OC/EC, WSOC and single organic compounds in size segregated aerosol particles from recent field experiments

Leibniz Gemeinschaft

Antje Plewka, Thomas Gnauk, Hartmut Herrmann

Institut für Troposphärenforschung
Permoserstr. 15
04318 Leipzig, Germany
mail to: plewka@tropos.de

LEIBNIZ-INSTITUT FÜR TROPOSPHÄRENFORSCHUNG

Introduction

During the last years a series of field experiments was performed in order to investigate the behaviour (i. e. emission, formation, modification, deposition) and sources of airborne aerosol particles. Measurements were carried out in urban and remote regions of Germany. This includes experiments in a Norway spruce forest area of the Fichtelgebirge with prevailing biogenic emissions, multiphase cloud passage experiments at the Schmücke summit in the Thuringian Forest or measurements in a street canyon in the city of Leipzig. Aerosol particles were collected on quartz fibre filters with high volume samplers, size resolved with Berner impactors and high size resolved with Micro Orifice Uniform Deposition Impactors (MOUDI). Cloud water was collected with a single stage Caltech Active Strand Cloudwater collector. The particles were analyzed for OC/EC, for biogenic organic compounds, PAHs and alkanes.

Chemical characteristics of aerosols from car exhaust and urban environment (FAT project)

The goal of this project is to determine the distribution of EC, OC and organic compounds between different particle sizes in view of car exhaust emissions and urban air quality. The chemical composition of the ultra fine nanoparticles are of special interest. MOUDI-measurements were carried out in a background station (Melpitz), in a urban background station (IfT) and in a street canyon. Here are shown high size resolved measurements from OC, EC and organic single compounds in a street canyon in summer and winter.

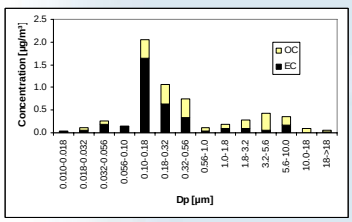

Fig. 1: EC/OC concentrations of a MOUDI summer run in a street canyon, traffic profile

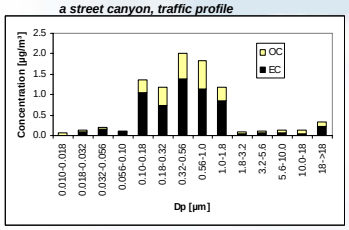

Fig. 2: EC/OC concentrations of a MOUDI winter run in a street canyon, traffic and domestic heating profile

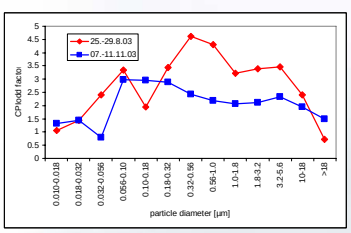

Fig. 5 : CPI_{odd} factors of alkanes for various particle sizes during summer and winter

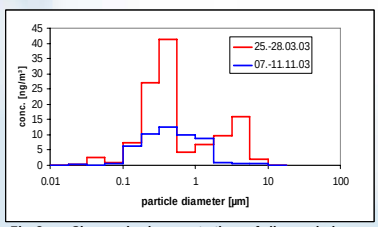

Fig. 3: Size resolved concentrations of alkanes during summer and winter

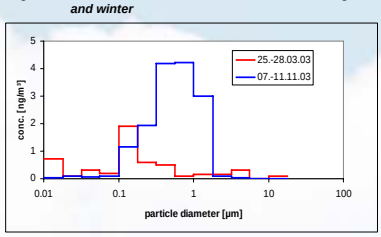

Fig. 4: Size resolved concentrations of PAHs during summer and winter

Analytical method for PAHs and Alkanes:
- were measured with a Curie point pyrolysis (CPP) GC/MS system: the aluminium foils were wrapped in a Curie point foil (50% Fe, 50% Ni), deuterated PAHs and d_{24} tetracosane were added before
- the ferromagnetic foil with the particles is heated very rapidly to the Curie point temperature by eddy currents in the presence of a high frequency magnetic field
- the organic compounds were evaporated, not pyrolyzed and introduced by a helium carrier into the GC/MS.

Determination of OC/EC:
- thermographic two step method: 650°C/N_2 for OC; 650°C/O_2 for EC (Ströhlein)

Determination of WSOC:
- combustion, catalytic oxidation/NDIR method (Shimadzu TOC-VCPH)

The difference in the EC/OC patterns, shown in Fig. 1 and 2, between summer and winter reveals the contribution of domestic heating to the total carbon load of aerosol particles especially in the size range of 0.32 - 1.8 µm. In the size range of 0.056 to 0.10 µm the EC fraction increases to about 80% of TC due to traffic emissions. Domestic heating causes the abundant EC in the size range up to 1.8 µm.
The alkanes show a bimodal distribution during summer (Fig. 3), which is caused by traffic (small particles) and a biogenic contribution by plant waxes (large particles). As expected, the PAHs (Fig. 4) are higher concentrated in winter due to domestic heating and are to find on larger particles than in summer. Fig. 5 shows the increasing fraction of alkanes of biogenic origin with particle size in summer, expressed by the CPI_{odd} (carbon preference index).

Impactor stage 3, 420 nm – 1200 nm, 234 µg particle mass

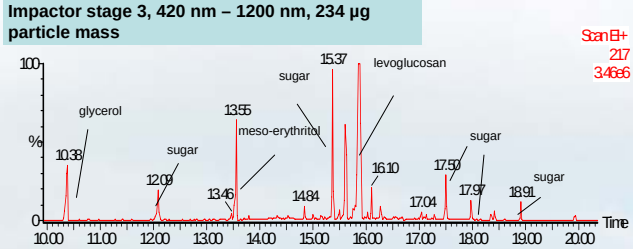

Fig. 6 : Chromatogramm of a silylated particle sample, collected in summer 2004

New method development:
- derivatisation CPP/GC-MS: silylation or methylation directly on the Curie point foil
- measurement of polar compounds in high size resolved aerosol samples should be possible
- this project is supported by Deutsche Forschungsgemeinschaft (DFG)

Biogenic organic compounds (BEWA)

BEWA: Regional biogenic emissions of reactive volatile organic compounds (BVOC) from forests: Process studies, modeling and validation experiments (AFO 2000)

The aim of this project was to investigate the particle modification and formation from BVOC emissions above coniferous forests in Germany. Particles were collected with high volume filters in (12 m height) and above (24 m height) the canopy of a Norway spruce forest in a day/night rhythm. The main focus of the measurements was the identification and quantification of terpene and isoprene oxidation products on particles.

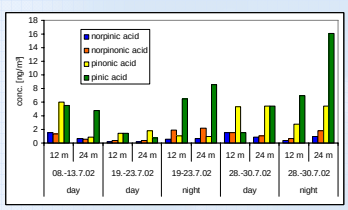

Fig. 7: Terpene acid concentrations

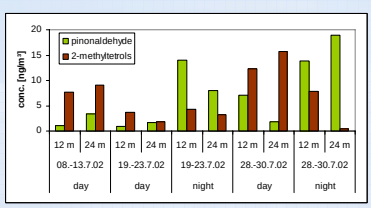

Fig. 8: Concentrations of pinonaldehyde and the 2-methyl-tetrols (threo + erythro)

Pinic acid shows the highest concentration of the terpene acids, shown in Fig. 7. The night concentrations are slightly higher than the day concentrations. The same is true for pinonaldehyde (Fig. 8). One reason for the higher night concentrations of pinic acid and pinonaldehyde could be the lower ambient temperatures during the night. A second reason could be a possible formation by the nitrate radical during the night. Except during the first sampling period the concentration of pinic acid was higher above the canopy of the forest than in the forest.
For the two methylterols, no clear trend could be observed between the two sampling heights, but the averaged day concentrations (8.4 ng m^{-3}) are higher than the night concentrations (4.0 ng m^{-3}).
A survey including all results will be pubslished soon in Atmospheric Environment.

OC and WSOC during a hill-capped cloud experiment (FEBUKO)

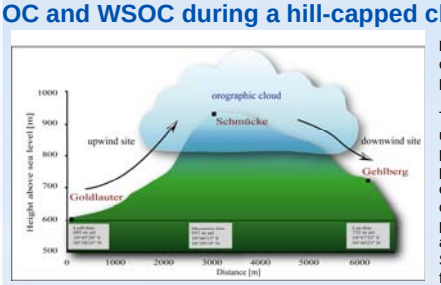

Fig. 9 : Schematic view of the sampling sites

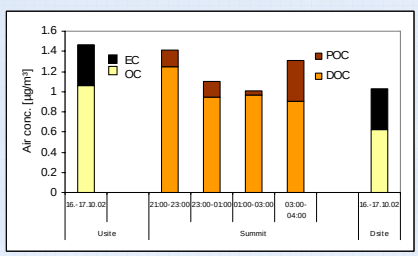

Fig. 10 : Particulate (OC/EC) and cloud water (DOC/POC) carbon concentration during one selected cloud event

FEBUKO: Field investigations of budgets and conversions of particle phase organics in cloud processes (AFO 2000)

This project intends to improve the understanding of tropospheric multiphase processes including interactions of aerosol particles and clouds. Field hill-capped cloud experiments were performed to investigate the chemical and physical transformations of particles by a cloud passage. For this purpose a upwind, summit and downwind site at the Mt. Schmücke (Thuringian Forest) were installed for measurement of gaseous and particulate trace components during orographic cloud events with connected flow (Fig. 9).
At the summit cloud water was sampled using Caltech Active Strand Cloudwater Collectors. Meteorological data were also measured at all three sites.
Particulate OC and cloud water TOC agree in the presented event III (Fig. 10). TOC consists in 80-95% Dissolved Organic Carbon (DOC) and 5-20% Particulate Organic Carbon (POC) adsorbed on particles in cloud water. Particulate OC losses at the downwind site are assumed to be caused by deposition or dilution of the air mass. A survey including the results of all selected events for all components analysed and the comparison with model calculations is in preparation and will be published in Atmospheric Environment.