Size Segregated Characterization of Fine Particulate Matter in a Triple Site Experiment - Leipzig-City, Leipzig-Outskirts, and Melpitz

A contribution to subproject AEROSOL

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Summary

The European standard for suspended particulate matter in air (PM_{10}) will lead to strict regulations with regard to the atmospheric mass concentration of PM_{10} and later $PM_{2.5}$. For Saxonian cities the observance of these new regulations will be problematically. So the Sächsisches Landesamt für Umwelt und Geologie charged the IfT to measure the size segregated particulate matter at three sites in NW Saxony to identify sources of the small particles during two measurement campaigns in winter 1999/2000 and in summer 2000.
The three sites selected for particle collection were a central cross road near the main railway station, the measuring platform of the IfT building at the North-Eastern outskirts and the rural IfT research station in Melpitz.
Nine typical dry winter days and eight typical dry summer days have been selected for the 24 hour collection of particles by five stage BERNER impactor (only four size fractions have been investigated: 0.05 – 0.14 µm, 0.14 – 0.42 µm, 0.42 µm – 1.2 µm and 1.2 – 3.5 µm), and $PM_{2.5}$ high volume filter collection on quartz fibre filters.
The chemical characterization of the impactor and filter samples was performed with regards to their ionic content, OC-EC, trace metals and selected organic single species.
Reflecting the specific regional source structure the most important sources of particulate matter have been identified for the four impactor stages in a winter and a summer period. The meteorological situation during both periods was not typically for the region with very mild winter with good exchange conditions. The summer measurement period in July was untypically cold. During both periods days with continental air masses from the East could not be observed, which have shown higher particle loads in the past (K. Müller, 1999).
An extrapolation of the data to the PM_{10} standard of the European Union established that compliance will be problematically in the Saxonian cities. The most important anthropogenical sources of small particles have their origin in traffic and household emissions.

Stage	mass proportion [%]	maximum [%]	minimum [%]	absolute standard deviation [%]	variation coefficient [%]
1	6	3	15	4.6	77
2	21	16	24	3.3	16
3	51	43	57	5.1	10
4	22	17	27	4.1	10

Table 1: Mean values of the PM distribution between the four size fractions of the investigation

The main amount of particulate matter, nearly 80 %, is found in small particles below 1.2 µm, which are most important because of their atmospheric stability, lung penetrating and toxic effects. The OC-EC content in particles decrease with the particle diameter. The smallest particles contain up to 80% carbon in winter samples whereas in stage 4 the carbon content decreased under 20%, mostly.

Selected Results

Between the two measurement campaigns not only important differences but also comparabilities have been identified. The traffic emissions were stable at both campaigns. During the winter campaign the particulate matter composition was heavily influenced by individual household heating with brown coal briquettes, output from coal fired electrical power plants and heating power plants, and by the lower mixing height. During the summer campaign the influence of biogenic emissions must be taken into account.

Stage 1 particles (50 – 140 nm)
The smallest particles mainly consist of elemental and organic carbon directly from traffic emissions or from gas to particle conversion or condensation of organics on particle surfaces. At the city of Leipzig, which is predominantly influenced by traffic the mean winter concentration for Total Carbon (TC = OC+EC) is 77% of mass. From Leipzig city to the IfT and, further far to Melpitz a strong decrease in mass is observed for summer and winter.
During winter measurements nitrate was observed at all sites as the most important ionic component (13-17% of stage mass) whereas in the summer campaign sulfate was dominating (5-20% of stage mass).

Stage 2 particles (140 – 420 nm)
These particles are older than the smaller ones and therefore contribution from the transport from outside the direct measurement region begins to play a role. During the winter at the IfT and in Melpitz the emissions from individual heating systems and from power plants are responsible for the main part of the EC/OC content and not the traffic emissions. In the summer at all sites submicron crustal material and oxidized organic carbon represent 7 to 23 % of mass. The nitrate concentration during the winter was between 18 and 21 % of the total mass whereas for sulfate only 8 to 10 % have been measured. In the summer campaign for nitrate 5-6 % and for sulfate 16 to 25 % were observed. The water content was estimated to 10 %.

Stage 3 particles (0.42 – 1.2 µm)
About 51 % of the mass have been found at this stage, at which the ionic components dominate (33 – 55 %). The winter carbon fraction was found to be between 31 and 14 % dominated by the traffic only at the city measuring point. The total carbon amount measured at these particles decreased to 31 – 14 %. At the other sites the household emissions and the long range transport from power plants dominate (Fig. 1). During the summer 5 to 6 % of the mass have their origin in biogenic sources. Following the results of McInnes et al., 1996, the water content was estimated to 20 %. Crustal materials reach 22 – 25 % during the summer.

Stage 4 particles (1.2 – 3.5 µm)
Aged particles and greater primary particles (sea salt, crustal material) dominate here. About 22 % of the total mass have been found in this mode. The mass concentration decreases in winter and summer from the city over the institute to Melpitz but the differences are small. The carbon fraction decreased to a minimum (23 – 13 %). Considering metal concentrations the origin of most particles was estimated as re-suspension of crustal materials which are modified anthropogenically (e.g., tire abrasion). The summer content reaches 29 – 35 %. The ionic component concentration was detected to 26 – 35 % in summer and during the winter campaign to 40 – 51 %. According to the content of ionic and crustal material the water content was estimated to 20 %. In the summer the content of biogenic material was found to be between 6 and 8 % for all sampling sites.

Comparison of impactor and filter sampler
For filter sampling quartz fibre filters (Munktell, MK 360) have been used. During the winter measurements both methods have shown good conformity with some exceptions for the cations ammonium, potassium and calcium. These ions were overestimated by the filter sampling method. For ammonium the uptake of gaseous ammonia is possible because the winter aerosol is more acidic.
During the summer campaign the main differences were found for nitrate and chloride. The filter samples showed less nitrate and more chloride than the impactor samples. Depending on the temperature the nitrate loss from quartz fibre filters was observed.

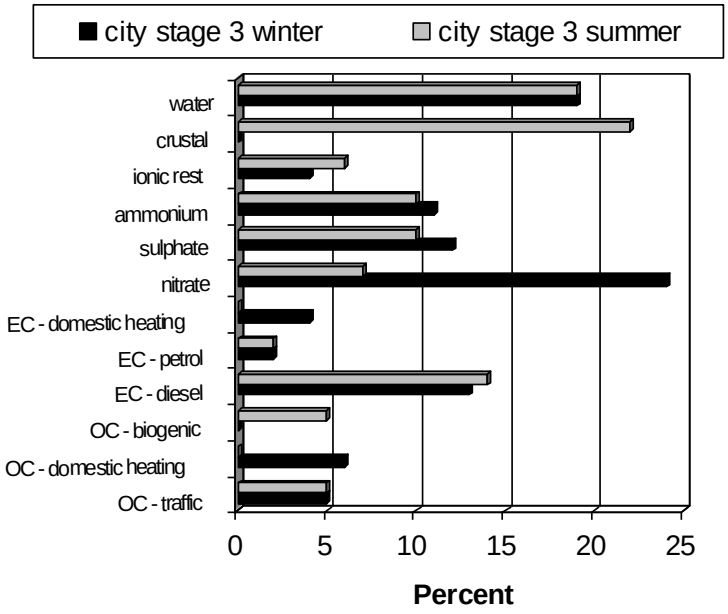

Figure 1: Estimated origin of particulate matter at the mainly traffic influenced measuring point in the city of Leipzig in the both periods of the project at the mass rich stage 3 (0.42 - 1.2 µm) of the impactor, where the older particles from traffic, long range transports or households are the most important source of particles.

Group specific results

Ionic components
During the winter and summer periods significant changes have been observed. Whereas the nitrate is the dominant ion during the winter time in the summer sulfate is the main ion in all samples. The ionic content decreases from winter to summer significantly, in mass concentration and percentage. The history of the air mass is important for the ionic content of the PM because main parts of the ionic components were from long range transports - the SO_2 oxidation to sulphate is a slow process.

OC-EC analyses
The carbon content of particles as a fraction of the stage mass decreases with increasing particle size. At the smallest stage of the impactor the differences between winter and summer are very small. With increasing particle diameter differences between summer and winter were observed depending on output from households and biogenic emissions. At the mass rich particles of the third impactor stage the difference in carbon concentration between summer and winter at all sampling sites was noticeably.

Source assignments of carbonaceous aerosol particles:
Based on the following assumptions the calculations of source assignment were performed.
1) Traffic emissions were supposed to be nearly constant throughout the year (no seasonal variation)
2) TC of the fine particles on stage 1 at the city station B was supposed to originate entirely from traffic emissions. In this case the OC/EC ratio (mean value = 0.34) is set to be typically for pure traffic exhaust particles.
3) TC parts on the higher impactor stages were assumed to be composed of
Winter: EC = part of aged traffic emissions, part of domestic heating (lignite fires)
OC = like EC
Summer: EC = aged traffic emission particles, i.e. EC(summer) = EC(traffic)
OC = part of altered traffic emissions, part of biogenic emissions.
4) Diesel engine vehicles were found to produce about 90% of the traffic particle emission in Saxony (see Gerike et al., 2000).
5) In the summertime the mixing layer height (MLH) is believed to be roughly twice as during wintertime. Performing winter/summer comparisons a normalization to the same MLH is required, therefore MLH was reduced to 50% doubling summer concentration values.
Calculations of the parts of OC and EC for traffic (segregated in diesel and gasoline part), domestic heating and biogenic emissions were performed for each stage.

Organic single species
The analysis of samples was performed for polyaromatic hydrocarbons (PAH), selected oxy-PAH and the n-alkanes (C20-C32).
Some important results are:
1. PAH have their origin mainly in the individual heating by coal burning processes (about 80%) during the winter. The winter concentrations are typically much higher at all sampling stations. The differences between the three locations were small during the wintertime whereas in the summer campaign a strong decrease of PAH concentrations was observed from the city over the IfT to Melpitz.
2. During the winter period the PAH had their highest concentrations on the stages 2 and 3 (household heating) – during the summer on stage 1 (traffic emission).
3. The alkanes had their origin during the winter mainly from burning processes. During the summer they are partly of biological origin indicated by the CPI at impactor stages 3 and 4 in the range of three to six (CPI - carbon preference index = c_{odd}/c_{even}).

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