Determination of Organic Species during the FEBUKO hill-capped cloud experiment

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Introduction

Within the joint research project FEBUKO (field investigations of budgets and conversions of particle phase organics in tropospheric cloud processes) two series of ground-based cloud experiments were performed in 2001 and 2002. The aim of the project is to obtain a better insight into aerosol-cloud interactions and chemical conversions especially for organic compounds in tropospheric multiphase processes. To this end, a detailed physical and chemical characterisation of air masses before, while and after passing an orographic cloud took place at three stations in a forestal region in Germany (Thuringian forest). Figure 1 shows a scheme of the three sampling sites. All the obtained data is used in a sister project MODMEP (modelling of tropospheric multiphase processes: tools and chemical mechanisms) to initialise and validate a complex microphysics and multiphase chemistry model.

This presentation focuses on some results on the dicarboxylic acid (DCA) measurements . Because of their low vapour pressure these acids, like oxalic acid, malonic acid, succinic acid and even the higher homologues as well as some of their hydroxylated homologous compounds are frequently found in tropospheric condensed phases such as aerosol particles, rain, cloud water or snow [Saxena and Hildemann, 1996]. They are formed at least partly from a variety of chemical reactions in either the gas or condensed phase environment [Ervens et al., 2003; Kawamura and Ikushima, 1993]. As water soluble organic compounds they are discussed to participate in cloud formation processes by altering the hygroscopicity of cloud condensation nuclei [Cruz and Pandis, 1998].

Experimental

At the valley stations five-stage cascade impactors (Berner-type with 50% cutoffs: 0.05, 0.14, 0.42, 1.2, 3.5, and 10 µm) for size resolved sampling of particles were used. A humidity-controlled tube bundle served as the inlet device. Complementary, spray collectors (scrubbers) sampled the complete aerosol (gas and particle phase) in a time resolved manner (2 hour interval). For cloud water sampling different cloud water collectors were used. Results shown in this contribution were obtained from samples of the Caltech Active Strand Cloud water Collector 2 (CASCC2, Colorado State University, Ft. Collins, USA), which collects droplets with a 50% cut off diameter of 3.5 µm by inertial impaction on several rows of teflon strands [Demoz et al., 1996]. After the campaign the samples were analysed using analytical equipment such as GC/MS, HPLC/MS, ion chromatography or capillary electrophoresis. For the determination of dicarboxylic acids we applied capillary electrophoresis with indirect UV detection.
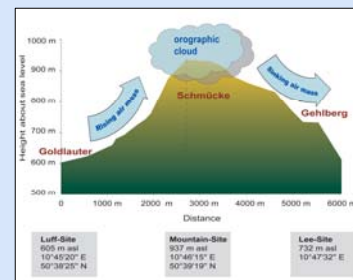

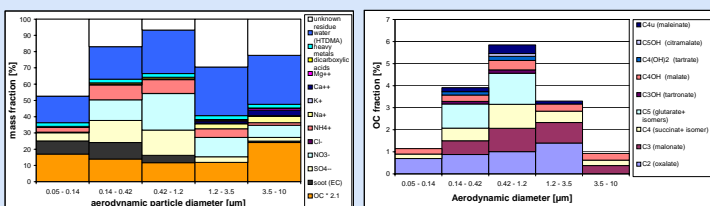Figure 1: Schematic view of the sampling sites

Results

Figure 2: Chemical mass balance for aerosol particles at upwind station during event 1.
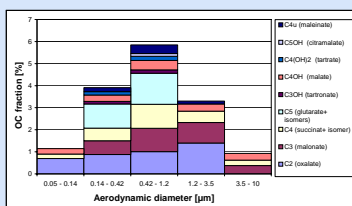

Figure 3: Contribution of dicarboxylic acids (carbon mass) to organic carbon for event 1.
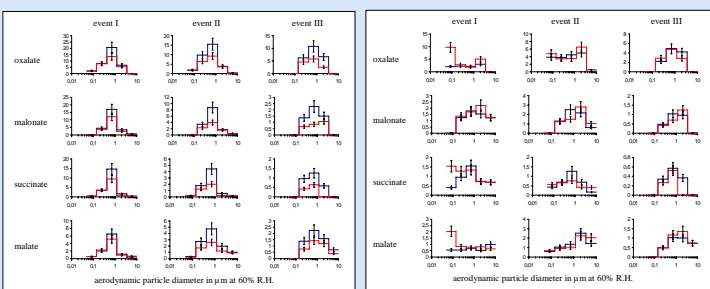

Figure 4: Atmospheric concentrations (per impactor stage) of the most abundant dicarboxylic acids in ng m⁻³, blue line for upwind station, red line for downwind station (error bars represent the analytical error).
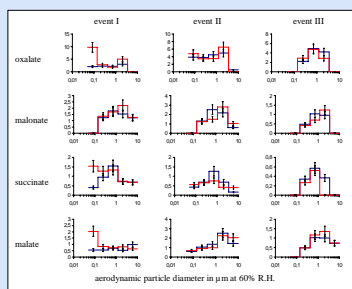

Figure 5: Mass fractions (in ng/µg stage mass) of the most abundant dicarboxylic acids, blue line for upwind station, red line for downwind station (error bars represent propagated analytical errors).
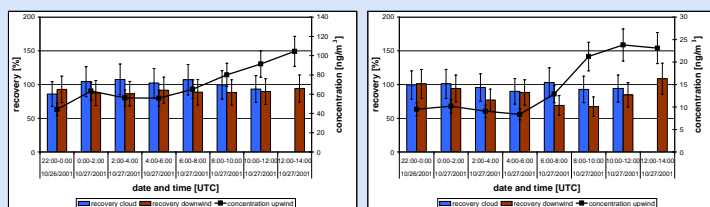

Figure 6: Temporal distribution of oxalate concentration at upwind station and recoveries at summit and downwind station for event 1 (error bars represent analytical error).
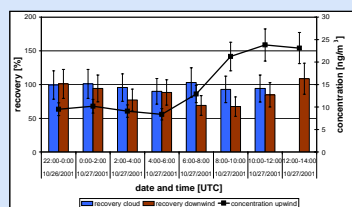

Figure 7: Temporal distribution of malonate concentration at upwind station and recoveries at summit and downwind station for event 1 (error bars represent analytical error).

Within the two measurement campaigns in 2001 and 2002 14 cloud events occurred. Table 1 shows three events for which meteorological and micro-physical parameters were fulfilled best to have a connected flow between all 3 sampling sites.

Figure 2 shows a chemical mass balance from the impactor samples for event 1. Water content of the particles was calculated using growth factors obtained by HTDMA (hygroscopic tandem differential mobility analyser) measurements at 60 % RH. The mass of organic carbon was converted to a mass of organic material using a factor of 2.1 as suggested in literature for non-urban, aged aerosol particles [Turpin and Lim, 2001].

During all events 9 dicarboxylic acids could be identified in the particle phase (Table 2) and their contribution to the total organic carbon can be as high as 6 % for event 1 (Figure 3). All exept one of the diacids could be determined in the liquid phase of the summit cloud, too.

Size distributions of the 4 most abundant diacids look similar at the upwind station during one event (Figure 4). The downwind station usually shows lower concentrations, possibly due to losses of particle mass by deposition or entrainment. To account for this the mass fraction of the compounds was calculated as ng compound per µg particle mass on the respective impactor stage (Figure 5). For the smallest particles during event 1 substantially lower particle mass was found at the downwind station, which led to a clearly higher mass fraction on impactor stage 1.

The temporal distributions of oxalic and malonic acid at the upwind station for event 1 are given in Figures 6 and 7, together with the corresponding recovery rates of the upwind concentrations in the summit cloud and at the downwind station. A clear trend to higher concentrations during the day and nearly 100% recovery were found for most samples.

Averaged oxalate concentrations over the entire event 1 and for different sampling systems are given in Figure 8. Concentrations from impactor samples are significantly lower than those from the spray collectors, which might be due to evaporation losses on the low pressure stages. Also, gaseous oxalic acid, which would be sampled by the spray collectors only, could be a reason.

Table 1: Top events during the FEBUKO campaigns.

event	date	time (UTC)	duration
1	26/27-10-01	22:00–13:00	15 hrs.
2	6-10-01 7-10-01 7/8-10-01	10:30–14:15 13:15–15:15 18:00–11:15	23 hrs.
3	16/17-10-02	21:00–5:30	8:30 hrs.

Table 2: Concentration ranges for DCA from impactor samples and cloud water (events 1 – 3)

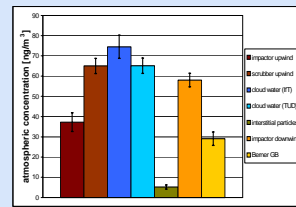| diacid	upwind concentration (ng/m³)	cloud water concentration (µmol/l)
C2 (oxalate)	23,6 – 35,3	1,4 – 7,7
C3 (malonate)	5,2 – 25,6	0,3 – 3,1
C4 (succinate+ isomer)	2,8 – 20,6	0,2 – 1,1
C5 (glutarate+ isomers)	0 – 23,1	0 – 1,7
C3OH (tartronate)	0,3 – 3,8	0 – 0,2
C4OH (malate)	5,9 – 10,9	0,1 – 1,1
C4(OH)2 (tartrate)	0,8 – 4,5	0 – 0,4
C5OH (citramalate)	0 – 2,0	0
C4u (maleinate)	0 – 6,8	0 – 0,4

Figure 8: Comparison of oxalate concentrations at all 3 stations for event 1 (summed up for impactor samples, averaged for scrubber and cloud water samples, error bars represent propagated analytical errors).

Summary and Outlook

During the FEBUKO hill-capped cloud experiments a huge set of data was collected. Special emphasis was laid on the determination of organic compounds in gas phase, particle phase and liquid phase in a natural environment. Out of these, dicarboxylic acid measurements are reported in this work. Both size and time resolved information could be obtained by applying different sampling techniques. This data will help to further elucidate the fate of diacids in atmospheric processes. The complete set of measurements during FEBUKO will be published in a special issue of Atmospheric Environment together with complex multiphase modelling of the field data in the sister project MODMEP.

References

Cruz, C.N., and S.N. Pandis, Journal of Geophysical Research-Atmospheres, 103, 13111-13123 (1998).

Demoz, B. B., Collett, J. L., and Daube, B. C., Atmos. Res. 41, 47-62 (1996).

Ervens, B., George, C., Williams, J.E., Buxton, G.V., Salmon, G.A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H., J. Geophys. Res.-Atmos. 108, doi:10.1029/2002JD002202 (2003).

Kawamura, K., and K. Ikushima, Environmental Science & Technology, 27, 2227-2235 (1993).

Saxena, P., and Hildemann, L.M., J. Atmos. Chem. 24, 57-109 (1996).

Turpin, B.J., and Lim, H.J., Aero. Sci. Tech. 35, 602-610 (2001).

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