# SIZE SEGREGATED CHARACTERIZATION OF $PM_{10}$, $PM_{2.5}$ , $PM_1$ AND LONGTERM MEASUREMENTS OF $PM_{10}$ DOWNWIND OF A LARGE CONURBATION IN GERMANY


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AFO 2000 VERTIKO


## Introduction and experimental methods

For a period of ten years (1993 to 2002) filter samples $PM_{10}$ were collected at the IfT-research station Melpitz located in the downstream plume of the Leipzig conurbation in Central Europe (Figure 1). Sampling devices were a modified *high volume* sampler ($PM_{10}$ Sampler, Anderson Samplers Inc., Atlanta, USA, quartz fibre filters, Munktell Filter, Grycksbo, Sweden,) for daily samples since 1993 and for weekly filter samples $PM_{10}$, $PM_{2.5}$, and $PM_1$ a *low flow* sampler ("Partisol 2000" air sampler, Rupprecht and Patashnik Co. Inc., Albany, USA, since 1995 for $PM_{10}$ and $PM_{2.5}$, since 1999 also for two $PM_1$ impactors) additionally. The second $PM_1$ impactor acts in parallel operation and was used for OC/EC collection on quartz filters. The determination of organic carbon (OC) and elemental carbon (EC) was done with a thermographic method using a Ströhlein C-mat 5500 carbon analyser. OC was detected at 650 °C in $N_2$ and EC after them during a new heating step at 650 °C in $O_2$. The sampling volumes were 1400 (hig volume, daily) and 84 m³ (low volume, weekly), respectively. The filters for the three impactors in the low flow sampler are 47 mm diameter Teflon filters (Millipore, Eschborn, Germany, Type 470 and 3 µm pore size). After a conditioning time at least 24 hours (50 % relative humidity, 20 °C) the particle mass was determined gravimetrically (Mettler AT 261 Delta Range balance, Mettler Toledo GmbH, Germany). Water soluble ions were determined from each filter. Standard ion chromatography with columns from Dionex, USA and Metrohm, Switzerland was used for that purpose.

The particle mass distribution, content of water soluble ions and carbon content in different size fraction were discussed. The mass concentration data were compared with gravimetric mass data from stations located in Saxony (former Southeast of the German Democratic Republic, GDR). The results show an decreasing particle mass concentration and a change in the ion content, especially for sulfate and nitrate after the German unification, caused by changing anthropogenic emissions.

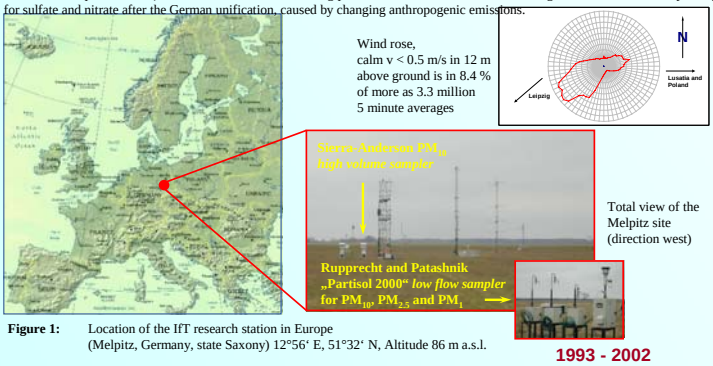
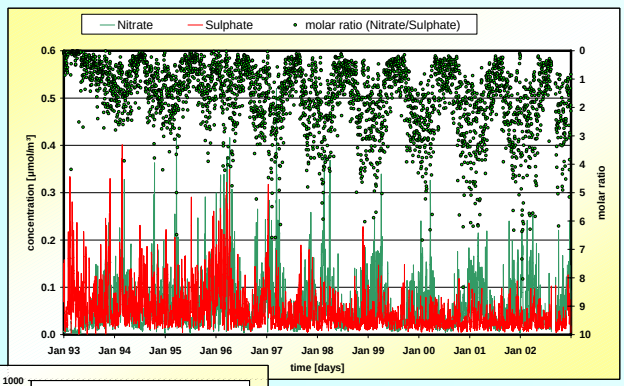



**Figure 1:** Location of the IfT research station in Europe (Melpitz, Germany, state Saxony) 12°56' E, 51°32' N, Altitude 86 m a.s.l.

**1993 - 2002**



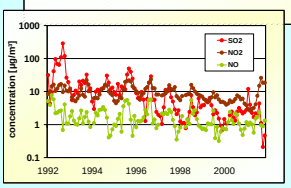




**Figure 3a:** (top) Daily $NO_3^-$ and $SO_4^{2-}$ molar concentration in particles $PM_{10}$ (high volume sampler. The molar ratio $NO_3^-$ / $SO_4^{2-}$ is plotted inverse.

**Figure 3b:** (left) Concentration time course for trace gases $SO_2$ and $NO_x$

## Nitrate and sulphate in particles $PM_{10}$

Since 1993 particle filter samples $PM_{10}$ were collected daily. The concentrations of sulphate and nitrate are decreasing (Figure 3a). The sulphate concentration decreases much more stronger caused by a strong decrease of the $SO_2$ concentration in the last 10 years. The $NO_x$ concentration (NO and $NO_2$) for this time shows only a moderate decreasing trend (Figure 3b). The inverse plotted $NO_3^-/SO_4^{2-}$-ratio in Figure 3a shows a typical increasing trend caused by the decreasing $SO_4^{2-}$-mass concentration in $PM_{10}$ which originates in the strong decrease of $SO_2$ concentrations with seasonal variation (Figure 3b) but also in $NH_4NO_3$-losses by evaporation from the filters during higher temperatures in summer.

## Size segregated characterization of $PM_{10}$, $PM_{2.5}$ , $PM_1$ (1999 – 2002)

Since 1999 particles have been collected also as weekly samples on filter packs for $PM_{10}$, $PM_{2.5}$ as well as $PM_1$ (two inlets) using the "Partisol 2000" low flow air sampler. As a result a 4 year study for particle concentration and content of water soluble ions of fractions $PM_{10}$, $PM_{2.5}$ and $PM_1$ (additionally with the OC and EC content) is available. Figure 4a shows the size segregated weekly particle mass concentration.. In the summers (highlighted by a sun) more coarse particles ($PM_{10}$-$PM_{2.5}$) exist. A reason can be found in a reemission from dry surfaces. The mean mass distribution for the period 1999 up to 2002 is: 11.1 µg m$^{-3}$ for particles $PM_1$ with a part of water soluble ions of 55 %, 3.4 µg m$^{-3}$ for particles ($PM_{2.5}$ – $PM_1$) with a part of water soluble ions of 50 % and 6.1 µg m$^{-3}$ for particles ($PM_{10}$– $PM_{2.5}$) with a part of water soluble ions of 22.8 %. The mean content of TC (OC+EC) in $PM_1$ is between 16 and 17 % of mass, with no significant difference between summer and winter. The percentage of OC from TC shows an increasing trend in summer from 1999 to 2002 (Figure 4b) and no trend in winter.

A reason can be found in a increasing emission of diesel soot because these is the main source in summer.

In Table 1 graphs for the size segregated seasonal relative content of water soluble ions are plotted (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 as 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. A reason can be found in evaporation of nitrates caused by higher temperatures in summer. The mean seasonal mass is near equal for all seasons, but the absolute part of coarse mode particles is highest in summer and also higher in fall and spring, also the sodium part is elevated. A hint for reemitted material is the high mass content of potassium, magnesium and calcium ions (black part, 18 % in the bigger circle). The Magnesium content is elevated in the $PM_{2.5}$-$PM_1$ mode in winter, that can be a hint of an anthropogenic impact from road defrosting. The content of chloride is highest in the coarse mode in winter due to sea salt. In summer the content is very low by possible exchange of chloride by nitrate (photochemistry).

**1983 - 2002**

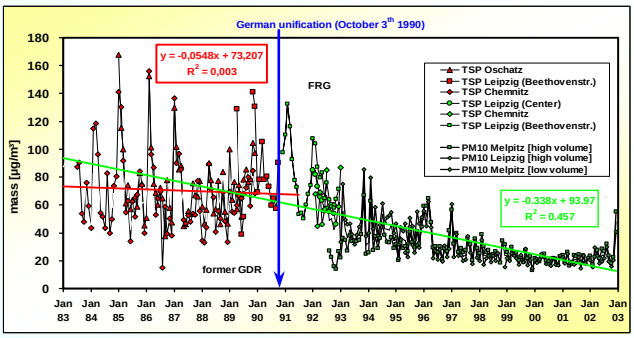
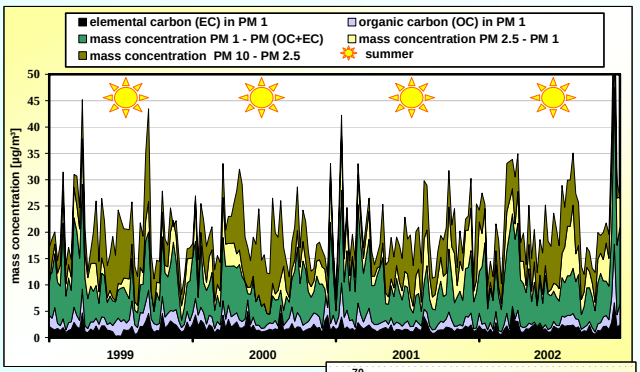



**Figure 2:** Reconstruction of the aerosol mass concentration time course 1983-2002 (1983-1992 TSP and from1992 $PM_{10}$ )

## Reconstruction of the aerosol mass concentration time course 1983-2002

For an observation of the aerosol mass concentration in coarse mode (total suspended particles, TSP and $PM_{10}$) over a large period of time a historical time course of particle mass concentration was reconstructed (Figure 2). From 1983 to 1992 TSP gravimetric mass data of four stations located in the vicinity of the Melpitz site in Saxony (former south-east of the GDR) were used. For these monthly means from 1983 up to the German unification (red points) no significant trend was found (red line in Figure 2). The mean TSP particle mass concentration was found between 60-80 µg/m³ and shows a big scatter. The different monthly means from 1990 up to 2002 show a significant decreasing particle mass concentration (green line). Monthly particle mass concentrations for $PM_{10}$ from Leipzig and Melpitz are highlighted with dark green symbols in Figure 2. The causes for the decreasing particle mass after 1990 are very complex and can be found in a shutdown of the obsolete factories, the decreasing importance of the brown coal processing industry, the modernisation of power plants and individual house heating systems. This trend was also balanced by a strong increase of road traffic (number of cars and miles travelled). Since 2000 the mean particle mass concentration stagnates between 20-30 µg/m³. In the relatively cold last winter higher monthly means were found caused by dry and cold weather conditions with high pressure systems and a transport of air masses from eastern Europe to the Melpitz site (continental climate, see wind rose in Figure 1).

**1999 - 2002**



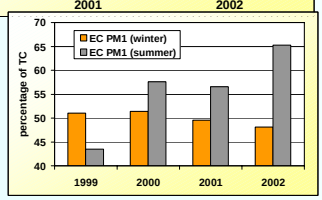




**Figure 4a:** (top) Size segregated weekly particle concentration (low flow sampler) fraction $PM_{10}$, $PM_{2.5}$ and $PM_1$ (additional with the OC and EC content), the weeks 29,31,41 (1999), 14,15 (2000), 12 (2001) and 12, 33,34 (2002) are interpolated.

**Figure 4b:** (right) Percentage of EC from TC (OC+EC), yearly means for summer (April - September) and winter (October - March)

**Table 1:** Size segregated seasonal relative ion content (mean 1999 to 2002)

| size | winter (months 12,1,2) | spring (months 3,4,5) | summer (months 6,7,8) | fall (months 9,10,11) |
|---|---|---|---|---|
| PM1 | 5% | 4% | 7% | 5% |
| % Mass ($PM_{10}$ = 100%) | 61.5 | 52.0 | 41.9 | 54.4 |
| PM2.5-PM1 | 1% | 2% | 6% | 2% |
| % Mass ($PM_{10}$ = 100%) | 19.9 | 18.4 | 12.9 | 18.1 |
| PM10-PM2.5 | 11% | 13% | 18% | 11% |
| % Mass ($PM_{10}$ = 100%) | 18.9 | 29.6 | 45.2 | 27.5 |
| mean seasonal mass [µg/m³] | 20.7 | 22.1 | 20.0 | 19.4 |

Cl⁻, $NO_3^-$, $SO_4^{2-}$, $Na^+$, $NH_4^+$, part of following ions, $K^+$, $Mg^{2+}$, $Ca^{2+}$


## Acknowledgements

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