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The FEBUKO team

MOTIVATION

The FEBUKO research project with the AFO 2000 programme will improve the understanding of tropospheric multiphase processes and especially the interaction of aerosols and clouds with an emphasis on organic particle constituents. Field experiments on aerosol and cloud chemistry and physics and model application are combined to investigate chemical and physical transformation of particles within a cloud passage. The main focus of the FEBUKO field studies is to lay the groundwork for the further development of tropospheric cloud chemistry models, which may also serve as the basis for mechanism development for the tropospheric aqueous aerosol. A complex experimental data set was provided by two field campaigns.

RESULTS

In both campaigns in 2001 and 2002 a total set of 14 cloud events was identified for intensive measurements (see Table 1). The most important conditions (i) connected flow, (ii) an orographic cloud and (iii) good data coverage were best fulfilled during three events (red in Tab. 1). The results within the present contribution refer to a 15 hours measurement period on 26/27-October 2001 (22:00 to 13:00 UTC).

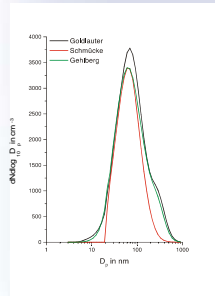


Fig. 1

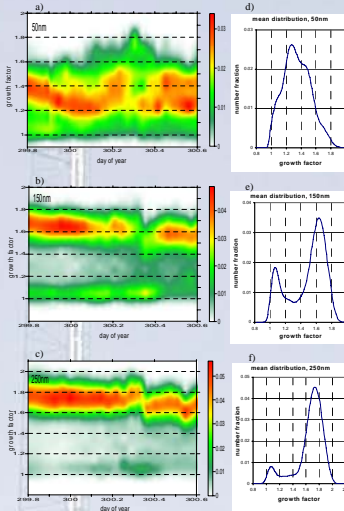


Fig. 2

EXPERIMENTAL

At the two valley measurement sites (Goldlauter (GL) – upwind site, Gehberg (GB) – downwind site) and at the mountain site (Schmücke (SM)) a set of meteorological parameters, trace gas components, cloud parameters and particle characteristics was determined. The sampling of particles using filter samplers (HVA) and impactors (BI) for the chemical constitution measurements was carried out at the valley stations together with measurements of particle number concentrations, size distributions and hygroscopic properties. On top of a 20 m research tower a variety of different cloud water (CW) samplers was operated on the Schmücke. These measurements are complementary to the interstitial particles (INT) and drop residues (by Counter Flow Virtual Impactor - CVI). The flow connection between the three stations is an important prerequisite for the whole experiment. Hence, special tracer experiments, measurements of number and size distribution of particles as well as trace gas concentrations were performed. In addition, the synoptic experimental conditions were carefully investigated and flow simulations for the complex terrain area are ongoing.

Table 1: Cloud events

Date	Time (UTC)
02-10-2001	08:00 - 12:45
06-10-2001	10:30 - 14:45
07-10-2001	13:15 - 15:15
07/08-10-2001	18:00 - 11:15
08-10-2001	20:00 - 21:30
09-10-2001	08:00 - 10:45
10-10-2001	04:45 - 10:30
11-10-2001	04:00 - 09:45
21-10-2001	07:15 - 08:30
	14:15 - 16:30
22-10-2001	05:00 - 13:30
23-10-2001	09:30 - 11:00
25-10-2001	03:00 - 05:45
26-10-2001	08:30 - 16:30
26/27-10-2001	22:00 - 13:00
29-10-2001	09:00 - 11:00
03-10-2002	09:00 - 12:35
	13:00 - 15:00
	17:30 - 18:10
14-10-2002	12:00 - 13:00
15-10-2002	06:30 - 10:45
16-10-2002	03:30 - 09:30
16/17-10-2002	21:00 - 04:10
17-10-2002	11:50 - 12:25
18-10-2002	08:00 - 10:30
18/19-10-2002	16:00 - 00:50
21/22-10-2002	21:30 - 01:20
23/24-10-2002	21:30 - 04:55

Fig. 1 shows averages of the particle size distribution at the three measurement sites over the whole cloud period on 26th/27th October 2001. Compared to the valley sites, the scavenging of particles > 160 nm on summit can be seen. This can be traced back to the fact that the cloud on top of the mountain activates such particles by condensation of cloud water onto the particle surface. Thereby, the particles grow up to a size that is undetectable by the instruments used for.

Fig. 2: a) to c) show time series of hygroscopic growth curves for 50, 150 and 250 nm particles at 90% RH measured with a HTDMA. The mean growth spectra for this time period are displayed in Fig. d) to f). The spectra for 150 and 250 nm particles reveal a bimodal behaviour with a growth factor (GF) around 1.1 for the hydrophobic mode and a GF around 1.7 for the more hygroscopic particles. A bimodal growth characteristic for 50 nm particles was not evident for this cloud event. The peak of the growth curve for 50 nm particles was found around a GF of 1.3.

The total mass concentration of particles on the impactor foils (summarized five BERNER impactor stages) is classified as low and amounts to 17 $\mu\text{g m}^{-3}$ at upwind site (GL) and 11.5 $\mu\text{g m}^{-3}$ at downwind site (GB). In the case of transport over the ridge of the Thüringer Wald a loss occurs mainly by deposition and dilution by entrainment (Figure 3). The distribution of particle mass is typically in the ranges of size and shows for particles with diameter from 0.42-1.2 μm the highest mass concentration. The effect of mass decrease can be observed for the most size-ranges of all events, too.

About 90% of the total particle ionic mass concentration consist of sulfate, nitrate, and ammonium. A comparison of nitrate, sulfate, and ammonium concentrations in size-segregating samples and in the sum PM_{10} in GL and GB with those obtained by the averaging over different cloud water samples is presented in Figure 4 for all sampling techniques applied. In cloud water the sulfate concentration agrees reasonably well with the concentration in particles. A possible SO_4^{2-} and NH_4^+ production after the cloud passage could be verified at about 15% by comparing the SO_4^{2-} and NH_4^+ concentration of the GL and GB aerosol (BI - for $\text{PM}_{0.05-0.14}$) with the concentration of cloud droplets and interstitial aerosol particles (CVI-INT) at SM (10%). This is within the error margin of the measurement but very well consistently with the model findings. Nitrate and ammonium are clearly higher concentrated in the cloud droplets than in the particles sampled by BI, HVA filter sampler, and droplet CVI and INT. Only the nitrate concentration in particles sampling by the Steam-Jet collector (SU) agrees with that in cloud water. The difference of these samplers might be due to uptake and evaporation processes of gaseous and semi-volatile compounds during collection.

Figure 5: The total carbon (TC) concentration summarized over all stages of BI found at the GL station was 2.1 $\mu\text{g m}^{-3}$ consisting of 1.1 $\mu\text{g m}^{-3}$ organic carbon (OC) and 1.0 $\mu\text{g m}^{-3}$ elemental carbon (EC). OCEC concentrations in the cloud were also determined by CVI and INT, the sum of both should correspond to the GL particulate carbon. CVI + INT for EC (1.1 $\mu\text{g m}^{-3}$) are in good agreement with the GL value, whereas CVI + INT for OC (2.8 $\mu\text{g m}^{-3}$) exceed the GL value one and a half times. This may be a hint to gas to liquid phase transfer of organic compounds on their upwind way from GL to the Schmücke summit. On the downwind way to GB this process can be reversed. Losses can also occur during collection.

With this described field measurement equipment it was possible to create an extensive pool of data for dozens of organic substances in their respective most relevant atmospheric phases. The possible photooxidation products of carbonyls and VOCs such as higher oxygenated species like monocarboxylic acids in the gas phase and in cloud water and dicarboxylic acids in the particle phase and in cloud water were analysed in a time-resolved manner. Size distributions before and after the cloud passage as well as the corresponding liquid-phase concentrations are as well available for lower vapour pressure compounds such as long-chain alkanes, alcohols, sugars, fatty acids, dicarboxylic acids, and several biogenic compounds such as pinaldehyde, squalene, and others. Bulk concentrations from filters for interstitial particles allow us to calculate directly the in-cloud scavenging for some of these compounds.

In Figure 6 are shown the concentrations of pinaldehyde, alkanes and pinic acid in particles and cloud water. The concentrations are always higher in cloudwater than the particle concentrations. The reason for this enrichment could be the high vapor pressure of these substances, especially for pinaldehyde and pinic acid. These compounds are predominantly in the gas phase and are washed out by the cloud water.

In Figure 7 comparison for the example of oxalic acid concentration measured by Berner impactor (BI) and spray collector (from Technische Universität Darmstadt) with the respective cloud water content is presented. The oxalic acid concentration of particles from BI show lower values than measured by spray collector and in the cloud water much higher concentrations. This might be due to uptake and evaporation processes of gaseous oxalic acid during impactor sampling. Oxalic acid present in the gas phase is on the one hand unlikely because of the low vapour pressure of dicarboxylic acids on the other hand it cannot be fully ruled out as an explanation for the observed phenomena. This issue is controversially discussed in literature.

SUMMARY

This complex data set is of great importance for the MODMEP model initialisation and validation. Besides it can be interpreted by comparing, correlating and balancing concentrations of selected species for different atmospheric phases, different times and different particle sizes. In combination with the model results we may now be able to achieve a better understanding of phase partitioning and chemical multiphase processes of tropospheric organic material.

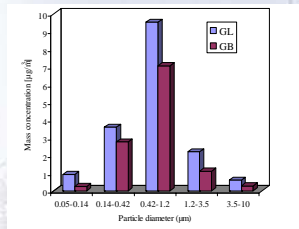


Fig. 3

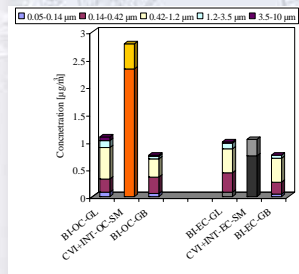


Fig. 4

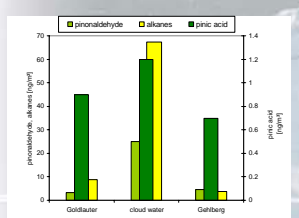


Fig. 5

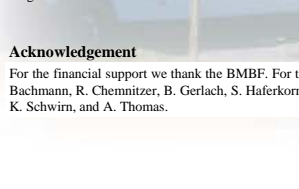


Fig. 6

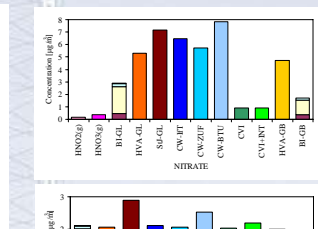


Fig. 7

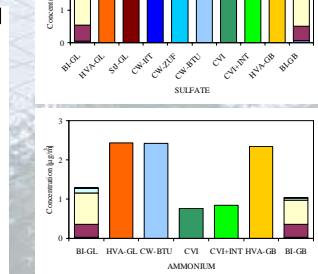


Fig. 7

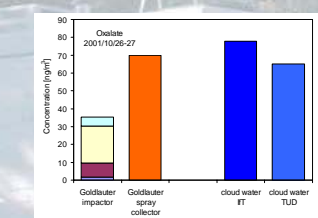


Fig. 7

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