

Size-segregated physical and chemical long-time characterization of particles depending from air mass origin at German lowlands (Saxony, Melpitz site)

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Summary

In the 1980s and 1990s the region around the city of Leipzig (West-Saxony) was one of the most polluted regions in central Europe. There were a number of sources contributing to the pollution during that period: emission from brown coal open mining, environmentally irresponsible industry, old power plants, old fashioned heating systems and mostly cars with two stroke engines without efficient exhaust fume cleaning techniques. The TSP concentrations in these periods show a large scatter with a mean value about 75 µg/m³. Since the re-unification of Germany in 1990, a continuous decrease in PM₁₀ concentration till 1998/99 was observed.

Long-time measurements of PM₁₀ has started in 1993 at the IfT-research site Melpitz located in the lee side of the Leipzig conurbation in Saxony near the city of Torgau (12°56'E, 51°32'N, 86 m above sea level). The mean wind direction is Southwest; the second-class wind direction is East.

The measured PM₁₀ concentration in 1993 was about 38 µg/m³ in summertime and about 44 µg/m³ in wintertime. The PM₁₀ level decreased to 24 µg/m³ and 28 µg/m³ for winter and summer in 1998 and 1999, respectively. The yearly variation of the mean concentration was lower in summer than in winter.

Since 1995 weekly low volume samples of PM_{2.5} (since 1999 also PM₁) show that the percentage of coarse particle (PM₁₀-PM_{2.5}) in summer is higher than in winter with an increasing trend till the end of the 1990s. This is a hint for an increasing influence of local emissions caused by agriculture and wind blowing dust from dry surfaces in summer. The particle mode between PM₁ and PM_{2.5} mostly accounts the highest percentage of the PM₁₀ during winter months. The concentration of the particles between PM₁-PM_{2.5} together with the fraction smaller than PM₁ can reach higher than 80% of the PM₁₀ in wintertime. This is a hint of the influence of long range transport.

With the decrease of anthropogenic emissions in the Saxon cities and whose direct surroundings at end of 1990s the influence of the long-range transport especially with air masses from the East during high pressure situation with low mixing heights in winter became more and more evident and is the cause for distinctive episodes with elevated particle concentrations in wider areas. The mean sources regions for wintertime anthropogenically influenced air masses are inside and outside of the European Union. The mean concentrations in the Melpitz area for PM₁₀, PM_{2.5} and PM₁ was 19.9, 15.2 and 12.7 µg/m³ in 2004 and 22.4, 17.6 and 12.9 µg/m³ in 2005, respectively.

Therefore, particles were physically and chemically characterized for two years after size-segregated sampling in a project between the German Environmental Protection Agency (Umweltbundesamt, UBA) and the Leibniz-Institute for Tropospheric Research (IfT). The main results of the project the differences in the mean particle mass concentration, the chemical distribution and the physical properties of particles distinguished for air masses transported from West or East in summer and winter by classification of the daily results. These differences show the possible influence of long-range transport from the east, mostly in wintertime, to the region of Saxony near the Polish boarder. In the winters 2004/05 and 2005/06 the PM₁₀ mass concentration at the rural Melpitz site exceeded the limit value of 50 µg/m³ for 8 and 9 days, respectively. These concentrations were mostly accompanied with a strong elevated percentage of PM_{2.5} in PM₁₀. These days contributed to the 35 days with exceeding the limit value of 50 µg/m³ allowed in cities. The detailed investigations also give clues to naturally emitted precursors for secondary particle mass formation especially in summer. A single event in May 2006 shows the strong influence of forest fires in Russia on the particle concentrations in wide areas of Germany with a strongly elevated percentage of PM_{2.5} in PM₁₀.

1. Introduction

In the 1980s and 1990s the region around the city of Leipzig (West-Saxony) was one of the most polluted regions in central Europe. There were chemical industry and power plants without efficient waste gas cleaning systems, wide open coal mines with large erosion areas and domestic heating systems mostly based on brown coal briquettes. After the German reunification in 1990 fast and comprehensive modernization of power plants was initiated. Many old factories and metal processing facilities were closed. The remaining industry and a large fraction of the household heating systems were reconstructed within the last decade. Now the main sources for anthropogenic air pollutants are the traffic, the remaining brown coal open mining areas, power plants, households, and agricultural activities leading to primary particle emissions from surface erosion and secondary particle mass formation.

Long-time characterization of particles starts at the research site of the Leibniz-Institute for Tropospheric Research (IfT) Melpitz in 1993 with PM₁₀ high volume samplers (Müller, 1999). Low volume samplers for PM₁₀ and PM_{2.5} were added in 1995 and for PM₁ in 1999. Figure 1 shows the particle concentrations before the German reunification and the decrease after the reunification in Saxony (Spindler et al., 1999 and 2004).

With the dramatic decrease of anthropogenic emissions in the Saxon cities and their direct surroundings at the end of 1990s the influence of long-range transport of trace gases and particles, especially from Eastern Europe became more and more apparent as a cause for distinctive episodes with elevated particle concentrations, mostly in wintertime. During high-pressure conditions dry air masses may be transported over long distances to Saxony, often with moderate wind velocity and low precipitation. The main source regions for these air masses are located outside (Russia, Belarus and Ukraine) and inside (Poland, Czech Republic and Slovakia) the European Union. Such situation with long-range transport from the east (continental air masses) can occur particularly in wintertime with daily PM₁₀ concentrations > 50 µg m⁻³. Long-range transport during these meteorological conditions can increase the number of days with mean PM₁₀ concentrations > 50 µg/m³ (limited to 35, EU-Commission, 1999) in wide areas and Saxon cities. Under the dominating wind direction (SW to NW) the particle concentrations are low in Saxony, because continental air masses from the European Union or maritime air masses from the Atlantic Ocean with showers are transported, often during low pressure conditions with high turbulence to Saxony. Because of the long distance to the sea the influence of sea salt particles is low.

In a two year joint study (2004-07-01 until 2006-06-30) between the Umweltbundesamt (UBA) and the IfT, size-segregated particles were characterized chemically and physically using high-volume samplers, five stage BERNER-type impactors and physical online instruments at Melpitz site. The main aim of the project is to show the differences in particle mass concentration, chemical distribution and physical properties by classification of daily particle characterization results for air masses from west (maritime and/or continentally influenced) and east (continentally influenced) with a distinction between winter and summertime. The PM size distributions from 3 nm to 10 µm was also investigated to address the toxicological aspects of PM (Samoli et al., 2005)

The IFT took part in the EMEP summer campaign in June 2006, with daily high-volume measurements of PM₁, PM_{2.5} and PM₁₀ and five stage BERNER type impactor measurements. The particles were analyzed for water soluble ions, organic carbon and elemental carbon (OC/EC). The size distributions and the absorption of the particles were continuously monitored using a tandem differential mobility particle sizer (TDMPS) system and a Multi Angle Absorption Photometer (MAAP), respectively. The EMEP winter campaign for January 2007 with identical instrumentation to the EMEP summer campaign is part of a one year continuation of the joint project with the UBA.

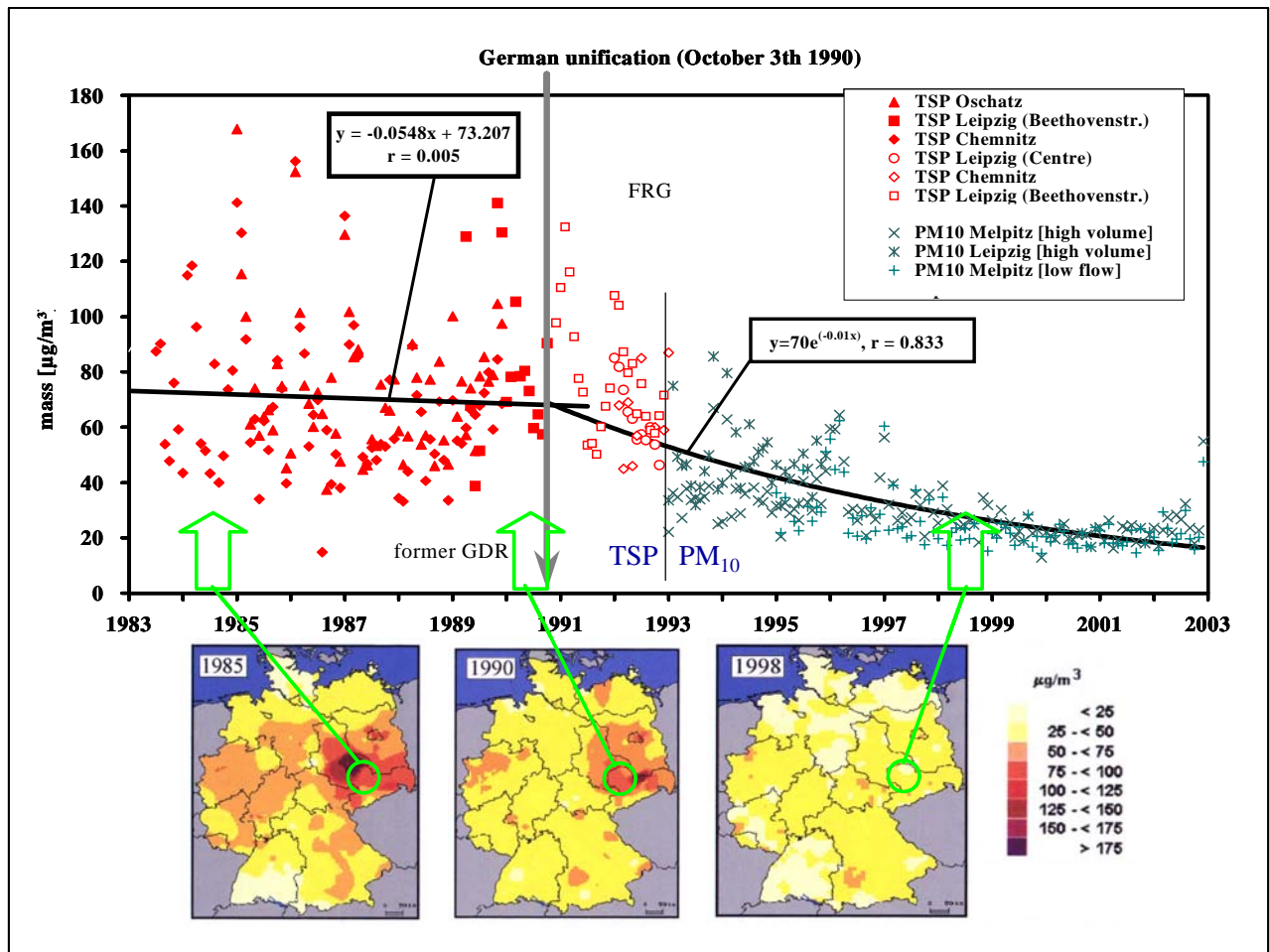


Figure 1 Mean aerosol mass concentration during 1993-2002 for west Saxony. The data shown are monthly means (1983-1992, TSP from different places in Saxony, source: SLUG, Sächsisches Landesamt für Umwelt und Geologie, 1992-2002 own high-volume PM₁₀ measurements from Leipzig and Melpitz). The model calculations for 1985, 1990 and 1998 are from the Umweltbundesamt (UBA)

2. Measurement site, sampling methods, analysis, and determination of air mass origin

Measurement site

All measurements described in this report were performed at the IfT-research station Melpitz (12°56' E, 51° 32' N, 86 m a.s.l.). IfT and the research station Melpitz are integrated in the new EU activities ACCENT (Atmospheric Composition Change, the European Network of Excellence) and EUSAAR (European Supersites for Atmospheric Aerosol Research, Flossmann et al., 2006) (Figure 2). Melpitz is located about 50 km in north-easterly direction from the city centre of Leipzig near Torgau, between the *Dübener Heide* and the *Dahlener Heide* in a representative region for rural sites of the German low lands. There are no major anthropogenic sources of PM near the site

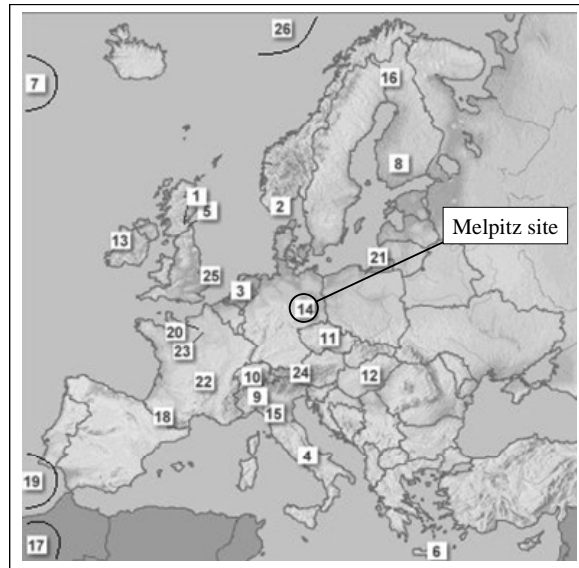


Figure 2 Location of the Melpitz site in Europe (EUSAAR network)

(Figure 3). During several national and international projects of the IfT the site was characterized meteorologically (Spindler et al., 1996, Brüggemann and Spindler, 1999, Erisman, et al., 2001, Stratmann et al., 2003), for trace gases (Gnauk et al., 1997, Spindler et al., 2001, Spindler et al., 2003) and for PM concentrations (Heintzenberg et al., 1998, Spindler, et al., 1999, Müller, 1999, Neusüss et al. 2002, Plewka et al., 2004, Spindler et al., 2004a, Herrmann et al., 2006, Engler et al. 2006). Comparisons to other European sites are given in Putaud et al., 2004, Van Dingenen et al., 2004 and MacDougall et al., 2005. Long-time measurements since 1993 and an intensive joint test project with the UBA in November and December 2003 (Spindler et al., 2004b) have shown that Melpitz is a representative site for a continuous size-segregated physical and chemical PM characterization and is suitable for the classification of days with different origins and history of air masses.

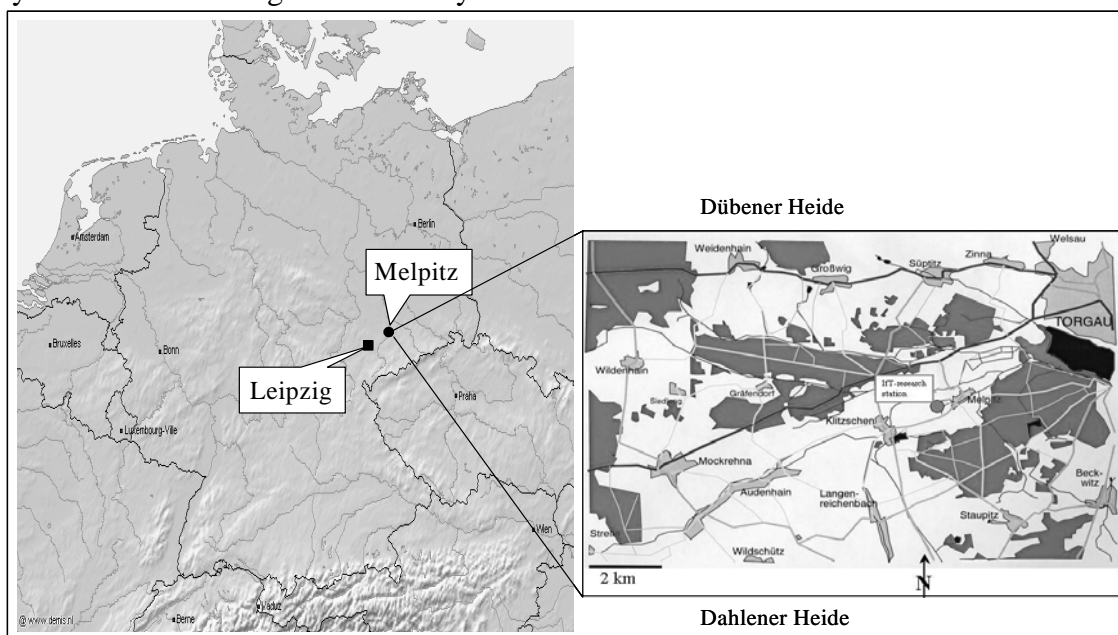


Figure 3 Location of the Melpitz site in Germany and surroundings

Long-time measurements

For the long-time measurements (Müller 1999, Spindler et al. 2004), the daily samples were taken by a modified Sierra-Anderson-PM₁₀ high volume sampler (Anderson Samplers Inc., USA). The sampling volume was approximately 1340 m³. The filters were rectangular quartz fibre filters (MUNKTELL, Sweden). Since 1995 weekly filter samples for PM₁₀ and PM_{2.5} were taken using a low-volume sampler ('Partisol 2000', Rupprecht & Patashnik Co. Inc., USA) with 47 mm diameter Teflon filters (Type 4700, 3 µm pore size, Millipore, USA). The low volume sampling starts every Monday 12:00 MEZ. Since 1999 a PM₁ sample was taken simultaneously.

Two years intensive measurements

The PM size spectrum from 10 µm down to 3 nm was investigated for two years (winters 04/05 and 05/06 and summers 05 and 06) using different sampling systems combined with physical-chemical off-line analysis and physical on-line instruments.

High-volume sampling

Three identical samplers, DIGITEL DHA-80 (Walter Riemer Messtechnik, Germany), were used to determine PM₁₀, PM_{2.5} and PM₁ (Gnauk et al. 2005). The sampling velocity was 30 m³/h for all systems. The filter was made from quartz fibre (MK 360, MUNKTELL, Sweden). The sampling time for each filter was 24 hours. The automatic filter change took place at midnight. PM₁₀ and PM_{2.5} were measured every day and PM₁ every sixth day (except during intensive measuring campaigns, e.g., EMEP in June 2006, when PM₁ was measured daily too).

BERNER-type impactors

In parallel to the filter sampling, size-segregated PM sampling using five-stage BERNER type impactors was carried out with a sampling velocity of 75 l/min for selected days. The impactors consist of six successive impactor stages with decreasing cut-off diameters (D_{pa} : 10, 3.5, 1.2, 0.42, 0.14, and 0.05 µm). Aluminum foils were used as a substrate (Gnauk et al. 2005). Particle mass and chemical size distributions were determined by weighing the mass of particles impacted on the stages and from the analysis of the particle phase chemical composition. On stage 1 (0.05-0.14 µm) freshly emitted particles were typically found (e.g., traffic emitted soot). On stages 2 and 3 aged particles were found though the particles from other sources were also found (e.g., long-range transport particles or from domestic heating). In the coarse mode fractions 4 and 5 the sea salt particles, primary biogenic material, and resuspended crustal material were found. The chemical composition of the particles in different size classes varied with sources of PM and the meteorological conditions during the sampling periods.

High time resolution measurements with TEOM®

Additionally, a high time resolution PM₁₀ concentration (half-hourly-means) were measured using a TEOM® 1400a (Rupprecht & Patashnik Co., Inc., USA). The TEOM operates at 50°C and quasi-continuously measures PM₁₀ mass by collecting particles on an oscillating microbalance. The air stream is regulated by a mass flow controller. The relatively high operating temperature (50 °C) for the TEOM microbalance is necessary to avoid the condensation of water vapor (positive artifact) but can also generates systematic errors by evaporating volatile compounds (negative artifacts) such as ammonium nitrate (Charron et al., 2004). The TEOM is used only for the monitoring of short time effects. The mean mass for 24 hours would be corrected by a daily comparison with the PM₁₀ data from high-volume sampler (DIGITEL DHA-80).

Mass determination and Ion-chromatography

The mass, the concentrations of main ionic species (Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}), the elemental carbon (EC) and the organic carbon (OC) in all size fractions were determined from impactor samples and the PM_{10} , $\text{PM}_{2.5}$ and PM_{10} samples. The impactor foils and filters were equilibrated for 48 hours in the weighing room under controlled temperature and relative humidity (20°C and 50% RH.). The impactor foils were weighed using a microbalance UMT-2 and an AT-261 for filters (both Mettler-Toledo GmbH, Germany). Anions and cations from filter samples were analyzed by ion chromatography (Metrohm, Switzerland) after two hours extraction in Milli-Q grade water. Different procedures were used for anion determination from the impactor samples and the filter samples. Cations in the impactor samples were analyzed using IC but the anions in the impactor samples were analyzed by capillary zone electrophoresis (Spectra Phoresis 1000-Thermo Separation Products, USA).

OC and EC determination

OC/EC separation can be achieved in different ways as reviewed by Penner and Novakov (1996). In this study the particulate carbon fraction was determined by a two step thermographic method using a carbon analyzer C-mat 5500 (Ströhlein, Germany). The method applied in this study is a variation of the German official VDI guideline (VDI 2465, Part 2, 1999). In a first step nitrogen was used as carrier gas for the OC volatilization at 650°C for eight minutes. Those carbon compounds that evaporate under N_2 atmosphere at 650°C conditions and converted to CO_2 by a catalyst are addressed as OC in this study. In a second step the remaining carbon was transformed to CO_2 by combustion under oxygen for eight minutes at 650°C and detected by IR absorption is addressed as EC in this study. A NDIR detector was used for the detection of CO_2 . This temperature was selected to avoid melting of the aluminum substrates, decomposition of carbonates (Petzold and Nießner, 1996) as well as to minimize charring processes during the volatilization step. The method discussed in detail can be found in Neusüß et al. (2002) and Plewka et al. (2004). The method was involved in the Germany-internal VDI/DIN - comparison experiment (Neuroth et al., 1999) as well as the International Round Robin Test Carbon Shoot out Stage I (Schmid et al., 2001) and Stage II (Puxbaum, TU Vienna, unpublished).

Carbon preference index (CPI)

The determination of selected non-polar semivolatile organic species was carried out by CPP-GC-MS (Curiepoint pyrolysis gas chromatography mass spectrometry) directly from the impactor foils. The CPP system (JPS-350, Japan Analytical Industry, Ltd.) acts as a fast thermal desorption injector. The evaporation of species occurs at 500 °C under helium after adding internal standards (two deuterated alkanes). The detection limits are in the lower pg/m^3 range for the most compounds.

The concentration of n-alkanes is used to distinguish biogenic and anthropogenic sources of carbonaceous PM. The CPI (Carbon preference index) is determined as follows:

$$\text{CPI}_{\text{odd}} = \frac{\text{mass concentration of odd n-alkanes (C}_{21} - \text{C}_{33})}{\text{mass concentration of even n-alkanes (C}_{20} - \text{C}_{32})}$$

Alkanes from anthropogenic sources have the CPI close to 1 and the CPI of alkanes from biogenic origins is typically between 5 and 20. Additionally to the CPI index, the mode where alkanes are found can give information on the sources. For example, plant waxes have been found typically in coarse mode PM (Sicre et al., 1990; Kavouras et al., 1998) but fresh traffic emission PM, e.g., is found in the submicron PM.

TDMPS/APS-system with thermodenuder

A tandem differential mobility particle sizer (TDMPS) was used for continuous online particle number concentration determination in the size range 3 to 800 nm (twin differential mobility particle sizer, Birmili et al., 1999) in combination with a thermodenuder (TD). This system is suitable to measure dry number size distributions of ambient aerosol particles and those of non volatile particle fraction in an alternating manner. The system is equipped with automatic valves which enable measurements with and without TD. The valves are switched computer controlled. The TDMPS system consists of two Hauke type DMAs (differential mobility analyzer) in combination with two CPCs (condensation particle counter). One DMA (ultrafine DMA) is operated at an aerosol flow rate of 2 lpm, a sheath air flow of 20 lpm and it measures particle size between 3 and 22 nm (mobility size). The number concentration of the quasi monodisperse aerosol fraction behind the UDMA is measured by an ultrafine CPC (UCPC, model 3025, TSI Inc., USA). The second DMA is operated at an aerosol flow rate of 0.5 lpm, a sheath air flow of 5 lpm and it measures particles between 22 and 800 nm. The particle number concentration was measured behind the DMA by a CPC (model 3010, TSI Inc., USA). The measurements are controlled by LabView®-based software. Both systems start the measurements overlapping at 22 nm and continue stepwise up- and downwards to their upper and lower limits with a size resolution of 16 channels per decade. The system measures a complete size distribution from 3 to 800 nm within 10 min, thus there are 3 measurements with and without TD available per hour. An inversion routine is used afterwards to calculate the real number size distributions using the real DMA transfer function (e.g, Stratmann and Wiedensohler, 1996). The TD removes a volatile fraction of particles by thermal desorption (Wehner et al., 2002). The TD consists of two units, a heating and a cooling section. In the first part of the instrument, particles are heated to a certain temperature (maximum ~ 300 °C) where all the volatile material is evaporated. The subsequent cooling tube is filled with active carbon for the adsorption of evaporated gas phase compounds. The aerosol flow inside the heating section is maintained at constant temperature and controlled and regulated using a thermal resistor (Pt 100) which is placed halfway along the aerosol line on the outside of the stainless steel tube. A second Pt 100 is located at the entrance of the cooling section to monitor the temperature of the aerosol flow downstream of the heater. The aerosol tube (stainless steel, 20 mm ID) is surrounded by a second tube (copper, 35 mm ID) filled with fine sand to maintain a homogeneous and uniform temperature distribution between wall and aerosol line. The tubing inside the cooling unit consists of stainless steel gauze which permits the gases to transfer to the carbon section. It is supplied with a thin-walled stainless steel tubing system wrapped spirally around the aerosol line to actively cool the aerosol flow if needed.

The number size distribution between 0.8 and 10 µm was measured using an aerodynamic particle sizer (APS, model 3321, TSI Inc, St. Paul, USA). Within the APS particles are separated according to their inertia. The sample flow is accelerated through a critical orifice and the following time of flight measurement provides the aerodynamic diameter. The time resolution of the APS is identical to the TDMPS system 10 min, but measurements have been performed with ambient aerosol (without TD) only.

Figure 4 shows the size cuts of high volume samplers, the impactor, the TDMPS and the APS, which took part in this study.

Determination of air mass origin

A determination of air mass origin of measurement days was carried out because particle mass concentration, physical and chemical properties and their size distribution depends mainly on the air mass history, the origin, and the seasons (winter or summer). The classification was based on 96-hour backward trajectories from the NOAA-Hysplit-Modell (source: <http://www.arl.noaa.gov/ready/hysplit4.htm>). Backward trajectories were plotted

twice a day (10:00 and 18:00 CET) and for 200, 500 and 1500 m above ground level for the measurement periods (winters 04/05, 05/06 and summers 05 and 06). The measurement days from May to October were assigned to the summertime and measurement days from November to April were assigned to wintertime. The days with westerly air mass transport was classified as continental and/or maritime and the days with easterly air mass transport was classified as continental. Figure 5 shows the two broad sectors used for the classification of long-range transported air masses by backward trajectories. The days with low wind velocity and more local influences and the days with air mass transported from North or South were not considered in the different means for air masses from West (maritime and/or continentally influenced) and from East (continentally influenced).

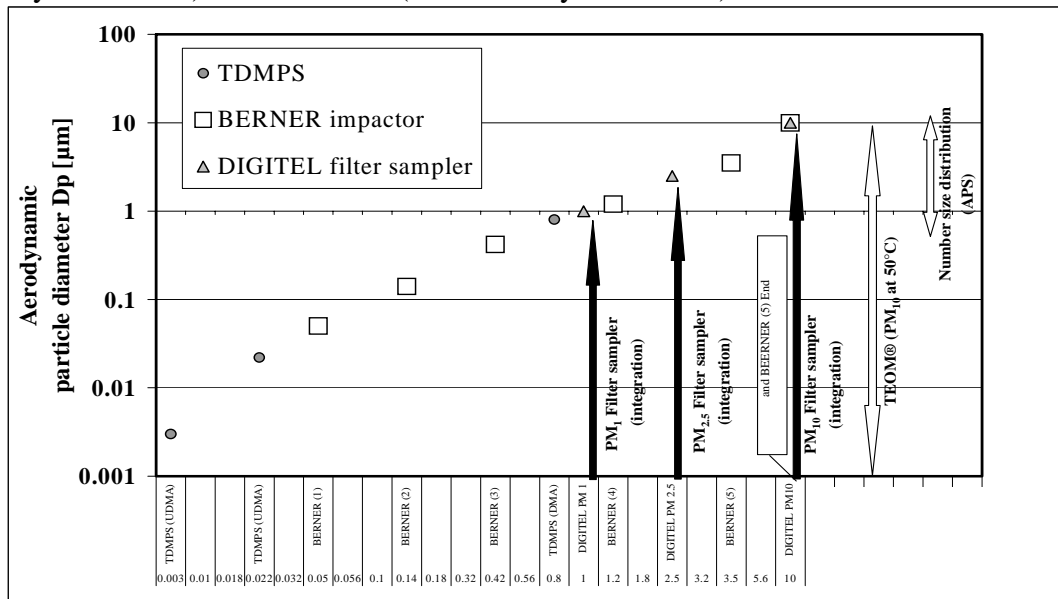


Figure 4 Size-segregated chemical and physical characterization of particles with different sampling systems and online devices

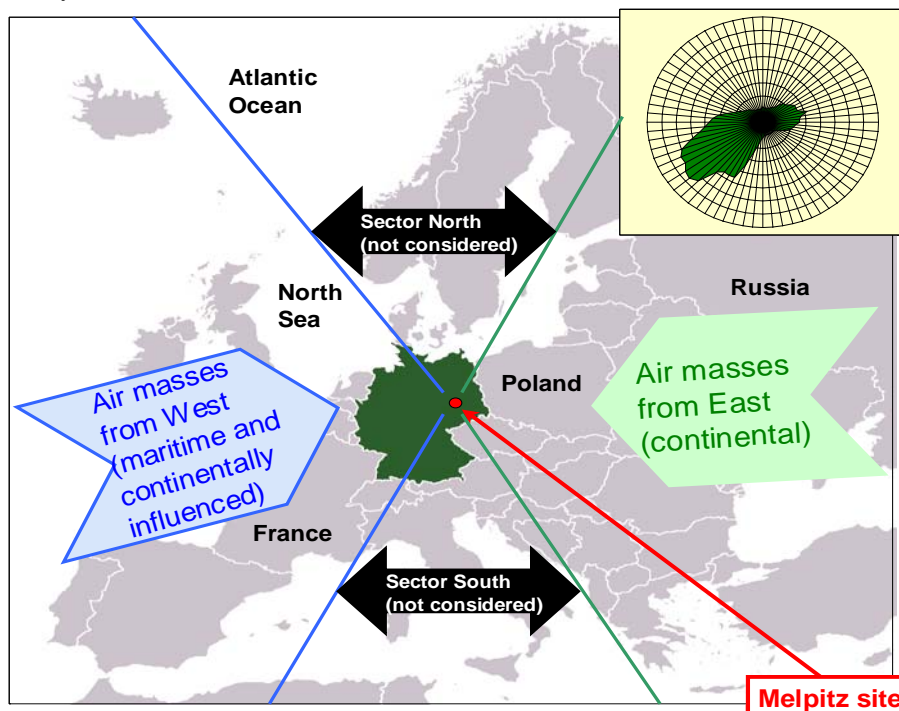


Figure 5 Classification of daily samples for two major long-range transport patterns - air masses from West (maritime and/or continentally influenced) and air masses from East (continentally influenced) and wind rose for the Melpitz site (more than 4.2 million 5 min averages considered, calm wind velocity $< 0.5 \text{ ms}^{-1}$ in 12 m above ground is 8.6% of the measurement time)

3. Results

3.1. Long-time measurements

Long-time characterization of particles started at the Melpitz site in 1993 with PM₁₀ high volume sampling. Figure 6 shows the course of average half-yearly particle mass concentration of PM₁₀ for winter and summer combined with the half-yearly means of precipitation sum over 14 years. The elevated PM₁₀-concentration (1993 till 1997) was mostly caused from local emission in the Saxon cities and surroundings. A decreasing PM₁₀-mass concentration can be observed till about 1998/99. From about 1999 up to now the influence of the long-range transport of particles, especially from Eastern Europe became apparent. This is now the major cause for distinctive high PM episodes in wide regions in Saxony. The winters show the higher inter annual pattern caused by lower turbulence as in the summers. This means the general influence of different meteorological conditions is more pronounced in winter ($r^2 = 0.47$), than in summer ($r^2 = 0.90$). The correlation with the total precipitation is weak but winters with relatively high mass concentrations show low total precipitations, these are hints of a more continentally influenced climate in these winters with a low mixing height during cold high pressure weather situations.

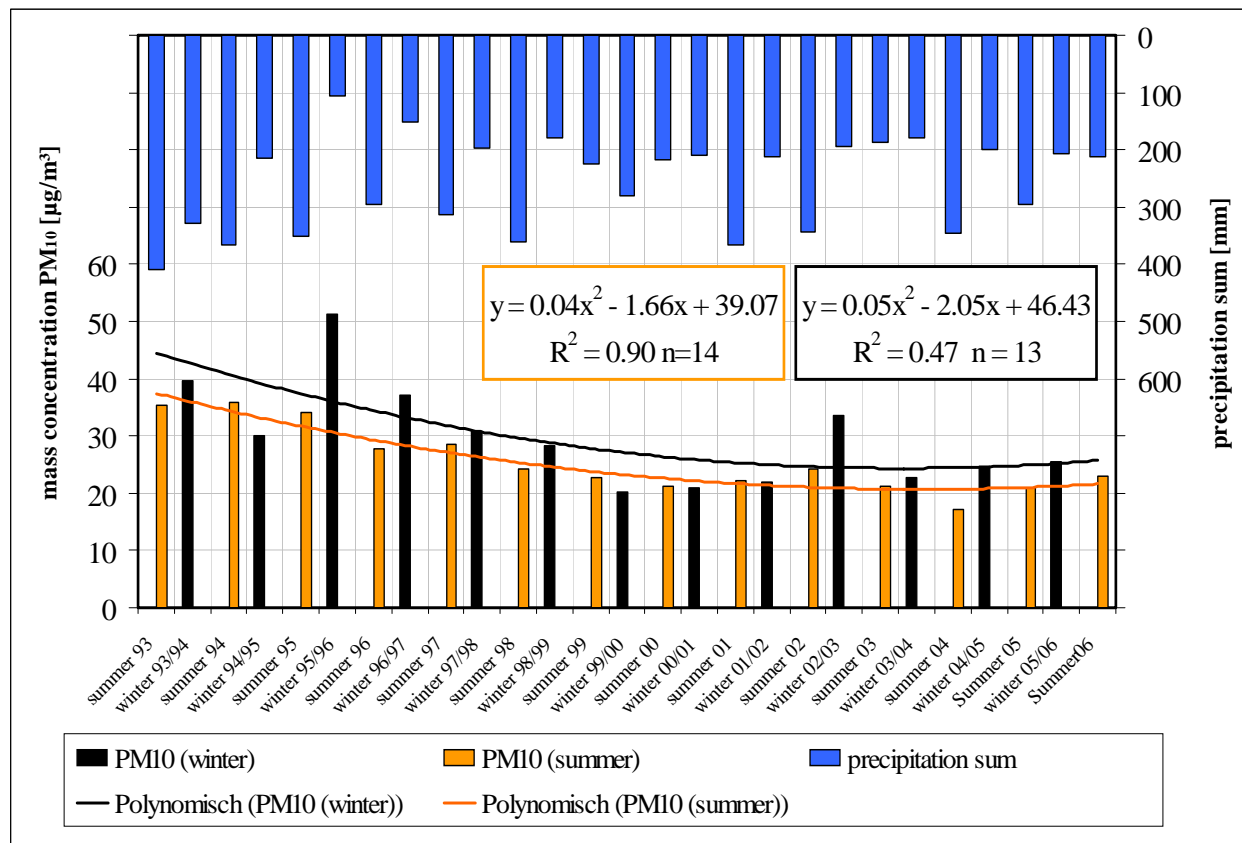


Figure 6 Evolution of half-hourly PM₁₀-mass concentration and precipitation in winter (November until April) and summer (May until October) at Melpitz site in the least 14 years. The half yearly precipitation sum is plotted as inverse.

Weekly low-volume filter samplers for PM₁₀ and PM_{2.5} since 1995 and PM₁ since 1999 are available for a size-segregated chemical characterization at Melpitz site. The percentage of PM₁₀-PM_{2.5} concentration in PM₁₀ since 1995 and the relative parts of PM_{2.5}-PM₁₀ and PM₁-PM_{2.5} concentrations in PM₁₀ since 1999 are plotted in Figure 7. These size segregated measurements show a typical pattern with significantly higher percentages of coarse particles

PM₁₀-PM_{2.5} in summers. The reason is, at one hand, the regional re-suspension of coarse particles from dry surfaces in summer by agricultural activity and/or blowing wind. On the other hand, the particles smaller than PM_{2.5} were emitted from domestic heating systems in winter which were transported over long distances. The re-suspension of coarse mode particles from wet or snow-covered surfaces is depressed in winter. The increase of the percentage of coarse mode particles PM₁₀-PM_{2.5} from 1995 till 1998 may be caused by decreasing emissions of coarse particles in the surroundings. This means that local coarse mode emissions account comparably higher fractions of the coarse mode now than the time when the site was influenced by much worse pollution episodes.

Additionally, the particle fraction PM_{2.5}-PM₁ is available since 1999 (Figure 7). These particles are mostly from long range transport. Generally, higher percentages of fine particles PM_{2.5}-PM₁ were detected in winter than summer. The percentage of the particles smaller than PM₁ and the fine particles PM_{2.5}-PM₁ can reach more than 80 % of PM₁₀ especially during times with snow covered surfaces and with low mixing heights in winter. Low contribution of PM₁₀-PM_{2.5} can be explained by negligible coarse particle emissions in the near surroundings. This means that high PM₁₀ particle mass concentrations in winter outside a conurbation are made of 80 % or higher PM_{2.5} masses (compare chapter 3.2.1. and 3.2.3.).

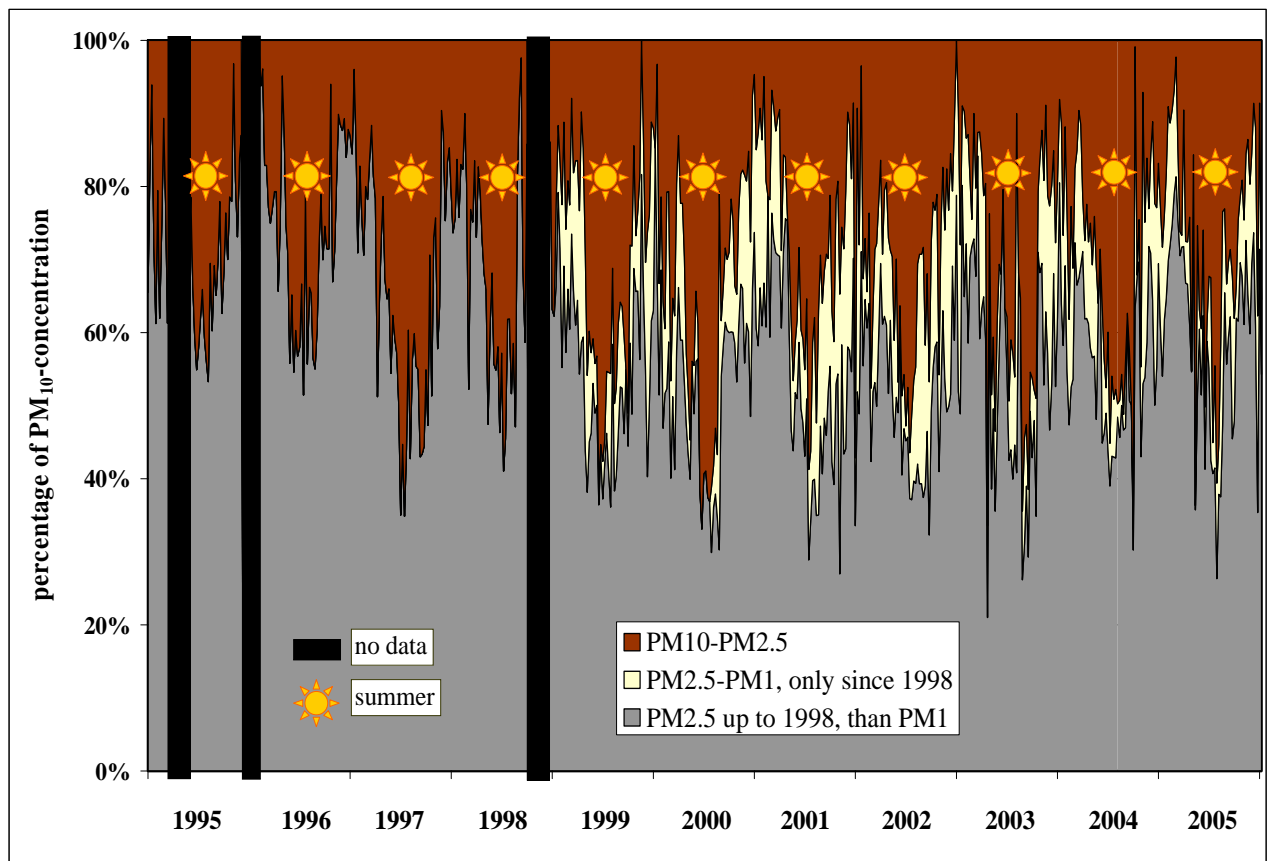


Figure 7 Time series of the percentage of PM₁₀-PM_{2.5} and PM_{2.5}-PM₁ mass concentration in PM₁₀ since 1995 at Melpitz site (from 1995-98 only PM₁₀-PM_{2.5}). The data are weekly averages.

3.2. Characterization of particles – comparison for air mass transport from West and East in winter and summer

3.2.1. PM₁, PM_{2.5} and PM₁₀ measurements with high-volume samplers

Three identical high volume samplers (DIGITEL) were used to determine PM₁₀, PM_{2.5} and PM₁ since May 2004 till now. PM₁₀ and PM_{2.5} were measured every day and PM₁ every six days (except during intensive campaigns with daily PM₁ measurements). The yearly mean concentrations for PM₁₀, PM_{2.5} and PM₁ were 19.9, 15.2 and 12.7 µg/m³ in 2004 and 22.4, 17.6 and 12.9 µg/m³ in 2005, respectively. The time series since May 2004 together with an indicator for air mass direction from West or East are plotted in Figure 8.

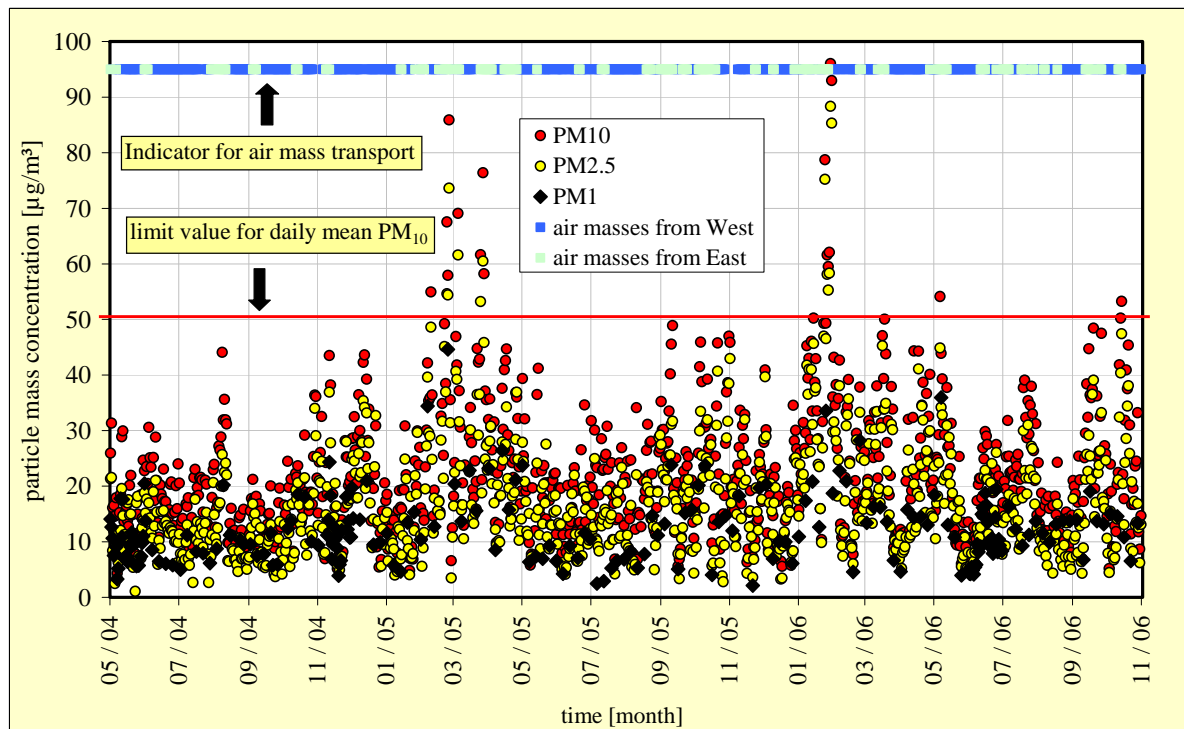


Figure 8 Time series of daily particle mass concentration PM₁, PM_{2.5} and PM₁₀ (May 2004 until October 2006) with indicator for air mass origin.

In winters the PM₁₀ but also the PM_{2.5} particle mass concentrations at the rural Melpitz site exceed the limit value of 50 µg/m³ for PM₁₀ (8 times in winter 04/05 and 9 times in winter 05/06). These numbers of days with large area exceedings of the PM₁₀ concentration limit of 50 µg/m³ contribute to the limit number of 35 days in cities nearby the Melpitz site. Additionally, the numerous days with elevated background concentrations higher than 30 µg/m³ are a problem in view of the limits. The elevated PM₁₀ values for the very hot and dry July 2006 in Germany and the warm and dry October 2006 are also recognizable. The high PM concentrations in May 2006 were caused by a long-range transport from partly anthropogenically caused vegetation fires in Russia. During this episode from May 5-9 in 2006, when the particle mass concentration exceeded 50 µg/m³ in wider areas, the percentage of the PM_{2.5} fraction in PM₁₀ was strongly elevated and reaches 84%, typical for long range transport episodes. Figure 9 illustrates this special situation. From the data plotted in Figure 8, the daily and monthly percentage of PM_{2.5} in PM₁₀ was calculated and plotted in Figure 10. As Figure 10 shows, the higher percentages for PM_{2.5} in winter can be also caused by long range transport, especially during air mass transport from east during dry high pressure situations with low mixing height.

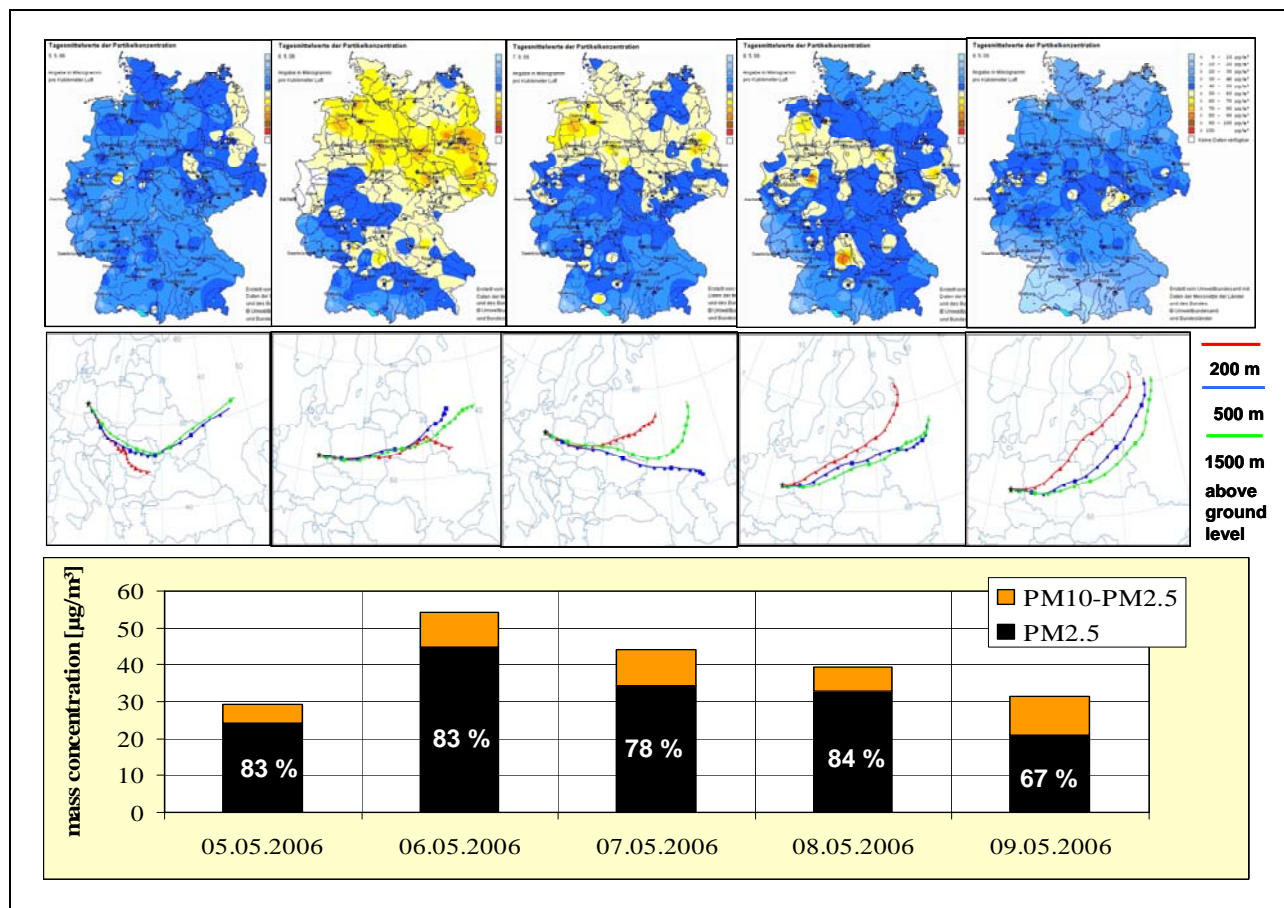


Figure 9 PM₁₀ concentrations in Germany with a high percentage of PM_{2.5} at five days in May 2006 caused by long-range transport from East. (sources: concentration maps, Umweltbundesamt, 96-hour backward trajectories, NOAA-Hysplit-Model)

The highest percentage of PM_{2.5} in PM₁₀ at Melpitz was between 92 and 96% during a smog episode over Germany in winter 2006 (January 22 till February 7). At the same time the mean percentage of PM_{2.5} in PM₁₀ was 67.4% (average of 6 sites) in North-Rhine-Westphalia (Bruckmann et al. 2006). These data show that the air masses near the Polish border were negligibly influenced by locally caused coarse particle emissions and the percentage of PM_{2.5} in PM₁₀ decreased over Germany because locally produced coarse particle were added to the air masses during the transport from East to West. Figure 11 shows the time series of daily particle mass concentration of the main ions (nitrate, sulfate and ammonium) and the total carbon content (TC) in PM₁, PM_{2.5} and PM₁₀. The concentrations in winter samples were higher than in summer samples for all species. The secondary aerosol components (NH₄⁺, SO₄²⁻ and NO₃⁻) were a significant fraction of PM and dominated in the samples which had influence of the long range transport (compare also with Figure 12). The strong variation of the ammonium nitrate concentrations between summer and winter can be explained by the vapor pressure of ammonium nitrate over the corresponding particles (Hildemann et al., 1984). Ammonium nitrate shows a temperature and relative humidity dependent phase distribution (Lammel and Leip, 2005, Plessow et al., 2005, Vayenas, et al., 2005) but also volatilization from filters in summer is possible.

Ammonium, hydrogen sulfate and sulfate can exist as NH₄HSO₄ and (NH₄)₂SO₄ in the condensed phase, therefore a reasonable concentration of NH₄⁺ and SO₄²⁻ was observed in the condensed phase in summer. The TC concentration in the winter was often strongly elevated and corresponded to the episodes of high particle mass concentration (see Figure 9). The reason is the air mass transport from East, especially in winter.

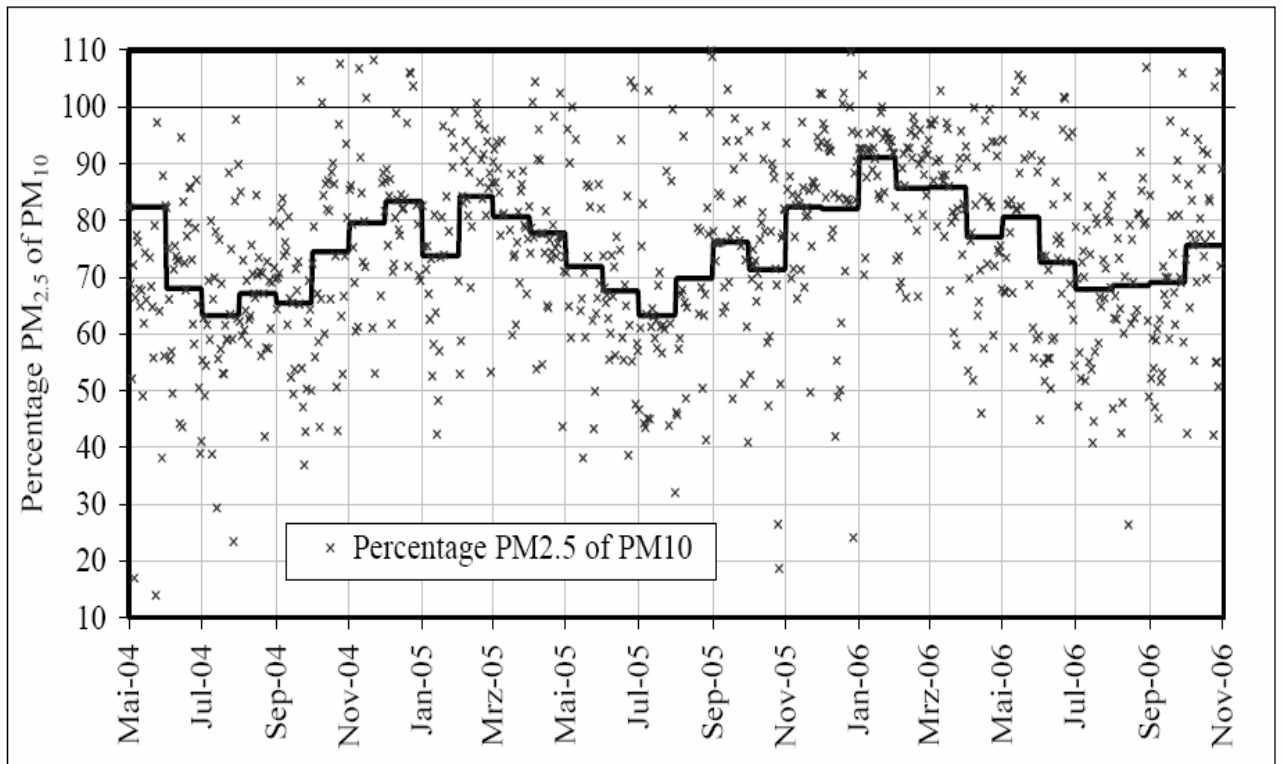


Figure 10 Time series of daily and monthly percentage of $PM_{2.5}$ in PM_{10} (May 2004 until October 2006) (Values greater than 100 % can be calculated in the range of spreading)

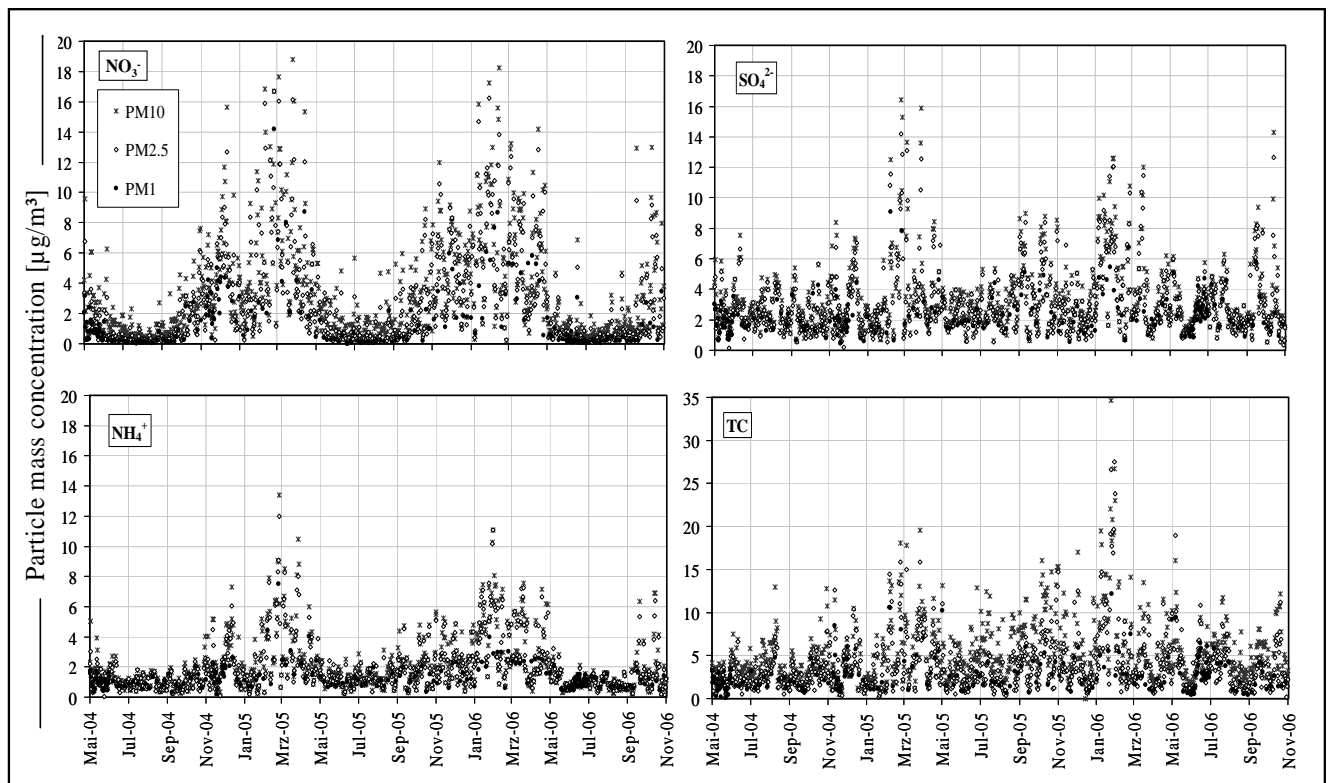


Figure 11 Time series of daily particle mass concentrations PM_1 , $PM_{2.5}$ and PM_{10} for the main ions (nitrate, sulfate and ammonium) and total carbon content (TC)

Figure 12 shows the average summer and winter particle phase mass concentrations of the main water soluble ions (nitrate, sulfate and ammonium) and organic and elemental carbon (OC and EC) in PM₁, PM_{2.5} and PM₁₀ for days with air mass transported explicitly from East or West. The average particle mass concentrations in Melpitz were higher in winter than in summer. The highest PM concentrations were observed during air mass transport from East (continentally influenced) in winter, caused from long range transport but also from a low mixing high pronounced during high pressure situations. The air masses from East were mostly dry and stable. The main source regions for these air masses are located in Russia, Belarus, Ukraine, Poland, Czech Republic and Slovakia. The high contents of sulfate, OC and EC indicate that there were also from anthropogenic emissions (power plants, industry, households and older automobiles). The wintertime OC/EC ratio was lower than in summer (i.e. higher EC fractions in winter), especially for the air masses from East, possibly caused by additional emissions from combustion processes. This observation is not valid for nitrate because the main source of nitrate is the NO_x-emission of cars. The difference in nitrate concentration between winter and summer was caused by the volatility of ammonium nitrate in summers.

The unidentified mass was mostly mineral dust. Unlike unidentified mass, the fraction of water soluble ions was higher in PM₁ than PM₁₀ and also was higher in the summer samples than in the winter samples. One reason is the re-suspension of coarse particles from agricultural activities and wind blowing dust in the surroundings. The re-emission is preferred in the summer as surfaces are drier and also dry much more faster after precipitation events than in winter. Generally, the PM concentration is lower under air mass transports from West (maritime and/or continentally influenced) because they are often combined with precipitation (wet deposition) and higher mixing volumes in more turbulent air masses.

3.2.2. PM₁₀ measurements with TEOM®

With a TEOM® a high time resolution PM₁₀ time series can be monitored additionally. Possible positive or negative sampling artifacts of the device were corrected daily in this project by a comparison with PM₁₀ data from the PM₁₀ high volume sampler.

The investigations of the high time resolution time series confirm the results discussed in chapter 3.2.1. Figure 13 shows the mean diurnal variation of half-hourly PM₁₀ measurements for air masses transport from West and East, and for winter and summer. In Figure 14 the relative frequency distributions of half-hourly PM₁₀ concentrations are plotted. The mean daily time series for days with air mass transported from East in winter shows the highest half-hourly PM₁₀ concentration, with a negligible variation, which is typical for long range transport. In summer the concentrations were lower for the air mass transported from east with a weak daily variation (lowest mean concentration in the early morning about 21 µg/m³) and highest in the late afternoon about 33 µg/m³). Also the concentrations during air mass transported from West in summer were observed at a level that is about 10-15 µg/m³ lower than in the winter with a weak daily variation (lowest mean concentration in early morning about 14 µg/m³ and highest in the late afternoon, about 18 µg/m³). A reason for this variation can be found in the re-suspension of particles from dry surfaces in the surroundings of the Melpitz site in summertime. The mean concentration time series for the air mass transported from West in winter was about 20 µg/m³ lower than for the air mass transported from East and was also nearly equal over the whole day. This is a hint for pronounced long range transport.

In consequence the relative frequency distributions (Figure 14) show clearly the higher percentage for elevated PM₁₀ concentrations especially for wintertime and air mass transported from the East. The smallest frequency distribution was observed from the measurements during air mass transported from west in summer.

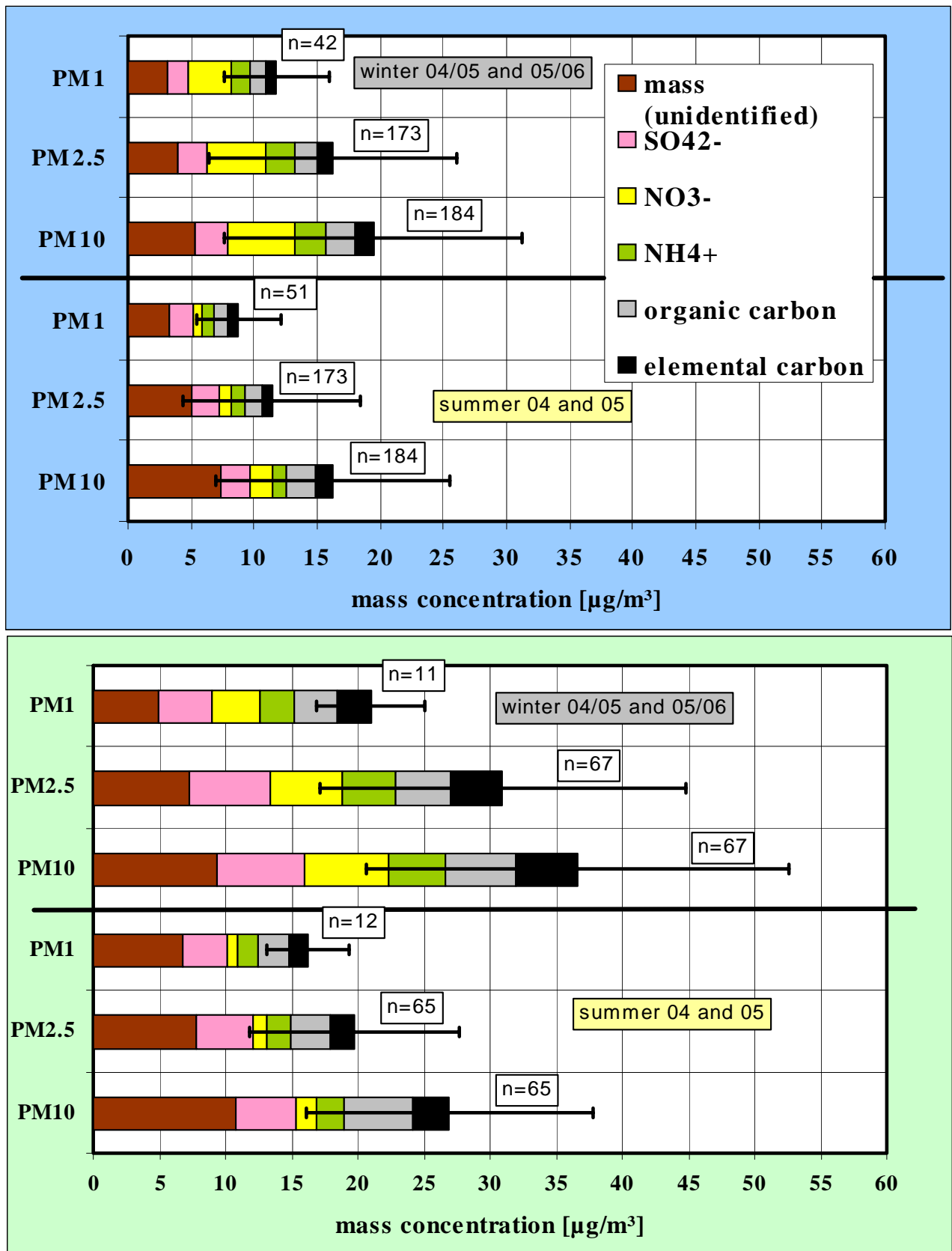


Figure 12 Mean PM_{10} , $\text{PM}_{2.5}$ and PM_1 mass concentrations and the concentrations of the main ions (nitrate, sulfate and ammonium) and organic and elemental carbon content (OC and EC) in winter and summer. Only days with air mass transport explicitly from West (blue frame) or from East (green frame) are considered. The error bars are the standard deviation for the particle mass concentration. "n" is the number of days. Averages of two winters (2004/05 and 2005/06 and two summers (2005 and 2006) are shown.

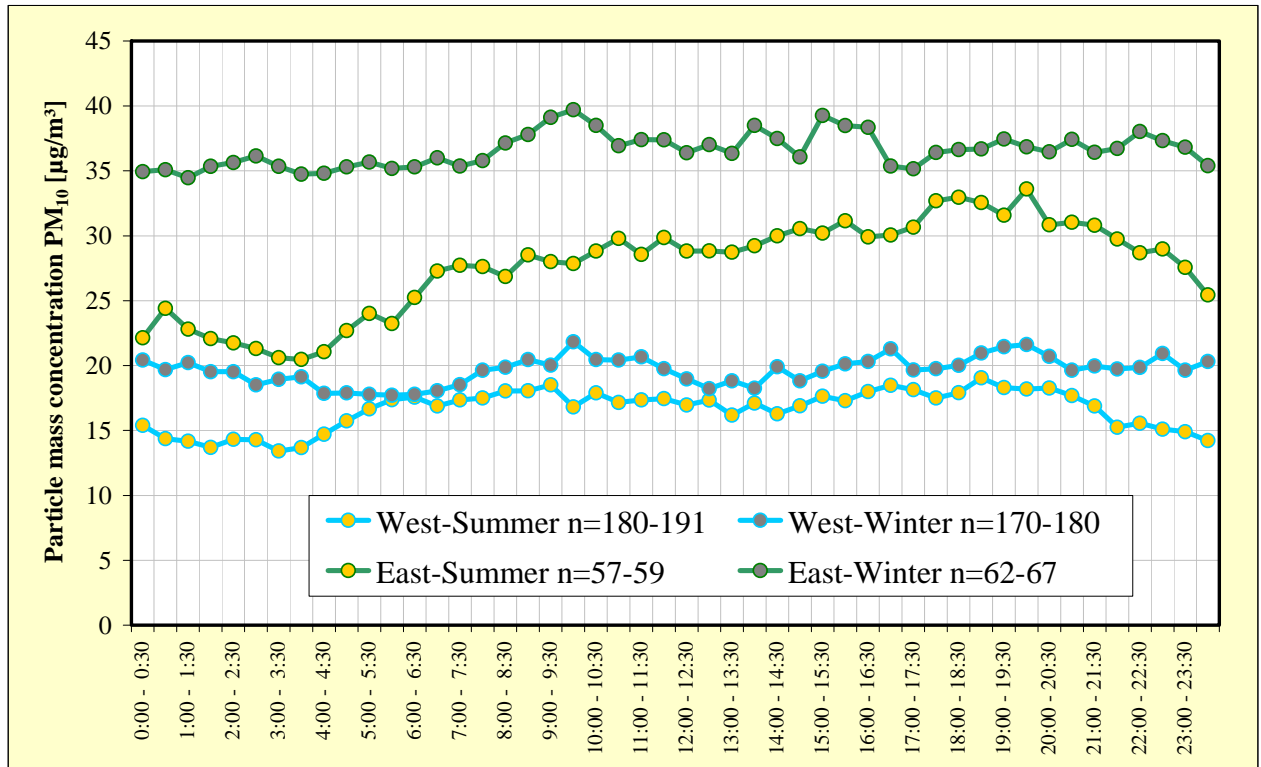


Figure 13 Mean daily time series of half-hourly PM_{10} measurements with a TEOM®, divided for winter and summertime. Only days with air mass transported explicitly from West or from East are considered.

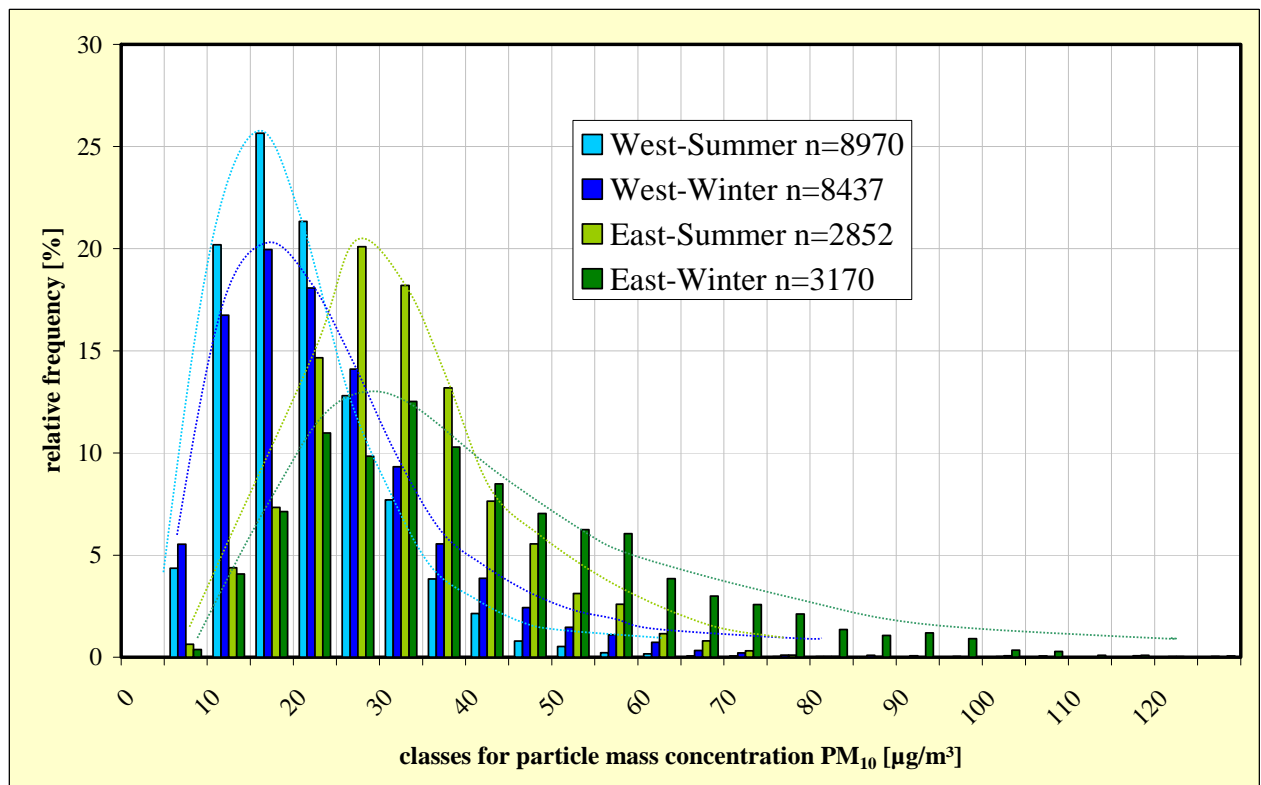


Figure 14 Relative frequency distributions of half-hourly PM_{10} measurements from Figure 13

3.2.3. PM characterization with five stage BERNER-type impactor

Selection of measuring days

PM sampling using the impactors was carried out during selected dry days with stable maritime and stable continental air mass transports according to the definition made in Figure 5. The impactor samples were taken over 24 hours. The days were selected by the weather forecast and the origin of air masses which was determined by 96-hours back trajectories. During the two years of the measurements 14 maritime and 8 continental summer days and 12 maritime and 12 continental winter days have been selected for mass determination and chemical analysis.

Mass, content of water soluble ions, OC/EC, and organic species

For these measurements all the above mentioned samples have been used. The Figure 15 shows the means of the determined mass of the size classes for summer and winter and air mass transported from West and East. Differences between seasons and source regions are evident. Summer concentrations are lower than winter concentrations and air masses transported from Eastern Europe carry higher amounts of PM. The highest concentration of PM was typically found in the size fraction 0.42-1.2 μm which is known for their atmospheric stability. This PM fraction is characteristic for long range transported particles. During wintertime also aged PM from domestic heating using coal was found mainly in this fraction. The percentage of coarse mode particles (size fraction 3.5-10 μm) was higher during summers because of the natural re-suspension by turbulence and the anthropogenic re-suspension of PM from dry surfaces by agricultural activities near the sampling site.

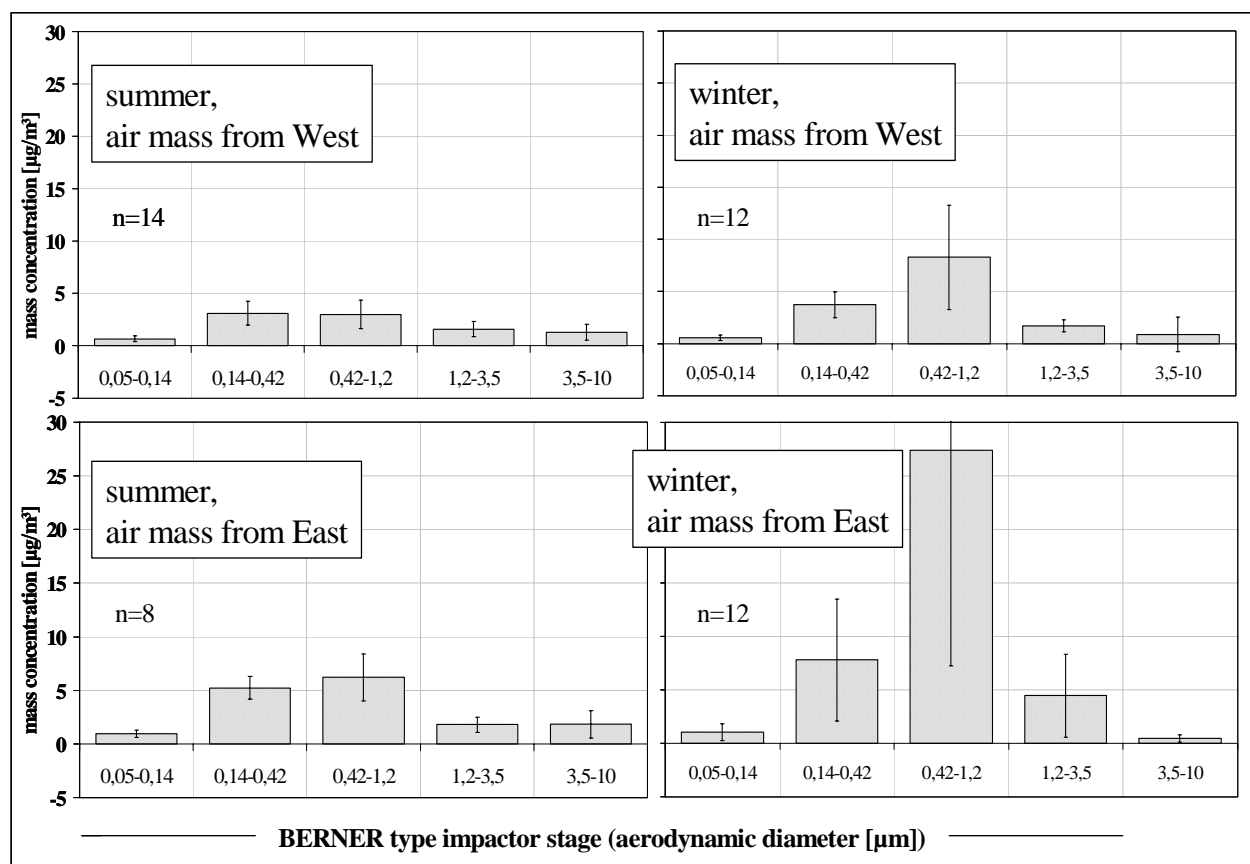


Figure 15 Mean PM mass concentration from the five stages of BERNER type impactor, divided for winter and summer days and air mass transported from West (continentally and/or maritime influenced) or East (continentally influenced). The error bars are the standard deviation, n is the number of days used for the average in winters 04/05 and 05/06, and summers 05 and 06.

In Figure 16 striking differences were found in the relative constitution of PM in the five size classes. During the summertime the non-resolved part of PM (mainly mineral dust) was the major fraction in all size classes for both source regions. Sulfate was found only in fine particles during summers but during winter sulfate was observed also in super-micron particles and in higher concentration in continentally influenced samples. The concentration of sulfate in winter often reached $10 \mu\text{g}/\text{m}^3$ in stage 3 particles. Similar patterns are seen for the other main ionic components such as ammonium, nitrate and chloride but not for the metal ions such as sodium, magnesium and calcium. Their content in PM is mainly influenced by sea salt. During winters chloride was also emitted by burning processes and by re-suspension of KCl from roads. Nitrate was the major ionic component (NH_4NO_3 in $\text{PM} < 1 \mu\text{m}$ and NaNO_3 in coarse mode PM) during winter sampling periods with maritime air masses whereas nitrate was found at a similar concentration to sulfate in PM of continental origin. In the summer samples nitrate was found mainly in the coarse mode particles, typically as the stable NaNO_3 whereas NH_4NO_3 decomposes to ammonia and nitric acid during summers leading to smaller fractions. Sodium nitrate was formed from sea salt by the exchange of chloride by nitric acid. Ammonium concentrations were low in coarse mode particles but in fine PM only ammonium sulfate was found in summer. However, both ammonium nitrate and ammonium sulfate were found in PM in winter.

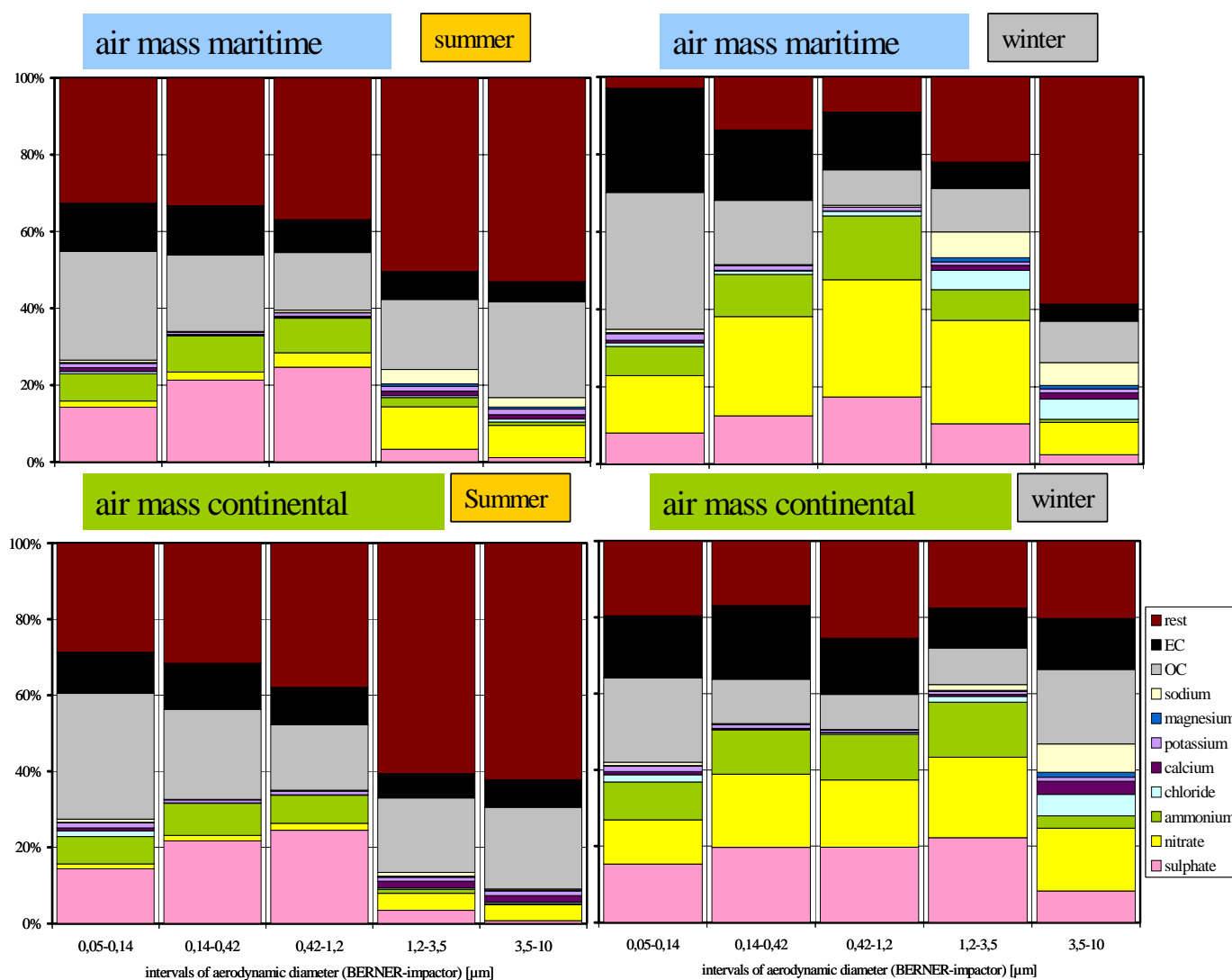


Figure 16 Percentage of mass of water soluble ion mass concentrations, mass concentration for organic carbon (OC) and elemental carbon (EC) and unidentified mass (rest) from the five stages of BERNER type impactor, divided for winter and summer days and air mass transported from East or West. Average values for winters 2004/05 and 2005/06 and summers 2005 and 2006.

The concentrations of organic carbon (OC) and elemental carbon (EC) show the identical behavior to sulfate because they have identical sources – all types of burning processes. The size distribution of EC and OC typically shows highest concentration at stage 3. Notable is the high percentage of OC/EC in the smallest particle which was mainly influenced by local or regional traffic emissions and SOA (secondary organic aerosol) from gas to particle conversion. The relatively high percentage of OC in coarse mode summer samples had the origin in biogenic material. Figure 17 shows the CPI values as a measure for biogenic hydrocarbons. In summer samples the CPI increases with the size of PM independently from the source region. The small differences have their origin in the traffic which is the influence from the Leipzig-Halle region. CPI from winter samples (near 1) indicates the anthropogenic origin of the alkanes because the biogenic material was clearly only a minor part of the alkanes and most of hydrocarbons were released from domestic heating and traffic.

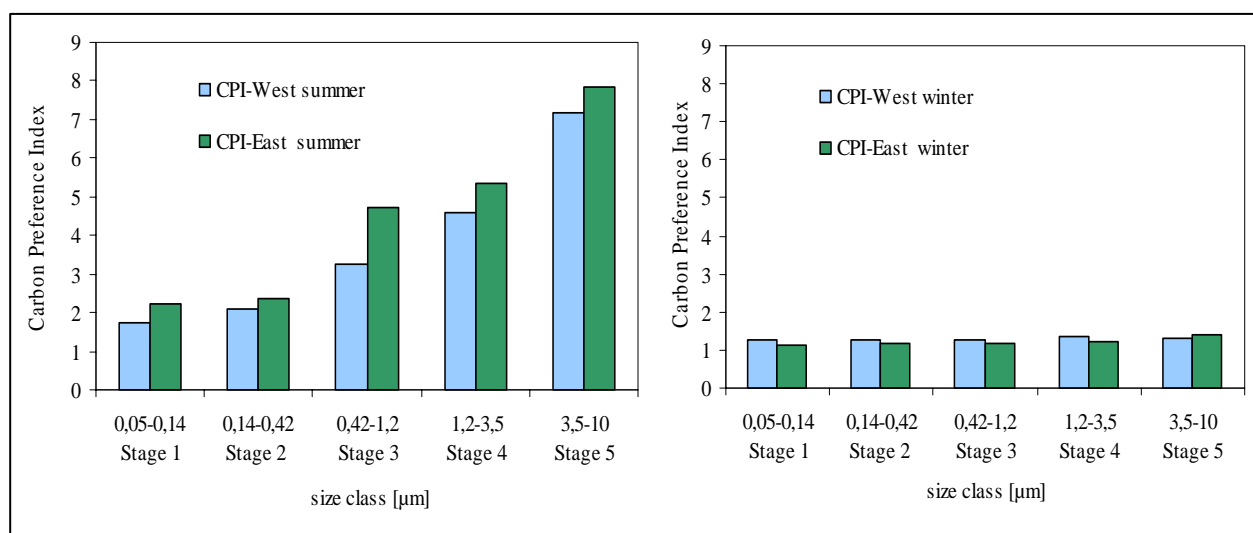


Figure 17 Carbon Preference Indices (CPI) from winter and summer and source regions in the West and in the East

3.2.4. PM characterization by TDMPS/APS

The TDMPS system measures number size distributions for particle diameters from 3 to 800 nm alternating with and without thermodenuder. The time resolution for one scan is 10 min, thus every 20 min a number size distribution for ambient and non-volatile aerosols is available. Larger particles (0.8 – 10 μm) are measured using an APS but for ambient aerosols only. The diurnal variation of the number size distributions was averaged for days with air mass transport from West and East and for summer- and wintertime. Results are shown in Figure 19. The variation of number size distributions shows significant differences. This was caused by variations in natural and anthropogenic aerosol sources but also in variations in meteorology. Air masses arriving from western directions (continentally and/or maritime influenced) are typically characterized by higher wind speeds and higher chance for precipitation compared to continental air masses coming from the East (continentally influenced). Continental air masses are usually connected with weather conditions dominated by long term high pressure influence without precipitation, higher amplitude of the temperature cycle between day and night and also dry air. Such high pressure systems occur also in wintertime and cause frequently a low mixing layer height during the cold season. During summer months the measurements show higher concentration of coarse particles due to re-suspension of crustal material from dry areas (compare Chapter 3.2.1. and 3.2.2.). These particles appear within the range of APS measurements (> 800 nm). Concentrations of very

small particles (< 10 nm) show on average a maximum around noon time and represents the so-called new particle formation events which occur frequently mainly under influence of solar radiation, i.e. on days with only little cloud coverage. In summer the new particles were measured after a well mixed boundary layer has been developed and the nocturnal inversion has been removed (9:00 – 10:00 CET). Later on the particles grow up to sizes of 100 nm in diameter. This phenomenon has been also observed after the thermodenuder but at smaller diameters meaning the newly formed particles contain some non-volatile material. In air masses from West the number concentration after thermodenuder seems to be decreased significantly, but for continental air masses number concentration of newly formed particles seem to be nearly identical. Since this process is connected with intensity of global radiation it is not clearly recognizable for wintertime. But the general observation that particles after the thermodenuder appear at smaller size is valid for winter and summer and both types of air masses.

In winter sometimes another phenomenon was observed: when the size distribution without thermodenuder was unimodal it was split into two modes after the thermodenuder. The mean plots are not suitable to show this behavior very clearly but it is still recognizable for winter and air mass transport from West. The mean maximum diameter in wintertime is shifted to larger sizes compared to summer months.

Figure 18 shows mean number size distributions averaged over whole days in summer and winter between July 2004 and June 2006 divided into air mass from West and air mass from East. The most significant difference is the higher number concentration in continental air masses at diameters between 50 and 1000 nm. This is the size range where mainly anthropogenic and aged anthropogenic aerosols appear and thus the result indicates that more polluted air was advected from eastern directions. This is in agreement with the results for the high-volume samplers, the TEOM® and the Berner type impactor.

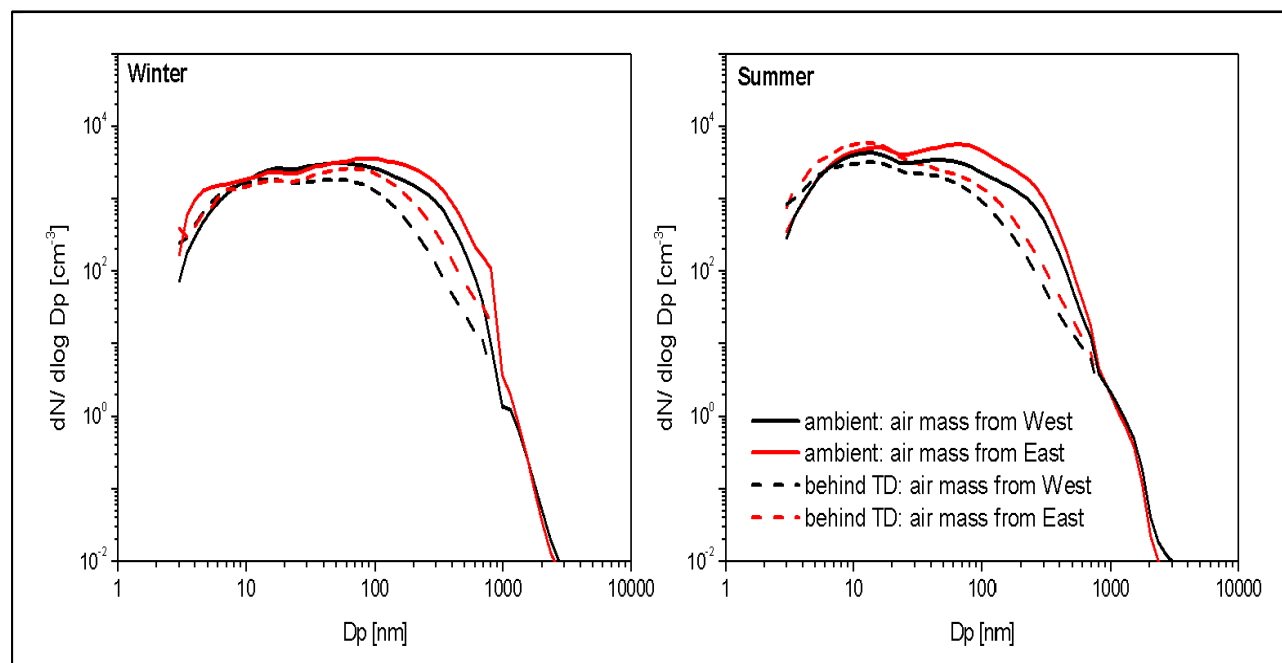


Figure 18 Mean number size distributions averaged for days in summer and winter divided into air mass from West and from East. Means for winters 04/05 and 05/06 and summers 05 and 06.

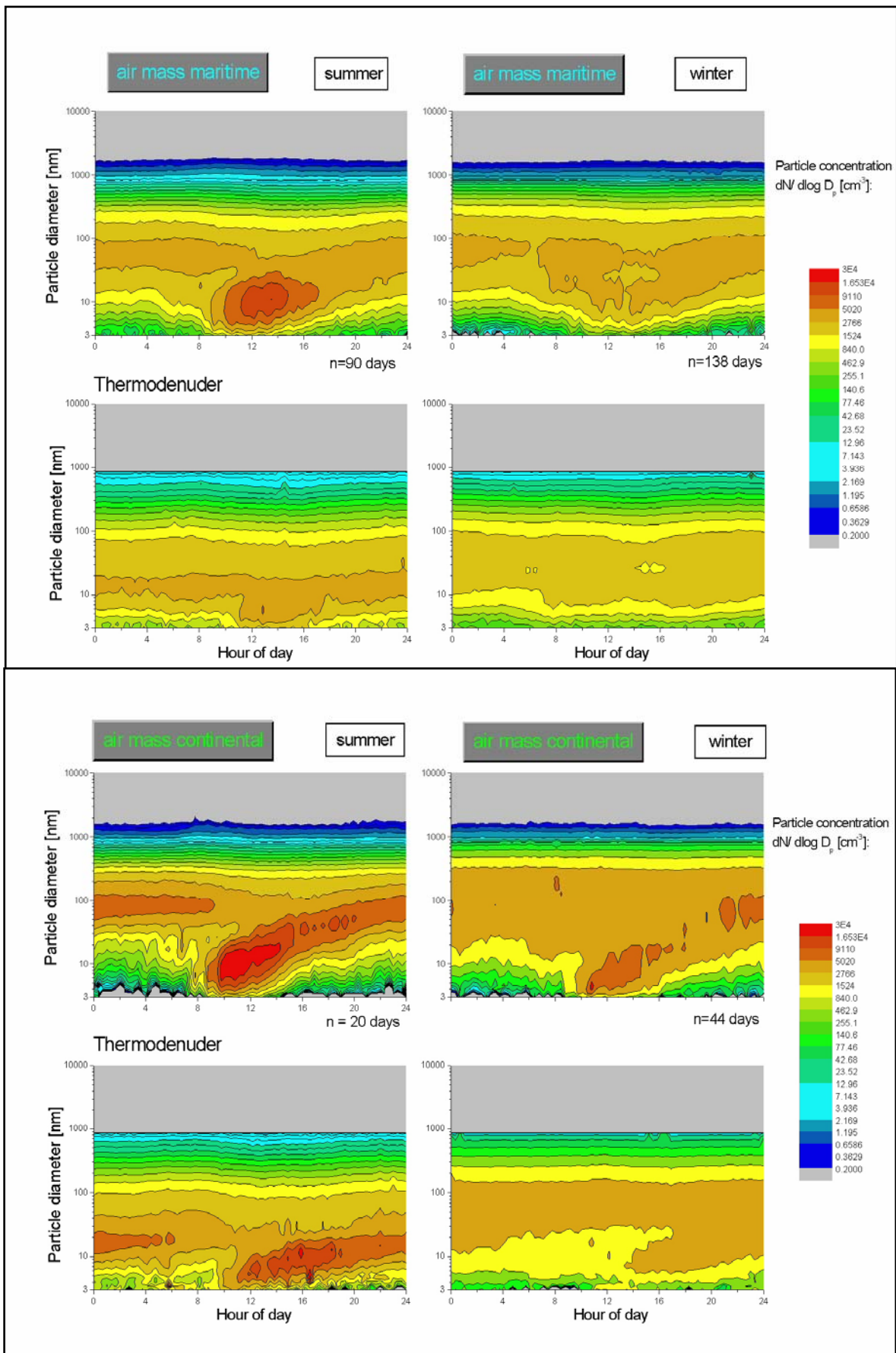


Figure 19

Evolution of number size distributions of ambient aerosols (upper figures) and of non-volatile particle fractions behind the thermodenuder (lower figures) for air mass from West (upper Plot) and air mass from East (lower Plot) divided for summer and winter days. Means for winters 04/05 and 05/06 and summers 05 and 06.

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