

## Cloud physics and cloud water sampler comparison during FEBUKO

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### Abstract

Optical methods for counting and sizing cloud droplets and a wide range of cloud water sampling methods were used to characterize the atmospheric liquid phase during the FEBUKO cloud experiments. Results near cloud base as well as more than 300 m inside the hill cap clouds are presented, reflecting their inhomogeneous nature. The cloud droplet number varies from 50 to 1000 cm<sup>-3</sup> and drop sizes between 1 and 20 μm diameter are most frequent. Variations in the liquid water content (LWC) and in the total ion content (TIC) are much smaller when the measurement position is deeper in the cloud. Near cloud base variability in updraft strength and, near cloud top, entrainment processes (droplet evaporation by mixing with drier air, aerosol and gas scavenging) disturb the adiabatic conditions and produce large variations in LWC and chemical composition. Six different active cloud water collectors and impactors were running side by side; they differ in the principle of sampling, in the throughput of cloudy air per unit time and in the calculated 50% cutoff diameter, which influence also their sampling efficiency. Two of them are designed to collect cloud water in two droplet size fractions. Three cloud events were selected by the FEBUKO team for detailed cloud physical and chemical analyses because they serve best the modelling demands concerning connected flow between the upwind, summit and downwind sites for process studies. Frequency distributions of the LWC and, also of the cloud base height are given as statistical parameters for both FEBUKO experiments.

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**Keywords:** Cloud water sampling; Liquid water content; Cloud base height; Droplet size distribution; Cloud chemistry

### 1. Introduction

Ground-based cloud experiments were performed in autumn 2001 and 2002 at a mountain ridge in the Thuringian Forest (Germany) to study the airflow over hills, the cloud microphysics, and air and cloud

chemistry. Air approaching the ridge is forced to rise, cools by adiabatic expansion, and forms low clouds in the boundary layer. During south-westerly winds, the air is characterized at an upwind site before it enters the cloud, in the cloud at the summit and at a downwind site after cloud processing. Details about the investigations conducted are given in Herrmann et al. (2005).

Typically 50–1000 cloud droplets are found per cm<sup>3</sup> air together with about 200–3000 non-activated particles

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in *cumulus* or *stratus* clouds at a given supersaturation (Arends, 1996). Droplet number is highest at cloud base. Above cloud base existing droplets take up available supersaturated water vapor produced by the updraft leading to an increase in liquid water content (LWC) and droplet diameter with height above cloud base (Pruppacher and Klett, 1978). It is known from many field measurements (Junkermann et al., 1994; Wiegprecht et al., 1995; Möller et al., 1996; Acker et al., 2002) and expected under wet adiabatic conditions, that the LWC of a low cloud increases almost linearly with the height above cloud base, reaching a maximum at about 80–90% of the cloud thickness. Variations in LWC and in cloud water composition are much smaller if the measurement position is located well inside the cloud. Near cloud base variability in updraft strength and, near cloud top, entrainment processes (droplet evaporation by mixing with drier air, aerosol and gas scavenging) disturb the adiabatic conditions and produce large variations in LWC and chemical composition. Studies conducted over the last two decades have clearly demonstrated the important role clouds and fogs serve as processors of inorganic fine aerosol particles, contributing both to production of new particle mass and particle removal. Different cloud droplet collectors for research purposes have been developed during the last decade in order to sample fog or cloud water droplets (Daube et al., 1987; Fuzzi et al., 1997; Schell, 1997a; Moore et al., 2002; Straub and Collett, 2002). In addition to samplers that collect cloud droplets as liquid water samples there exists another technique, using a counterflow virtual impactor (CVI) (Ogren et al., 1985) where the individual sampled droplets are evaporated and the released cloud droplet residuals analyzed. Various cloud water samplers were tested in several field campaigns (Schell et al., 1997b; Herckes et al., 2002; Laj et al., 1998; Mertes et al., 2001) and some intercomparison campaigns have been carried out under different fog and cloud conditions (e.g., Schell et al., 1992). Sampling characteristics of some cloud water collectors have been determined in the laboratory (Straub and Collett, 2002) and wind tunnel experiments (Schwarzenböck and Heintzenberg, 2000). During planning for the FEBUKO field experiments, it became clear that different participants had needs which could not be fulfilled by a single type of cloud water sampler.

Some of these needs included

- a very well characterized cloud water sampler (cutoff calculated and tested in wind tunnel, cloud chamber and field experiments),
- cloud water sampling in two or more droplet size fractions,
- simultaneous sampling of cloud water and interstitial aerosol,

- large volume of cloud water for the analysis of trace organic species,
- half hour time resolution to permit comparison between cloud water composition and aerosol composition measured by a steamjet chamber,
- short time between cloud water sampling and analysis of reactive compounds (e.g., peroxides, nitrite),
- special CVI inlets for microphysical and chemical characterization of cloud droplet residual particles.

The decision was made to use cloud and fog water samplers of different designs to adequately address the identified requirements. This paper is intended to demonstrate the benefits of, and address issues of comparability resulting from, this multi-sampler approach.

## 2. Experimental

Cloud water sampling was carried out during the field campaigns on a tower platform approximately 20 m above ground at the summit site (S). The meteorological sensors and the sensors (see below) measuring LWC, effective droplet diameter and, droplet size distribution were also located on this platform. The tower was constructed of aluminum scaffolding in order to permit an undisturbed airflow around the samplers and instruments. Cloud LWC was measured every 10 s using a forward-scattering particulate volume monitor (model PVM100) for droplet diameters from 3 to 45  $\mu\text{m}$  (Gerber, 1991). Cloud drop size and number distributions were measured at the same frequency using a forward-scattering spectrometer probe (Particle Measurement Systems FSSP-100) equipped for ground-based operation. This laser-based light scattering instrument measures droplet number in 16 different size bins. From the drop distribution, the total volume of liquid water can be calculated.

At a distance of about 20 m from the tower but at the same height above ground, the inlets of two CVI and an additional PVM100 were mounted at a window and on a roof platform of the weather service building, respectively. The analyzers and sampling units connected downstream of the CVI (see below and Mertes et al., 2005) were deployed inside for protection from the weather. Additional information, including cloud base altitude (derived from ceilometer data), cloud coverage (obtained from NOAA satellite data) and backward trajectories (NOAA) for air mass history, are available for data analysis. At the upwind study site (U) a Vaisala CTK25 laser ceilometer (resolution in time 15 s, in space 30 m) was operated for continuous determination of cloud base height by backscattering of a vertically directed laser beam.

Discrete periods of several hours, which meet the right experimental conditions, were selected as cloud monitoring events. Criteria to initiate measurements included cloud occurrence only at the summit site with  $LWC > 100 \text{ mg m}^{-3}$  for more than 15 min, connected airflow at the three sites (south-westerly winds) and temperature  $> 1^\circ \text{C}$  without rain at all sites. Generally, a sampling time of 2 h was utilized in order to sample enough cloud water for the planned chemical analyses. For some special needs a shorter sample time of  $\frac{1}{2}$  h was used in 2001 (Acker et al., 2003). The amount of collected cloud water was determined by weight (most cloud collectors) or by using Ly alpha measurements of evaporated cloud water (for the CVI, see Mertes et al., 2005). Chemical analysis of collected samples was completed by various FEBUKO participants. For details see other FEBUKO-related papers in this special issue (Gnauk et al., 2005; Müller et al., 2005; Brüggemann et al., 2005; van Pinxteren et al., 2005).

The various cloud water collectors used in the study are briefly described below.

### 2.1. CASCC2\_4: Caltech Active Strand Cloudwater Collector Version 2

The design of this sampler is described by Demoz et al. (1996). The CASCC2 is a compact version of the original CASCC which in turn was based on a similar collector developed by Daube et al. (1987). Air containing cloud droplets is drawn by a fan through the CASCC2 where the droplets are collected by inertial impaction on six rows of 508  $\mu\text{m}$  diameter Teflon strands. The size cut (droplet diameter collected with 50% efficiency) was estimated to be approximately 3.5  $\mu\text{m}$ . The collector design was adopted by IfT with a 220 V frequency controlled fan used to generate a stable airflow of  $348 \text{ m}^3 \text{ h}^{-1}$ . Four CASCC2 samplers were mounted side by side in order to collect a larger cloud water volume for analysis of trace organic compounds.

### 2.2. SAJ-16: Set of Active round Jet collectors—16 samplers)

The sampling head of this fog impactor has 16 single-jet collectors arranged in a circle. A single collector consists of a round nozzle for the formation of a jet and a collection disc and funnel assembly underneath the nozzle. This collector has been described in some detail by Berner (1988). All single-jet collectors were connected to a common exhaust tube, equipped with a throttle for limiting the flow to the desired amount, and with a tap for measuring the pressure ahead of the throttle. Assuming uniform flow conditions for individual jets, the cut diameter of the collector has been calculated as

$D_{p,50} = 4.5 \mu\text{m}$ . This sampler was used primarily for  $\text{H}_2\text{O}_2$  analysis in the cloud water.

### 2.3. SSI: Single-Stage slit jet Impactor

The low-volume SSI sampler consists of two parallel slit jets, air is drawn through the impactor with a total sample volume of  $120 \text{ m}^3 \text{ h}^{-1}$  using a vacuum pump. The airflow was tested and set before and after each FEBUKO campaign. The calculated 50% cutoff diameter for cloud droplets is 5  $\mu\text{m}$  (Winkler, 1992). The cloud water collected by this sampler was used for analysis of inorganic anions and cations, (Acker et al., 2003) water-soluble organic compounds (WSOC), organic peroxides (see Valverde-Canossa et al., 2005), and for measurements of pH and conductivity.

### 2.4. TSCI: Two Stage Cloud water Impactor

The TSCI cloud water sampler operates on the principle of internal impaction on plane surfaces, used widely in aerosol particle sampling, as reported by Marple and Willeke (1976). The TSCI consists of three vertical slit impactor stages. The first stage collects larger droplets, followed by two identical stages in parallel to collect smaller droplets. The 50% cutoff diameter in the first stage was fixed at 12  $\mu\text{m}$  and the second stages at 4  $\mu\text{m}$ . The airflow through the sampler was  $180 \text{ m}^3 \text{ h}^{-1}$ . The sampler was equipped with an isokinetic inlet (Schell et al., 1997a, b) and a wind vane to keep the inlet directed into the wind.

### 2.5. Sf-CASCC: Size-Fractionating Caltech Active Strand Cloud water Collector

The size-fractionating Caltech Active Strand Cloud water Collector collects cloud drops in two size ranges (Demoz et al., 1996). The first stage (referred to as the fractionating inlet) consists of a bank of four rows, each containing eight 12.7 mm diameter Teflon rods. Each row is offset from the one in front of it so that rods are not shadowed by those in the previous row. Mounted downstream of the inlet is the second stage, which contains a bank of six rows each containing 102 Teflon strands (508  $\mu\text{m}$  diameter) spaced 2.3 mm apart (center to center). By removing the large drops from the air stream in the fractionating inlet (modelled 50% size cut of  $\sim 16 \mu\text{m}$ ), a second sample of cloud water comprised of smaller cloud drops is collected on the second stage (50% size cut of 4  $\mu\text{m}$ ). Consequently, the operator can simultaneously collect independent large and small drop size fractions from the sampled cloud. Cloud water sampled by this high-volume two-stage sampler was analyzed for inorganic cations and anions and several different WSOC.

## 2.6. CVI: Counterflow Virtual Impactor

A CVI was deployed to collect cloud droplets in the size range between 5 and 50  $\mu\text{m}$  (Schwarzenböck et al., 2000). By means of a counterflow directed out of the inlet (opposite to the sampling direction) interstitial particles and gases are pre-segregated. Upon collection, cloud drops are evaporated in a dry and particle-free carrier stream of air releasing all dissolved, volatile substances into the gas phase and non-volatile components as residual particles. Downstream of the CVI and an interstitial inlet, two particle counters (TSI-3010) and two differential mobility particle sizers measured the residual and interstitial particle concentrations ( $D_p > 12 \text{ nm}$ ) and dry size distributions ( $22 \text{ nm} < D_p < 900 \text{ nm}$ ). Filter units and cartridges were combined to sample material for chemical analysis. More details about the CVI systems used in this study are given in Mertes et al. (2005).

## 3. Results and discussion

### 3.1. Liquid water content and cloud base height

Based on the LWC measurements made at Mt. Schmücke tower (957 m above sea level (a.s.l.)) between 02 October and 05 November 2001, the mean value of cloud LWC was determined to be  $221 \pm 130 \text{ mg m}^{-3}$ . The mean LWC of clouds intercepting this site between 22 September and 31 October 2002 was  $187 \pm 121 \text{ mg m}^{-3}$ . These 10-min averages varied between 10 and 670  $\text{mg m}^{-3}$ . The summit was in cloud 40% of the study time in 2001 and 51% in 2002. Fig. 1 shows frequency distributions of LWC for both FEBUKO experimental periods. Knowledge of the distance between the

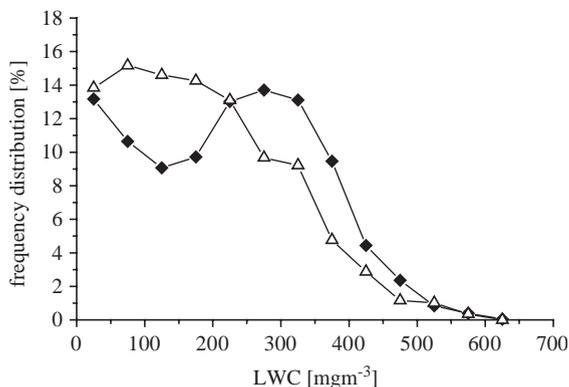


Fig. 1. Frequency distribution of liquid water content of low clouds observed at Mt. Schmücke during the two FEBUKO experiments: 02 October–05 November 2001 (solid line with closed diamonds) and 22 September–31 October 2002 (solid line with open triangles).

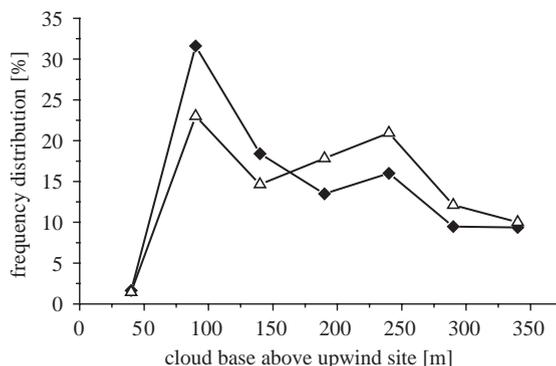


Fig. 2. Frequency distribution of the cloud base if Mt. Schmücke (tower) is in cloud for the two FEBUKO experiments: 02 October–05 November 2001 (solid line with closed diamonds) and 22 September–31 October 2002 (solid line with open triangles). The vertical distance between measurement platform at Mt. Schmücke and ceilometer position is 352 m.

sampling position and cloud base is essential for any physico-chemical interpretation of cloud data. Ceilometer measurements from a point 352 m below the Schmücke tower were made continuously. It was found, that about 65% of all low clouds (clouds observed up to 2500 m a.s.l.) had their cloud base below the Mt. Schmücke tower (957 m a.s.l.). As can be seen from Fig. 2, Mt Schmücke tower was often (25–35% of the time) 250–300 m deep in the cloud and in about 20–25% of the cases near the cloud base. Unfortunately, there are no observations of cloud top height. In an undisturbed (stratus) cloud, the condensation conditions inside the cloud are strongly correlated with decreases in temperature above the cloud base altitude.

### 3.2. Selected cloud events

Three out of 14 cloud events observed during the two measurement campaigns were selected for detailed cloud physical and chemical analyses and modelling activities (using synoptic parameters, airflow analysis, and meteorological, chemical and physical data): 26/27 October 2001 22:00–13:00, called E I; 07/08 October 2001 19:00–08:00, called E II; 16/17 October 2002 21:00–04:00, called E III. These events featured connected flow between the study sites with continuous advection of air masses of maritime origin from the south-west. During long distance transport over Western Europe the aerosol should be altered and become more continental (e.g., Tilgner et al., 2005; Heinold et al., 2005). Air masses during these selected episodes featured low to medium pollution levels. On average concentrations of  $\text{SO}_2$  below 1 ppb and of  $\text{NO}_2$  below 10 ppb were observed.

Time series of LWC, its distribution between two different droplet size ranges (4–12  $\mu\text{m}$  and 12–32  $\mu\text{m}$ ),

and the altitude of the cloud base above the upwind site are presented for two events in Figs. 3a (E I) and 3b (E III). Cloud drop number distributions for these events are given in Figs. 4a and b.

Mt. Schmücke summit was already in cloud when intensive measurements started at 22:00 UTC on 26 October 2001 (E I). At about 00:00 UTC the summit is approximately 150–200 m above cloud base and the two droplet size ranges are comparable contributors to total cloud LWC (see Fig. 3a). Later, the base of the stratus descends. At approximately 03:00 UTC a summit LWC of  $500 \text{ mg m}^{-3}$  was measured and, at this position 300 m deep in the cloud, most of the water was found in the drops larger than  $12 \mu\text{m}$ . The droplet size distribution of E I given in Fig. 4a reveals a droplet number reduction

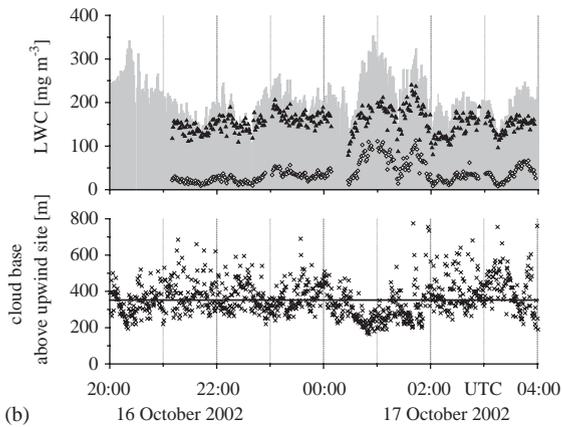
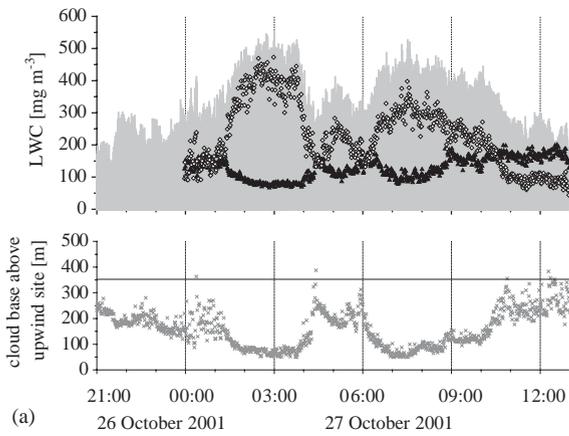


Fig. 3. Relationship between liquid water content of cloud, droplet size distribution and the position inside the cloud. Upper diagram: LWC for all droplets (gray area, PVM100), for the droplet fraction  $4\text{--}12 \mu\text{m}$  (closed triangles, FSSP100) and the droplet fraction  $12\text{--}32 \mu\text{m}$  (open diamonds, FSSP100). Lower diagram: height of the cloud base above the upwind site ( $605 \text{ m a.s.l.}$ ). The solid line presents the level of measurement platform at Mt. Schmücke tower ( $957 \text{ m a.s.l.}$ ): (a) cloud event E I; (b) cloud event E III.

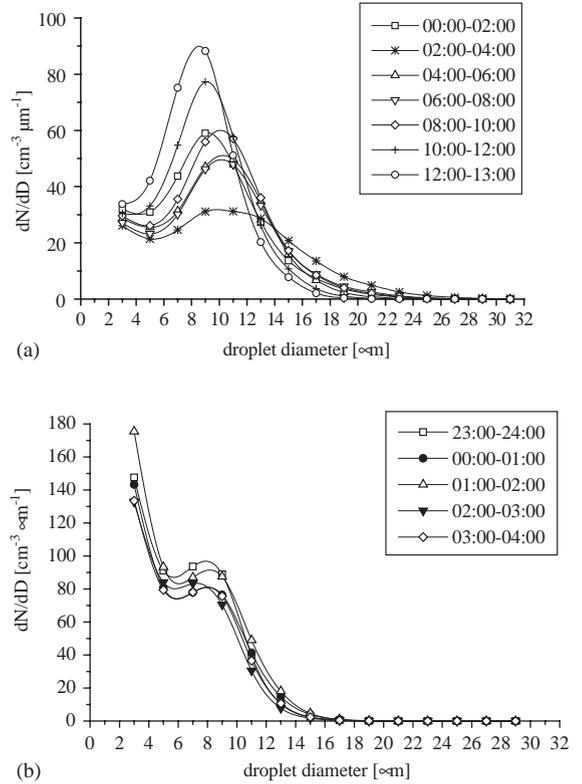


Fig. 4. Cloud droplet number distribution during two sampling periods: (a) 26/27 October 2001 (E I); (b) 16/17 October 2002 (E III).

and a shift of the droplet volume to bigger droplets in the sampling period 02:00–04:00 UTC. The increase in LWC per meter of height is about  $2 \text{ mg m}^{-3}$ . Colville et al. (1997) expected similar values during adiabatic changes in the temperature of air parcels flowing over the hill. During the whole event E I a strong correlation between LWC and height above cloud base was observed ( $r = 0.78$ ). At 13:00 UTC, after several hours of cloud lifting, the Mt. Schmücke tower was located near cloud base. The observed decrease in LWC is connected with a shift of the droplet size distribution to smaller drops after 10:00 UTC (Fig. 4a).

Cloud physical properties during event E III (Fig. 3b) were significantly different than observed in E I. A much lower LWC is related to a much smaller vertical distance between our sampling position and cloud base, averaging only  $50\text{--}100 \text{ m}$  during the measurement period. Very little correlation between LWC and height above cloud base was found ( $r = 0.08$ ) during this event. Reasons for the little correlation may be among others the principle of cloud base detection (overflow over complex orographic terrain) and the cloud base structure during E III (very inhomogeneous concerning droplet number density). Reflections of the laser beam often from more than  $100 \text{ m}$  inside cloud (above the

sampling position) were registered. Any time delay caused by the horizontal distance between both measurements (3 km) was already corrected in the data. Near cloud base, mixing with unsaturated air cannot be excluded. Little liquid water was found in droplets larger than  $12\ \mu\text{m}$  and, cloud drops with diameter  $D > 15\ \mu\text{m}$  were rarely observed. Throughout E III the droplet number distribution was relatively stable, as indicated by Fig. 4b. As expected near cloud base, mainly small cloud droplets were observed with a broad maximum in the size range  $4\text{--}10\ \mu\text{m}$ .

Cloud event E II can be divided into three sampling periods (Müller et al., 2005) including times near cloud base and other times higher inside the cloud. This event is not discussed here in detail.

As already mentioned, cloud droplets were sampled by CVI and evaporated to permit drop residual characterization. Agreement between the FSSP drop number concentration and the CVI residual particle concentration was found during all three focus episodes (E I–E III) indicating that on average one evaporated droplet released one residual particle. The number of interstitial (non-activated) particles ( $< 5\ \mu\text{m}$ ) inside cloud was also determined (Mertes et al., 2005).

### 3.2. Cloud water sampling at the summit

All cloud water samplers as well as the instruments for the measurement of LWC, cloud droplet size and number concentrations were concentrated side by side on the measurement platform at summit. One important feature of cloud water samplers is their sampling efficiency. The efficiency  $\varepsilon$  can be defined as the ratio of sampled water volume to the *real* cloud water volume in air, i.e.,  $\varepsilon = 1$  if the sampler collects *all* cloud droplets in a given air volume. There are some difficulties in estimating the efficiency. First, no sampler can collect all cloud droplets by several methods and secondly, each sampler has different characteristic (which even depends from atmospheric conditions, namely wind speed) in the droplet-size resolved sampling efficiency. It follows that each sampler must have always  $\varepsilon < 1$ . This is not a problem in characterising the chemical composition of clouds when the sampling efficiency is only weakly dependent from droplet size, which, however, cannot be presumed. Consequently, by using the total cloud water based on integrated measurement methods (LWC) the sampler efficiency cannot be calculated theoretically (not even taking into account data quality objectives) but only approached. In comparing different samplers in this experiment, we calculated  $\varepsilon$  as the relation between the predicted cloud water volume and the real sampled cloud water. The predicted cloud water volume was calculated for these samplers by

$$V_{\text{pred}} = \overline{\text{LWC}} V_{\text{air}} \Delta t, \quad (1)$$

where  $\overline{\text{LWC}}$  is the cloud droplet water volume (calculated from FSSP measurements) integrated over the droplet spectra starting at sampler  $D_{50}$  cutoff,  $V_{\text{air}}$  airflow through the cloud water sampler and  $\Delta t$  sampling time. Sampler using the impaction of the cloud droplets at a plane plate with a defined droplet velocity have a sharp  $D_{50}$  cutoff, normally calculated for cloud droplets at  $4$  or  $5\ \mu\text{m}$  diameter. Two active strand collectors (CASCC2\_4, sf-CASCC) used the principle of cloud drop impaction on cylinders (rods and strings). These samplers offer very high air sampling rates at low pressure drop, but do not feature sharp collection efficiency curves. Use of Eq. (1) for these samples will result in an overestimation of the predicted cloud water sample volume. Therefore, the cloud water volumes collected with the two-stage sf-CASCC were compared with those expected from the collector's performance characteristics and the observed drop size distributions. Collector performance characteristics for the first stage of the sf-CASCC were based on a computational fluid dynamics simulation (FLUENT) of the air and droplet flow through the collector. The collection performance of the second stage was based on the treatment by Demoz et al. (1996).

Observed and predicted cloud water sampling volumes of three high-volume and one low-volume cloud water sampler are presented in Fig. 5 for all events E I–E III. Measurements were made with the sf-CASCC only in 2002. Total sf-CASCC sample volumes (large + small drop fractions) have been used for the presentation in Fig. 5. As discussed above, there are systematic and random deviations from the “theoretical” efficiency (1:1 line). Closest to the 1:1 line lies the low-volume SSI. This sampler was tested in a wind tunnel and well characterized in many field campaigns. The sampling efficiency of the string collectors appears to decrease (Fig. 5) when there is a shift to bigger droplets and higher LWC. This may reflect loss of droplets off the collection strands

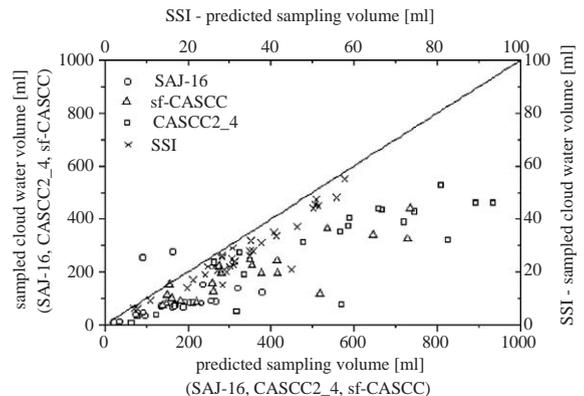


Fig. 5. Sampling efficiencies of low- and high-volume cloud water samplers during E I–E III.

and/or losses to interior collector walls, a phenomenon observed previously in large drop fogs.

The sampling efficiency for the two stages of the size fractionating samplers is presented in Fig. 6. Close to the 1:1 line is the sf-CASCC collector's first stage (17–32  $\mu\text{m}$ ). Actual collected volumes for the second stage, however, consistently fall below the “theoretical” line. This pattern also has been observed at other locations and appears to reflect inter-stage droplet losses during collector operation (Demoz et al. 1996). In the TSCI-first stage (12–32  $\mu\text{m}$ ) the sampling efficiency as defined above was on average 56% (45–70%). The cloud water sampling efficiency was higher in the TSCI-second stage (4–12  $\mu\text{m}$ ) averaging 76% (58–96%). The biggest differences between predicted and collected cloud water volume were observed during E III in both stages of the TSCI and in the second stage (4–17  $\mu\text{m}$ ) of the sf-CASCC collector. This event was characterized by the dominant occurrence of small droplets and large variations in LWC due to sampling near the cloud base. CVI sampling efficiencies were calculated on event basis. During the three main events the CVI 2 sampling efficiency has shown no variations with 70% and somewhat lower (about 55%) for CVI 1 (see Table 1).

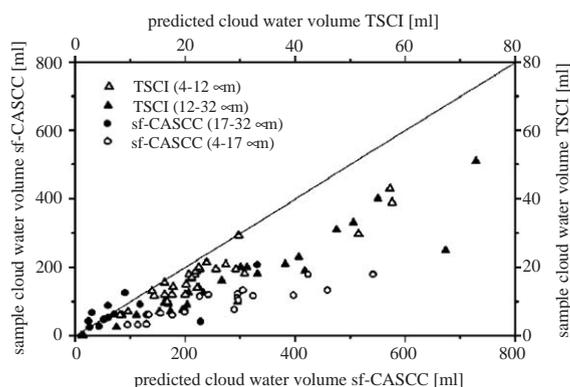


Fig. 6. Sampling efficiencies of the two size fractionating cloud water samplers.

Cloud water sampling performed by high- and low-volume samplers at Mt. Schmücke showed different sampling efficiencies from sampler to sampler and, in some cases from event to event. As already mentioned, the reasons for the variation of the sampling efficiencies are several. High wind speeds (gusts) near  $10 \text{ m s}^{-1}$  produced an environment where cloud drop sampling was often non-isokinetic. Differences in sampler design certainly influence sampler efficiency. Observed sampling of efficiencies near 50% and higher were judged adequate since sufficient water was collected for all planned analytical processes. Important is a representative sampling over the whole droplet spectra or the selected droplet fraction. Chemical cloud water composition results are described below using observations from the low-volume SSI and the high-volume CASCC2\_4 collectors, the TSCI two-stage impactor and the CVI.

### 3.3. Cloud water ionic composition

Aerosols comprised of water-soluble compounds are often efficient cloud condensation nuclei (CCN). However, each particle may have a different chemical composition and hence, hygroscopicity. Inorganic salt particles, for example NaCl,  $\text{NH}_4\text{NO}_3$ , and  $(\text{NH}_4)_2\text{SO}_4$ , are often quite effective CCN (e.g., Lohmann et al., 2004). The role of organic compounds as CCN is more uncertain. However, organic compounds with oxygenated functional groups, such as carboxylic and dicarboxylic acids, that contribute to their water solubility may also act as CCN. This confirms results from the Schmücke experiment (van Pinxteren et al., 2005; Müller et al., 2005; Wolke et al., 2005). The main factors controlling the cloud droplet number concentrations and hence the effective radius of the droplets are the chemical size distribution of the aerosol and the updraft speed at cloud base (Bower et al., 1997).

The ion concentrations of a cloud water sample are influenced by the cloud LWC. For intercomparisons at different sampling locations and times, therefore, it is important to account for dilution due to changing LWC. This can be done by multiplying the aqueous solute

Table 1  
Cloud water samplers used at the summit site during the FEBUKO experiment

Sampler ID	Operator	Airflow ( $\text{m}^3 \text{ h}^{-1}$ )	Sampling efficiency (%)	Sampling direction
CASCC2_4	IfT	1392	$56 \pm 17$ , $n = 56$	Horizontal
SAJ-16	ZUF	400	$51 \pm 37$ , $n = 53$	Vertical
SSI	BTU	120	$79 \pm 11$ , $n = 92$	Horizontal
TSCI	BTU	180	$66 \pm 13$ , $n = 45$	Horizontal
sf-CASCC	Collett Jr./IfT	1140	$45 \pm 11$ , $n = 21$	Horizontal
CVI-1	IfT	6	$53 \pm 11$ , $n = 22$	Horizontal
CVI-2	IfT	6	$64 \pm 17$ , $n = 21$	Horizontal

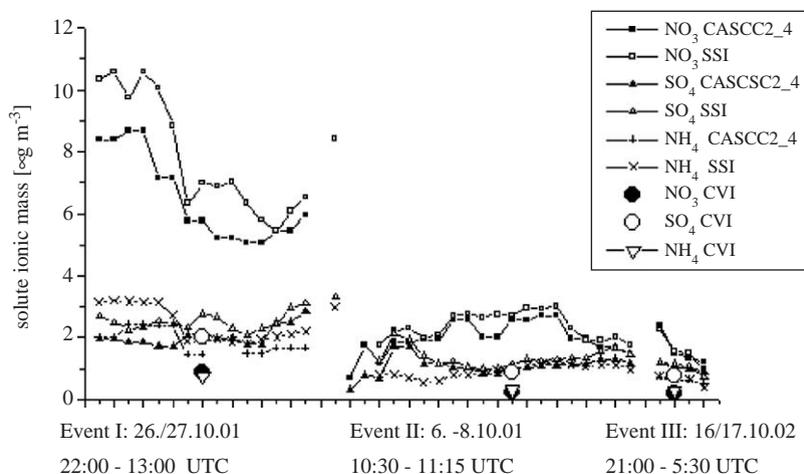


Fig. 7. Comparison of solute ionic mass in the cloud water collected by the low-volume samplers SSI and CVI and the high-volume sampler CASCC2\_4.

concentration by LWC to obtain the amount of solute present in cloud drops per unit volume of air:

$$m_{\text{isol}} = c_{\text{isample}} \times \overline{\text{LWC}}, \quad (2)$$

where  $m_{\text{isol}}$  is the solute mass of compound  $i$  (i.e.  $\mu\text{g}$ ) in cloud per  $\text{m}^3$  air,  $c_{\text{isample}}$  the aqueous concentration of compound  $i$  (i.e.  $\text{mg l}^{-1}$ ) in cloud water, and  $\overline{\text{LWC}}$  is the LWC averaged over the sampling time.

Temporal variations of the concentrations of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  observed during cloud events E I–III are shown in Fig. 7, where results for two different samplers are given. Comparing the three events, solute masses in “E I” are nearly a factor of 2–3 above those in “E II” and “E III”. Differences in meteorology and air composition between these events are discussed by Brüggemann et al. (2005). A systematic small difference in the ion concentrations was found between samples collected by the SSI low-volume jet impactor and the high-volume CASCC2\_4 string collector; the solute ionic mass in cloud water sampled by the SSI was on average about 8–15% higher than in CASCC2\_4 samples. The sulfate content of the cloud droplets sampled with the CVI agree well with the solute sulfate in the cloud water samples; not surprisingly, the nitrate and ammonium concentrations in cloud drop residuals were about ten times lower compared to the cloud water samples, likely reflecting evaporative losses of these more volatile constituents during drop evaporation in the CVI (Mertes et al., 2005).

The cloud water collected by the both SSI and CASCC2\_4 samplers was also analyzed for WSOC. Analyses were completed by the BTU central laboratory (SSI samples) and the IfT-laboratory (CASCC2\_4 samples). Results for events E I and E II are presented in Fig. 8, the data agree well. Further discussion of

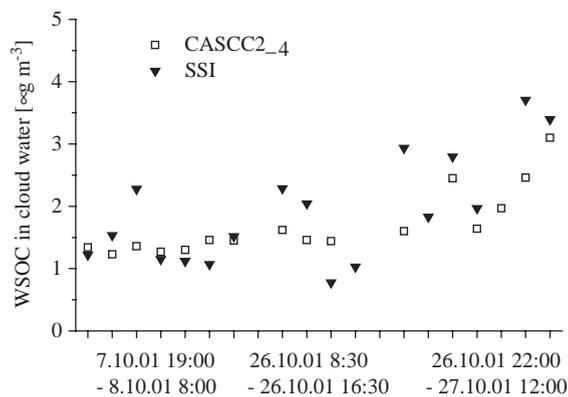


Fig. 8. Mass of water soluble organic carbon (WSOC) in the cloud water sampled by the string collector CASCC2\_4 and the droplet impactor SSI during E I and E II.

WSOC data is given in Brüggemann et al. (2005). The WSOC content in the cloud water was in the same range as the solute concentrations of the  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , indicating the potential importance of these clouds in the processing of organic matter in the atmosphere (see also among others Feng and Möller, 2004; Mészáros, 1999; Novakov and Penner, 1993).

The time available for the droplets to grow is important for the size dependence of solute concentrations. Size resolved cloud water sampling was made during events “E I” and “E III”. Data from the Two-Stage Cloud water Impactor (TSCI) are presented here (see Figs. 9a and b and 10a and b). During both events nitrate was the dominant inorganic anion, followed by sulfate and ammonium. During E I the solute ionic mass per  $\text{m}^3$  air was a factor 2–4 higher in the big droplets

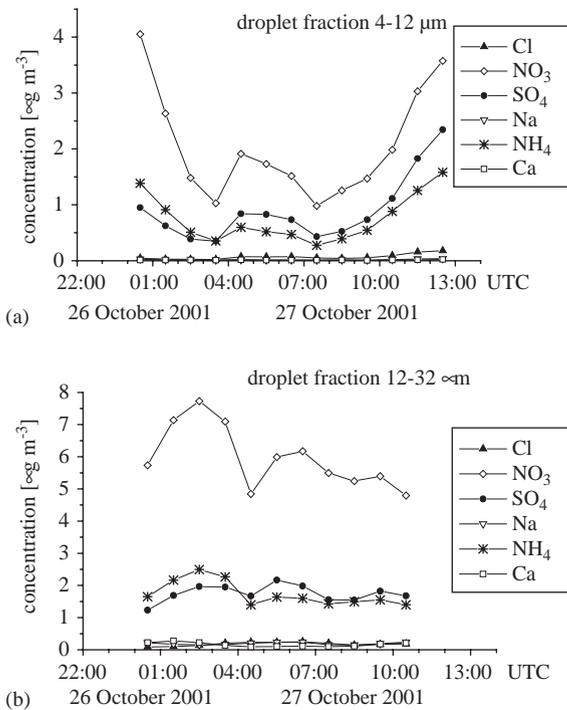


Fig. 9. Ionic composition of event E I: (a) in the small droplet fraction of the TSSI; (b) in the fraction of big droplets of the TSSI.

(12–32 μm) compared to the small ones (Figs. 9a and b). This could be an indication that the cloud droplets were formed by orographic lifting of the air at Mt. Schmücke. The observed time series are very similar for the main inorganic ions and follow changes in LWC and droplet spectra (Section 3.1, Figs. 3a and 4a). Concentration changes observed between 03:00 and 05:00 UTC may be caused also by changes in the particle number concentration observed simultaneously at the upwind site (Mertes et al., 2005) and changes in height above cloud base (see Fig. 3a). Sodium and chloride were observed in both size ranges at low concentration, indicating the loss of sea salt dominance in the air mass during cross-continent transport.

During “E III” cloud droplets were collected all the time near cloud base and concentrations of all main ions (esp. sulfate, nitrate and ammonium) are about three times larger in the small droplet fraction (Figs. 10a and b). With no significant changes of the droplet spectra (Fig. 4b) and of particle number concentration below cloud or of interstitial particles in the cloud (Mertes et al., 2005), no significant changes resulted in the chemical composition of both drop size fractions (Fig. 10b). The observed drop size-partitioning of sodium and chloride (indicating the marine influence of the air mass) suggest that (larger) sea salt aerosol particles served as activa-

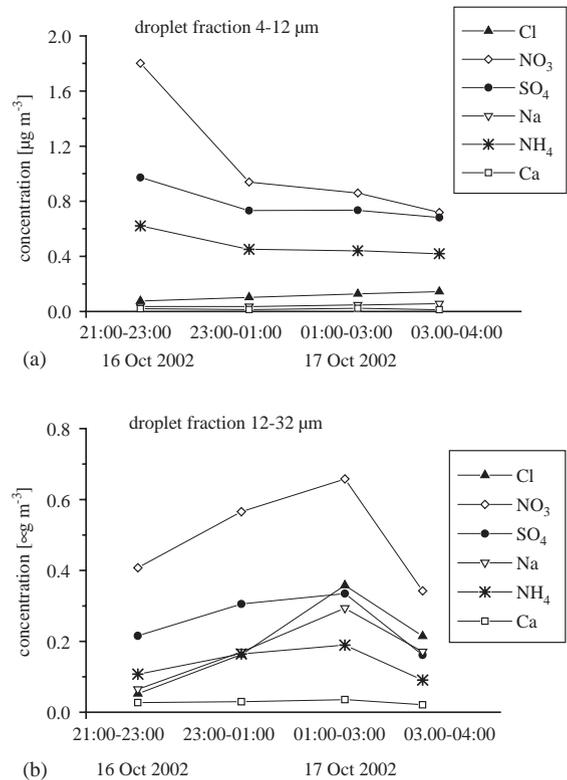


Fig. 10. Ionic composition of event E III: (a) in the fraction of small droplets of TSSI; (b) in the fraction of big droplets of the TSSI.

tion sites for larger droplets than observed for (smaller) ammonium sulfate or ammonium nitrate particles.

#### 4. Summary

For the first time at Mt. Schmücke in the Thuringian Forest (Germany), measurements of cloud liquid water content and cloud base height were made simultaneously. About two-thirds all low clouds (up to a height of 2000 m above ground at the upwind site) observed in October 2001 and October 2002 had their cloud base below Mt. Schmücke summit. The station was in cloud nearly half of both experimental periods. Summit LWC in these clouds averaged approximately  $200 \text{ mg m}^{-3}$ .

The observations done at this site confirm the increase in liquid water content with the height above cloud base. During event E I a high correlation between LWC and height above cloud base was found ( $r = 0.78$ ), these LWC measurements were made often 300 m deep in the cloud. Throughout E III the Mt. Schmücke summit was near cloud base, only 50 to 100 m deep in cloud. Conditions for adiabatic condensation are probably disturbed close to cloud base by processes like droplet

evaporation by mixing with drier air, and aerosol and gas scavenging. The drop size spectrum was very stable in this event, mainly droplets between 2 and 10  $\mu\text{m}$  diameter were observed. Differences in sampling position within the cloud between these two events provide a nice contrast for planned numerical simulations of cloud development and pollutant processing. Several cloud water collectors were in use during the field campaign. Cloud collectors sampling efficiencies ranged from 45% to 79% when averaged over all cloud events of the FEBUKO campaigns. A good agreement between the high-volume strand collectors and the low-volume cloud droplet impactors was found in the LWC range between 100 and 350  $\text{mg m}^{-3}$ . At higher liquid water contents with higher number of bigger droplets, the sampling efficiency of the strand collectors decreased. On average, a difference of approximately 10% was observed between measured cloud water chemical compositions from these two collector types.

The chemical composition of cloud droplets varies as a function of size because of the inhomogeneous chemical composition of the cloud condensation nuclei (CCN) on which the droplets grow and the sampling height above cloud base. Size-resolved ionic cloud water composition in two cloud drop classes ( $4 \mu\text{m} < D < 12 \mu\text{m}$  and  $D > 12 \mu\text{m}$  diameter) are presented for sample times near cloud base (E III) and deep inside cloud (E I).

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