2 AEROSOL CHARACTERISTICS IN BERLIN

2.1 AEROSOL FORMATION

Particles in the atmosphere which are dispersed in air may consist of a single continuous unit of solid or liquid containing many molecules held together by intermolecular forces and are primarily larger than molecular dimensions (> 0.001 µm). Aerosol particles may also be considered to consist of two or more such unit structures held together by inter-particle adhesive forces such that it behaves as a single unit in suspension or upon deposit (Seinfeld et al., 1998).

The particles in the Aitken mode (< 0.1 µm in diameter) are produced mainly by reactions between gases. A small proportion is emitted directly in the atmosphere. The products of these reactions have a low vapour pressure, as a result of which homogenous or heterogeneous condensation occurs. During homogenous condensation a gas condenses from itself, unlike heterogeneous condensation where a gas condenses onto an existing particle. The Aitken particles can coagulate with other Aitken particles or with bigger aerosols to thus form bigger particles. Coagulation is the most important removal mechanism for Aitken particles and the most important source of particles in the accumulation mode. In addition to coagulation of or with Aitken particles, heterogeneous condensation plays a part in the formation and growth of particles in the accumulation mode. Particles may also coagulate with one another in the accumulation mode. Particles from the accumulation mode are least effectively removed from the atmosphere. Wet deposition plays a big part in the removal of these particles. Dry deposition and sedimentation are less important for the removal of particles in the accumulation mode.

Aerosols from the coarse mode (> 2.5 µm) are largely emitted directly from the earth's surface. These are primary aerosols. Wind erosion is the most important source. Coarse particles consist mainly of quartz and minerals and are reasonably chemically inert. These big particles are mainly removed from the atmosphere by sedimentation.

Sedimentation is the removal of aerosols under gravity. An aerosol may be transported over great distances through the atmosphere before it is removed. During its residence in the atmosphere the composition of an aerosol may be

changed by chemical reactions, condensation and evaporation or by interaction with clouds.

Reactions between gases in the atmosphere cause the formation and growth of secondary aerosols. An important source of aerosols is the neutralisation of (gaseous) sulphuric acid and nitric acid by ammonia. In particular ammonium (bi) sulphate and ammonium nitrate aerosols are formed. The concentrations and the phase of the aerosols are dependent on the concentrations of the reactants, the relative humidity and the temperature.

Sulphuric acid in the atmosphere is formed by the oxidation of sulphur dioxide. The most important oxidation agent in the gas phase is the hydroxyl radical. The net reaction equation is:

$$OH + SO_2 + O_2 + H_2O \rightarrow H_2SO_4 + HO_2 \,.$$
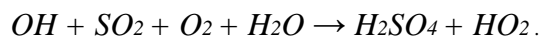
The first step is the reaction of OH with sulphur dioxide. This is also the rate-determining step in the reaction mechanism:

$$OH + SO_2 + M \rightarrow HOSO_2 + M$$
$$HOSO_2 + O_2 \rightarrow HO_2 \rightarrow + SO_3$$
$$SO_3 \rightarrow + H_2O \rightarrow H_2SO_4$$
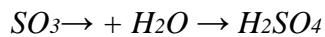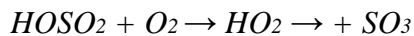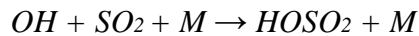
where M represents a non-reactive species.

Sulphuric acid has a very low vapour tension as a result of which the concentration of sulphuric acid in the gas phase is very low. The sulphuric acid formed will condense directly or react with a base. Roughly the entire oxidised sulphur dioxide will become aerosol sulphate. Except in the gas phase sulphur dioxide can also be oxidised in clouds. Sulphuric acid is very hygroscopic. Sulphur dioxide then dissolves in cloud droplets. In the droplet sulphur dioxide reacts with hydrogen peroxide or ozone. Catalysed by metals sulphur dioxide can also be oxidised by oxygen into sulphate (Restad et al., 1998). When air flows through clouds the composition of this air will then be modified.

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$$
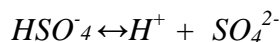
Nitric acid in the atmosphere acts as a sink for nitrogen oxides (NO + NO_2 = NOx). Nitric acid may be formed from gas-gas reactions and from

heterogeneous reactions. In addition nitric acid is also formed by reactions of NO_3 with organic hydrocarbons.

By day the reaction of NO_2 with OH is the most important removal mechanism for NOx and hence the most important source of nitric acid:

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

Nitric acid reacts with OH to form water and NO_2:

$$HNO_3 + OH \rightarrow H_2O + NO_2$$
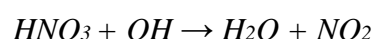
Part of the nitric acid formed will be converted by photolysis back into NO_2 and OH:

$$HNO_3 + h\nu \rightarrow NO_2 + OH$$
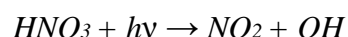
The photolysis rate in the troposphere is so small that the majority of the nitric acid is removed by dry and wet deposition (Dentener and Crutzen, 1993). Also the reaction rate is lower than the removal rate of nitric acid by dry and wet deposition. At night these reactions are not significant because they are dependent on photolysis. As at night the rapid photolysis of NO_3 also stops, the formation of this radical becomes important. NO_3 is in equilibrium with N_2O_5. This equilibrium is very temperature-dependent. At low temperatures the equilibrium is on the side of N_2O_5. NO_3 may react with aldehydes and substituted benzenes (Warneck et al., 1988). Nitric acid is formed by this.

In most cases the reactions of NO_3 during the night cannot explain the short atmosphere life time of NO_3 measured (Dentener and Crutzen, 1993). Platt et al. (1984) observed that the short life time of NO_3 is correlated with relative humidity higher than 50%. This indicates that reactions of NO_3 or N_2O_5 with water may be important. N_2O_5 can react with water vapour:

$$N_2O_5 + H_2O\ (g) \rightarrow 2\ HNO_3$$
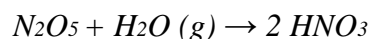
Nitric acid in the atmosphere may react with ammonium hydroxide to form ammonium nitrate. This is an equilibrium reaction. Whether ammonium

nitrate is formed, and if so to what extent, depends among other things on the sulphate concentration.

Carbonaceous particles consist of two major components – black carbon (referred also to as elemental carbon) and organic material. Elemental carbon can be produced only in combustion and is therefore exclusively primary, while organic carbons can either be emitted from sources or produced from atmospheric reactions involving gaseous organic precursors. Black carbon is the most abundant light-absorbing aerosol in the atmosphere. Both forms of carbonaceous particles have been shown to be carcinogenic in animals and mutagenic in in-vitro bioassays, especially organic matter if containing polycyclic aromatic hydrocarbons (PAHs) (WHO, 2000)

Secondary organic aerosol (SOA) is formed in the atmosphere when the oxidation of gas phase organic compounds leads to the formation of low-volatility reaction products, that partition into the particle phase. SOA can comprise a major part of ambient aerosols with various gaseous biogenic and anthropogenic precursors. The chemistry of these precursors in the atmosphere is complex and apart from the initial reaction steps not well understood. Reactions with hydroxyl radical, ozone, nitric oxides and light form products that nucleate and/or condensate to aerosols. The organic aerosol compound is produced in the gas phase during the reaction of parent organic gases. Then, the organic compound partitions between the gas and particulate phases, forming secondary organic aerosol. The organic compound gas-phase production depends upon the gas-phase chemistry of the organic aerosol precursor, the various compounds present in both phases.

Distinguishing between primary and secondary components of measured particulate organic matter is difficult. There is still a lack of direct chemical analysis method. Thus, indirect methods have been developed including the use of tracer compounds for either the primary or the secondary organic carbons (OC). Elemental carbon (EC), for instance, has often been used as a tracer of primary OC (Turpin et al., 1991). The main hypothesis is that EC and OC have both the same sources and thus there is a representative ratio OC/EC for the primary aerosol. If the measured OC/EC – ratio threshold is exceeded then the additional organic carbon can be considered to be secondary. The main shortcoming of this approach is that carbonaceous emission rates depend on the

source and therefore the primary OC/EC – ratio is influenced by meteorology, diurnal and seasonal fluctuations in emissions and anthropogenic behaviours. On average, primary OC dominates, but secondary OC depends strongly on photochemical activity and can exceed the primary OC concentrations during peak episodes.

Primary carbonaceous particles are emitted by combustion (meat cooking, fireplaces, forest fires etc.), chemical commercial products, fossil fuels (Diesel, non-catalyst and catalyst-equipped automobiles) and biogenic sources (plant leaves via leaf wax) (Rogge et al., 1996, Simoneit et al., 1990).

2.2 THE AIR OVER BERLIN: THE HOVERT-PROJECT

2.2.1 General Introduction

Berlin air has been analysed in different measurement campaigns since more than 30 years. However, during this time period the Berlin air has changed significantly, due to historical events like the re-unification and the therefore changed industrial situation in the former German Democratic Republic, due also to new German, European and global legislation and due to a higher sensibility towards environment (Lenschow et al., 2001). Thus, between September 2001 and September 2002 a one year lasting measurement campaign has been carried out with the special aim at analysing particulate matter with aerodynamic diameter less than 10 μm (PM10) and its components in and around the city of Berlin.

The objective of the HoVerT -study ("Untersuchung von vertikalen und horizontalen Transportprozessen und deren Einfluss auf die bodennahe Belastung durch Ozon und Staub" – "Investigations on vertical and horizontal transport processes and their influence on surface Ozone and aerosol concentrations") was to investigate the effect of vertical exchange and horizontal transports on the concentrations of aerosols over the greater Berlin area. The most important challenge was to improve the knowledge about the contribution of anthropogenic urban sources and of long range transports of anthropogenic and natural constituents of air to local pollution levels. The observation campaign was a joint project in collaboration with the Brandenburg Technical University (BTU) – Cottbus and with the Berlin Senate Department for Urban Development.

A High-Volume PM10 measurement sampler DIGITEL (Wieprecht et al., 2001) has been installed on the Frohnauer Turm at 321 m above ground and at its base (Figure 1). Contemporaneously, aerosols have been measured at several surface stations in and around Berlin. At the tower platform the device has been installed by BTU using a special constructed inlet system via the container roof to provide an undisturbed sampling. Glass fibre filters have been used on daily sampling basis for gravimetric estimation of the total aerosol burden. The samples have been analysed for inorganic main ions (sulphate,

nitrate, chloride, ammonium, sodium, potassium, calcium, magnesium), total organic carbons (TOC), water soluble TOC and selected trace metals.

Figure 1 Measurement sites of the HoVerT-campaign 2001-2002. Red squares indicate traffic sites (Frankfurter A. [MP174] and Beusselstr. [BS]), green triangles city edge stations (Marienfelde [MP27] and Buch [MP77]), the light – green arrow indicates the urban background station (Neukoelln – Nansenstr. [MP42]), the blue sign the tower station at 321 m above ground (Frohnau T. [FT]) and the dark-green arrows indicate the rural background stations (Paulienenaue [PA] and Hasenholz [HH])

During the HoVerT campaign nine additional special observational sites in the Berlin and Brandenburg area (Figure 1) were equipped with dedicated instruments to perform daily measurements of PM10 and its chemical speciation, including inorganic ions, elemental and organic carbon. Two traffic sites were chosen in the centre of Berlin, one urban background site was installed within the urban area (some km south-east of the city centre), two suburban sites were placed at the southern and northern edge of the urbanised area and two rural sites were installed in order to obtain a rural counterpart to the urban samples. Measurement sites were often part of regional or national air quality networks. Measurements started right in September 2001 at the urban and suburban sites MP27 (Marienfelde), MP42 (Nansenstr.), MP77 (Buch.) and MP174 (Frankfurter Allee) and were after several months extended to other

measurement stations (Paulinenaue in January 2002, Hasenholz in February, Beusselstr. in July). OC measurements are available from May 2002 on. Samples from MP27 and MP77 have been analysed depending on the wind direction in order to sample cases with minimal pollutions from the city (for about half of the cases).

Daily samples of atmospheric PM10 fractions have been collected on quartz filters conditioned according to usual regulations. Defined air volumes are sucked through filters and the particles are deposited on the filter material. The sampler has been placed in an air-conditioned container while the cut-off sampling head was placed 1.5 m above the container roof. Thus, the observations were performed at 3.5 m above the surface. The filter change was executed weekly. A single-stage impactor was used to separate particles smaller than 10 μm in aero-dynamic diameter (d_{p50}) from the aerosol-inflow in order to collect only particulate matter < 10 μm on the quartz-filters. The gravimetrical mass concentration determination has been executed under well-defined conditions comparing weights before and after the aerosol exposure. The inflow was limited to 30 m^3/hour of air. Subsequently, filter parts were chemically analysed by means of ion chromatography SYKAM in order to measure main ions as well as by means of thermo-graphimetry to measure EC and OC, following VDI regulation 2564, Blatt 2. In this method, elemental and organic carbon are determined from one and the same filter sample using the sequential thermal desorption properties of OC and EC and applying an Infra-Red-Detection of the developed CO_2. In a first step, the sample is heated gradually in a helium-atmosphere up to 600° Celsius evaporating organic C-compounds, which are then catalytically transformed into CO_2. In a second step, EC is transformed into CO_2 in a 20% O_2 / 80% He atmosphere. Moreover, trace metals (Fe, Cu, Zn, etc.) were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP MS).

2.2.2 Interpretation of observational data set

Highest yearly PM10-values have been measured at the traffic sites (MP174 and BS); the concentrations measured at the city edges (MP27 and MP77) are slightly lower than at the urban background site (MP42), and the lowest values are measured in the rural areas far outside Berlin (PA and HH). Even lower values are revealed at the top of the 321 m high Frohnauer Turm (FT) (Figure 2).

PM10 Annual Mean
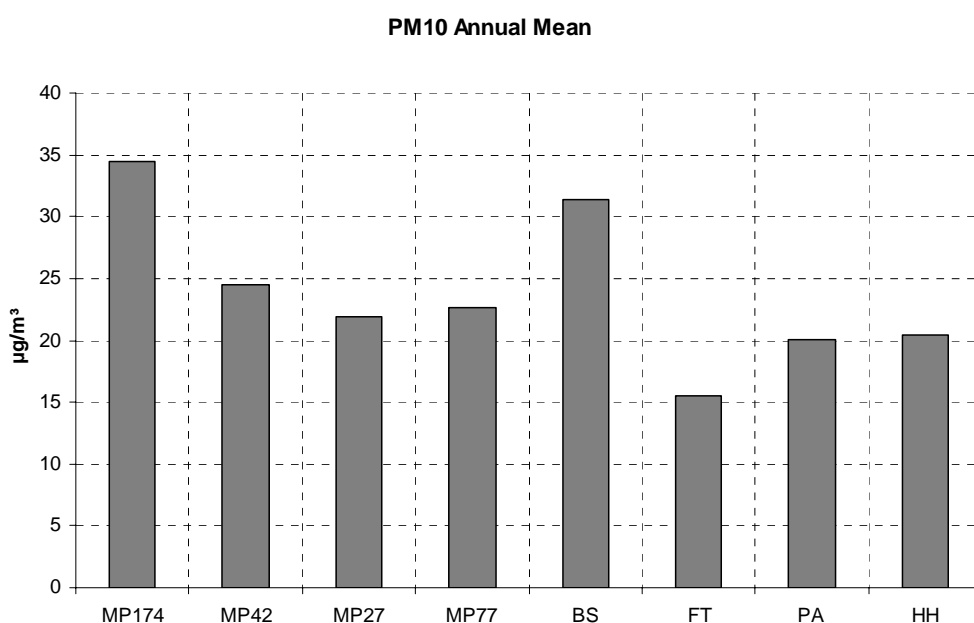
Figure 2 Yearly average PM10 concentrations at MP174 (Frankfurter Allee), MP42 (Nansenstr.), MP27 (Marienfelde), MP77 (Buch), Beusselstr. (BS), FT (Frohnauer Turm – 321m), Pa (Paulinenaue) and HH (Hasenholz)

Total continental PM10 background, measured at 321 m height, is about 15 $\mu g/m^3$, as seen at FT. PA and HH, both ca. 50 km outside the Berlin centre, show some 30% higher values than at the upper station. Considering that these rural stations are only indirectly experiencing the Berlin influence, this 30% higher value with respect to the upper air station is explainable only through local surface sources like minerals from the agricultural activities or organics

from natural origins (leaf debris, pollen etc.). Traffic and other anthropogenic sources are of negligible importance considering the position of the rural monitoring stations. The urban edge stations exhibit 43% higher values than the tower value. As mentioned for the rural stations, again surface influence is the reason for these higher values. Anthropogenic sources are very likely to be the main contributor, being the measurement site in the immediate vicinities of human settlements and activities. The annual mean PM10 concentration measured at the urban background station in Berlin (MP42) is 57% higher than the concentration measured at the FT. A first conclusion is that 57% of the PM10 concentrations are attributable to Berlin sources, i.e. 15 µg/m³ are continental airborne background and some 9 µg/m³ are urban increment. MP42 measures only 10% higher values than MP27 or MP77, the city-edge monitoring sites, and 17% higher values than HH and PA, the rural sites. So, all background surface values lie within 20 and 25 µg/m³, whether they are measured in the countryside or in the middle of the urbanised area of Berlin. This is an indication that aerosols are strongly influenced by surface sources, whether they are anthropogenic or natural. Surface decoupled values, measured at 321 m height, as a result, stem from other sources and must be influenced strongly by long range phenomena. The measurement sites near main traffic roads, at the other hand, show some 112% higher annual PM10 concentrations than the air station FT and some 35% higher values than the urban background station. Again, attributing ca. 24 µg/m³ PM10 concentrations to the urban background, traffic contributes some 8 µg/m³ to the annual PM10 concentration at the road measurement sites. The underlying hypothesis of the considerations is the relatively slow transformation rate of PM10, the concurrent measurements and the relative vicinity of the monitoring sites. Thus, excessive pollutants concentrations can be attributed to the relative monitoring site.

In general, except of the unknown part, the biggest contribution to the total PM10 mass is given by inorganic ions nitrate, sulphate and ammonium (25-42%) (Figure 3). The traffic site exhibits the lowest inorganic ions contribution. There, EC is higher (13%) than at the other stations (5-9%). The rest constitutes a considerable part of 35–43% of the mass closure which is not specified. The main components of this not analysed part is believed to be water, silicon, aluminium and oxygen (Tsyro, 2005). Most strikingly, the absolute value of secondary inorganic aerosol components changes only very

little over different types of monitoring stations, while the percentages augment in rural area compensating the reduced importance of elemental carbons there. That is again a strong indication of the low direct contribution of the urban agglomeration to the annual secondary inorganic aerosol concentration field.

PM10 composition
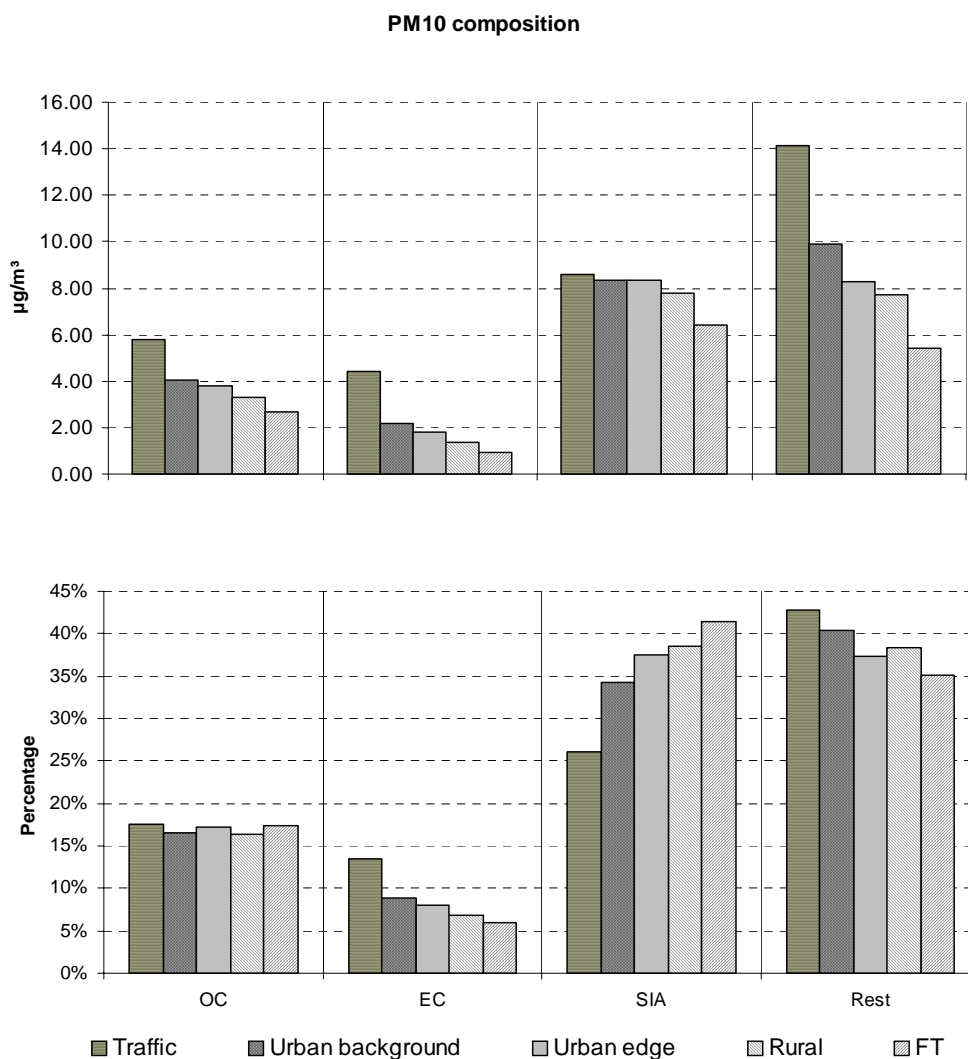
Figure 3 Yearly average PM10 components concentrations at Traffic sites (MP174 and BS), urban background (MP42), urban edge (MP27 and MP77) rural (PA and HH) and FT (tower station at 321 m height) in μg/m³ (upper panel) and in percentages of total mean values (lower panel)

Measured elemental carbon is double near traffic compared to regional and also to urban background values. This shows the importance of traffic and thus of local contribution to annual EC and therefore to annual aerosol concentrations in the city. Compared to the 2 µg/m³ measured EC in the rural and on the upper air station, there are additional 2 µg/m³ PM10 coming exclusively from anthropogenic urban sources. The ratio between elemental and organic carbon gives an interesting picture showing that the primary part of the organic carbons decreases rapidly from the urban toward the rural. Chow et al. (1994) have used an OC/EC ratio exceeding 2.0 to indicate the presence of secondary organic aerosols (SOA). This holds in the HoVerT – dataset only for urban edge, rural and upper air stations, attributing again to urban anthropogenic sources a high degree of responsibility for augmented PM10 concentrations.
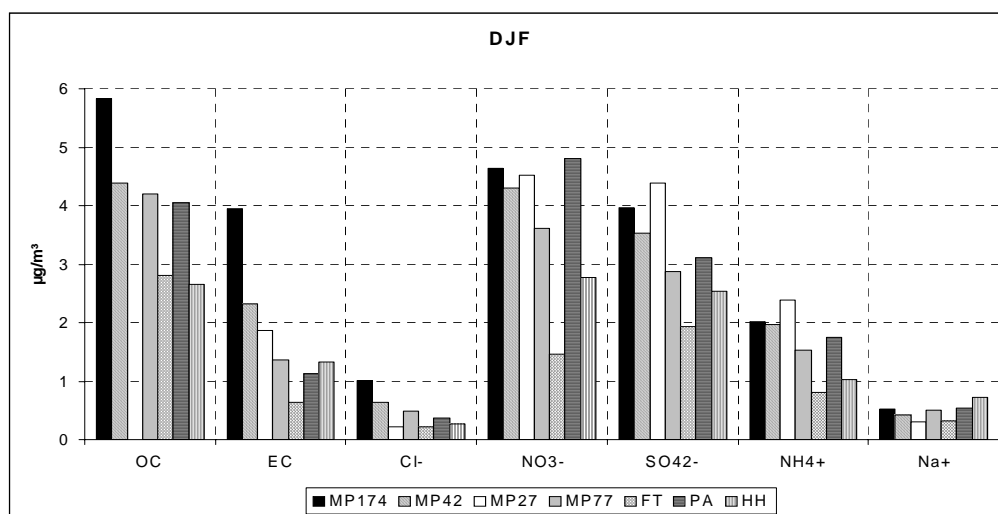
Figure 4 Winter average (December, January, February – DJF) PM10 components concentrations at MP174 (Traffic station), MP42 (urban background.), MP27 (southern city edge), MP77 (northern city edge), FT (tower station), PA (rural) and HH (rural)

Seasonal analysis of PM10 components shows a predominance of inorganic ions during the cold season (Figure 4). This is due to the semi-volatility of nitrate which is more stable at cold temperatures. Also EC and OC

are higher during winter at the urban sites while organic carbons show higher values during summer (Figure 5) at rural sites. Biogenic secondary organic aerosols are responsible for higher values in summer, while wood-burning is most probably an important source of organic carbon accumulation in winter (Fine et al., 2001, 2002, Schauer et al., 2001, Hedberg et al., 2006).
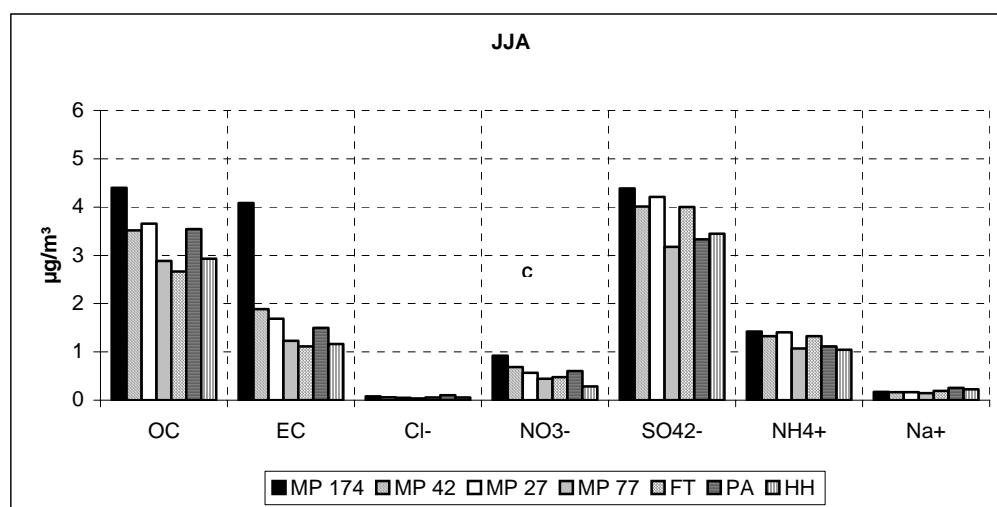

Figure 5 Summer average (June, July, August – JJA) PM10 components concentrations at MP174, MP42, MP27, MP77, FT, Pa and HH

Sulphate ions show no distinct seasonal dependency, ammonium ions follow the seasonality of the negative ions being neutralised by these species. Chloride and sodium ions, although not important in the overall mass budget of the PM10 observations being some order of magnitude smaller than the other components, are much higher during the cold season than during summer. This is a strong indication of sea-salt which comes mainly with strong winds from the North-Sea during the winter and less during summer.

The OC/EC-ratios for the warm as well as for the cold season shows again a strong primary part for the traffic related sites (1.4 during summer and 1.3 during winter). The urban background shows an increased secondary organic influence during summer (OC/EC=2.1), while the winter is still predominated by primary organic carbons (OC/EC = 1.8). The city edges and the rural regions exhibit a more pronounced secondary part during summer than during winter. FT OC and EC measurements exhibit an interesting behaviour:

EC is smaller during winter (0.8 µg/m³) than during summer (1.1 µg/m³), OC is almost stable throughout the year (2.4 µg/m³ in winter and 2.9 µg/m³ in summer). This is explainable by considering the mixing properties of the atmosphere. While summer exhibits more vertical mixing than winter, EC is more likely to arrive at 300 m height at summer than during winter. This holds also for the primary part of OC. The secondary part is distributed more stably throughout the lower atmosphere than the primary part. Thus, the secondary organic carbons are more important during winter at altitudes of about 300 m than during summer. Nevertheless, the absolute value of OC is higher during summer than during winter. This stems from the fact that secondary organic aerosols are formed preferentially during warm and sunny days.
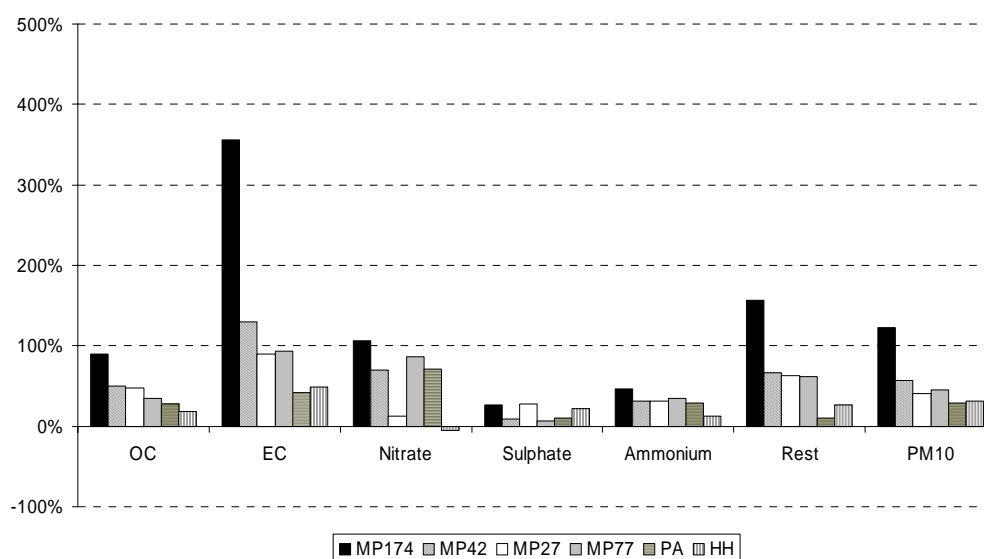
Figure 6 Relative annual concentrations of PM10 components at individual stations with respect to FT, yearly mean [%]

Figure 6 shows the mean annual concentrations of PM10 scaled by the correspondent measurements executed at FT. The percentages give an indication of how much pollution is not found in the air-mass at 300 m height. Moreover, considering the upper air concentration as a regional background, the percentages give an indication of how much of the measured PM10 components

are due to local phenomena. Most strikingly elemental carbon at traffic sites altogether with the non-analysed rest is more than double as high as in the free atmosphere. However, also nitrate ions, averaged over the whole year, are mainly locally influenced: at the traffic site, but also at the urban background-site and at the northern edge of the city, more than 70% higher values are measured than at the air-station FT. Comparing sulphate which is less than 30% higher at all surface stations than at the air-station, this high nitrate measurements are due to local effects and can be explained by the faster reaction of nitrogen oxides to aerosol nitrate.
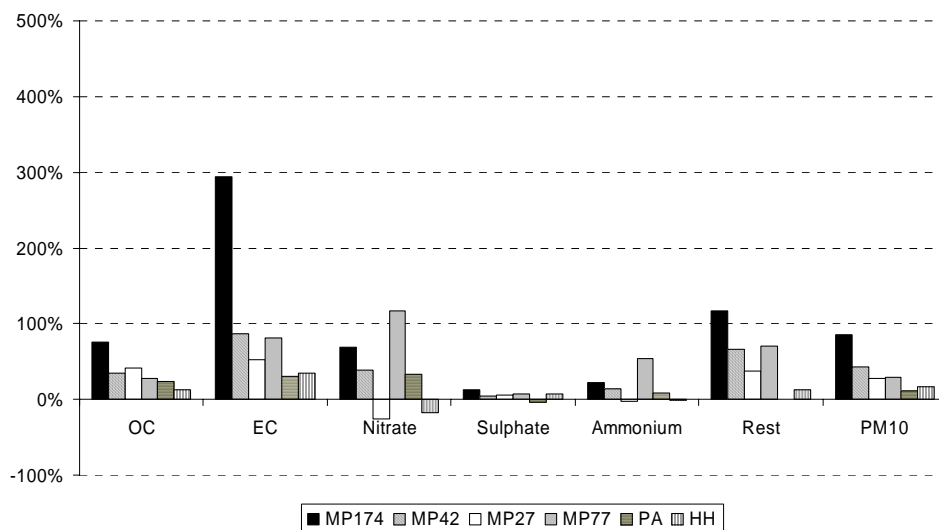
Figure 7 Relative summer concentrations of PM10 components at individual stations with respect to FT, yearly mean [%]

Figure 7 and Figure 8 show these relative concentrations with respect to the air-station, subdivided into summer and winter mean concentrations, respectively. The traffic contribution of EC to the regional background is more pronounced during winter than during summer. This is first of all due to meteorological stability in the boundary layer. This is intelligible looking at the EC measurements at the other surface monitoring stations. At the Berlin stations, EC winter concentrations are at least 100% higher than at 321 m height. Also the rural EC measurements are higher during winter than during summer. Nitrate, again, shows its increased stability properties depending on

temperature: during summer, for instance, nitrate concentrations measured at MP27 are even lower than those measured at FT.
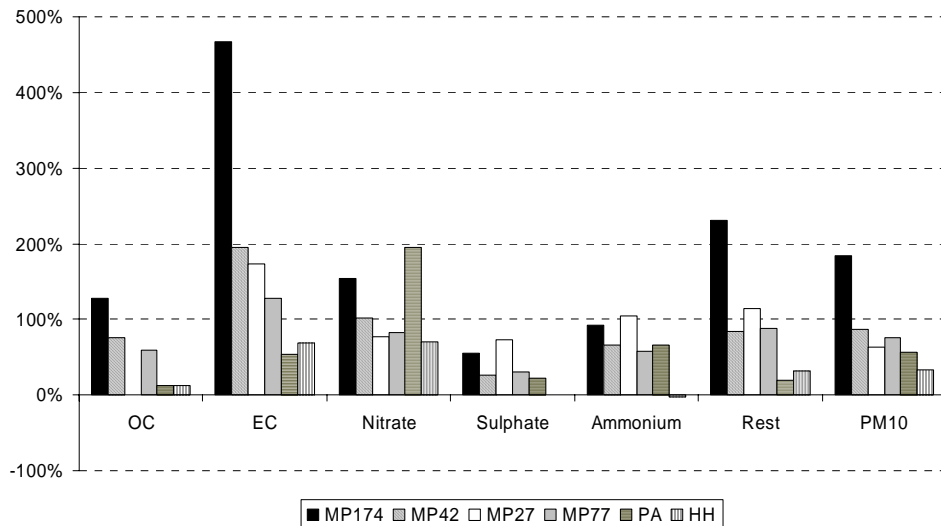
Figure 8 Relative winter concentrations of PM10 components at individual stations with respect to FT, winter mean [%]

Sulphate ions are distributed more homogeneously in the lower atmosphere during summer than during winter: while there are more or less the same SO_4^{2-} concentrations at different heights and at different land-use-stations during summer, this is not the case during winter: upper air station FT measures some 30–50% lower concentrations than any other surface station. This again indicates the stronger disconnectedness of air-masses during winter than during summer.

Correlation coefficient matrices show the process oriented similarity of the measurement sites. Correlations between the concentrations measured at the urban background station MC42 and at the other measurement sites have shown a strong relationship between city-edge-stations and urban background (r=0.93 for MC27 and 0.95 for MC77) and a slightly weaker relationship between traffic stations and urban background (0.90 for MC174 and 0.84 for BS) (Table 1). On the other side, the temporal relationship between PM10-concentrations in Berlin and in the rural background is lower (r = 0.87 for PA,

r = 0.78 for HH and 0.74 for FT). The temporal course at the urban background is very similar to the traffic related PM10. It is less similar to regional and continental PM10 measurements. PA, whoever is showing a different behaviour than HH. Also consider the correlation coefficient which is one of the smallest within the HoVerT-stations (0.68).

Table 1 Correlation coefficient between the HoVerT-measurement sites for PM10 over the whole measurement campaign time extension.

PM10	MP174	MP42	MP27	MP77	BS	FT	PA	HH
MP174		0.90	0.82	0.87	0.87	0.62	0.82	0.71
MP42			0.93	0.95	0.84	0.74	0.87	0.78
MP27				0.94	0.91	0.80	0.85	0.76
MP77					0.90	0.80	0.89	0.77
BS						0.88	0.64	0.87
FT							0.75	0.75
PA								0.68
HH								

PM10 shows a homogeneous pattern over a wide range of distances, if considered only the surface stations. Again, the least correlation could be found between the upper air station FT and any other monitoring side. The separation between the air masses is the reason for this low relationship. Nevertheless, the correlation coefficient is never less than 0.62, indicating a non-negligible overall continental influence also on urban PM10 pollution events.

PM10 is a composite of individual species which stem from anthropogenic and natural sources, influenced by local sources and long-range transported. EC is emitted directly mainly by Diesel engines and is a strong indicator of local sources, while sulphate ions is transported over long ranges and its life-time is several days (Seinfeld and Pandis, 1998). Thus they have been considered separately.

Table 2 Correlation coefficient between the HoVerT-measurement sites for EC over the whole measurement campaign time extension.

EC	MP174	MP42	MP27	MP77	BS	FT	PA	HH
MP174		0.76	0.66	0.73	0.57	0.54	0.64	0.58
MP42			0.85	0.89	0.56	0.66	0.78	0.72
MP27				0.88	0.50	0.83	0.92	0.82
MP77					0.38	0.81	0.82	0.86
BS						0.29	0.38	0.18
FT							0.80	0.85
PA								0.79
HH								

Table 2 shows the correlation coefficients of measured elemental carbons between the HoVerT monitoring sites. Most strikingly, the highest correlation coefficients are not seen between the two traffic sites (MP174 and BS). It must be kept in mind that BS together with PA and HH, have joined the HoVerT campaign only in a second stage. Considering only the stations which participated from the beginning in September 2001 and monitored the air throughout the whole measurement period unit September 2002, the lowest correlation is seen between FT and MP174. Elemental carbon is a tracer for traffic, being related to a high degree to diesel combustion and tire abrasion (Rauterberg-Wulff, 1998, 2000). The correlation coefficients between the urban background station MP42 and the urban edge stations are rather high (> 0.8) indicating a more homogeneous behaviour of EC over the city. Local transport of EC is responsible for this.

Table 3: Correlation coefficient between the HoVerT-measurement sites for sulphate ions over the whole measurement campaign time extension.

| SO_4^{2-}	MP174	MP42	MP27	MP77	BS	FT	PA	HH
MP174		0.95	0.95	0.89	0.95	0.74	0.94	0.95
MP42			0.97	0.98	0.98	0.81	0.95	0.95
MP27				0.98	0.99	0.82	0.93	0.91
MP77					1.00	0.89	0.96	0.97
BS						0.97	0.93	0.77
FT							0.80	0.89
PA								0.89
HH								

Table 3 shows the correlation coefficients of sulphate ions measurements between the HoVerT monitoring stations. All the correlation coefficients, except upper air-station FT vs. a variety of monitoring sites and traffic station BS vs. rural site HH, are higher than 0.9. This, again, is a very strong indication of a homogenous behaviour of long-range indicator sulphate.

Seasonal differences in the correlation coefficient between concentrations measured at the urban background station MC42 and at the top of the FT reveal the importance of the boundary layer height which is lower during winter and higher during summer. Thus, the correlation coefficient is much lower during winter than during summer. During cold winter days, mixing height extension is lower than the measurement site at 321 m and therefore the two sites are representative for individual disconnected air-masses. As the PM10-concentrations measured at FT are considerably lower during winter than during summer and concurrently the mixing layer is more often lower than the FT height during winter than during summer, the air mass reaching the monitor is less influenced by the local urban sources during winter than during summer.

In order to analyse the influence of wind directions (Figure 9 and Figure 10) and thus of preferred pathways toward the city of Berlin form outside, measurements of EC (Figure 12) and sulphate ions (Figure 11) have been analysed depending on wind fields. The favourite wind direction during the HoVerT-measurement campaign in Berlin-Dahlem is West-South-West

(Figure 10). This is also the wind direction where highest wind speeds are measured from.

In order to analyse the dependency of measured pollutants on the wind-direction, measurements at MP42, MP27, MP77 and FT have been weighted by the wind-direction-frequency. Both considered PM10-components, sulphate and EC, show a characteristic influence from the south-eastern directions for all considered monitoring sites. The dependency of sulphate on south-easterly winds is thereby stronger than the dependency of EC from that influx direction. This is a hint to attribute sulphate concentrations in Berlin to sources in the south-east of Berlin. EC, however, shows the same behaviour. Nevertheless, EC is also known as a local-source tracer. Thus, meteorological phenomena like low-wind speeds connected to south-eastern wind-direction may explain an accumulation effect during south-eastern-wind-situations.
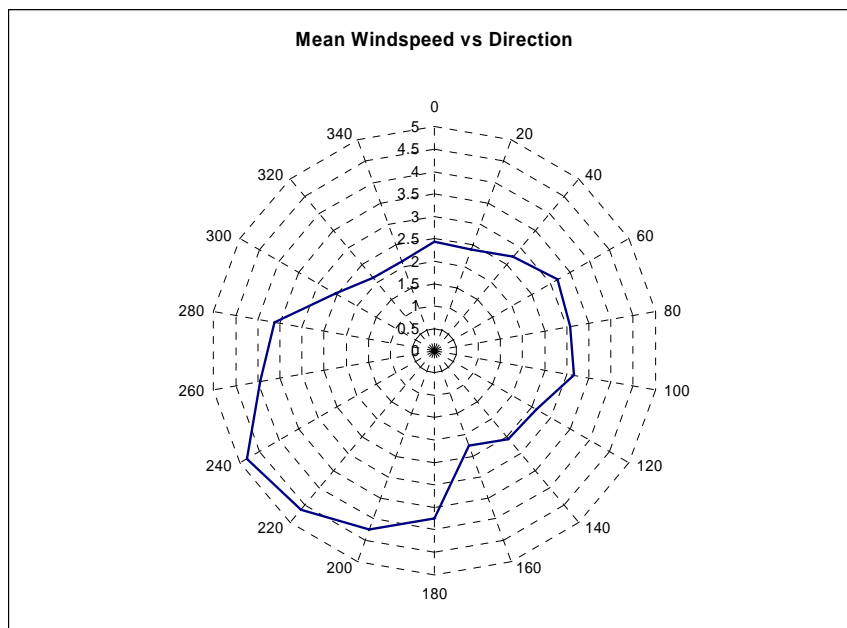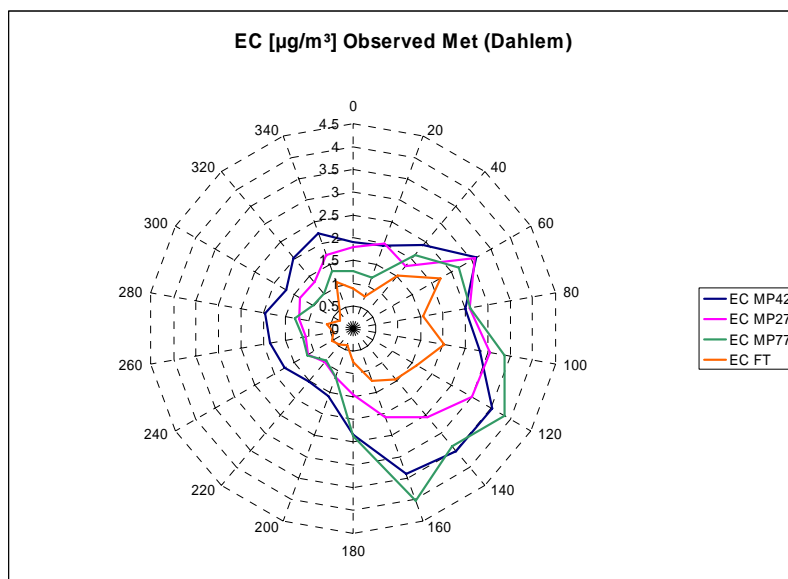

Figure 9 Mean wind speeds [m/s] vs. wind directions at Berlin-Dahlem. [0° = North, 90° East, 180° = South, 270° = West].
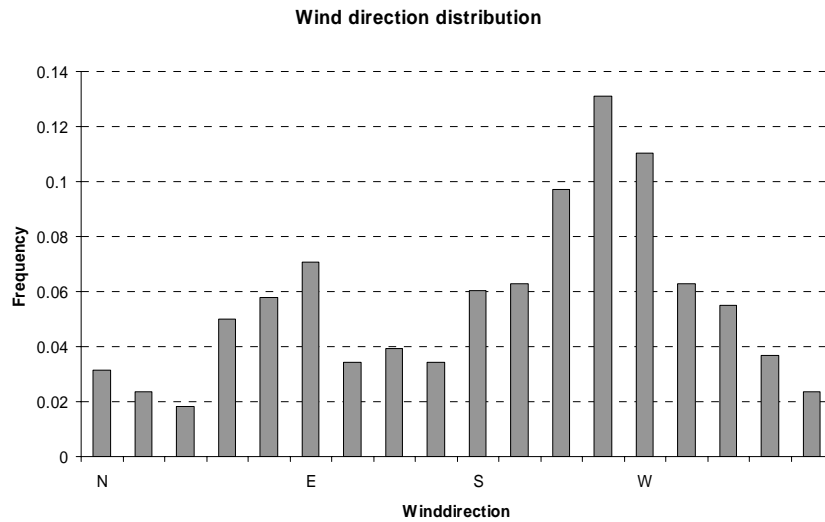
Figure 10 Wind direction distribution at Berlin-Dahlem during the HoVerT-Campaign 2001-2002 [N = North, E East, S = South, W = West].
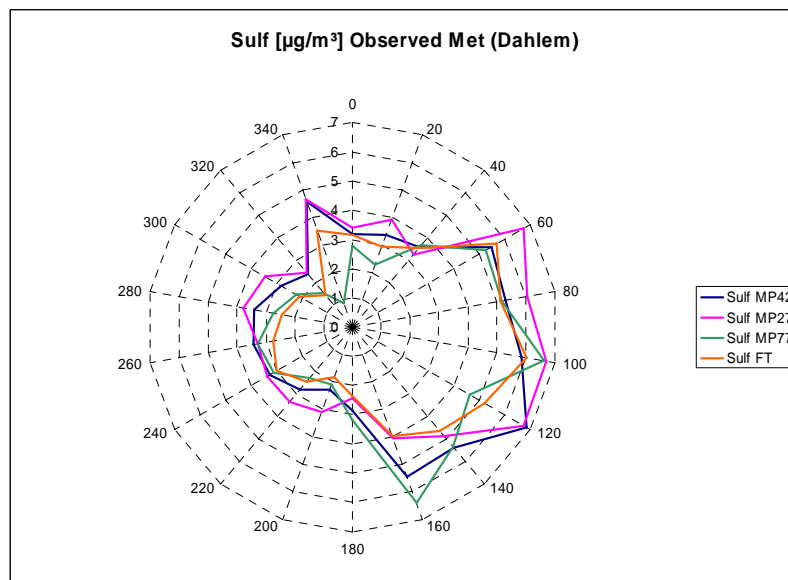
Figure 11 Mean sulphate concentrations in MP42 [µg/m³] vs. wind directions at Berlin-Dahlem [0° = North, 90° East, 180° = South, 270° = West].

Figure 12 Mean EC concentrations in MP42 [μg/m³] vs. wind directions at Berlin-Dahlem [0° = North, 90° East, 180° = South, 270° = West].

2.2.3 Qualitative budget analysis from the measurements during the HoVerT-Campaign

The HoVerT PM10 measurement campaign has primarily shown the net distinction between primary - anthropogenic influenced - aerosol concentrations and secondary inorganic – again, due to human activities – and organic – due to nature – aerosols. As a tracer for human activities the primary component elemental carbon could be isolated. Again, EC is produced mainly locally and can thus be used also as a tracer for short range transport. On the other side, secondary inorganic aerosols and especially sulphate ions have a much longer life-time and genesis, and can thus been seen as a tracer for long range transport. The contribution of organic aerosol components is strong in the aerosol concentration and its origin is twofold: a considerable part has its sources in human activities while the remaining part stems from biogenic precursors. Keeping in mind these findings one can try to make a qualitative budget analysis of the PM10 concentrations found in Berlin based on observations:

- PM10 mass concentration differences between the individual monitoring stations in, around and above Berlin have shown that the "free" air over Berlin has approximately 15 µg/m³ aerosol burden, the rural background is some 30% higher and the urban agglomeration contributes with ca. 30% higher PM10 values than the rural background. Near traffic areas show 112% higher values than the "free" air or 35% higher values than the urban agglomeration.
- Apportionment of PM10 shows the influence of primary to secondary aerosols to be ca. 1/3 secondary inorganic PM, 1/3 primary PM and 1/3 organics.
- Winter exhibits more local influence and stronger local generation of nitrates.
- Higher concentrations are measured during synoptic wind-patterns from south-east.

2.2.4 Former Berlin Aerosol measurements, analyses and interpretation.

Israël et al. (1992) differentiated Berlin Aerosol samples according to traffic-related and rural characteristics. They found out that primary constituents' concentrations were higher at kerbside-measurement sites than secondary. They analysed sulphate, nitrate chloride and ammonium and elemental and organic carbons attributing them ca. 70–75% of the total PM10-mass. This was sufficient to give a net distinction between primary and secondary aerosol components and to relate PM-constituents to short and long range origin. Israël et al. (1996) and Schlums (1998) applied a concentrations-difference-technique to the Berlin PM-measurements taking observed values from an urban background-station and a rural upwind and downwind station contemporaneously. The main hypothesis was that long-range components do not change from rural station to urban background stations, while local influenced pollutants do change strongly. The relatively short distances between the rural upwind station and the urban background station and thus the time the polluted air parcel stayed over the city was negligible compared to the chemical building process time range. Analysing the measurement time series from 1989 to 1991 they attributed a 70% of total PM10 concentrations at the urban background station to long range transport and only 30% to the city related emissions. Hainsch (2004) analysed PM10 measurements at a Berlin background station in the vicinity of the Technical University (TU-Berlin) executed in 2001 and attributed 70% to long range transport, again. He, too, adopted the technique proposed by Israël et al. (1992).

The same technique was applied also by Lenschow et al. (2001) to measurements in Berlin. The time period they analysed was form 1998 to 1999. They confirmed that at least 50% of urban background aerosol concentrations are imputable to long range influenced PM10 concentrations.

Lenschow et al. (2001) analysed Berlin-PM10 and TSP (total suspended particles) time series from 1990 to 1998 at different measurement sites finding out a general reduction of about 34% of coarse PM10 and about 23% of fine mode PM10, while TSP diminished by 44%. This is a strong indication that the reduction strategies were more efficient for big particles than for small particles. Especially PM25 is related to traffic containing a substantial part of

EC while coarse PM10 is more related to heating systems based on coal firing. This type of heating has been substituted successfully by gas heating systems.

Also the change of the political system in the former Eastern European countries was accompanied with a strong destruction of industry plants reducing strongly the emissions. Other industrial complexes were brought to international emission standards installing filter systems for particles and substituting sulphur-containing fuels by cleaner substances.