SIZE SEGREGATED CHARACTERIZATION OF PM_{10}, $PM_{2.5}$ and PM_1 DOWNWIND OF THE LEIPZIG CONURBATION IN GERMANY – AN EIGHT YEAR STUDY

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Introduction and experimental methods

The collection and characterization of environmental particulate matter (PM) is in the focus of atmospheric sciences and environmental policy (Pope and Dochery, 1999; Grassian, 2002). Up to the end of the 80-ies the region around Leipzig was one of the most polluted areas in Central Europe (Spindler at al., 1999). A size segregated long term characterization is necessary because particles with different aerodynamic diameters show different residence times in the troposphere, are differently composed and have different human health effects e.g., particles smaller than 10 µm (PM_{10}) are able to pass the larynx whereas particles smaller than 2.5 µm ($PM_{2.5}$) reach the pulmonary aveoli.

Filter samples PM_{10} and $PM_{2.5}$ were taken weekly, using the 'Partisol 2000' low flow air sampler (Figure 2, RP, Rupprecht and Patashnik Co. Inc., Albany, New York, USA) on 47 mm diameter Teflon filters (Millipore, Eschborn, Germany, Type 4700, 3 µm pore size). The sampling starts every Monday 12:00 CET. Parallel samples for PM_{10} and $PM_{2.5}$ are available from 1995 to 2002. In addition samples for PM_1 are available from 1999 to 2002. Samples were also taken on 47 mm quartz fibre filters (Munktell, type MK 360) over a second PM_1 inlet for the investigation of the content of total carbon (TC), the sum of organic (OC) and elemental carbon (EC). These filters were preheated at 800 °C for at least 3 hours.

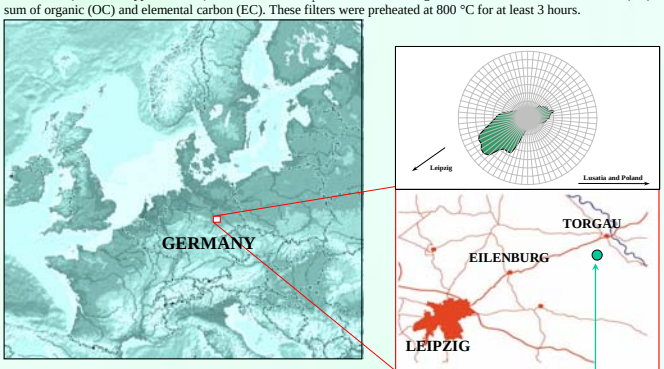

Figure 1: Location of the IfT research station in Europe (Melpitz, Germany, state Saxony) 12°56' E, 51°32' N, Altitude 86 m a.s.l. Wind rose, calm v < 0.5 m/s in 12 m above ground is in 8.4 % of more as 3.3 million 5 minute averages

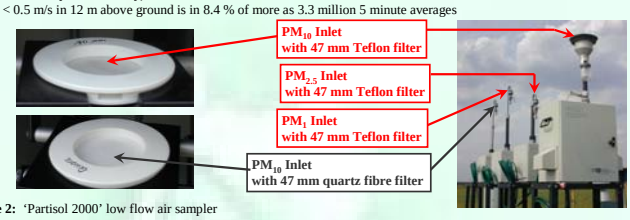

Figure 2: 'Partisol 2000' low flow air sampler

Time course of ratio for particle mass concentration in weekly PM_{10} and $PM_{2.5}$ low volume samples (1995 – 2002)

In the coarse fraction (PM_{10}-$PM_{2.5}$) mainly mineral ground material was found, which was not characterized chemically. Coarse dust from the ground is suspended especially in summer when surfaces dry faster and precipitation is more intense but of shorter duration as in winter. Additionally, anthropogenic turbulence from moving cars and agricultural activities leads to re-emission of soil. Strong re-emissions were found in the dry summers 1999 and 2000, the latter coincided with an drought in northern Saxony (Figure 5). The summers 1995, 2001 and 2002 were relatively wet and the (PM_{10}-$PM_{2.5}$)/PM_{10}-ratio is not very pronounced. From 1995 to 2002 the (PM_{10}-$PM_{2.5}$)/PM_{10}-ratio seems to increase somewhat stronger than expected from the intensity and distribution of precipitation. This can be caused by the strong decrease of permanent anthropogenic coarse dust emission in eastern Germany so that re-emission more strongly influences the (PM_{10}-$PM_{2.5}$)/PM_{10}-ratio.

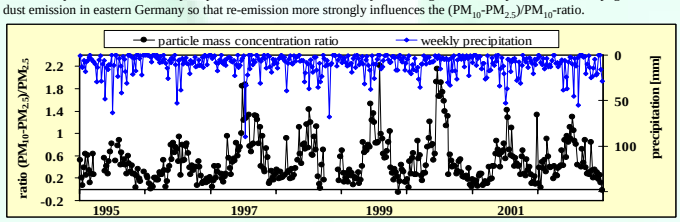

Figure 5 Time course for the mass concentration ratio (PM_{10}-$PM_{2.5}$)/$PM_{2.5}$, the sum of weekly precipitation is plotted inversly

Seasonal contribution of particle mass and ion concentration in weekly PM_{10}, $PM_{2.5}$ and PM_1 low volume samples (1999 – 2002)

In Figure 7 a seasonal ordered series of pie charts shows the size segregated seasonal relative content of water soluble ions and percentage of particle mass as four year mean (1999 to 2002). In the coarse mode (PM_{10}-$PM_{2.5}$) a high relative mass content was found for nitrate in all seasons. The sulphate content in the fine mode (PM_1) is higher than in the other modes. The lowest ammonium content was found in the coarse mode. Especially, in summer the sulphate content is relatively high in PM_1 and $PM_{2.5}$-PM_1 compared to nitrate. The content of coarse mode particles is highest in summer and also higher in fall and spring. A hint for re-emitted material is the high mass content of potassium, magnesium and calcium ions (white part, 18 % of the bigger circle in summer). The magnesium content is elevated in the $PM_{2.5}$-PM_1 mode in winter, possibly from road defrosting. Sodium is a minor ion but in the coarse mode samples it is the dominating cation. The summer concentrations for metal ions (potassium, magnesium and calcium) in the fractions $PM_{2.5}$-PM_1 and PM_1 were larger than in the others seasons. The content of chloride in the coarse mode in winter is highest due to sea salt transported during weather situations with wind direction from the Atlantic Ocean and the North Sea and low sun radiation. In summer the content is low by possible photochemical exchange of chloride by nitrate (e.g. Pio and Lopes, 1998). It can be clearly recognized that most of the mass of $PM_{2.5}$ is PM_1. The coarse mode mass fraction PM_{10}-$PM_{2.5}$ is elevated in the summer and has the lowest contribution to PM_{10} in the winter.

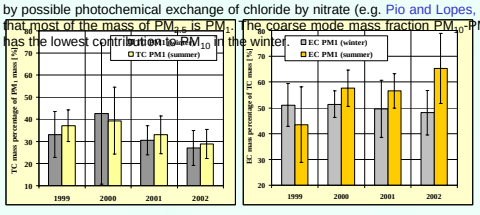

Figure 6 Percentage of TC in PM_1(left plot) and EC Percentage of TC in PM_1 (right plot). Mean values for the years 1999 to 2002 are given. Error bars are from standard deviation

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The particle mass concentration of the filter samples was determined gravimetrically under constant conditions (at 50% relative humidity, temperature 20°C). The conditioning time was at least 24 hours (Mettler AT 261 Delta Range balance, Mettler Toledo GmbH, Giessen, Germany). Water-soluble ions were determined from each filter. Standard ion chromatography with columns by Dionex, USA and Metrohm, Switzerland was used for that purpose.

The uncertainty of the ion analysis was estimated to 10 % using an ionic standard (Brüggemann and Rolle, 1998). The determination of OC and EC was performed by a 2-step thermographic method applying a Ströhlein C-mat 5500 carbon analyzer. OC was evaporated at 650 °C in N_2 for 8 minutes and oxidized to CO_2 by a catalyst, EC subsequently burned during a new heating step at 650 °C in O_2 for 8 minutes. The error of the method was found to be < 5 % for repeated EC analysis of quartz filter samples. The detection limit of the carbon analyzer was determined to be about 0.3 µg carbon.

The PM_{10} samples from the RP-sampler were compared with results from a modified Sierra-Andersen-PM_{10} high volume sampler (SA, Andersen Samplers Inc., Atlanta, Georgia, USA). The filters are rectangular (254 * 203 mm) quartz fibre filters (Munktell, Filter AB, Grycksbo, Schweden, type MK 360). The filters were preheated for 24 hours at 105°C. The sampling time for each day was 23.5 hours from 8:00 to 7:30 CET (central European time) on the following day.

The sampling site – IfT research station Melpitz

All samples were taken in central Europe at the IfT research station situated near the village of Melpitz in the vicinity of the city of Torgau in the river Elbe valley in Germany. This station is an air chemistry station with micrometeorological energy balance measurements located on a flat meadow (Spindler et al., 2003). For the location and details of the RP-sampler see Figure 1. The place is surrounded by agricultural land and there are no wind obstacles within a distance of at least one kilometre in all directions apart from a small sector in the east, with data acquisition containers and the village of Melpitz in a distance of 65 and 500 m, respectively. The grassland is semi-natural and there is no pest control. Plants cover the surface by more than 95%. The grassland was fertilized in the previous 10 years once in spring with 70 kg N ha^{-1} in a single application by calcium ammonium nitrate (60% NH_4NO_3, 35% $CaCO_3$, 5% H_2O). There are no grazing animals. A federal main road (B 87) crosses the region in a minimum distance of 1.5 km in northern direction. Edges of forests, Dübener Heide and Dahlener Heide, both with nature conservation status, lie 2.5 km to the north and 1 km to the south, respectively. The houses in both villages in neighbourhood (Melpitz and Klitzschen) were heated by natural gas, commonly. Under the dominating wind direction from southwest (Figure 1), the Melpitz station lies in the downwind plume of the city of Leipzig. in a distance of 50 km. The second important wind direction maximum is east. Hence during high-pressure conditions dry air masses are transported over long distances to Melpitz, often with moderate wind velocity and without precipitation. The main source regions for these air masses are Poland, Belarus, Ukraine and the north of the Czech Republic.

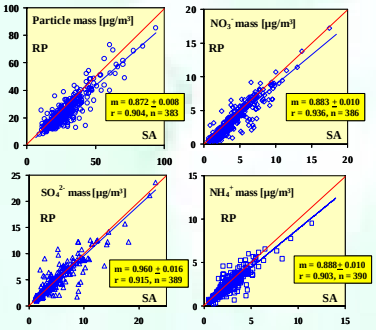

Figure 3 Comparison of SA (weekly means of daily samples) and RP (weekly samples) for 1995 to 2002 (linear fit y=mx)

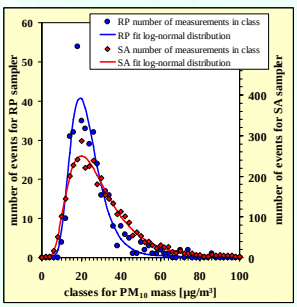

Figure 4 Histogram for particle mass concentration of PM_{10} SA-sampler (weekly means from daily samples) and RP-sampler (weekly means) with an approximation by a Gaussian fit. Both y-axes are comparably scaled

Comparison of PM_{10} measurements RP-sampler (low flow) with SA-sampler (high volume)

Daily high volume PM_{10} and weekly low volume PM_{10} measurements are available for eight years (1995 to 2002) in parallel. For an assessment of the RP low flow sampler technique and the SA high volume sampler technique the particle mass concentration and the mass concentration for the mean ions nitrate (NO_3^-), ammonium (NH_4^+) and sulfate (SO_4^{2-}) were compared. The calculated arithmetic weekly means from the daily SA samples and direct measured weekly samples from the RP sampler were used

The resulting scatters shown in Figure 3. Generally the RP sampler shows smaller values than the SA sampler. For particle mass concentration, NO_3^- mass, and NH_4^+ mass the difference is about 12 % and the slope of the regression line shows a very small error. For SO_4^{2-} mass the difference is smaller (about 4 %) and the error of the slope of the regression is hardly higher. The small but significant differences between the SA and RP sampler with regards to mass concentration, nitrate, and ammonium mass could result from different inlet systems (virtual impactors), different filter material and a larger absolute sampling time of the RP sampling process. Nitrates, especially ammonium nitrate, can evaporate from the filter depending on temperature and relative humidity during a longer sampling time and cause mass losses.

Figure 4 shows two histograms (example for particle mass concentration distribution) approximated with two fits of lognormal distribution. The SA sampler has a wider range in the distribution of classes and extreme concentrations can be detected in daily samples only. The weekly samples (RP sampler) give a more smoothed result for the distribution in classes around the mean value.

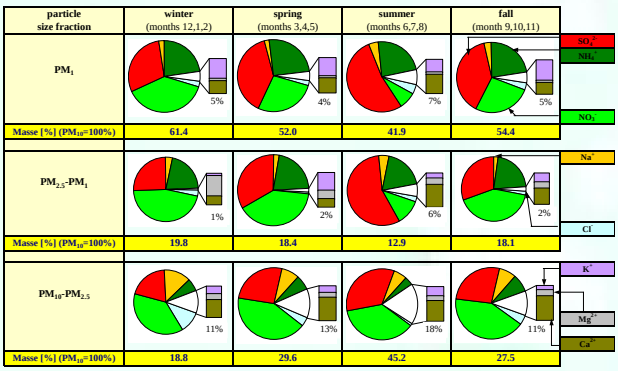

Figure 7 Seasonal ordered pie charts for the size segregated relative content of water soluble ions and percentage of particle mass concentration (four year mean 1999 to 2002)

Seasonal contribution of TC and EC concentration in weekly PM_1 low volume samples (1999 – 2002)

Figure 6 shows the percentage of TC in PM1 (left plot) and the EC percentage of TC in PM1 (right plot).

The mean content of TC = OC + EC in PM_1 was found between 27 and 42 % of mass, with a non-significant difference between summer and winter (Figure 6 left plot). The percentage of EC in TC shows a significantly increasing trend in the summers from 1999 to 2002 (Figure 6, right plot) and no significant trend in winter. On the one hand, a reason can be found in decreasing absolute particle mass and constant EC emissions from heavy-duty tracks during summers. On the other hand, a decreasing emission of VOC (Gnauk and Rolle, 1998) results in a lower concentration of secondary organic aerosol (SOA).