

SIZE SEGREGATED CHARACTERIZATION OF ORGANIC COMPOUNDS IN URBAN PARTICULATES

K. MÜLLER and A. PLEWKA

Leibniz-Institut für Troposphärenforschung e.V., Permoserstr. 15, 04318 Leipzig, Germany

Introduction

During a two year experiment the collection of particles was performed on the measuring platform of the institute building by a PM10 high volume sampler and during two intensive campaigns by two five stage Berner-type impactors. From the PM10 filters only the PAH were analysed whereas from the impactor samples PAH, oxy-PAH, alkanes, fatty acids and some ketones were quantified. The source apportionment was assisted by measurements of pure source aerosols of typical burning processes (lignite fired stove, heating power plant, diesel powered passenger car).

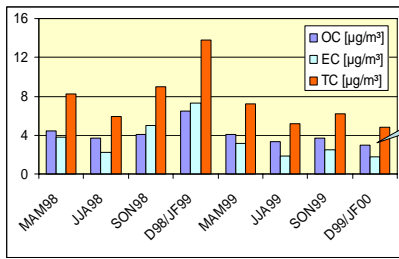
Experimental

Filter samples were collected as weekly (every seventh hour) samples over 24 hours for 2 years. During a summer and a winter campaign impactor samples were collected as daily samples. During these campaigns the filter samples were daily samples, too.

Filters were extracted by a hot extraction procedure with toluene/ dichloromethane over 2 hours. The HPLC analysis was performed using a TSP system equipped with autosampler, UV/VIS- and fluorescence detector. The analytical column was a Supelcosil LC-PAH (25 cm x 3 mm).

Curiepoint-Pyrolysis-GC-MS was performed directly from impactor foils (CP-temperature: 530°C) using a JHP-3S-Curiepoint Pyrolyzer coupled to a GC-MS (GC8000/Trio 1000, Fisons). The analytical column was a CP-Sil 5-CB (30m, 0.25mm, 0.1µm film).

OC-EC-Analyses were from a C-mat 5500 system operated for OC at 650 °C under nitrogen and in a second step under oxygen at 650 °C for 8 minutes each.



Very mild winter without inversion situations and mainly northern atlantic air masses

During winters coarse mode particles from domestic heating are the most important factor for the observed differences between both techniques.

Figure 1: OC-EC variations from high volume PM10 quartz fibre filter over the seasons of the experiment time

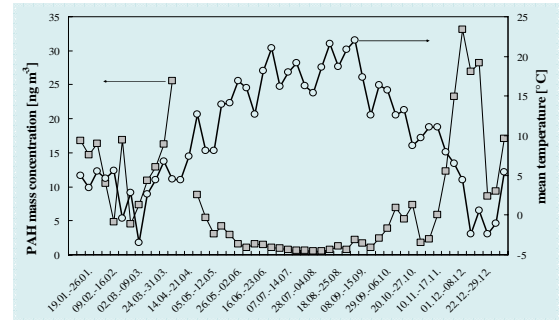


Figure 2: PAH mass concentration from weekly filter samples (yearly variation in 1998 and temperature course)

Results and discussion

The reported results are mainly from the first year of the campaign because the winter 1999/2000 was atypically warm (see TC concentrations in Fig. 1).

An extreme variation of PAH over the year was observed (Fig. 2 and 4). The origin of the high winter concentrations is the heating of individual households using brown-coal briquettes. Only 10-20 % of the flats in the region have used this type of domestic heating. From the beginning of the 1990ies the percentage is decreasing strongly.

The traffic affects the PAH content of the aerosol only to 4-10 % of the total content in the winter.

Measured PAH concentrations from PM₁₀ filters were higher than from PM_{3,5} impactors (Fig. 3). The sample preparation techniques do not influence the results: $C_{C3P}/C_{extraction-CPP} = 1.028$ (for PAH). Losses in the impactor samples, positive artefacts on filters and coarse mode particles from domestic heating can explain the differences between both techniques.

The alkane mix is during the summer mainly from biogenic sources not from traffic or other anthropogenic sources.

During the winter fossil fuels are the most important source of alkanes.

Between summer and winter differences were observed for nearly all components of aerosol (Fig. 5). The toxic PAH play an important role only during wintertime. They originate similar to carboxylic acids and ketones from domestic heating by brown coal briquettes, typically.

Carboxylic acids reach their maximum during summers in medium size particles (0.42-1.2 µm) whereas during the winters in smallest particles.

Table 1: CPI values for alkanes (C₂₁ – C₃₂) measured in summer and winter campaign in Leipzig versus typical data from anthropogenic and biogenic sources

Particle diameter	Summer CPI	Winter CPI	Heating power plant CPI	Norway spruce forest CPI
0.05–0.14 µm	2.2	1.1	1.0	2.3
0.14–0.42 µm	2.4	1.1	1.0	2.9
0.42–1.20 µm	3.3	1.3	1.0	3.9
1.20–3.50 µm	5.1	1.5	1.0	5.4

Acknowledgements

This work was supported by the BMBF in the German Aerosol Research Focus (AFS). For supplying the OC-EC data we thank T. Gnauk and for the excellent laboratory work we thank E. Neumann and S. Haferkorn.

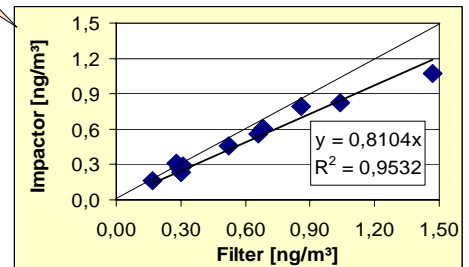


Figure 3: Mass concentration of Phenanthrene, Pyrene and Benz(a)anthracene during winter from PM₁₀ quartz filters versus mass concentration from impactors (PM_{3,5})

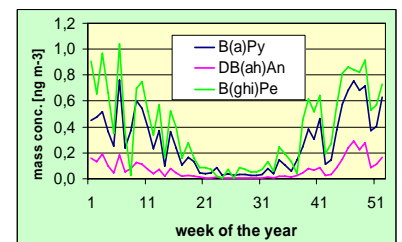
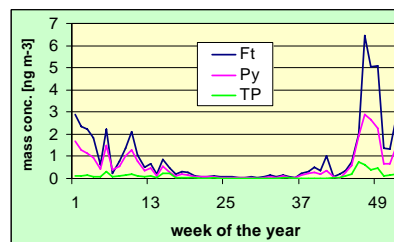


Figure 4: The diagrams present yearly concentration courses of more and less volatile PAH – phase partitioning depending on temperature is not the cause for measured concentrations in PM₁₀ particles! – The contribution of traffic is nearly constant over the year!

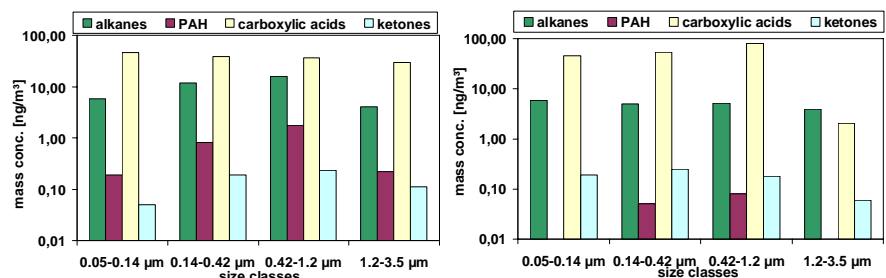


Figure 5: Concentrations of main components in four size classes during winter (left) and summer (right)