

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 locations. All the obtained data will be 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.

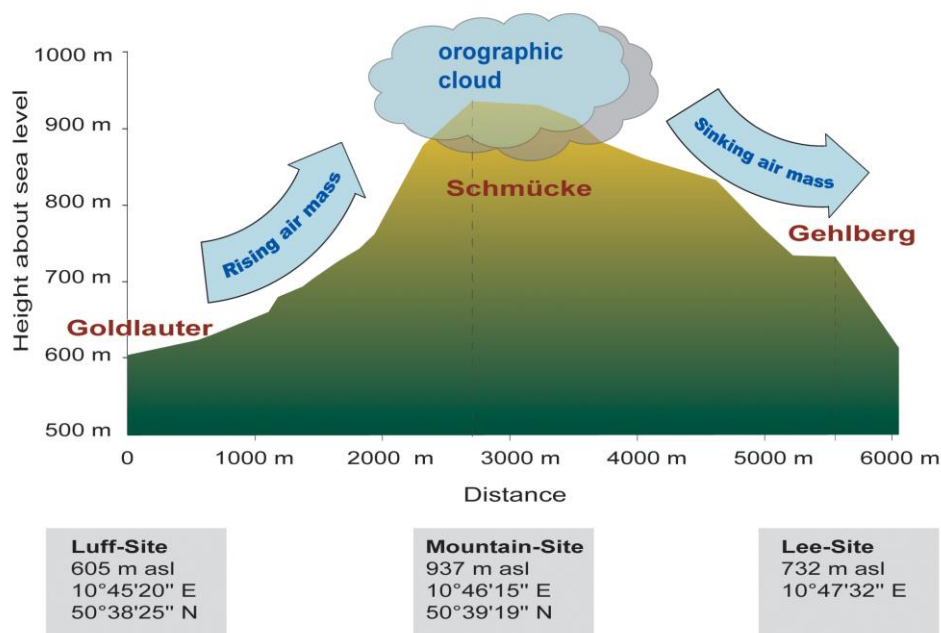


Figure 1: Schematic view of the sampling sites

With the experimental setup described below it was possible to create an extensive pool of data for dozens of single organic substances in their relevant atmospheric phases. Aliphatic and aromatic aldehydes and ketones as well as other volatile organic compounds (VOCs) like short chain alkanes, alkenes and volatile aromatics could be identified and quantified in the gas phase on a time resolved basis. Depending on their polarity some of them can be scavenged by the cloud and therefore they were also measured in the liquid phase. As possible

photooxidation products of carbonyls and VOCs the concentrations of higher oxygenated species like monocarboxylic acids in the gas phase and cloud water and dicarboxylic acids in the particle phase and cloud water were determined in a size resolved manner. Size distributions before and after the cloud passage as well as the corresponding liquid phase concentrations are available for high vapour pressure compounds like long chain alkanes, alcohols, sugars, fatty acids, dicarboxylic acids and several biogenic emitted compounds (pinonaldehyde, squalen and others). Bulk concentrations from filters for interstitial particles allow us to directly calculate the in-cloud scavenging for some of these compounds.

As sum parameters organic carbon (OC) and elemental carbon (EC) from size segregated impactor samples, and water soluble organic carbon (WSOC) and water insoluble organic carbon (WISOC) from cloud water samples were determined.

This presentation focuses on some results on the dicarboxylic acid 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 like aerosol particles, rain, cloud water or snow [Saxena and Hildemann, 1996]. They are formed partly from a variety of chemical conversion reactions in either the gas or condensed phase environment [Ervens *et al.*, 2003; Kawamura and Ikushima, 1993].

Experimental

Organics are usually trace compounds in different atmospheric phases, which makes their determination a difficult and challenging task [Turpin *et al.*, 2000]. To accomplish this, a variety of sampling devices was applied, some of them exclusively for organic speciation.

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 [Kramberger, 2003] sampled the complete aerosol (gas and particle phase) in a time resolved manner (2 hour interval). Quartz-fibre filter sampler gave information about the bulk chemical composition of particles both for the valley stations and for the interstitial phase at the mountain station.

Additionally, gaseous compounds were trapped on self-made sorbent filled cartridges (2,4-dinitro phenylhydrazin, DNPH) at the valley stations.

For cloud water sampling different cloud water collectors were used. Results shown in this contribution were obtained from samples of the Caltech Active Strand Cloudwater 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 like GC/MS, HPLC/MS or capillary electrophoresis.

For the determination of dicarboxylic acid we applied capillary electrophoresis (CE) with indirect UV detection. CE has some important advantages for the analysis of ions in aerosol particles compared to the commonly used ion chromatography or gas chromatography. It is a simple and fast technique, which needs no sample purification or preparation. The absolute detection limits are very low (below 1 pmole) and it has a large range of signal-to-concentration linearity (up to 4 orders of magnitudes) [Neusüß *et al.*, 2000]. Thus it suits to difficult matrices with strongly changing concentrations and compositions such as aerosol samples. The separation efficiency is usually much higher than in liquid chromatography and the required sample amount is low (< 1 μL).

Results

Within the two measurement campaigns in 2001 and 2002 14 cloud events occurred. After the campaigns a detailed analysis of meteorological and microphysical parameters took place to ensure connected flow conditions between the three stations and to validate the assumption of an orographic cloud. Table 1 shows three events for which these criteria were fulfilled best.

Table 1: Top events during FEBUKO 2001 and 2002

event	date	time (UTC)	duration
1	26/27 th October 2001	22:00 – 13:00	15 hours
2	6 th October 2001	10:30 – 14:15	23 hours
	7 th October 2001	13:15 – 15:15	
	7/8 th October 2001	18:00 – 11:15	
3	16/17 th October 2002	21:00 – 5:30	8:30 hours

Event 1 was the longest one without any interruptions. Figure 2 shows a chemical mass balance from the impactor samples for this event. 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 recent literature for a non-urban, aged aerosol [Turpin and Lim, 2001].

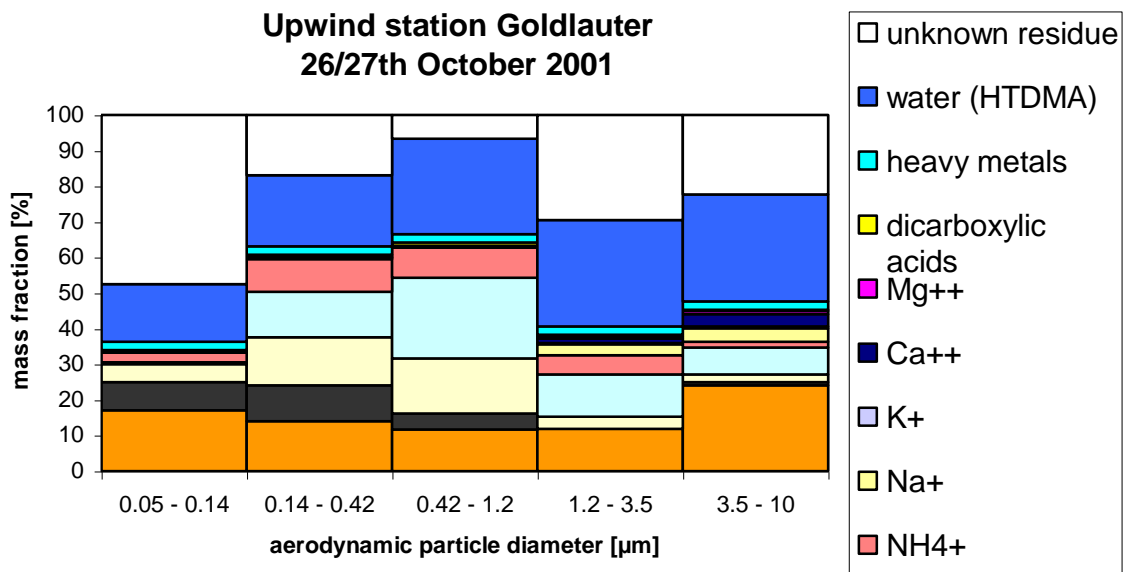


Figure 2: Chemical mass balance for aerosol particles during event 1

The relative composition shows the highest degree of identified constituents in the size range of $D_p = 0.42 - 1.2 \mu\text{m}$ where also absolute particle masses are highest. For the smallest sampled particles ($50 - 140 \text{ nm } D_p$) only 50 % of the weighed mass could be assigned to the analysed compounds.

During all events 9 dicarboxylic acids could be identified in the particle phase in different concentration ranges (Table 2). Their contribution to the total organic material can be as high as 10% (Figure 3).

Table 2: Concentration ranges of dicarboxylic acids during FEBUKO

acid	concentration (ng/m ³)
C2 (oxalate)	30 – 69 ng/m ³
C3 (malonate)	14 – 38 ng/m ³
C4 (succinate+ isomer)	7 – 21 ng/m ³
C5 (glutarate+ isomers)	0 – 23 ng/m ³
C3OH (tartronate)	0 – 4 ng/m ³
C4OH (malate)	6 – 24 ng/m ³
C4(OH) ₂ (tartrate)	0 – 6 ng/m ³
C5OH (citramalate)	0 – 2 ng/m ³
C4u (maleinate)	0 – 7 ng/m ³

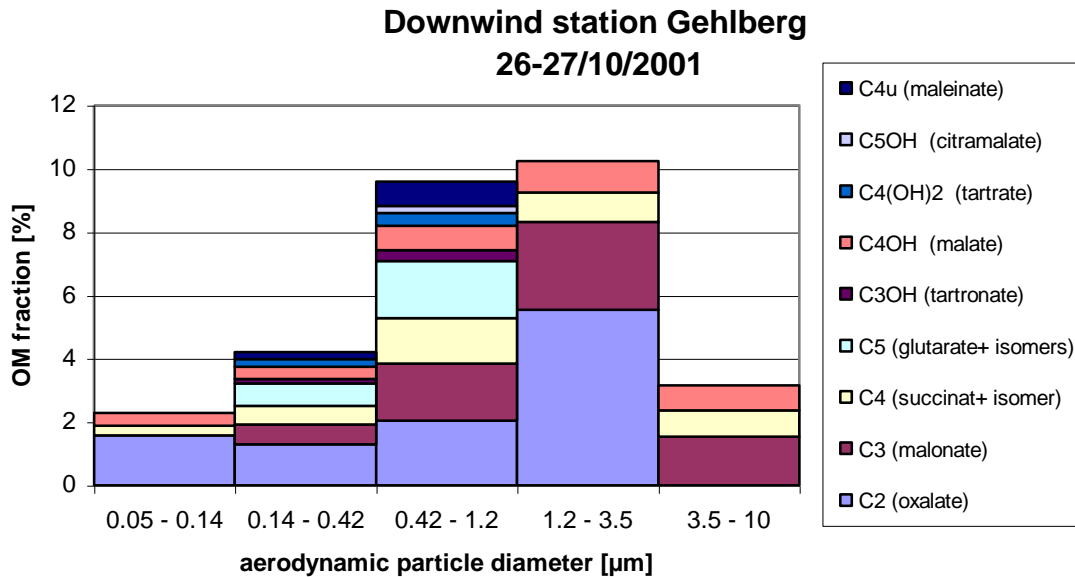


Figure 3: Contribution of dicarboxylic acids to organic material (OC * 2.1)

Size distributions of the acids look very similar for the upwind and downwind stations (Data not shown). Downwind station usually shows lower concentrations due to losses of particle mass by deposition of entrainment. For the smallest particles during event 1 substantially lower particle masses were found at the downwind station. As the concentrations of dicarboxylic acids did not decrease that much, this leads to a clearly higher mass fraction on impactor stage 1 (shown for oxalic acid in Figure 3).

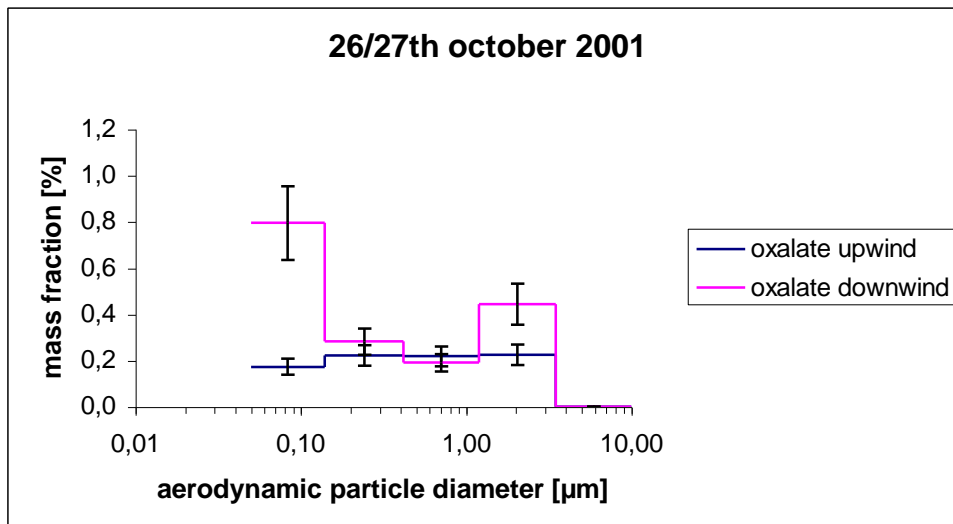


Figure 3: Mass fractions of oxalate at the valley stations during event 1

Comparing atmospheric concentrations of oxalic acid at all three stations reveals an interesting picture (Figure 4). Atmospheric concentrations in the cloud, which are obtained by multiplying liquid phase concentrations with the liquid water content of the cloud, are much higher than the particle concentrations determined from impactor samples. Spray collectors, which sample aerosol and gas phase simultaneously at the valley stations show similar concentrations to that in the cloud. This leads to the assumption that substantial fractions of oxalic acid could be present in the atmospheric gas phase. Due to their low vapour pressure oxalic acid is usually considered to be found almost completely in condensed phases, but the possibility of gaseous dicarboxylic acids is also discussed in the literature [Limbeck *et al.*, 2001; Saxena and Hildemann, 1996]. Another possible explanation for the discrepancy between impactor, spray collector and cloud water could be losses of oxalic acid due to the low pressure on the impactor stages or the elevated temperatures for RH control inside of the impactor inlet tubes.

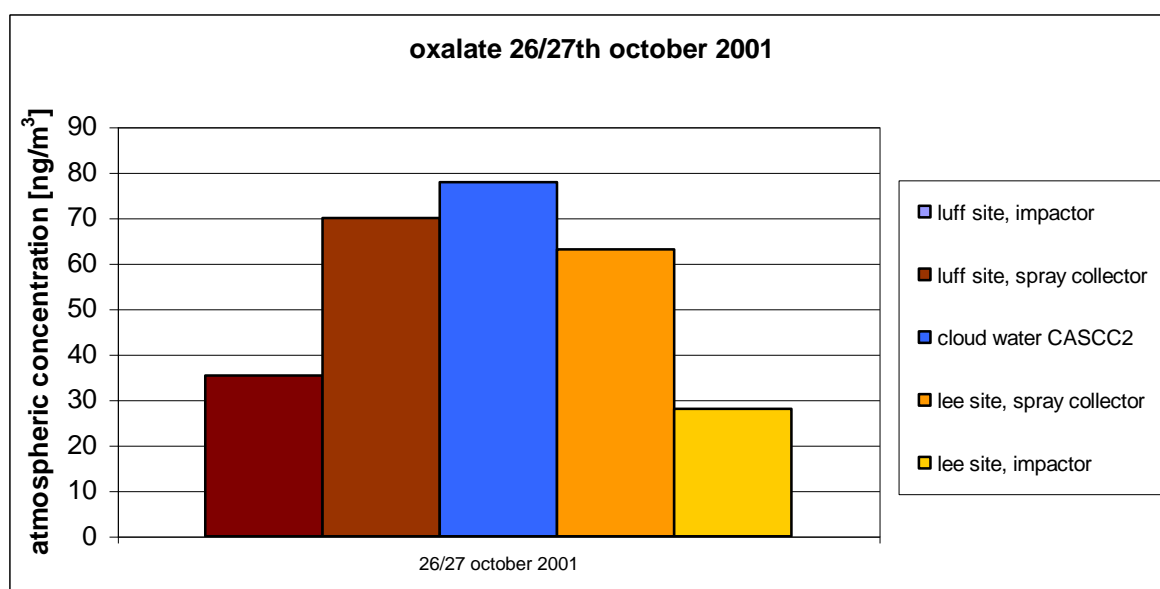


Figure 4: Comparison of oxalate concentrations at all three stations with different samplers

Outlook

The comprehensive data set from the FEBUKO field campaign is and will be used in coupled microphysics and complex multiphase chemistry models (SPACCIM and CAPRAM {Ervens, 2003 #670}). The models already show quite good agreement between the measurements and model results for some species, but need to be further developed especially for a better description of the organic chemistry. Furthermore, the Schmücke hill-capped cloud experimental site is ready for further ground based aerosol-cloud interaction experiments with special emphasis on organics.

Acknowledgment

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