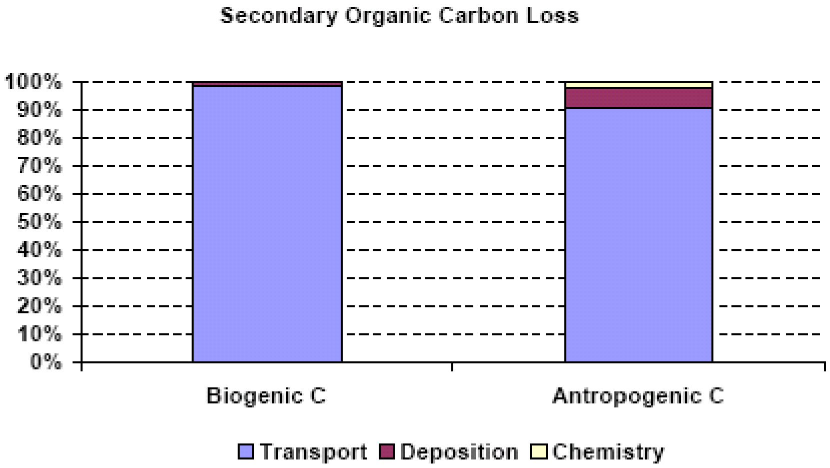

Figure 40 Removing Transport, Deposition and Chemistry Destruction for biogenic and anthropogenic secondary organic aerosols. (Whole Year)

5.3 HORIZONTAL TRANSPORT – ADVECTION+DIFFUSION

The same transport-related gross accumulation and gross removal analysis as in chapter 5.2 has been conducted with regard to wind-directional dependencies.

The horizontal annual transport of particulate matter is the most important process in accumulating and removing mass from the control volume. A high percentage of inflowing mass is also leaving the control volume. At the other hand, the PM10-mixture obtains different composition in different wind directions. On a yearly basis, primary particulate matter enters the city of Berlin mainly from the west and leaves the city toward the east. The opposite direction is negligible (Figure 41). Also the south-north flow direction is not as important for primary PM than for secondary aerosols. All secondary particles, inorganic as well as organic, have an important flow direction form the south toward the north (Figure 41). As for the primary particles, this opposite direction, i.e. from the north toward the south, is of no importance at all. The east-west-direction becomes important for secondary PM.

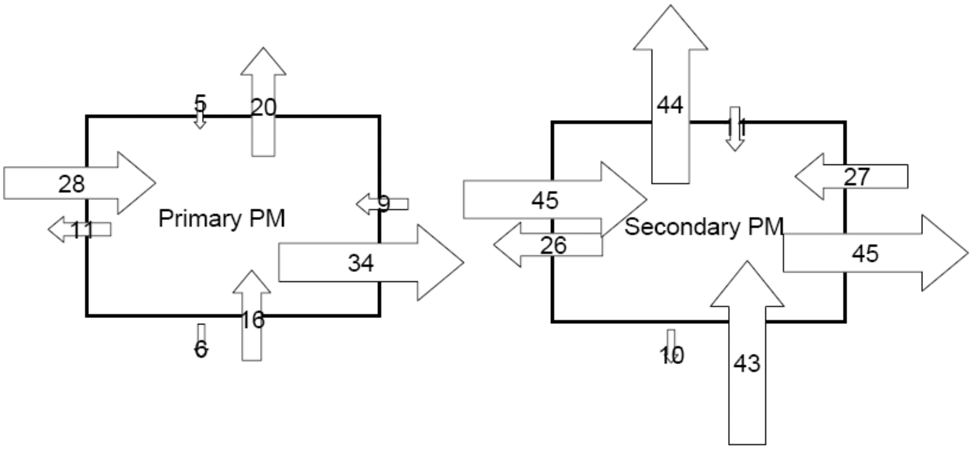

Figure 41 Directional inflow and outflow mass of primary (left) and secondary (right) PM10 components from the control volume [kT/yr]. (Arrow length is scaled by maximum flow strength)

While for primary PM this direction constitutes only about 25% of the longitudinal flow, somewhat less than 40% of secondary PM comes from the east over the whole year. Considering the absolute values of primary and secondary inflow-outflow behaviour, the faster mass exchange of primary particles becomes evident. While 28 kT/yr enter the western boundary, about 34 kT/yr leave through the eastern border. The same relation holds also for the south-north direction: 16 kT/yr enter the city through the southern border and 20 kT/yr leave the Berlin domain through the northern border. The opposite directions are negligible. Considering at a first attempt only the one-dimensional directions, a net difference of 8 kT/yr in the west-east direction and a net difference of 5 kT/yr in the south-north direction is attributable to the city of Berlin. The secondary particulate matter has a remarkably different behaviour: again, considering only the one-dimensional flows an almost equilibrium between inflow from the west and south, respectively, and an outflow toward the east and north, respectively, can be observed. The net increment for the secondary aerosol by the city of Berlin is almost zero, though negative. Discerning secondary inorganic and organic aerosol components, it becomes evident that long range indicator anthropogenic sulphate together with biogenic secondary organic aerosols have a strong tendency to be brought in from the east and from the south toward the urban control volume, while anthropogenic influenced secondary aerosol nitrate together with anthropogenic secondary organic carbons exhibit a more “primary-like” pattern.

Coarse fractions of PM10 have sufficiently large sedimentation velocities that they settle out of the atmosphere in a reasonably short time (Seinfeld and Pandis, 1998). They normally do not travel long distances except under some special cases like Sahara dust episodes (Schütz et al., 1981, Arimoto et al., 1995). Coarse particles are mainly mechanically generated; dust, resuspension, industrial processes and sea-salt. (Jaenicke, 1993).

Nitrate ions (Figure 42) enter the control volume from the west and from the south to the same amount as they leave Berlin toward the east and to the north, respectively. This was also observed with the primary aerosol components. The secondary aerosol characteristic, at the other side, is evident considering the local contribution to the transported mass which is almost zero, though positive (0.3 kT/yr). Sulphate ions enter the control volume, on a yearly basis, more from the south and leave Berlin city toward the north (Figure 42).

North-south-direction is not important as a sulphate pathway. The longitudinal direction becomes interesting for sulphate ions also on the east to west way, i.e. for SO_4^{2-} almost the same amount of mass enters the control volume from the west as from the east.

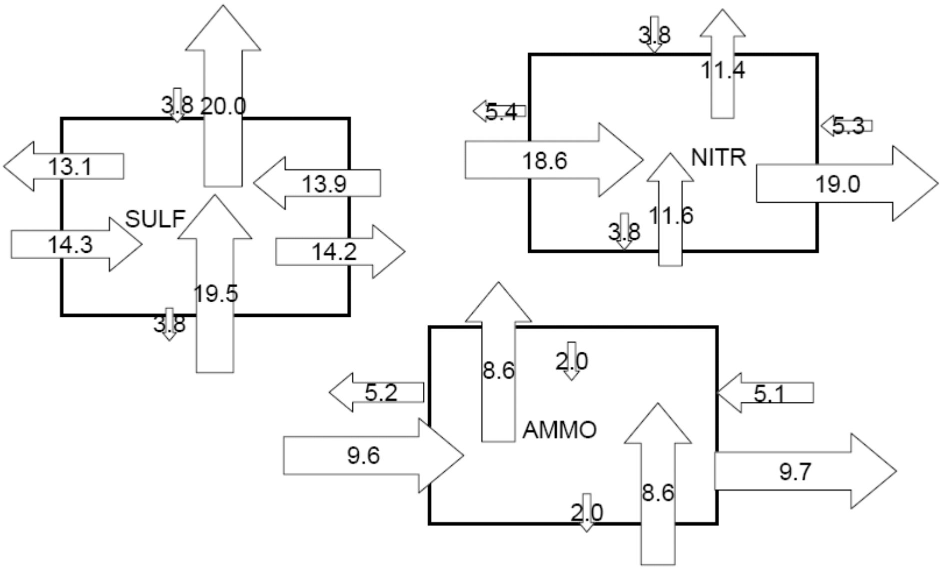

Figure 42 Directional inflow and outflow mass of sulphate (upper left), nitrate (upper right) and ammonium (lower) PM10 components from the control volume [kT/yr]. (Arrow length is scaled by maximum flow strength)

Analysing the prevailing wind direction in the Berlin region during the HoVerT campaign period, which was from the west toward the east (Figure 10), this behaviour becomes even more interesting. Reimer et al. (2004) attribute high PM10 concentrations to the strong influence of easterly winds. Stagnation effects of the atmosphere, when high pressure situations are the weather determining condition with low easterly wind-speeds and sunny and dry days in the winter and very hot days in the summer, contribute to high PM10 concentrations mainly via the higher sulphate content in the aerosol mass. Analysed trajectories indicate also a strong relationship between higher PM10 concentrations in Berlin and air mass surface contacts in South-Poland (Reimer et al., 2004). The long range transport pattern is evident also in our study, showing that the city of Berlin does not contribute substantially to the mass flow characteristics of sulphate.

The importance of sulphate in high PM10-concentrations in Berlin was also observed by Lenschow et al. (2001). The strong coincidence of higher sulphate ions concentrations and south-easterly wind directions has been evidenced. Also other studies (John et al., 2004) manifested this common picture of high PM10 values in Berlin and south-eastern winds. However, none of these studies took into account the chemical transformation.

A Lagrangian transport model could give an explicable picture of the sulphate faith on its way from the south-east toward Berlin. It could not be determined univocally whether the stagnation effects over Berlin, accompanied by easterly slow winds, or the high sulphate-using production industry areas in the south-east of Berlin are responsible for the high PM10 values observed. This mass budget analysis attributes a strong influence to the south direction, but shows at the other side also high production due to chemistry in the warm season. Nevertheless, accumulation due to chemistry is some order of magnitudes lower than transport processes, also if only flown through the city.

Ammonium transport (Figure 42) is coupled to nitrate as well as to sulphate flow characteristics. Again, the prominent west-east flow direction is found also in the ammonium way-path like for nitrate ions, but the south-north-flow is stronger than for primary and anthropogenic inflow patterns. This is explainable because the ammonium is bound to the sulphate and excess ammonium is bound by the nitrate ions. Again, the net uptake form the city of Berlin is negligible for ammonium on a yearly integration basis.

Considering the differences between anthropogenicly and biogenicly influenced secondary organic aerosol components it again becomes evident that PM-components related to the anthropogenic activities are brought more through the western border and leave Berlin toward the east, while biogenic secondary organic aerosols enter the control volume mainly through the eastern and southern border and leave the control volume toward the north and toward the west (Figure 43).

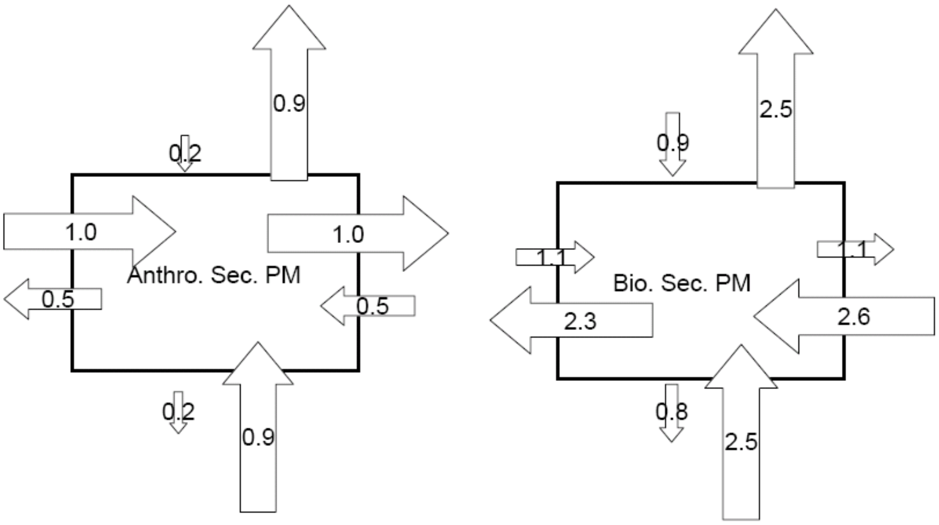

Figure 43 Directional inflow and outflow mass of anthropogenic (left) and biogenic (right) secondary organic aerosols from the control volume [kT/yr]. (Arrow length is scaled by maximum flow strength)

RCG simulated secondary organic particulate matter with an equilibrium approach starting from anthropogenic precursors which are related to olefin and aromatic emissions originated by vehicle exhausts, heating and industrial processes as well as from biogenic precursors from α-pinene and limonene emissions generated to a great extent by forest coniferous trees. Again, the characteristic of being a secondary pollutant is the same as in the inorganic case: the net contribution of the city of Berlin in the transport process is negligible.

Nevertheless, the wind direction dependency of anthropogenic and biogenic aerosols can give an indication about the organic aerosol sources. While nitrate and anthropogenic organic particulate matter have both a stronger local influence, it can be deduced that westerly winds contribute more to the flow-through than easterly winds. Westerly winds are more frequent in Berlin and are accompanied also with higher wind-speeds than easterly winds. Easterly winds are related more to slow wind speeds and thus to more stable situation over Berlin. Biogenic secondary organic aerosols exhibit a very similar pattern as sulphate ions. While sulphate precursors strongly are emitted in the south Poland region, this is not true for biogenic organic precursors. This might give an indication that the stagnation is at least as important in the accumulation of secondary sulphate aerosols as the source apportionment related to the south-polish industries.

5.4 SEASONAL BUDGET

Aerosol concentrations show no clear annual cycle in urban environments. Figure 44 shows the PM-components' time series at the urban background station in Berlin Nansenstr. (MP42). Total PM10 (blue line) shows a maximum at the end of March, 2002.

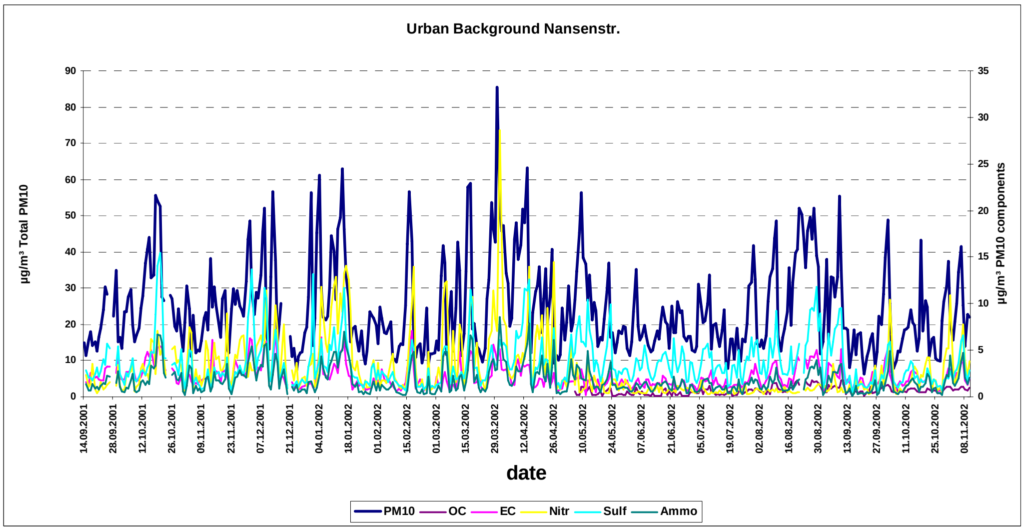

Figure 44 PM10 ([µg/m³] left y-axis) and PM10 components ([µg/m³] right y-axis) measured during the HoVerT campaign form Sep. 14th 2001 to Nov 11th 2002 (x-axis) at the Berlin urban background station Nansenstr.

In this period, also nitrate (yellow line) shows an absolute maximum of the whole measurement campaign HoVerT. Sulphate ions (light blue line), at the other side, do not contribute substantially to this high concentration situation. Another period of higher total PM10 observations occurs in winter (December, 2001 – January 2002) and during late summer (August – September 2002). Minima can be observed at the urban background station during February 2002 and during June-July 2002. So, while PM10 as a total does not show a distinct seasonal cycle, specific components of PM10 do show such cycles. The reasons why the aerosol composite eliminates the constituents' periodicity are manifold and have to be searched in the complex interaction between chemistry, meteorology and anthropogenic habits. Meteorological conditions seem to have a secondary influence on the particulate matter time series although mixing characteristics of the planetary boundary layer determine aerosol concentrations in a substantial way. Very stable meteorological conditions are distributed throughout the year though more frequently during winter than during summer. Secondary inorganic and organic aerosols depend very strongly on insolation and on temperature. These meteorological variables, at the other hand, show a very clear annual cycle, and the secondary aerosols contribute to a considerable part to the total aerosol mass. Thus, a more detailed view into building and removing processes depending on seasons is interesting and can help to understand the variations in the concentrations field.

While primary aerosols exhibit a very local characteristic and therefore are more influenced by anthropogenic daily behaviour, secondary organic and inorganic components show a more regional pattern. Primary and secondary aerosol components contribute to more or less the same extent to the total aerosol urban background concentration. Thus, the seasonality in the concentrations field is explainable only if considered separately the PM constituents. John et al. (2004), for instance, have attributed high sulphate concentrations to high total PM10 concentrations. This is especially true when high local concentrations measured for example at the traffic measurement site MP174 coincide with high regional secondary inorganic aerosol concentrations measured for instance at the tower station FT.

How much particles arrive to a certain location depends also on wet and dry deposition and cloud processes. Secondly, particle concentrations are affected by local mixing. If the planetary boundary layer is stable, locally emitted or resuspended particles stay in a smaller volume (Väkevä et al., 2000). Mixing depend on wind speed, turbulence, and relative humidity (Pohjola et al., 2000). Thirdly, meteorology and seasons affect also the emissions. This is especially true for resuspended PM10 which is related to springtime snow smelting which governs the release of sand from wintertime gravelling. Natural primary emissions like sea-spraying have a strong annual cycle as well, it is related to wind speeds. Also secondary aerosol particle formation is governed by the time of the year and meteorology (Mäkelä et al., 1997). The effect of season is related e.g. to house heating. Another example is traffic; in cities many people have their holidays in July which changes traffic emissions.

Nitrate particles show a substantial larger fraction in urban areas than in remote areas (Hueglin et al., 2005, Malm et al., 2004, Putaud et al., 2004). Thus, nitrate formation is expected to occur over urban areas. The measurements show also a significant seasonal variation in the nitrate abundance. A more difficult task than modelling non-volatile aerosol components in the atmosphere is to model semi-volatile aerosols, such as organics and nitrate aerosols. A large problem when modelling aerosol concentration of semi-volatile compounds is that their saturation vapour pressure is dependent on aerosol composition and temperature. The saturation vapour pressure of HNO_3 is also strongly dependent on temperature.

Chemistry is more subjected to seasonal differences than the other processes. While transport is dependent on meteorology and thus on the seasonal characteristics of wind field distributions in Berlin, aerosol chemistry is an interaction between temperature related vapour pressure, availability of neutralisation ions for the inorganic PM components and on the temperature related emission strength of biogenic secondary organic aerosol precursors (Simpson et al., 1999)

Figure 45 shows the chemical net production rate of secondary inorganic and organic aerosol components, simulated by the chemical transport model RCG. The red line (dashed: daily mass change due to chemical production and loss; full: moving average; unit scale at the right axis in tons/day) shows the ozone chemical transformation rate in the control volume over Berlin.

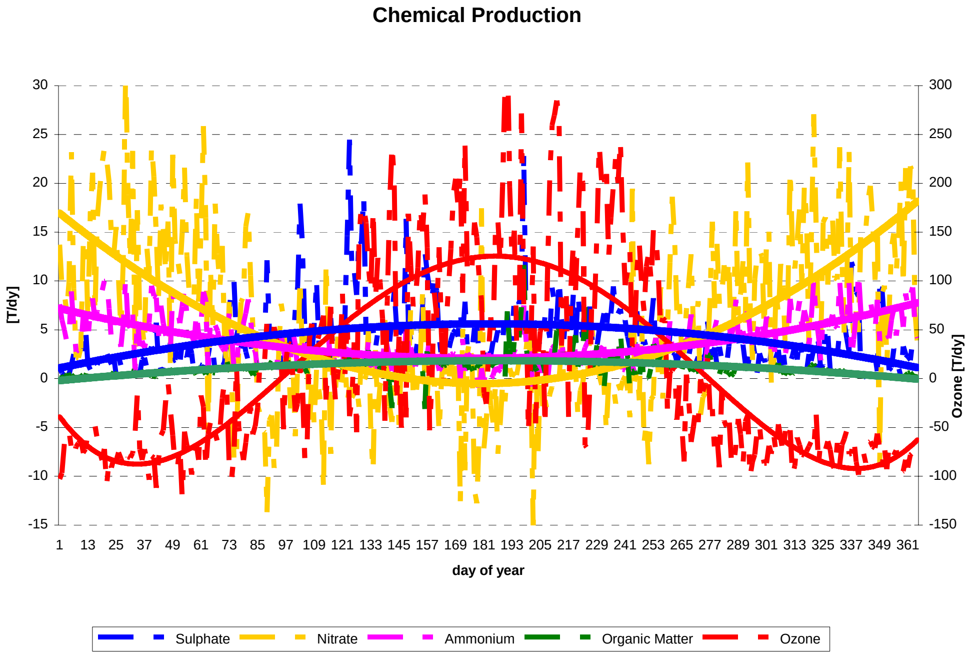

Figure 45 Chemical Transformation rate (positive net Production, negative net Destruction) of secondary inorganic aerosol components [tons/day] (left axis) compared to ozone chemical transformation rate (right axis). Red dashed line: ozone, blue dashed line: sulphate, yellow dashed line: nitrate; pink dashed line: ammonium. Continuous lines of corresponding colours indicate moving averages.

As expected, the yearly cycle is evident. Comparing this seasonal behaviour with the secondary inorganic and organic aerosol components' chemical production and destruction, only sulphate (blue line; unit scale at the left axis in tons/day) shows a somewhat similar behaviour as ozone. Highest production can be found during summer and lowest production during winter. More interestingly, particulate nitrate ions are net-produced chemically during winter and net-removed chemically during summer. The mean production rate during winter is an order of magnitude higher than the mean destruction rate of nitrate during summer. Nevertheless, nitrate chemical behaviour is anti-cyclic with respect to sulphate ions production rate. Ammonium production/destruction seasonal behaviour follows the nitrate behaviour: higher production rate during winter, lower production rate during summer. There is no net destruction during summer. Organic matter, again, shows a dependency on temperature with higher production during summer and lower production during winter. The order of magnitude in the control volume over Berlin urbanised area of the secondary organic aerosol components' chemical production rate is much smaller than the inorganic PM production/destruction rate in RCG.

5.4.1 Primary Aerosols

Primary aerosol components in RCG are related to a major fraction to traffic and resuspension for vehicle induced turbulence at street level bringing the abrasion of tyres and breaks into the atmosphere again. This holds especially for elemental and organic primary carbons. RCG distinguishes primary carbons and minerals. These non-carbon primary particles are attributed in the emission module to a considerable extent to constructing processes, industries, resuspension of mineral dust induced by surface winds and to other not yet known sources from the anthropogenicly modified environments like cities or agricultural activities (ploughing etc). On the other hand, wind-blown-dust is considered separately in RCG.

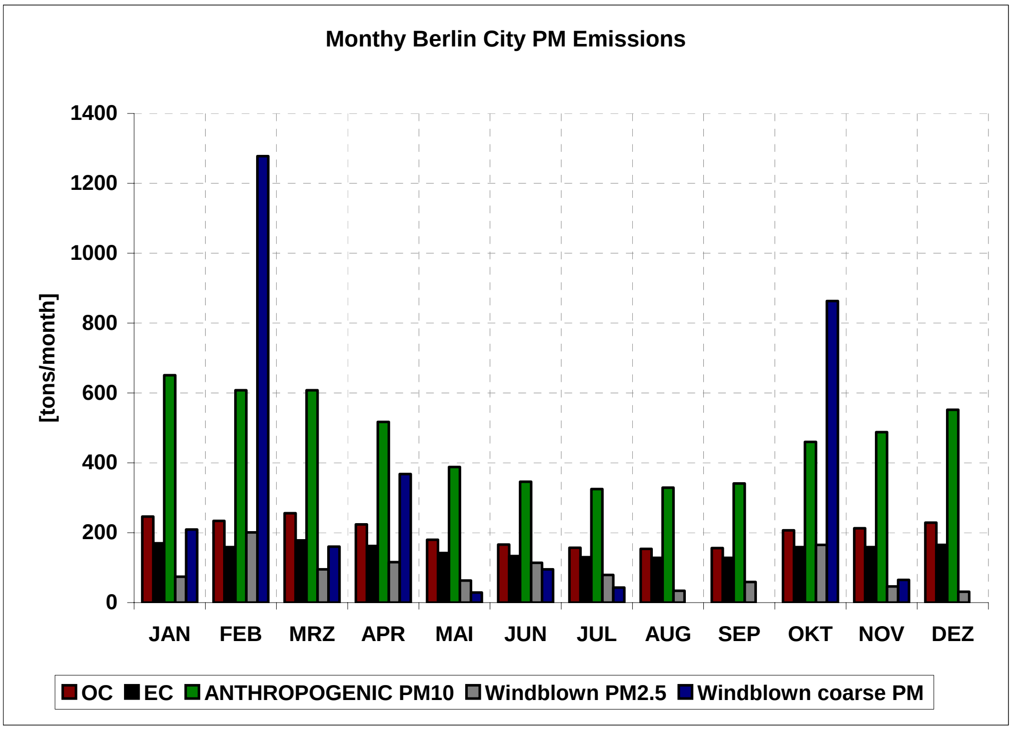

Figure 46 Monthly OC (brown bars), EC (black), anthropogenic total PM10, wind-blown-dust in the fine fraction below 2.5 µm (grew) and wind-blown-dust in the coarse fraction above 2.5 µm annual emissions in Berlin [tons/month]

Figure 46 shows the monthly emission strength of organic primary carbons, of elemental carbons and of anthropogenic particles comparing these components with the simulated coarse and fine wind blown dust emissions. RCG uses the Loosmore et al. (2000) approach to generate dust particles. While Loosmore et al. (2000) gave indications of dust contributions from wind induced resuspension starting from experiments done in the US these indications may to have been reconsidered in a European and especially urban environment. Figure 46 shows that wind-blown dust emissions in the city of Berlin, simulated by the Chemistry-Transport-Model RCG, are very important. This becomes also evident considering the budget analysis. In RCG, wind blown dust plays an important role also in the flow characteristics and thus in the contribution of Berlin related primary PM to the surrounding. Nevertheless, also the opposite holds considering the high importance of horizontal transport in the mass budget analysis over the year, over the different wind directions and over the seasons. PM10 simulations always underestimate urban observations, although secondary organic and inorganic aerosol components are calculated within an uncertainty of approximately 30%. The HoVerT campaign even has shown an overestimation of EC due to a too tight relationship of this species to the NOx emissions. All this very strongly indicates a not yet captured source of aerosols which contributes strongly to the total PM10 mass. RCG tried to overcome this lack of knowledge by introducing the species fine and coarse mode wind blown dust. Maybe these species should be named in a different manner making the uncertainty in the treated species more relevant.

Mossetti et al. (2005) applied the Chemical Mass Balance receptor model of the US-EPA to PM10 data obtained during a field study performed in the Milan urban area, including daily average concentrations, elemental carbon and ion concentrations. Four main source groups were identified: road traffic, with a 56% contribution, secondary particulate with 26%, soil dust (15%), and industrial emissions (3%). A more detailed treatment of the traffic source showed the important contributions of diesel exhaust and tyre and brake wear to ambient PM10 concentrations. Other studies, especially in southern metropolitan areas as Athens, attribute a somewhat higher contribution of dust to the emission budget in cities. Observed concentrations can be apportioned to wind blown dust up to 70-80% during special meteorological conditions related to Saharan wind storms (Rodriguez et al., 2001, Goudie et al., 2001), and these contributions may be also important on an average monthly emission inventory. Vautard et al. (2005), however, emphasised the importance of wind-induced resuspension of mineral particles and in general, that some important emission sources are still not captured in Aerosol-Chemistry-Transport-Models in general.

Summarising the findings above we feel comfortable with the conclusion that primary PM particles inside RCG and inside the chosen control volume over Berlin are to a high extent emission-driven. The considerable part of transported primary material toward the city has a negative budget if summed up with the primary material which leaves the Berlin area. Thus, local production - although in absolute magnitude less than transport- is determining for explaining the seasonal and daily primary PM10 components in Berlin. Scavenging processes are related to precipitation. A meteorological analysis has shown that Berlin experiences an annual rain sum of approx. 700 mm. Convective precipitation is more frequent during summer, stratiform precipitation during winter and thus also the deposition field is temporarily bound to the precipitation variation. Dry deposition of coarse particles is driven mainly be the settlement velocity. This removal process is important only for coarse PM (by ca. 30%), the other primary PM components are locally removed only by wet deposition.

5.4.2 Secondary inorganic Aerosols

Chemical production and loss in the Berlin control volume of sulphate ions is shown in Figure 47.

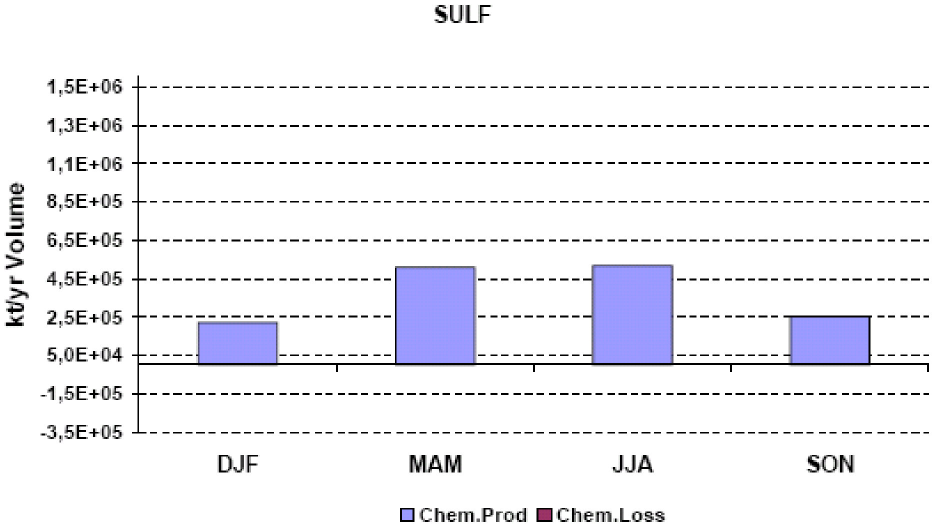

Figure 47 Seasonal chemical transformation rate (production: positive; destruction: negative) for sulphate ions in the control volume [k Tons / season]

As already mentioned sulphate chemical production is closely related to OH-availability and thus to temperature fields. Therefore it has a rather high correlation coefficient with Ozone production. Summer is the most active sulphate building season, winter is the weakest sulphate building season. The ability of undergoing a chemical bound with NH_4 is driven by the availability of this latter; but it does not determine the stability of SO_4. The precursor SO_2 is oxidised in clouds by H_2O_2 and O_3 into SO_4 and in the gas phase by the OH radical. Thus, the relationship between ozone-excess during summer and sulphate production during the same season is high in the chemical transport model RCG. Removal processes, again, are only wet and dry deposition where wet deposition is much more efficient than absorption on the ground. This process, again, is closely related to meteorology.

Sulphate particles pass into cloudy areas, take up water rapidly and grow to a size of cloud droplets (3 – 100 µm). The same particles leave the supersaturated cloudy region and loose water shrinking into accumulation mode aerosols (0.1 – 1 µm). Sulphate residence time considerations suggest that particles undergo this cycle many times before being removed from the atmosphere. They never dry fully unless relative humidity drops under 40% or even lower (Adams et al., 2001). Thus, most sulphate particles lie thermodynamically on the metastable branch of the aerosol.

Nitrate (Figure 48) and ammonium (Figure 49) exhibit a strong seasonality. Sulphate is the negative ion which is more likely to undergo a chemical reaction with ammonium than nitrate. Nitrate is bound to excess ammonium. That means NH_4 must be available in a sufficient amount in order to tie also the negative NO_3 ion. On the other hand, NO_3 has a rather high vapour pressure, i.e. the probability to reconvert into the gas phase is high.

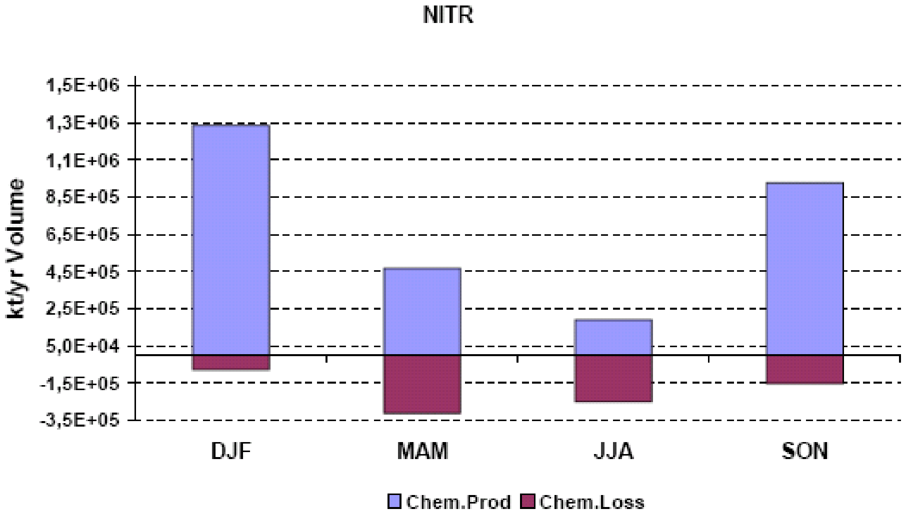

Figure 48 Seasonal chemical transformation rate (production: positive; destruction: negative) for nitrate ions in the control volume [k Tons / season]

This becomes evident considering the seasonal chemical production and removal process in RCG. During winter particulate nitrate chemical production is highest and during summer this production is smallest.

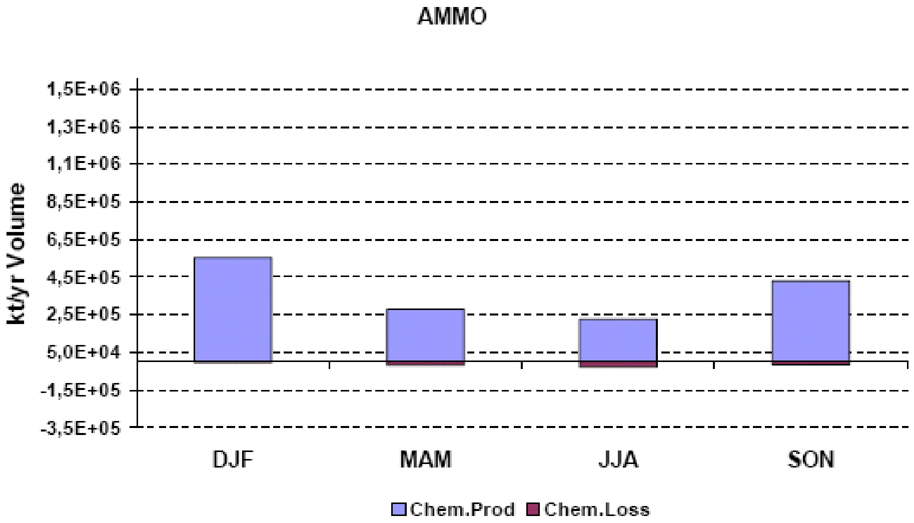

Figure 49 Seasonal chemical transformation rate (production: positive; destruction: negative) for ammonium ions in the control volume [k Tons / season]

RCG uses the thermodynamic equilibrium code ISORROPIA (Nenes et al., 1998) which partitions the total amount of ammonia and nitric acid between the gas and aerosol phases. The module computes the equilibrium composition of an internally mixed aerosol particle consisting of sulphate, nitrate, chloride, ammonium, sodium and water. ISORROPIA calculates the temperature dependence of equilibrium constants with the Van’t Hoff equation. With the assumption of linearity between the species’ enthalpies and temperature the equilibrium constant can be expressed as a function of temperature only:

$$K(T) = K_0 \exp\left[-\frac{\Delta H^0(T_0)}{RT}\left(\frac{T_0}{T}-1\right) - \frac{\Delta c_p{}^0}{R}\left(1+\ln\left(\frac{T_0}{T}\right)-\frac{T_0}{T}\right)\right]$$

where K is the equilibrium constant, K_0 the equilibrium constant at the reference temperature T_0, T is temperature, R is the gas constant, ΔH^0 is the standard enthalpy change of the reaction and $\Delta c^0{}_p$ is the difference in heat capacities between products and reactants at the reference temperature.

Sulphate has a sufficiently low vapour pressure that it can be assumed to reside completely in the aerosol phase. Ammonia and nitric acid, on the other hand, partition themselves between both gas and aerosol phase. At these conditions, nitric acid can exist in the aerosol phase in the form of the nitrate ions, but only when neutralised by ammonium. At low sulphate concentrations the ammonium nitrate aerosol represents about a third of the total ammonia in the system and nearly all of the nitric acid. Ammonium concentration increase with increasing sulphate concentrations until essentially all the ammonia is drawn into the aerosol phase. At this point, because of the lack of free ammonia, additional sulphate tends to force nitrate out of the aerosol phase. As a result of the thermodynamic competition between sulphate and nitrate, the total aerosol mass, dry or wet, is a nonlinear function of the amount of sulphate in the system.

5.4.3 Secondary organic Aerosols

Secondary organics have their origin either in anthropogenic precursors or in biogenic precursors. Anthropogenic precursors are mainly aromatic volatile carbons, alkanes and alkenes coming from burning processes i.e. traffic, heating and industry while biogenic precursors stem mainly from tree resins like α-pinene and limone or generic terpenes. These species are also the only species going into the secondary organic aerosol module (Schell et al., 2001). As organic gases are oxidised in the gas phase by species such as the OH radical, ozone and the nitrate radical, their oxidation products accumulate and some of these products have low volatilities and condense on the available particles in an effort to establish equilibrium between the gas and aerosol phases (Seinfeld et al., 1998). The chemistry module calculates the formation and partitioning of secondary organic aerosol based on (pseudo-)ideal solution thermodynamics. The code considers two cases:

i) initial absorbing mass is existent in the aerosol phase
ii) a threshold has to be exceeded before partitioning (even below saturation) will take place.

The temperature dependence of the saturation concentration is calculated using the Clausius-Clapeyron equation. It is assumed that the condensable vapors also evaporate if the saturation concentration lowers e.g. due to temperature effects. Therefore negative production (= evaporation) is possible.

Biogenic emissions are related to temperature (Simpson et al., 1999) while anthropogenic emissions are related to human activities. Nevertheless, the rather inhomogeneous behaviour of the chemical production and destruction of the secondary organic carbons in the city of Berlin, simulated by RCG, is indicating a strong dependency of the seasons also for anthropogenic emissions. The high vapour pressure of all volatile organic carbons makes the condensed phase highly unstable and temperature dependent. This is also a main problem in measuring secondary organic carbons running the risk of loosing mass on the way from the measuring device to the analyse-laboratory. The accuracy is rather low. The same holds for the simulation of secondary organics. The uncertainty in the biogenic as well as anthropogenic emissions is high, the mechanisms of obtaining stable particulate secondary organic carbons is not yet understood in great detail.

RCG simulates highest chemical production of anthropogenic secondary organic aerosols in the Berlin area during spring (Figure 50).

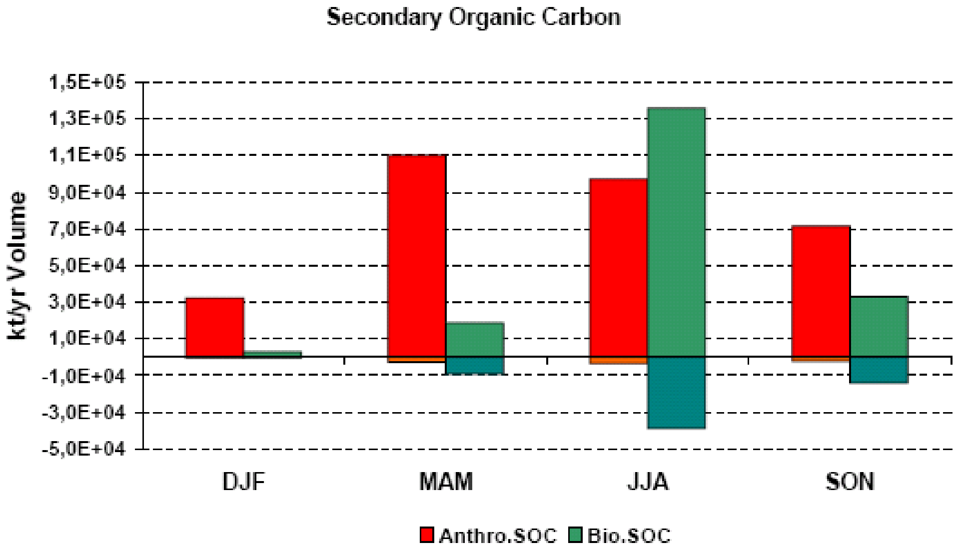

Figure 50 Seasonal chemical transformation rate (production: positive; destruction: negative) for for anthropogenic (red bars) and biogenic (green bars) secondary organic carbons in the control volume [k Tons / season]

There is almost no chemical removal of anthropogenic secondary organic aerosols, i.e. there is a rather stable PM10-part in the anthropogenic origin. This does not hold for biogenic secondary organic aerosols. Maximum chemical production occurs during summer, but there is also a maximum chemical re-conversion into the gas phase of this species. The chemical destruction of biogenic secondary organic aerosol occurs proportionally to the same amount throughout the year with higher negative transformation rate during summer and lower during spring and autumn. Winter shows almost no biogenic secondary organic aerosol activity. The fact that anthropogenic secondary organic aerosols are more stable than biogenic secondary organic aerosols is important in considerations about import/export of pollution from an urbanised area towards a rural area and vice-versa.

The linear correlation coefficient between secondary organic aerosol chemical production and ozone is greater then 0.7 indicating a strong relationship between the two production mechanisms. Transport mechanisms are in disagreement between the two considered species indicating different precursor positions in Berlin, although volatile organic carbons are important precursors for both species. While emissions of terpenes and isoprenes correlate well with the secondary organic aerosol chemical production (0.75 and 0.70, respectively), anthropogenic VOC-emissions show negative correlation coefficients (on average -0.6) except for xylenes (0.42), acetaldehydes (0.65) and olefins (0.64).

On a yearly average, anthropogenic VOC-emissions are two orders of magnitude higher than biogenic VOC-emissions in the Berlin urbanised area. Nevertheless, during the warm season biogenic VOC-emissions constitute up to 15% of total Berlin VOC-emissions.

Ozone chemical production rates show linear relations with the production rate of SOA gaseous precursor aromatics ($r = 0.65$), but there is much less relationship between the chemical production rate of ozone and gaseous SOA-precursor α-pinene ($r = 0.1$).

5.5 HEIGHT DEPENDENCE

In order to analyse the importance of the height where processes take place the mass budget analysis has been subdivided in two different regions: below the mixing height and above the mixing height. RCG uses the dynamical vertical co-ordinate system approach. This means that the vertical layers are not fixed in time but dependent on the mixing height which at the other side has a daily periodicity being higher during day and lower during night. The vertical structure is thus highly variable except for the first surface layer which is constrained to be 20 m high and the upper boundary to be 3000 m high. There are two equidistant layers below the mixing height and two equidistant layers above the mixing height. A minimum depth of the layers between the surface layer and mixing height and between the top layer and the mixing height is maintained in order to avoid numerical integration problems. This set-up makes it rather difficult to make mass budget calculations because the volume is changing during the day. Normalising the mass by the available volume in order to obtain mass densities is also dangerous because of the averaging effect of the individual mass changes due to different processes. For instance, calculating the mass change density due to emissions in the layers below the mixing height and in the layers above the mixing height would lead to wrong conclusions being the layers below the mixing height during summer much broader than during winter. The injected emission mass, at the other side, does not change substantially. The conclusion, that the emission mass change density during summer is lower than during winter is correct, but the underlying process of mixing due to vertical diffusivity is not taken into account. Thus, we decided to give only a qualitative picture of the mass budget changes due to individual processes below and above mixing heights.

There is a second specification needed in this consideration. Only the overall net mass budget due to transport has been considered. That is, the inflow and the outflow of mass due to horizontal advection through the walls of the control volume has been summed up over the integration time. A distinct differentiation between inflowing mass contributing to accumulation of mass in the control volume and outflowing mass contribution to loss of mass from the control volume has not been considered. The net difference of the inflowing and outflowing mass gives an indication of how much the city is affected by or responsible for the mass change due to airborne transport of pollutants.

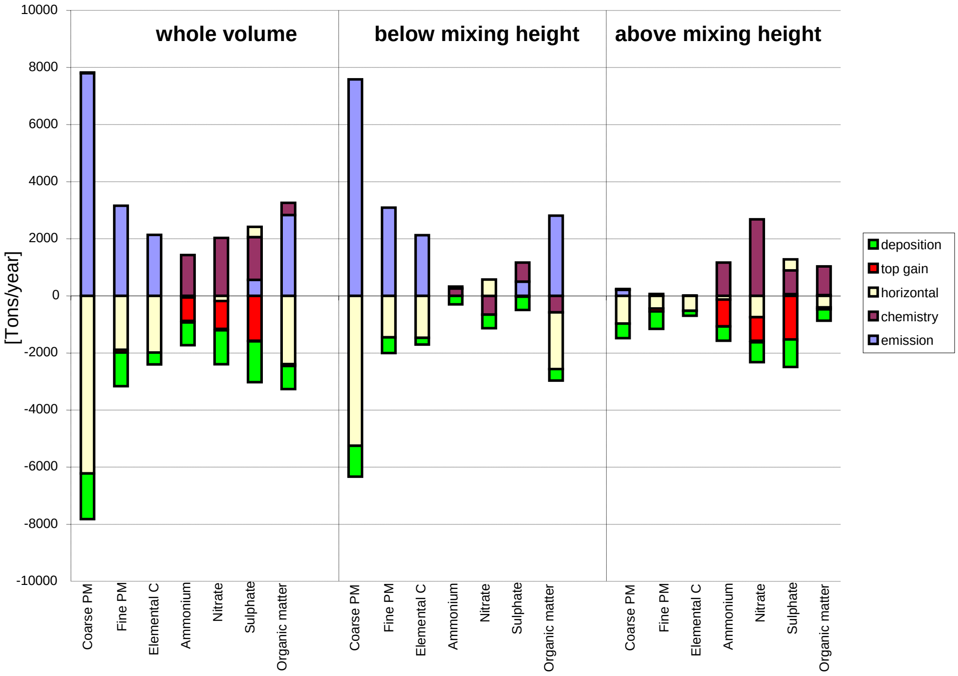

Figure 51 Net contribution to yearly accumulation and loss of primary and secondary PM10 components for the whole volume, for the volume below the mixing height and for the volume above the mixing height. [Tons/year].

Figure 51 gives an overview of the obtained results. The first set of bars at the left of the chart repeats the net contribution of the accumulation and the loss in the control volume due to emission, chemistry horizontal advection, flow through the upper boundary and deposition. The set of bars in the middle of the chart represents the net contribution to the mass change in the control volume below the mixing height and the set of bars at the right of the chart shows the net contribution due to the processes above the mixing height. As mentioned before, the horizontal transport counterbalances the accumulation due to emissions. This holds for all primary aerosol components. OM in this chart represents the total organic material, i.e. primary and secondary organic carbons. Comparing the importance of individual processes below and above the mixing height it becomes evident that the less important becomes emission as an accumulation process the more important becomes chemistry in storing mass in Berlin. Removal is driven below the mixing height mainly by horizontal transport, above the mixing height by vertical transport of mass into the atmosphere above the model domain and by scavenging effects in the wet deposition process. Analysing the aerosol components individually, sulphate is only accumulated in the chemistry module. There is no re-conversion into the gas-phase precursors of the component. Nitrate is built in the chemistry module also above the mixing height. Integration over the whole year shows a net destruction of aerosol nitrate in the boundary layer and a net accumulation in the atmosphere above the boundary layer, i.e. in the residual layer and in the free troposphere. Ammonium particles are net accumulated in the whole volume over the year.

Analysing the deposition process with more attention one can see that the dry deposition is relatively small compared to the wet deposition. This becomes evident if one considers the deposition in the layers above the mixing height to be wet and subtracting it from the total deposition in the control volume.

The net accumulation and loss due to horizontal transport is important only in the boundary layer. That means that the advection is the process which is opposite to the emission. In the layers above the mixing height net airborne export is of the same strength as wet deposition for primary particles. Advection at upper layers is still the strongest process; the flow velocity and the mass transported inside and exported are of the same magnitude leaving the mass budget unchanged due to advection. Secondary particles are net exported almost equally through the lateral as through the upper boundaries. Again, the advection consideration holds only on a net basis, i.e. there is very small accumulation or loss at higher levels due to horizontal transport through the walls. The flow-through character is much too strong as to leave space for a considerable amount of mass being stable at the higher levels.

5.6 INFLOW CHARACTERISTICS: LOCAL PRODUCTION VERSUS LONG RANG TRANSPORT

In order the evaluate the importance of local production versus advected pollution from outside the city domain of Berlin, integral mass ratios related to the emission and chemical production on one side and the net mass change due to advection and diffusion inside the control volume have been calculated.

First, the net transport contribution has been calculated for individual PM components - integrated over the whole year - in order to describe the flow characteristics.

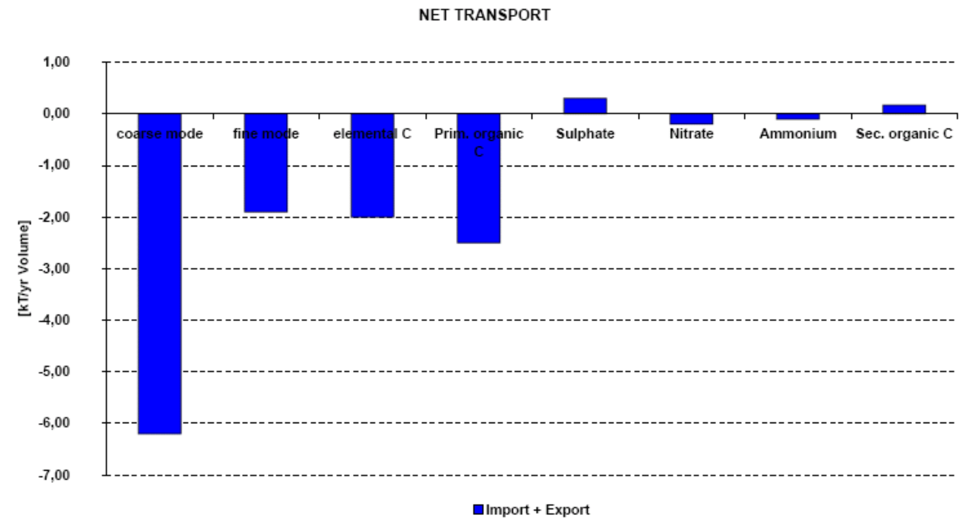

Figure 52 Net difference between inflow toward and outflow from the control volume over Berlin [kT/yr Volume]

Figure 52 shows the integral difference between inflow and outflow in the control volume; i.e. all inflowing mass through the lateral boundaries has been subtracted from all outflowing mass summed over the whole year. Recirculation could not be tracked back in this approach. That means that only net conclusions can be drawn. Nevertheless, the resulting picture shows again the highly different behaviour of primary and secondary PM components. RCG coarse primary aerosol is exported form the city of Berlin toward the surrounding areas. This is understandable considering that in the model there is a rather low natural background of this component. Furthermore, in RCG the emission module attributes a high contribution to the city, especially due to the estimation of wind-blown dust.

Fine primary mineral particles in RCG have their net integral source in the city, as well. The magnitude, however, is lower than for EC and for OC. Wind-blown dust, attributable to the fine fraction, is considerably smaller than to the coarse fraction. The apportionment of fine PM to EC, OC and rest is in line with emission inventories (Builtjes, 2003). Berlin exports a considerable part of EC and OC to the surrounding areas which are produced in the city by local anthropogenic emission sources.

The net transport analysis of the secondary inorganic and organic aerosol components, again, confirms the substantially flow-through characteristic. The net contribution of long-term indicator sulphate is positive, i.e. it is net-imported from outside, while nitrate, which has also a smaller residence time in the atmosphere, is to a small extend exported from the city of Berlin. Secondary organic aerosol components contribute to a very small part to the local accumulation inside the city due to production outside the city. This means, secondary organic aerosol components are built in the countryside and contribute to the PM10 accumulation in the urbanised area of Berlin because of transport.

Myhre et al. (2006) observed that ammonium-nitrate particles play a non-negligible role in the total aerosol composition in industrialised and urbanised regions. On a global scale the NH_4NO_3 particles contribute to a much smaller extent to the PM10-composition either due to a limited availability of ammonia or due to a lack of HNO_3 or NOx. Thus, remarkable gradients between urbanised and rural areas have been observed. This is in accordance with our finding of exporting nitrate ions from Berlin toward the rural. The magnitude, however, is not comparable to the primary contribution of the city to the PM10-burden in the surrounding areas only due to transport. Nevertheless, the net effect of the city in producing secondary PM precursors has to be taken into account in the contribution to non-urban contaminations.

Ammonium exhibits over the year a small export characteristic which can be connected to the nitrate behaviour. Ammonia emission is also attributed to a small part to vehicle exhausts, the emission strength, nevertheless, is much more intensive in the country-side. Again, the ammonium-nitrate bound as the only stable condensed matter form of this PM component is also shown in this transport consideration.

Production terms can be separated from removal terms when Aerosol-Chemistry-Transport-models are used to simulate pollutants concentrations fields. Also the transport characteristics can be analysed separately. A simultaneous consideration of local production via emission and chemistry and a long range transport of mass passing through the control volumes boundaries allows an estimate of the house-made pollution versus non–locally controllable concentration reduction strategies. Chemical destruction, deposition or outflow from Berlin toward Brandenburg has not been taken into account in this consideration.

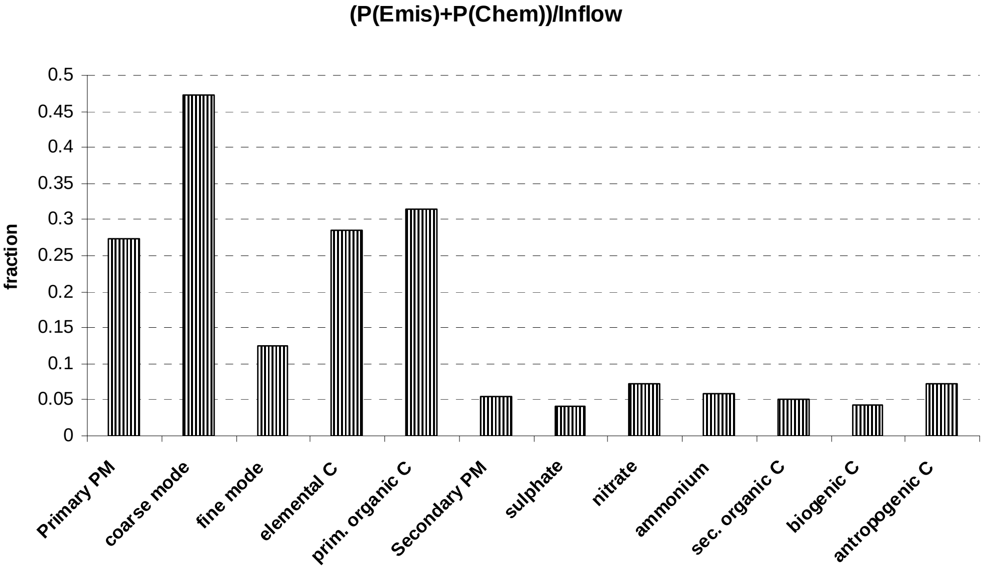

Figure 53 Ratio of local production vs. inflowing mass

Figure 53 shows the ratios of production in Berlin due to emission and due to chemistry and the gross mass inflow indistinctively through the four lateral boundaries around Berlin of primary and secondary PM10-components integrated over one whole year. The fraction (y-axis) indicates the part of local production in relation to imported mass.

Inflow of total primary pollutants is three times stronger than local production. That means considering the control volume over Berlin, primary particles are emitted in Berlin to ca. 24% and come form outside to ca. 76%. Analysing the primary PM10 components separately, this production percentage holds for EC and OC, too. Primary coarse mode aerosol is imported to ca. 66% while primary fine mode PM to ca. 87%. Again, this means that about 34% of coarse mode PM and only about 13% of fine mode particles are related exclusively to Berlin Emissions. The rather high difference between primary coarse and fine PM10 fraction again is explainable considering the apportionment of fine PM to EC, OC and rest and remembering the uncertainty in the coarse mode emission estimates. This lack of knowledge has been filled by the wind-blown-dust assumption. An important point in this assumption, again, is the underestimation of total PM10 and the rather good simulation of the total secondary inorganic and organic PM10 components.

Connecting the local production vs. inflow ratios to the net flow budgets in the control volume (Figure 53 and Figure 52) one finds again the importance of local production of primary aerosols. Summing the primary fine mode particles, the net outflow is about the same order of magnitude as the coarse PM fraction. Considering, at the other hand, the total primary PM production vs. inflow ratio, which is about 2/3 inflow and 1/3 local production, one must conclude that the anthropogenic EC and OC is contributing most to the local production and thus also to the export of these species toward the countryside. The fine mode rest (fine mode PM10) is attributed to emissions which are not EC or OC, i.e. minerals. This fraction again, is of high uncertainty, but other as for coarse PM which is attributable mainly to wind-blown-dust, resuspension, industries and constructing activities in Berlin, this might even be underestimated. Nevertheless, there is a net export toward the Berlin outskirts.

All secondary inorganic and organic aerosol local production are smaller than 1/10 with respect to the inflowing mass. Nevertheless, the city signal of humans' influenced nitrate ions and anthropogenic secondary organics is stronger than the city signals of long range indicator sulphate or biogenic organic carbons. For these latter the ratio of local production versus inflow is about 1/20. Again, combining these figures with the net inflow-outflow consideration (Figure 52) the overall flow-through is evident. There is a net accumulation signal for sulphate and a net loss signal for nitrate. While nitrate has a shorter life-time and thus also a shorter production time local and temporal accumulation is highly plausible during meteorologically stable winter periods. Stable winter times often are related to weak south-east-winds and high insolation in Berlin, which favours inflow of long-lasting sulphate ions coming from south-eastern regions. Stable local situations over the city of Berlin also contribute to a less pronounced outflow of primary particles, i.e. vertical mixing is inhibited. All these factors contribute to the strong accumulation of PM10 concentrations. This is in line with observations in Berlin (see e.g. Lenschow et al., 2001).

5.7 ION BUDGET

Adams et al. (1999) defined degree of neutralization (DON) as ($NH_4/2SO_4$) which equals 1 when sulphuric acid is totally neutralized by ammonia. Analogous to this definition, they defined NP (nitrate production) as the excess ammonia which is in the aerosols when all sulphuric acid is neutralized. NP is zero when all sulphuric acid is neutralized by ammonia (DON=1) and NP is larger than zero when there is excess ammonia in the aerosols. This excess ammonia is then associated with aerosol nitrate. They applied these methods to global aerosol simulations and showed that NP is larger than zero in the winter close to the ground in the northern hemisphere. In summer NP is rarely larger than zero anywhere meaning that the aerosols are rarely neutralized in summer. To interpret these results, they defined a nitrate Production Potential (NPP) and assumed that all gaseous ammonia can be used to formed nitrate. Areas with NPP larger than zero are areas where fine mode nitrate can be formed given that the temperature is low enough. Whenever NPP is smaller than zero, fine mode nitrate can not be formed even if the temperature is very low. The seasonal variation is significant and maximum in July in the southern hemisphere is partly due to very low sulphate (Adams et al., 1999).

We applied the Adams et al. (1999) method to the mass budget analysis in Berlin considering the production rate of secondary inorganic aerosols with ISORROPIA. Acidification of the Berlin aerosol has been evaluated considering the mol budget from the Berlin domain by summing positive and negative ions produced during the aerosol chemistry processes of the secondary inorganic aerosol components for the whole simulation time period and for the single seasons. Sulphate ions are counted twice or once depending on the preferred neutralisation process with ammonium ions and accounting for the re-building processes of ammonium-sulphate. ISORROPIA incorporates also chloride ions which are included in the mol-budget analysis.

Throughout the whole year the inorganic aerosol production in Berlin is in equilibrium between positive and negative ions when sulphate components are counted 1.6 times. Concentrations of $NH4^+$ and SO_4^{2-} are combined in the molecular ratio 3/2 to form two molecules of (NH4)1.6SO4 until all ammonia and sulphate is bound. This is in agreement with the equilibrium formulation, but differs, however, considerably during different seasons. Winter is characterised by predominance of ammonium ions giving an overall negative molar ion production rate term. Ammonium bisulphate is the favourite state during winter which holds also for autumn in Berlin. More acidic aerosol is the favourite state during the cold season. Summer is in an almost equilibrium state, while spring exhibits a preference for ammonium sulphate production.

Chemical inorganic aerosol production is dominated by nitrate ions throughout the whole year which contribute more than 60% of the total molar mass. Most evidently, winter shows a nitrate contribution of more than 70%, while sulphate ions contribute only approximately 8 % to the total negative inorganic ions molar mass production. Summer exhibits an opposite sign: sulphate ions production is about 60%, while nitrate molar mass production is about 33%. Autumn is simulated in a rather similar manner like winter, while spring is characterised by a gross 36% of inorganic aerosol ions coming from sulphate and ca. 50% coming from nitrate. ISORROPIA incorporates also chloride ions in the inorganic aerosol production. The net contribution of these ions to the particle production is rather high, ranging from ca. 8% during summer to approximately 20% during winter.

Seinfeld et al. (1998) attribute some importance to NaCl to urban aerosol including the reaction of NaCl with HNO_3. Measurements, at the other hand, have shown that the total contribution to the average PM10-composition of Cl is rather low, not exciding ca. 2% of the total PM10-mass (Wieprecht et al., 2004).

The sea-salt aerosol emissions (Na^+, Cl^-) are parameterized according to Gong et al. (1997) as a function of size and wind speed. This may give a strong over prediction of chloride emissions in Berlin which consequently brings an erroneous chloride contribution to the inorganic aerosol budget.

Kerminen et al. (2001) observed that the measured cation-to-anion ratios vary with particle size and sampling site so that in urban sampling sites aerosol was either neutral or alkaline throughout the size spectrum but in background areas the accumulation mode particles were acidic. This is in agreement with our findings of alkaline aerosols in Berlin urban area over the whole year.

5.8 UNCERTAINTIES

The uncertainties in Aerosol – Chemistry – Transport – Models are manifold. They arise mainly from uncertainties in emission data-bases, but also from not-appropriate resolution of integration domains, incomplete description of chemical and physical processes, like the treatment of wind-blown-dust-emissions or wet processes, from rough description of land-use-classes, and from a variety of other approximations. Often the only model evaluation is performed comparing grid-cell representative model outputs with station-representative measurements. As an additional point the uncertainty in the measurements has to be considered when validating models simulations. (e.g. Schaap et al., 2004). Process oriented validation of model calculations is done only considering time-slopes or linear correlation coefficients inspection. This is most often also the only possibility to validate model performances.

Process rates analyses and as a consequence mass budget analyses interpret the contribution of the individual processes to the final concentration fields. That means that neither the uncertainties in the input-data nor in the process-description can be avoided. Furthermore, the processes themselves are most often nonlinear. Thus, the exploited additive property of integrated process rates represents an additional approximation. That is, the model analysis via process inspection shows how the model simulates the individual species concentrations and reveals processes that are important.

As a preliminary starting point the model has to be evaluated positively. That means conventional model evaluation must provide confidence in the model’s prediction. Calculated concentrations have to agree with observations, mutual species ratios have to be correct and time-dependent and thus process-oriented features have to be reproduced in a satisfactory manner. However, there are no “observations of processes” which can be compared to simulated processes.

The uncertainties in the processes related numerical values are high. Again, numerical values for emission accumulation depend only on the input emission data, for instance. The numerical values for transported mass toward a considered volume depend on the simulated concentrations outside the volume, on the wind speed and direction and on the simulated concentration inside the volume. And chemical production and destruction depend on the mixing ratios of the participating species, on meteorological variables as temperature, humidity and radiation, on transport and on local emissions. Furthermore, the completeness of the chemistry description is assumed to be given.

Moreover, the budget analysis integrates contributions from individual processes over long time-periods. Thus, if there is a systematic even small error in the process description the final results will amplify this error according to the integration period. Mutual elimination of errors, which can happen in considering only the final concentration field, is not possible with the mass budget analysis approach. At the other hand, this is also the desired effect in order to reveal model's shortcomings.

Throughout this manuscript mutual importance of individual processes has been emphasised. This has also been done in order to minimise the uncertainty. Relative statements such as stressing the differences between different aerosol components in one individual process augment the confidence in the finding and may be more interesting than the absolute value of the process related accumulation or loss.

Thus we feel to give some indications how to connect uncertainties to statements:

1. Absolute values are affected by a very high degree of uncertainty. Too many variables, starting form the choice of the control volume and its freedom in deciding what is mainly rural and what is mainly urban and finishing with the input-data-uncertainties themselves make these figures only qualitative.
2. Inter-comparison of processes: Relative values and relative percentages have to be interpreted correctly. For instance, when we state that transport is predominant in accumulating and removing mass from the city of Berlin and this makes the other processes negligible, we must consider the net contribution, too. Then, the transport is still a very important process, but becomes the same order of magnitude as the other processes. The uncertainty attributed to the absolute statement may be enormous – considered, whoever, as a relative statement, the uncertainty is much less and reflects the uncertainties in the input-data again.

3. Smaller integration periods diminish the “accumulation effect of systematic errors”. Moreover, the inter-comparison of individual process contributions depending on different time-slices of the year makes a statement more reliable.
4. Individual process inspection for different aerosol components, considered during different seasons is the most reliable statement.

Also, processes may be more or less “certain”. Transport, for instance, comprises advection as well as diffusion. Thus, horizontal transport is more reliable than vertical transport. Again, the model set-up itself with its variable vertical layers makes a vertical analysis more complex and thus more uncertain than considerations about the whole considered box.

Chemistry is higher approximated for organic carbons than for inorganic aerosol components. Thus, the secondary inorganic aerosol building and destroying processes are more reliable than the same considerations about secondary organic aerosols.

Deposition of aerosols is mainly driven by wet scavenging processes. These are tightly dependent on the correct simulation of cloud, cloud-water and air moisture. Furthermore, the species specific scavenging coefficients should take into account the time-dependent hydrophobic and hydrophilic properties. These are only known to a very uncertain point.

As a conclusion, we recommend to give more importance to relative mutual and inter-seasonal statements than to absolute values.

5.9 DISCUSSION: RCG BUDGET ANALYSIS vs. OBSERVATIONS

Lenschow et al. (2001) gave a comprehensive source/receptor overview of the Berlin aerosol concentrations analysing observations over several years. They compared measurements obtained at different stations contemporaneously and with regard to the measurement sites location also with respect to the wind direction and speed. The main idea was that, neglecting the time needed for particles to flow over the city domain of Berlin, the concentrations measured at the upwind side of the city subtracted from the concentrations measured at the downwind side give a quantitative measure of the urban concentration contribution. The same approach was applied in considering concentrations measured at traffic related sites and concentrations measured at background sites. Again, differences explain the origin of the pollutants, or, at least, the attribution to the city of Berlin or the non-attribution to the same.

Lenschow et al. (2001) state that:

- the difference of urban background and regional background data shows that about 50% of the urban background pollution is caused by emissions specific to the city. Half of this contribution is due to traffic emissions and 15% to domestic heating and households.
- if the regional background concentration is attributed to all sources outside the agglomeration, about 55% of the urban background pollution is caused by long range transport from outside the region and by natural sources such as pollen and wind-borne soil.
- the average concentrations of Suspended Particulate Matter are much higher with south-easterly than with westerly winds. This is also valid for the PM10 concentration in the regional background. Therefore, it has to be taken into account that sources lying south to south-east of Berlin have high impact on PM10-concentrations in the town.
- Traffic is the most important group of sources (50%) causing high PM10 pollution in a busy street. About one quarter of the

traffic influence is exhaust emissions and tyre abrasion in the individual street, a further quarter is resuspension of soil particles in the individual street and the remaining half is traffic influence on the city background - containing also the regional background.

The HoVerT-measurements have been analysed according to differences between “upper air” concentrations, rural background concentrations, urban background concentrations and hot-spot concentrations distinguishing primary from secondary inorganic and to some extend also organic aerosol components. They essentially reveal the same findings as already asserted by Lenschow et al. (2001).

RCG-modelled process rates budget considerations over the whole HoVerT-campaign period, at the other side, have contributed to the Berlin air pollution description and explanation referring to an Aerosol transport model. The simulated processes and their mutual comparison have shown

1) Coarse primary aerosol accumulation in Berlin is to an important extent due to wind-blown dust. This process has not been investigated until now with the attention it should receive.
2) difference of locally emitted and import-export is positive for primaries and negative for secondary aerosols
3) the ratio between locally produced and from the surrounding areas imported mass of primary coarse and fine PM is. 0.3
4) EC and primary OC, which in RCG are treated as a part of primary PM, show high accumulation tendency and low dispersion tendency in the city.
5) Secondary inorganic aerosols are imported: but
6) Sulphate is produced outside and imported to the city although there are local emissions of sulphate in the city which contribute to the accumulation inside the city.
7) Nitrate behaves differently in the city than other secondary inorganic aerosols. Its main precursors are produced in the urban agglomeration and the reaction time to produce particulate nitrate is not as long as that of sulphate. Therefore, secondary inorganic aerosols are transported from

outside toward the city, but the local possibility to limit also secondary inorganics is not negligable.

8) Secondary organic aerosols are imported into the city