# Particle modification and formation from BVOC emissions above coniferous forests in Germany

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BEWA 2000
http://imk-ifu.fzk.de/bewa2000

**Validation**

AFO-Abschluss.2004 Bad Tölz

## Problem

Biogenic volatile organic compounds (BVOC) are estimated to exceed anthropogenic VOC emissions approximately by one order of magnitude on the global scale. In contrast to deciduous trees emitting mainly isoprene coniferous trees release predominantly $C_{10}$-monoterpenes, among them alicyclic (myrcene, ocxymene), monocyclic (limonene) or bicyclic ($\alpha$-pinene, $\beta$-pinene) monoterpenes being extremly reactive against ozone or radicals like OH and $NO_3$. Oxidation results in polar compounds showing substantially reduced volatility compared to their precursors. Such low volatile compounds are suspected to condense on existing particles modifying their surface or even to form new particles by homogeneous nucleation. Particles in the atmosphere are able to change radiative forcing directly by sun light absorption and scattering, and indirectly by influencing cloud formation by cloud condensation nuclei (CCN) activation. To understand the complex atmospheric multiphase chemistry it is necessary to perform both field measurements and laboratory experiments under controlled conditions. The results will contribute to the further development of multiphase models including particle modification and formation processes.

## Solution

The aim of this project is the investigation of the chemical composition of airborne particles in (12 m height) and above (24 m height) the canopy of a spruce forest (Waldstein/Fichtelgebirge - BITÖK site) by size-segregated particle sampling with BERNER impactors for three days running (eight hours centered around noon). For this purpose main components (inorganic ions, carbon as sum parameters OC and EC) have been determined. Additionally high-volume samples having sufficient particle mass were used for identification and quantification of organic compounds in airborne particles. Differences of the chemical composition in and above the canopy should show hints at primary emission or photochemical formation of BVOC as well as the formation of secondary organic aerosol.
In the 2002 campaign a day/night rhythm for impactor sampling was introduced in order to find day/night differences and source apportionment by trajectory analysis. Additionally mass closure after conversion of OC to OM and calculating the water content was carried out.

## Results

### Main components

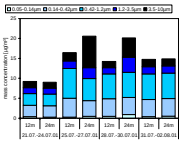


Fig. 1a

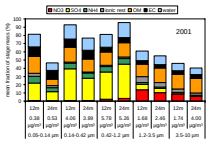


Fig. 1b

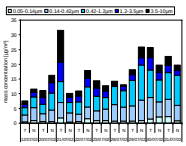


Fig. 2a

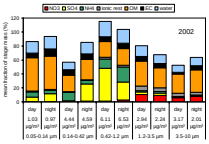


Fig. 2b

In the BEWA 2001 measurement campaign no significant differences were found between 12 m and 24 m height for mass (Fig. 1a) and main particle components like the ionic components nitrate, sulfate, ammonium or the sum parameters OC and EC (Fig. 1b). Differences on impactor stage 4 and 5 could be attributed to local contamination. Therefore impactor sampling was continued during the BEWA 2002 campaign only at the 12m level, but time resolved as day and night sampling. Differences of different days and also day/night in the composition of particles could be attributed to the origin of air masses determined by trajectory analysis (HYSPLIT, NOAA) and were not referred to any change in local emissions of the forest. Trajectories crossing the Bohemian basin or the Silesian district showed higher particulate sulfate and carbon concentrations (from 29 July), air from west showed higher values of nitrate and sodium, but on lower mass concentation level (until 28 July). Mass closure was tried including OM (converted from OC by a factor of 2.1) and water (estimated by a growth factor determined in other experiments) and found to be mostly sufficient in the range of +/-20%. Larger deviations on stages 4 and 5 can be attributed to non analyzed, resuspended coarse crustal material (Fig. 2a and 2b).

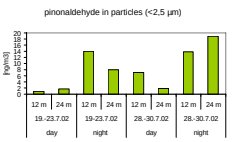


Fig. 3a

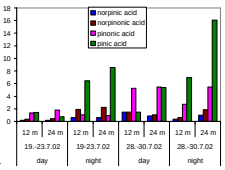


Fig. 4

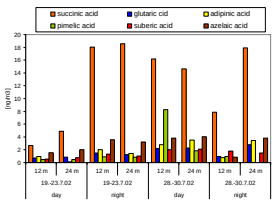


Fig. 5

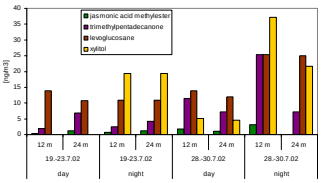


Fig. 6

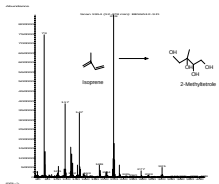


Fig. 7

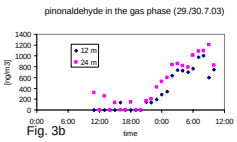
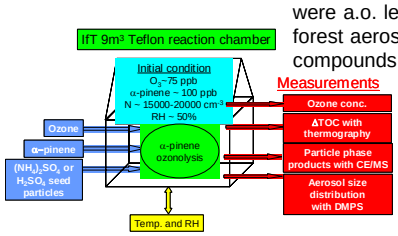


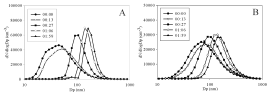
Fig. 3b

### Organic species

Particulate organic compounds found include alkanes, dicarboxylic acids and different terpene oxidation products. For alkanes (C20 - C33) no differences between day/night or 12m/24m height were found. Dicarboxylic acids showed no dependence of sampling height or daytime, but decreasing concentrations with the number of C-atoms (Fig. 5).The day/night difference of succinic acid during the period of 19 to 23 July is not yet clear. Terpene oxidation products account only for a small part of the particle mass. Concentrations of pinonaldehyde and pinic acid were higher in the night (Fig. 4), pinonaldehyde concentration in the gas phase much higher than in the particle phase (high vapor pressure and reactivity, Fig. 5). Other organic compounds identified were a.o. levoglucosan and xylitol (Fig. 6) as well as tentatively 2-methyl tetrols (Fig. 7), recently suggested for Amazonian rain forest aerosols by Claeys et al. in Science (2004), 303,1173-1176. Results of own determinations of particulate biogenic organic compounds have been published last year (Plewka et al. (2003), Chromatographia Suppl. 57, S 253 – S 259).




TOC yields found in particles from the ozonolysis of α-pinene with $H_2SO_4$ and $(NH_4)_2SO_4$ seed particles



The evolution of size distributions for the experiments with (A) ammonium sulphate seed particles and (B) sulphuric acid seed particles.

- A: $\Delta TOC_{(NH_4)_2SO_4}$ = 52.4 ± 8.5 µgm$^{-3}$ (n=3)
- B: $\Delta TOC_{H_2SO_4}$ = 72.3 ± 14.2 µgm$^{-3}$ (n=4)

• Sulphuric acid particles yielded nearly **40%** more OC compared with ammonium sulphate seed particles. The compounds with molecular weight over 300 (possible dimers and oligomers) are found from the CE/MS analysis of sulphuric acid particles samples.

### Chamber experiments

In experiments in a Teflon reaction chamber with α-pinene / ozone / seed aerosol-system the formation of SOA by α-pinene oxidation products could be shown by measuring the changing size distribution and the increasing carbon content of the seed aerosol particles.

First findings on SOA composition in dependence of the seed particle acidity have been published recently (Iinuma et al. (2004), Atmos. Environ. 38, 761-773).

## Summary

Two summer field measurement campaigns in a spruce forest were carried out with size segregated particle sampling in and above the canopy during sunny days and/or in a day/night rhythm.The chemical composition of the particles was determined for main components (anorganic ions, OC, EC) and single organic compounds.
Particulate main components showed no dependence of sampling height. Differences of successive days were attributed to different air mass origin verified by trajectory analysis.
Organic compounds showed no significant differences between 12m and 24m height. Only for pinic acid higher concentrations above the canopy were observable. Night concentration of pinonaldehyde was found to be higher because of its photochemical sensitivity and also the possible formation by nitrate radical chemistry in the night. In total identified biogenic organic compounds account only for a small part of the whole particle mass.
In chamber experiments the SOA formation in dependence of the particle acidity was observed.

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**Regional biogenic emissions of reactive volatile organic compounds from forests: Process studies, modelling and validation experiments**

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