Determination of dicarboxylic acids in tropospheric particles and cloudwater

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Introduction

During two field campaigns of the AFO 2000 project FEBUKO (*field investigations of budgets and conversions of particle phase organics in tropospheric cloud processes*) aerosol particle and cloudwater samples were taken in a forestal region in Germany (Thuringian Forest). Particle collection took place in autumn 2001 and 2002 at two valley sites (luff and lee) of the mountain Schmücke. On top of this mountain cloudwater was sampled (Figure 1). The aim was to collect and physically and chemically characterize air masses before, while and after passing an orographic cloud in order to provide information about possible multiphase interactions and chemical processing of the aerosol.

As part of the chemical characterization of particles and cloudwater the determination of dicarboxylic acids took place. Because of their low vapour pressure these acids, like oxalic acid, malonic acid, succinic acid, glutaric acid as well as some of their hydroxylated homologous compounds are frequently found in tropospheric condensed phases like aerosol particles, rain, cloudwater or snow[1,2]. They are formed partly from a variety of chemical conversion reactions in either the gas or condensed phase environment.

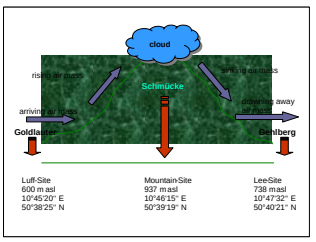

Figure 1: Schematic view of the sampling sites during the cloud experiments

Experimental

For sampling of the particles five-stage low-pressure cascade impactors (Berner-type with 50% cutoffs: 0.05, 0.14, 0.42, 1.2, 3.5, and 10 µm) were used. A humidity-controlled (60 % R.H.) tube bundle served as the inlet device. Tedlar foil was used as an impaction substrate then used for ion analysis.

For cloudwater sampling four cloudwater collectors of the California Institute of Technology design (CASCC2) were used, which collect droplets with a 50% cut off diameter of 3,5 µm by inertial impaction on several rows of teflon strands.

Determination of dicarboxylic acids was done by capillary electrophoresis with a Spectra Phoresis 1000 instrument from Thermo Separation Products (now Thermoquest). Main parameters of separation are shown in Table 1.

Table 1: Parameters of CE separation

capillary length	70 cm
capillary length to detector	63 cm
capillary inner diameter	75 µm
applied temperature	25 °C
applied voltage	- 29,4 kV
composition of electrolyte	10 mmol/l p-aminobenzoic acid
	8 mmol/l diethylenetriamine
	3,5 mmol/l NaOH (pH=9,6)
injection mode	hydrodynamic : 10,3 kPa for 30 s
detection mode	indirect at 254 nm

First results

Table 2: Top events of 2001 campaign

Event #	Date / Time (UTC)	Sampling time (h)
1	26.10.02 8:30 – 16:30	8
2	02.10.02 8:00 – 12:45	4,75
3	26./27.10.02 22:00 –13:00	15
4	02.10.02 8:00 – 12:45	4,75

Table 3: Concentration ranges of determined acids

Acid	Concentration range (ng/m³)
C2 (oxalate)	30 – 69 ng/m3
C3 (malonate)	14 – 38 ng/m3
C4 (succinate+ isomer)	7 – 21 ng/m3
C5 (glutarate+ isomers)	0 – 23 ng/m3
C3OH (tartronate)	0 – 4 ng/m3
C4OH (malate)	6 – 24 ng/m3
C4(OH)2 (tartrate)	0 – 6 ng/m3
C5OH (citramalate)	0 – 2 ng/m3
C4u (maleinate)	0 – 7 ng/m3

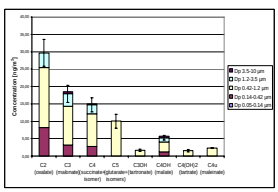

Figure 2: Concentrations of dicarboxylic acids for event #1

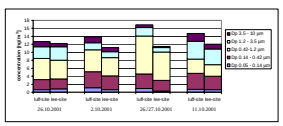

Figure 3: Concentrations of total particle mass for events #1 - 4

- Within the first measurement campaign in October 2001 17 cloud events occurred which were comprised into 9 periods. However, only 4 of them came with the right conditions for an orographic cloud (Table2). Event # 1 is considered as top-event, because meteorological conditions were nearly ideal.

- During the events 9 dicarboxylic acids could be identified in the particle phase in different concentration ranges (Table 3).

- Highest concentrations of the acids were found on impactor stage 3 (Dp=0.42-1.2 µm), where also total particle mass was highest (Figures 2 and 3).

- Total particle mass concentration (PM_{10}) decreases in the case of the transport from upwind side to downwind station with nearly all events (Figure 3), which is probably caused by deposition and a dilution by entrainment.

- For events # 1 and 2 the concentrations of the acids decrease more than the total particle mass concentrations, which results in decreasing mass fractions of the compounds (Figure 4).

- To compare particle phase with cloud water concentrations, liquid concentrations [µmol/l] are converted with the liquid water content [g/m³] to atmospheric concentrations [ng/m³]. In Figure 5 these recoveries are shown for the two most abundant acids. The concentrations given in this figure are mean values which include data of different aerosol and cloudwater samplers at the luff-, hill- and lee-site. As for oxalic and malonic acid the recoveries of other dicarboxylic acids are usually around 100 %.

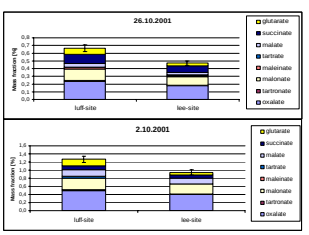

Figure 4: Mass fractions of dicarboxylic acids for events #1 and 2

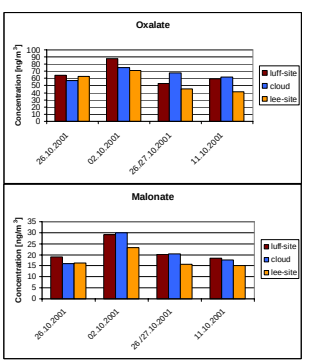

Figure 5: Comparison of concentrations before, inside and after the cloud for oxalic and malonicacid

Acknowledgment

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References

1 SAXENA, P. und HILDEMANN, L. M.; (**1996**); Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds; *Journal of Atmospheric Chemistry*; 24 (1); 57-109

2 SEMPERE, R. und KAWAMURA, K.; (**1994**); Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere; *Atmospheric Environment*; 28 (3); 449-459