Schmücke hill cap cloud and valley stations aerosol characterisation during FEBUKO (I): Particle size distribution, mass, and main components

E. Brüggemann[a,*], T. Gnauk[a], S. Mertes[a], K. Acker[b], R. Auel[b], W. Wieprecht[b], D. Möller[b], J.L. Collett Jr.[c], H. Chang[c], D. Galgon[a], R. Chemnitzer[a], C. Rüd[a], R. Junek[d], W. Wiedensohler[a], H. Herrmann[a]

[a]*Leibniz-Institut für Troposphärenforschung e.V., Permoserstr. 15, D-04318 Leipzig, Germany*
[b]*Brandenburgisch-Technische Universität, Abt. Luftchemie, Vollmerstr. 13, D-12489 Berlin, Germany*
[c]*Department of Atmospheric Science, Colorado State University, Ft. Collins, CO 80523, USA*
[d]*Umweltbundesamt, Messstelle Schmücke, D-98559 Gehlberg, Germany*

Abstract

Hill cap cloud field experiments were performed during autumn 2001 and 2002 in the Thüringer Wald (Germany). Gas phase trace compounds were determined at an upwind, summit, and downwind sites and major particulate components at an upwind and downwind site. Cloud water and total cloud components (drop residuals and interstitial particles) were determined at a summit site. Three events were fulfilling the criteria for the best conditions defined by during a connected flow upwind–summit–downwind sites and further detailed analysis was performed on these events. Cloud water components were compared with particle concentration at upwind and downwind site. The concentrations of non-volatile components in cloud water were found to be in good agreement with corresponding particle phase concentrations at the upwind site. Downwind site particulate component concentrations of non-volatile compounds were lower than in cloud water indicating loss processes during transport such as deposition. The concentrations of volatile components were found to be higher in cloud water than in the particle phase concentrations at up- and downwind site samples probably due to a loss from impactor sampling technique as well as a transport loss. Indications for changes of aerosol composition by cloud processes were found from a limited number of cases. Elevated sulphate and ammonium concentrations from upwind to downwind site in the smallest particle size range ($PM_{0.05-0.14}$) were found during event I (20% and 17%) and event III (70% and 150%), respectively. In the particle size range of $PM_{0.14-0.42}$ an increase of OC by about 20% for event I was observed. Considering the relative contributions of components to the single size range mass (avoiding physical sink processes), comparatively higher increases for sulphate, nitrate, ammonium, OC, and EC could be observed. Indications of an increase of aerosol mass can be derived in some cases from the aerosol number and volume size distributions. Results from a complex multiphase model (SPACCIM) are consistent showing an increase in concentrations of some compounds for some cases.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Size-segregated particle characterisation; Cloud water; Major ions; OCEC; Metals

---

*Corresponding author. Tel.: +49 341 235 2535; fax: +49 341 235 2325.
E-mail address: erika@tropos.de (E. Brüggemann).

1. Introduction

The chemical and physical characterisation of trace gases and aerosol before, during, and after a cloud passage is important to understand the cloud chemistry and the interaction between gases, aerosol, and cloud droplets. Most of such characterisation studies in the past focused mainly on inorganic components and only a small number of organic species (e.g. MSA, formic and acetic acid) were included. On the other hand, the knowledge of organic components is necessary for the development of better physico-chemical multiphase models.

During the last decades, a number of cloud investigations have been carried out to characterise mainly cloud water. In Europe, investigations of cloud water were carried out for different parameters and processes, e.g. in Germany—Brocken (Plessow et al., 2001; Acker et al., 2002), Switzerland—Jungfraujoch (Oberholzer et al., 1992; Baltensperger et al., 1998), Austria—Sonnblick (Kasper et al., 1998, Hitzenberger et al., 2000), England—Holme Moss (Dore et al., 2001), France—Puy de Dome (Voisin and Legrand, 2000).

The FEBUKO research cluster (Field investigations of budgets and conversions of particle phase organics in tropospheric cloud processes) within the German Atmospheric Research Programme AFO2000 (www.afo-2000.de) intends to improve the understanding of tropospheric multiphase processes and especially the interaction of aerosols and clouds with an emphasis on organic particle constituents. Therefore, a hill cap cloud experiment was carried out in order to investigate the changes of major particulate inorganic components and a wide spectrum of organic species.

2. Experimental setup

A set of meteorological parameters, trace gas components, cloud parameters and particle characteristics were determined at the two valley measurement sites (upwind site U, 605 m asl and downwind site D, 732 m asl) and at the summit site S, (937 m asl). The following meteorological conditions had to be met for the measurements: wind direction 210–250°, wind speed 5–12 m s^{-1}, LWC > 0.1 g m^{-3}, and no precipitation. Trace gas concentrations (SO_2, NO_x, O_3) are available for E I (event I), E II (event II), and E III (event III), CO concentrations are only available for E III (see Table I, Electronic Supplemental Material, ESM). An overview of the FEBUKO experimental design is given by Herrmann et al. (2005).

The collection of particles for chemical characterisation using filter samplers and impactors was carried out at the valley stations (U and D), where an equal set of particle samplers was used (BERNER impactor—BI) (50% cut-offs: stage 1: 0.05–0.14, stage 2: 0.14–0.42, stage 3: 0.42–1.2, stage 4: 1.2–3.5, stage 5: 3.5–10 μm aerodynamic diameter) and High Volume Andersen filter sampler—HVA (PM_{10}). BERNER impactor samples were collected at 60% RH using a relative humidity conditioner. Only at site U, the Steamjet technique (Acker et al., 2003) with online ion chromatography—StJ was used. A Twin Differential Mobility Particle Sizer (T-DMPS) within the particle size range of 3–900 nm was used to measure the number size distribution (NSD) of particles at U and D sites (Birmili et al., 1999).

On top of a 20 m research tower different active cloud water collectors operated at the summit site: four single stage samplers CASCC2_4 (Caltech Active Strand Cloud Water Collector in 2001 and 2002, see Demoz et al., 1996) from the Colorado State University (addressed CW-IfT), a Single Stage slit jet Impactor (SSI, Winkler, 1992) from the Brandenburgisch-Technische Universität Cottbus (in 2001 and 2002), (CW-BTU), and a size fractionating sampler sf-CASCC (Demoz et al., 1996) from the Colorado State University, (called CW-CSU), used only in 2002 for the determination of ionic components, water-soluble carbon and metals. A detailed description of collectors is given in Wieprecht et al. (2005). The interstitial aerosol (I) and the cloud droplet residues (R) were collected by means of a counterflow virtual impactor (CVI) and an inlet for interstitial particles (INT) as well (Schwarzenböck et al., 2000).

Particle mass concentrations were gravimetrically determined using a Mettler-Toledo micro-balance UMT2 after 48 h conditioning of the samples at 20 °C and 50% RH. The ionic components Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+} of particles were analysed using ion chromatography (Metrohm), Cl^-, NO_3^-, SO_4^{2-} using capillary electrophoresis (Spectrophoresis), (Neusüß et al., 2000a, b) as well as from the StJ samples with online analysis using IC (Dionex) (Brüggemann and Rolle, 1998; Acker et al., 2003). The particulate organic carbon (OC) and elemental carbon (EC) concentration were determined by a two step thermographic method (C-mat 5500, Ströhlein) (Plewka et al., 2004). From HVA samples the metals (Fe, Cu, Mn, Zn) were analysed by atomic absorption spectrometry (Perkin Elmer) (Chemnitzer, 2002; Rüd, 2003). The components in cloud water were determined using the same analytical methods as the particle components. For the water-soluble OC a Shimadzu TOC-V CPH analyser was used. Total organic carbon (TOC) was separated in dissolved organic carbon (DOC) and particulate organic carbon (POC) by filtration of the liquid samples (0.45 μm pore size).

The successful participation in international ring analysis by WMO-EPA each year since 1991 (http://marble.asrc.cestm.albany.edu/qasac/) ensures the high quality of the ion analysis. The International Round

Robin Test Carbon Shoot of Stage I (Schmid et al., 2001) and Stage II (Puxbaum, TU Vienna, unpublished) served as quality assurance for the used OCEC method.

Analytical uncertainties were determined in different concentration ranges by replicate analysis of ionic and carbonaceous components. The repeatability (95% confidence level) was found to be about 15% for nitrate, sulphate, and ammonium and about 20% for OCEC for stages 1 and 5 and about 5% and 10% for stages 2–4.

3. Results and discussion

In both campaigns a total set of 14 events was identified for intensive measurements (Herrmann et al., 2005). Among these 14 events connected flow conditions were fulfilled during three events (E)—E I: 26 October 22:00–27 October 13:00 UTC (2001), E II: Part 1: 06 October 10:30–14:15 UTC (2001), Part 2: 07 October 13:15–15:15 UTC (2001), Part 3: 07 October 18:00–08 October 11:15 UTC (2001), and E III: 16 October 21:00–17 October 4:10 (2002). A connected flow condition was demonstrated by a profound meteorological analysis including all information available (e.g. data of synoptic and local scale meteorological conditions, satellite data, trace gas concentrations) (Tilgner et al., 2005a; Heinold et al., 2005). These periods were selected for further discussion. Additionally, tracer experiments before and during the campaigns were carried out to investigate the real flow conditions.

In all events a particle mass concentration loss from site U to D was observed (Fig. 4). The losses (in total about 30% to 40%) were due to physical sink processes during transport or sampling losses. The estimation of entrainment for the three events discussed in Herrmann et al. (2005) reveals that no significant entrainment occurred. The particle sampling techniques may cause errors, e.g. flow (bounce-off in impactor, volatilisation and/or adsorption in filter) and/or temperature and pressure effects (change of gas to particle equilibrium) (Gnauk et al., 2005). BI particle sampling was performed under controlled relative humidity (60% RH) in order to maintain size cuts independent of the changing ambient RH and to minimise bounce-off effects (Neusüß et al., 2000a). These effects were investigated, e.g. in the INTERCOMP 2000 campaign (e.g. Müller et al., 2004; Hitzenberger et al., 2004).

Physical loss processes influence the particulate trace components and are able to mask results of chemical cloud processing. The use of percentage of the size range particle mass seems to be the better way to find out cloud effects avoiding the influence of physical losses. Therefore, the mass fraction values are included in the following discussion.

3.1. Cloud water

Cloud water samples were taken in 1 and 2 h intervals at summit site by bulk sampler (CW-IfT and CW-BTU). In Fig. 1 the cloud water time series of liquid water content (LWC, measured by a PVM100, see Wieprecht et al., 2005), nitrate, sulphate, ammonium (CW-BTU sampler), as well as DOC, POC, and pH value (CW-IfT sampler) are shown. All values for the cloud water components (including chloride, sodium, potassium, magnesium, calcium, and metals) are listed in Table III and pH and LWC values in Table IV (ESM).

The variability and the level of the LWC in E I was higher than in E II and III. Measurements of LWC in droplets of 4–12 and 12–32 μm diameters as well as the cloud base height (Wieprecht et al., 2005) showed that the sampling site S was located alternating in cloud and at cloud base during E I. The LWC in E I decreased simultaneously with the increase of cloud base height. The change of cloud base height was possibly caused by mixing of another air mass (frontal process) between 4 and 6 UTC (Tilgner et al., 2005a).

The pH values range between 4.0 and 5.0 (E I), 4.3 and 5.1 (E II), as well as 4.1 and 4.6 (E III). The LWC was found to be on average 334 ± 77, 230 ± 50, and 196 ± 19 mg m^{-3} for E I, II, and III, respectively. In E I the initial increase of LWC was associated with a decrease of acidity from 50 to 10 μeq l^{-1} of [H$^+$], corresponding to pH 4.3 and 5.0, respectively. This was followed by an increase up to 100 μeq l^{-1} (pH 4.0) and a drop of the LWC by about 30%. Simultaneously, a decrease of the nitrate concentration by about 50% was observed.

Cloud water TOC was separated to DOC and POC by filtration with syringe filters of 0.45 μm pore size. TOC in cloud water was found to be 80–95% of DOC. The time resolved cloud water samples show higher variations (TOC = 2–3.7 μg m^{-3}) during E I compared to E II (1.3–1.7 μg m^{-3}) and E III (1–1.4 μg m^{-3}). In E I an increase of DOC by nearly 100% was observed during the most acidic period of cloud water (pH about 4). It is difficult to compare the carbonaceous concentrations with other hill cap cloud experiments performed in Europe during the last 15 years (Kleiner Feldberg Cloud Experiment 1990; Great Dun Fell Experiment 1993 and 1995; ACE-2 HILLCLOUD Experiment 1997) because the past studies focussed on the ionic composition and OCEC data are not available. Other cloud investigations addressing carbonaceous material indicate similar levels to this study: e.g. 1.4–3.3 μg m^{-3} OC and 0.04–0.36 μg m^{-3} EC in the liquid phase were found at the Mount Brocken (Harz, Germany) in 1998 (Acker et al., 2002); 0.31–3.65 μg ml^{-1} Black Carbon (BC) in 1996 and 0.55–3.0 μg ml^{-1} BC in 1997 were detected at the Mount Sonnblick (Alps, Austria) (Hitzenberger
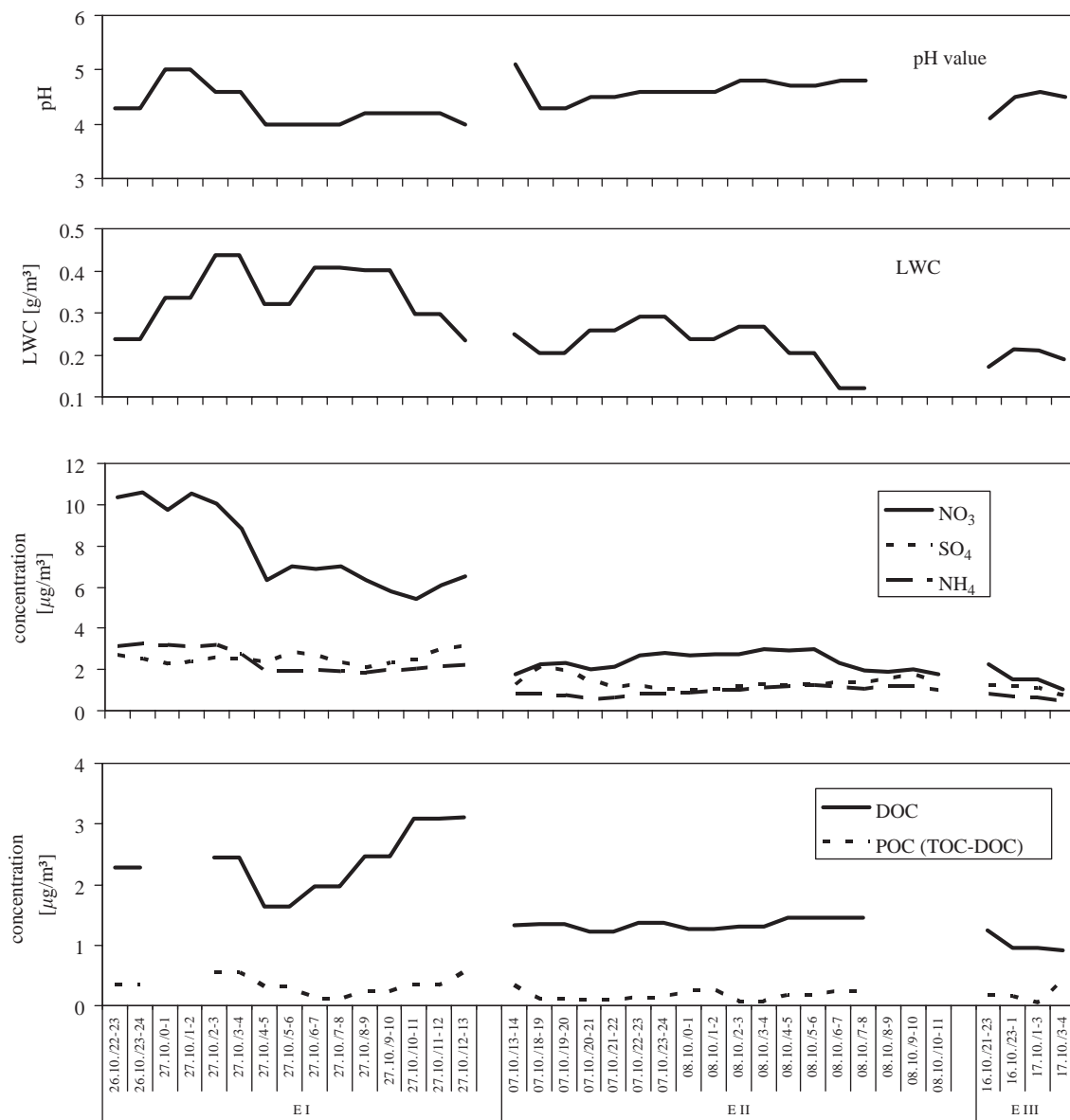
Fig. 1. Time series of pH value, LWC, nitrate, sulphate, ammonium, and DOC in cloud water for events I, II, and III at S site (E I: Part 1: interval not considered due to data gap).

et al., 2000). Polluted samples like Po Valley fog water showed WSOC air concentrations of $3.0–14.3\,\mu g\,m^{-3}$ (Facchini et al., 1999).

The mean concentrations of water-soluble metals were of the following order Zn (36, 26, $56\,ng\,m^{-3}$) > Fe (17, 18, $10\,ng\,m^{-3}$) > Cu (3, 2, $1\,ng\,m^{-3}$) ≈ Mn (2, 1, $2\,ng\,m^{-3}$) for all three events. In E II and III no significant changes of metal concentrations were found besides analytical variations. In contrast, the Fe concentration in E I was found to be increased probably due to the observed decrease of the pH value in cloud water. It is known that the solubility of different Fe species increases with

decreasing pH in the range of 5–4 (Finnlayson-Pitts and Pitts Jr., 2000).

Little information is available on CW trace element concentrations. In a study at Mt. Brocken (Germany) a number of trace metals was investigated (Plessow et al., 2001, and references therein). The ranges of total metal contents were found to be 21–3950 (Fe), 0.8–60 (Mn), 0.42–60.6 (Cu), and 2.5–421 (Zn) $ng\,m^{-3}$. In the Great Dun Fell Experiment (Sedlak et al., 1997) average total Fe and Cu concentrations in CW were 27 and $0.24\,ng\,m^{-3}$. The CW concentrations determined in this study are found to be in the same range.

3.2. Comparison of cloud water with upwind and downwind site particulate chemical composition

The ionic components and OCEC of droplet residues (R) and interstitial particles (I) in the cloud were determined. Additionally, in E III (campaign 2002) a two stage sampler (CW-CSU) was used and the results are presented as volume-weighted total values. Particles were measured as size-segregated (BI) and PM_{10} (HVA) at the upwind (Gnauk et al., 2005) and downwind site. Additionally, at the site U the Steamjet technique was used for anion determination (avoiding sampling losses of volatile components).

In Fig. 2 results are shown for average concentrations of nitrate, sulphate, and ammonium (about 90% of the total ionic concentration), OCEC, and metals. All impactor stages were summed up forming PM_{10} in order to compare this concentration with those of the HVA, StJ, cloud water components, R and I of clouds. All measured particulate concentrations of the upwind and downwind sites are listed in Tables II and IV (ESM).

Component concentrations in cloud water sampled by different collectors roughly agree for all events. Time series from cloud water components are given in Table III (ESM). Further comparisons between the different cloud water samplers are discussed in Wieprecht et al. (2005).

The sulphate concentration of R corresponds to the concentration of other CW collectors. However, nitrate and ammonium concentrations are smaller. By evaporation of the droplet water the R were released and thereby a fraction of volatile components can be lost. In all three events only 10% of CW nitrate and 30–50% of CW ammonium were found in R. In E I and II a similar concentration of OC for both in CW and R were found, but in E III a considerably higher content (about 80% more) in R, probably due to contamination, was observed. The ionic components were dissolved in CW droplets (more than 90% in E I and II). In E III a considerable part of ionic components was found in the interstitial phase: 40%, 30%, and 30% for nitrate, sulphate, and ammonium, respectively. This means that in comparison to e.g. E I a larger part of small particles was present as non-activated interstitial particles. This is consistent with the finding of the dry particle size distribution inside cloud which showed a shift of a mean diameter to smaller particles (see Mertes et al., 2005). The comparison of OCEC contents in R and I particles shows that in all events the OC/EC ratio was higher in R (R: 3.12, 2.40, 8.14; I: 1.54, 1.72, 1.91 for E I, II, and III, respectively). This means that particles acting as cloud condensation nuclei (CCN) contain more OC and non-activated particles contain more EC in agreement with Gieray et al., 1997.

The CW chemical composition depends on the particulate composition of the activating CCN from the upwind site, the uptake of gaseous components and, finally, components produced by in-cloud reactions. In Table 1 the component fractions of the U and D site particulate samples are related to cloud water concentrations. For the non-volatile components, sulphate (all events) and EC (E I and E III) show approximately the same concentrations in particles at the upwind site as in clouds. The particulate EC deviation in E II is caused possibly by contamination. For the volatile components, nitrate, ammonium, and OC show different behaviour. The particulate nitrate concentration determined by Steamjet technique added with the gas phase concentration of HONO and HNO_3 reaches the nitrate concentration of CW, by the HVA sampler about 60–75%, and by the BI only about 25–40%. Ammonium from the HVA samples was in good agreement with CW, but only 50–90% of CW concentrations were found from BI samples. The particulate OC amounted to 40–90% of CW-TOC.

The concentrations of component determined at the downwind site were found to be lower than that of the upwind site for BI. This also concerns non-volatile components like sulphate and therefore additional physical sink processes can be assumed. The HVA samples from U and D sites show the same concentrations as from CW except nitrate which exhibits smaller values. The HVA collects under 'natural' conditions and can adsorb gaseous components in contrast to the BI which is conditioned to 60% RH producing additional losses by heating of the sample air stream. The expected overestimation of sulphate by HVA in comparison to BI can be seen in event III (difference about $0.3\,\mu g\,m^{-3}$) at the U site, whereas in E I and E II this effect could not be observed. No explanation can be given for these differences at this moment. The measured SO_2 concentrations of about 0.5 ppb are sufficient to produce the excess sulphate of HVA during sampling at the D site of 0.37, 0.70, and $0.35\,\mu g\,m^{-3}$ in E I, II, III, respectively.

Despite all drawbacks mentioned impactors are the only instruments for size-segregated particle sampling and analysis of components especially in the size range $D_p < 1\,\mu m$. Losses caused by sampling technique (BI) are the same at U and D sites and were corrected accordingly using the data from other particle samplers for model initialisation.

Particulate metals can be dissolved in cloud droplets. Metals solved in CW can catalyse chemical reactions and contribute to the radical formation and interconversion in atmospheric liquid phase systems (see Herrmann et al., 2005). The water-soluble metals (Fe, Cu, Mn, and Zn) were determined in particles (PM_{10} by HVA filter collector) before and after the cloud passage and in CW samples (CW-IfT).

The particle phase concentrations of Fe, Cu, and Mn were rather similar in the all three events. Zn showed the highest concentrations especially in E III. The particle
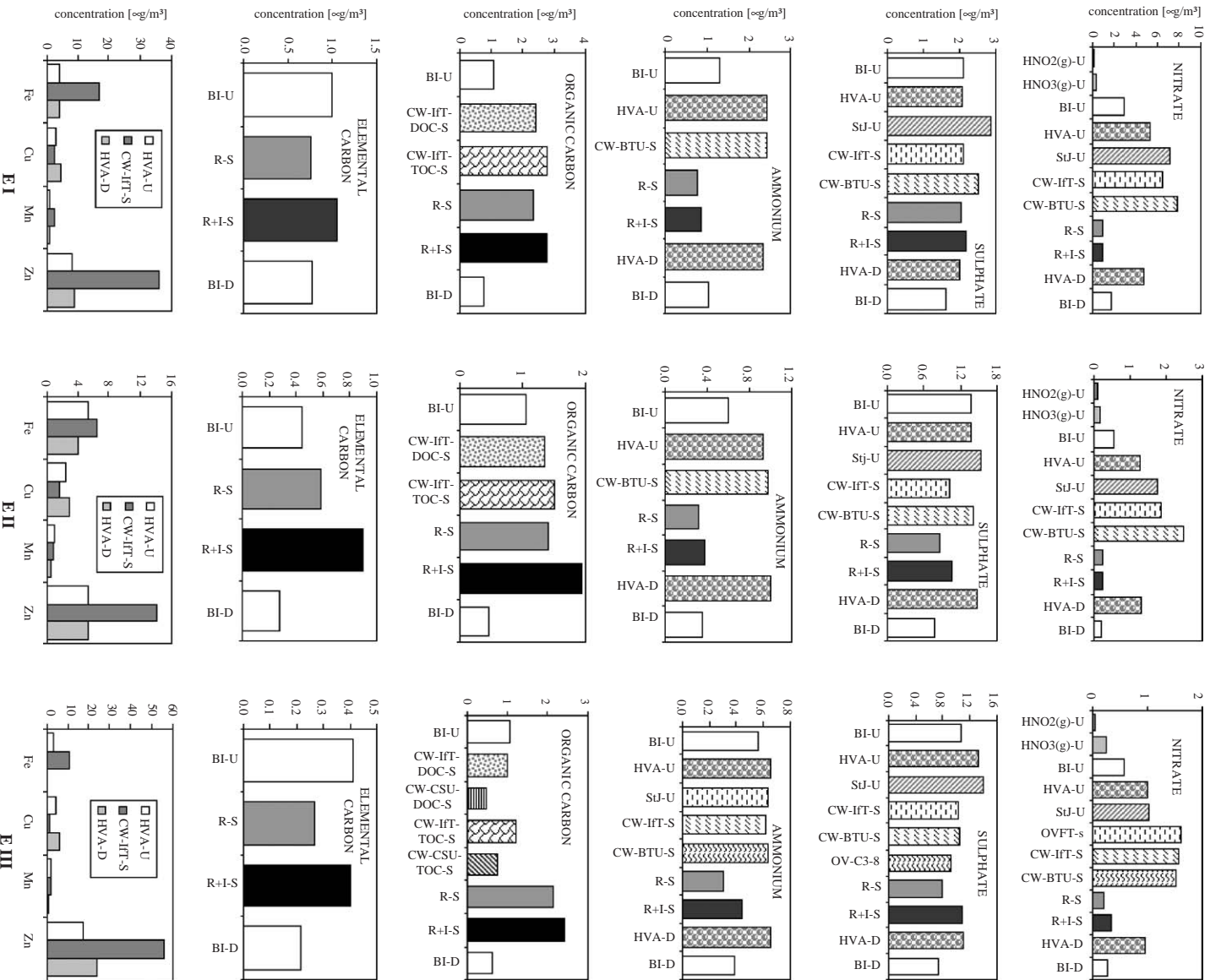
Fig. 2. Comparison of total (PM$_{10}$) particulate (at U and D sites) with cloud water components (at S site), TOC = DOC + POC (BI: BERNER impactor, HVA: high volume Andersen filter sampler, CW-IfT: CASCC2_4, CW-BTU: Single Stage slit jet Impactor, CW-CSU: sf-CASCC, R: residual particles, I: interstitial particles). Note that the scales are different.

Table 1
Components fractions of upwind and downwind site particulate samples referred to cloud water concentrations

Event	Component	Upwind			Summit	Downwind	
		BI particle (%)	HVA particle (%)	StJ particle (%)	cloud water (%)	BI particle (%)	HVA particle (%)
E I	SO_4^{2-}	≈	≈	≈	100	70	≈
	NO_3^-	40	75	≈	100	25	65
	NH_4^+	50	≈		100	40	≈
	OC/TOC	40			100	30	
	EC	≈			100*	70	
E II	SO_4^{2-}	≈	≈	≈	100	60	≈
	NO_3^-	25	60	≈	100	10	60
	NH_4^+	60	≈		100	40	≈
	OC/TOC	70			100	30	
	EC	50			100*	30	
E III	SO_4^{2-}	≈	≈	≈	100	70	≈
	NO_3^-	40	60	≈	100	20	60
	NH_4^+	90	≈		100	60	≈
	OC/TOC	90			100	50	
	EC	100			100*	50	

≈: Roughly equal amounts; *: sum of residual and interstitial particulate EC; OC/TOC: particulate OC, cloud water TOC.

concentrations for Fe, Cu, Mn, and Zn were between 3 and 5, 2.5 and 6, 0.5 and 1.5, and 5 and $24\,\mathrm{ng\,m^{-3}}$, respectively. The comparison between summit (cloud water) and upwind sites (particle phase) results in different findings: At the U site the water-soluble particle phase concentrations of Fe were about 20%, 80%, and 30% of the concentrations in cloud water, about 85%, 60%, and 20% for Cu, and about 20%, 40%, and 30% for Zn for E I, E II, and E II, respectively. Mn concentration in particles for EI shows about 30% of CW concentration but the concentrations are similar in E II and E III. The dissolution mechanisms of the metals from particles often include complexation with organic ligands. For iron dissolution it is well known that complexation with organics (mainly oxalate) is responsible for the concentration of dissolved iron in atmospheric droplets (see, e.g. Pehkonen et al., 1993; Faust and Zepp, 1993). Also the pH-value and the photo-chemistry contribute to the solubility of the metals (e.g. Deutsch et al., 2001).

The comparison of the water-soluble metal concentration in particles before and after the cloud passage results in the following: an increase in Cu concentration (about 30% on average) was observed at the U site in all events. This could be caused by automobile traffic (Sedlak et al., 1997) from a road near the D site. The concentrations of Fe and Mn in E I remained the same, but their concentrations dropped by 30% (E I) and 100% (E II) for Fe and 20% (E I) and 30% (E II) for Mn; the Zn concentration were stable in E I and E II, and 25% increase was observed in E III after the cloud.

3.3. Changes in particle size distribution and composition

3.3.1. Particle size distribution

NSD was measured continuously in the size range from 3 to 900 nm at upwind and downwind sites. Possible aerosol transformation processes can be found using this NSD with a time resolution of 15 min. Furthermore, the NSD observed at the U site can be used as input parameters for models determining cloud formation and processing. The NSD can be also used to calculate the volume size distribution (VSD) assuming spherical particles. The VSD can provide information if there was an increase in aerosol particle volume or mass during a certain period of time.

To make the NSDs comparable at sites up- and downwind of the orographic cloud, the NSDs taken at the U site are normalised to the peak maximum in the Aitken mode of the NSDs measured at the D site. This procedure can be done if the Aitken mode is not affected by passing the hill. As the Aitken mode is neither influenced by cloud activation nor by diffusion scavenging in the cloud, this assumption is valid. Since the differences between the two size distributions were within 10% (less than the uncertainty range of both instruments together), the corrections made for the NSDs of the D site were small and reasonable. In terms of the VSDs, these normalisations are important to discuss chemical cloud processing with a subsequent increase in aerosol mass.

During event I (Fig. 3), the average NSD at the D site decreased in accumulation mode compared to the U site.
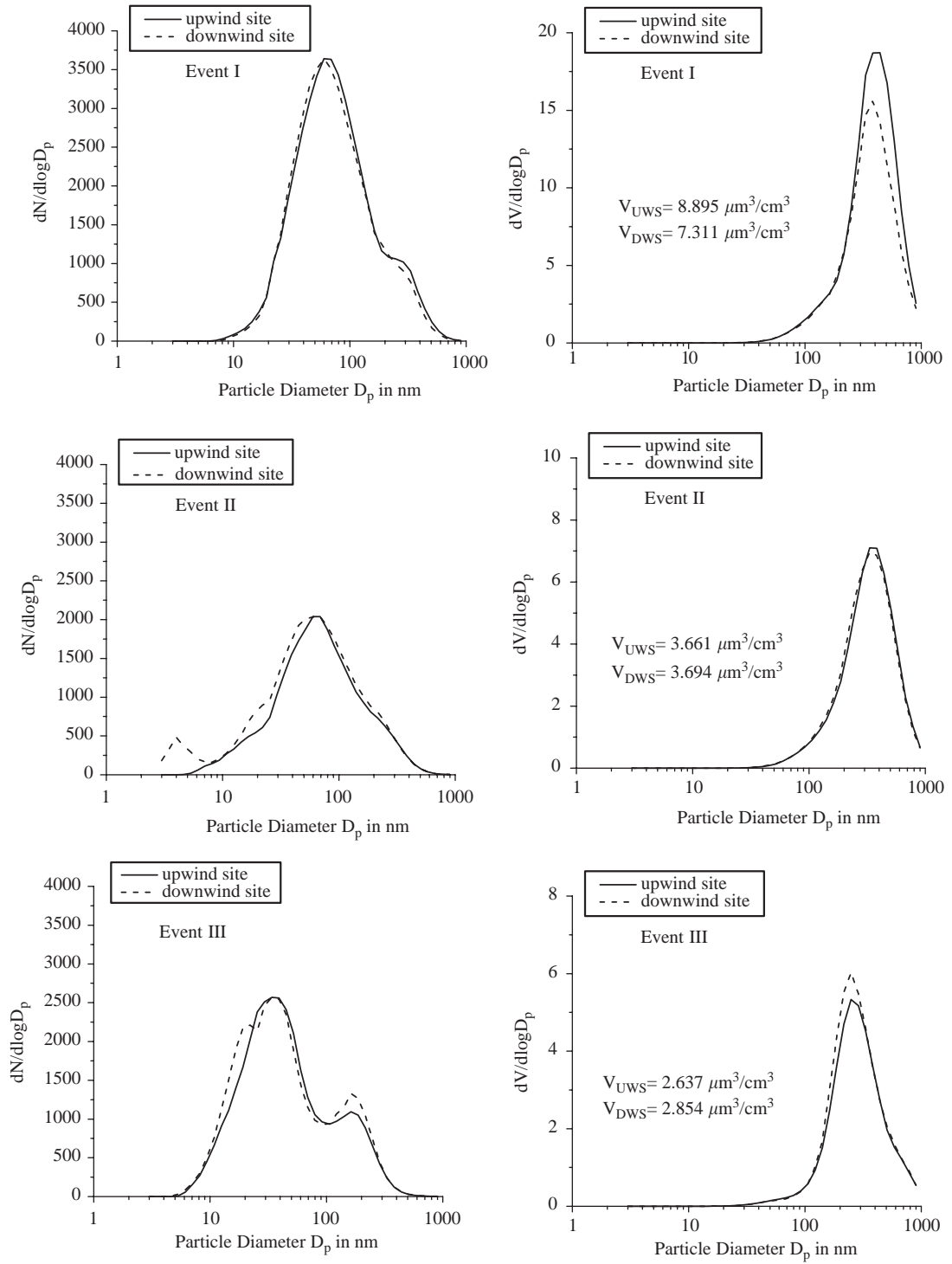
Fig. 3. Number and volume size distribution for events I, II, and III at U and D sites. Note that the scales are different.

Therefore, the VSD at the D site shows a significant decrease by approximately 15% in the accumulation mode range. The loss hints to deposition of droplets and particles during the transport to the D site.

The average NSD at the D site during event II (Fig. 3) shows some deviation at the smaller particle sizes. The nucleation mode particles below 10 nm are within the uncertainty range of the Poisson statistic, while the deviation around 20 nm is due to a poor overlap of the both mobility size spectrometers. The VSD (Fig. 3), however, is almost identical indicating no significant increase in aerosol mass.

During event III (Fig. 3), clear indications of an increase in aerosol volume due to cloud processing are visible from the NSDs and VSDs. The accumulation mode NSDs and VSDs are clearly lifted to higher concentrations. Different chemical components in $PM_{0.05-0.14}$ range show a clear increase in fraction, but observed increases in higher size ranges were found to be $< 50\%$. In contrast to former hill cap cloud experiments, a significant change in NSDs and VSDs can be noticed here for the average distributions for the whole experiment durations. Clearly, a volume increase can be noticed which is ascribed to chemical mass production given in Tilgner et al. (2005b). Further details of the increase in aerosol volume or mass are outlined in Mertes et al. (2005). The deviation in the NSD around 20 nm is again due to a poor overlap of the mobility spectrometers at the D site.

3.3.2. Size-segregated chemical particle composition

In order to find changes in the chemical particulate composition caused by possible cloud processing the different size ranges were compared between U and D sites. To avoid the physical loss processes from U to D site the fraction of mass at respective impactor stage was also considered.

The size-segregated concentrations and the fraction of mass, nitrate, sulphate, ammonium, OC, and EC of particles are shown in Fig. 4. All data are listed in Tables II and V (ESM) for both the U and D sites.

The comparison shows that the mass concentration of particles for all size classes is always smaller at the D than the U site. For E I the decreases in mass concentrations in the five size classes amount to between 25% and 50% (from stages 2 to 5) and 75% (stage 1), for E II from 20% to 35%, and for E III about 45% (from stages 2 to 5) and 60% (stage 1). Considering the fraction of stage mass to the total mass concentration no significant difference between U and D sites can be observed except for the smallest particles of E I and III.

The concentration of the particle components is generally decreased at the D site. Nevertheless, in the smallest size range ($PM_{0.05-0.14}$) with nanogramme concentrations increases of sulphate and ammonium in E I and E III and nitrate in E III were observed. This

represents about 20% (E I) and 70% (E III) for sulphate, about 17% (E I) and 150% (E III) for ammonium. The remaining ionic components rose about 150% in E I. It should be noted that an increase below 20% is in the analytical error range. In the Great Dun Fell Experiment (1993), a sulphate production by cloud processing on the particles in the range from 0.2 to 1.1 µm and a simultaneous ammonium increase were observed (Laj et al., 1997). Ammonium increase could be a consequence of the neutralisation of the formed sulphuric and/or nitric acid by gaseous ammonia.

Increases in sulphate, nitrate, and ammonium concentrations found in this experiment were in part found from a result of SPACCIM model calculations (Spectral Aerosol Cloud Chemistry Interaction Model—Tilgner et al., 2005b). Coincidence of increasing trends is marked by an asterisk (*). Differences between experiment and modelling are discussed in Tilgner et al. (2005 b).

Considering the fraction of stage mass (avoiding the physical loss processes) the same cases of increases were found in the $PM_{0.05-0.14}$ (see Fig. 4). Sulphate shows 5-fold (E I* and E III*), ammonium 4-fold (E I) and 6-fold (E III*), and nitrate 6-fold (E III*) increase. More increases in stage mass fraction were observed: about 3-fold in stage 1* (E I) and 1.5- and 2-fold in stage 1* and 5 for nitrate, in E II, respectively, to about 1.5-, 2-, and 1.5-fold in stage 4, 5, and 5* for sulphate in E I, E II, and E III, respectively, to about 1.5-fold in stage 5* for ammonium in E II. Minor changes (< 1.5-fold) were not considered and attributed to analytical variation.

In E I a significant increase of OC concentration by 20% in stage 2 was observed, the OC fraction of particle stage mass rose by 1.5-fold. Furthermore, an increase of OC in stage 1 by about 3-fold (E I) and 1.5-fold (E III) as well as for EC to about 2-fold (E I and E III) was observed. The increase of OC could be attributed to secondary organic aerosol (SOA) formation from organic precursor substances processed in cloud droplets. SOA formation was found to be stronger in clear sky episodes than in cloudy events, but Strader et al. (1999) also found that under conditions of reduced photochemical activity a third to a half of the maximum SOA quantities was produced. On the other hand, the simultaneous increase of OC and EC in stage 1 in E I and E III hints at a more local contamination.

The fraction of the stage mass is related to the weighed mass. Although the standard deviation of weighing was about 1%, possible random error could have influenced the accuracy especially within the range around 10 µg mass mainly appearing in stage 1.

4. Summary

Size-segregated particle and cloud water measurements were performed during a hill cap cloud experiment in
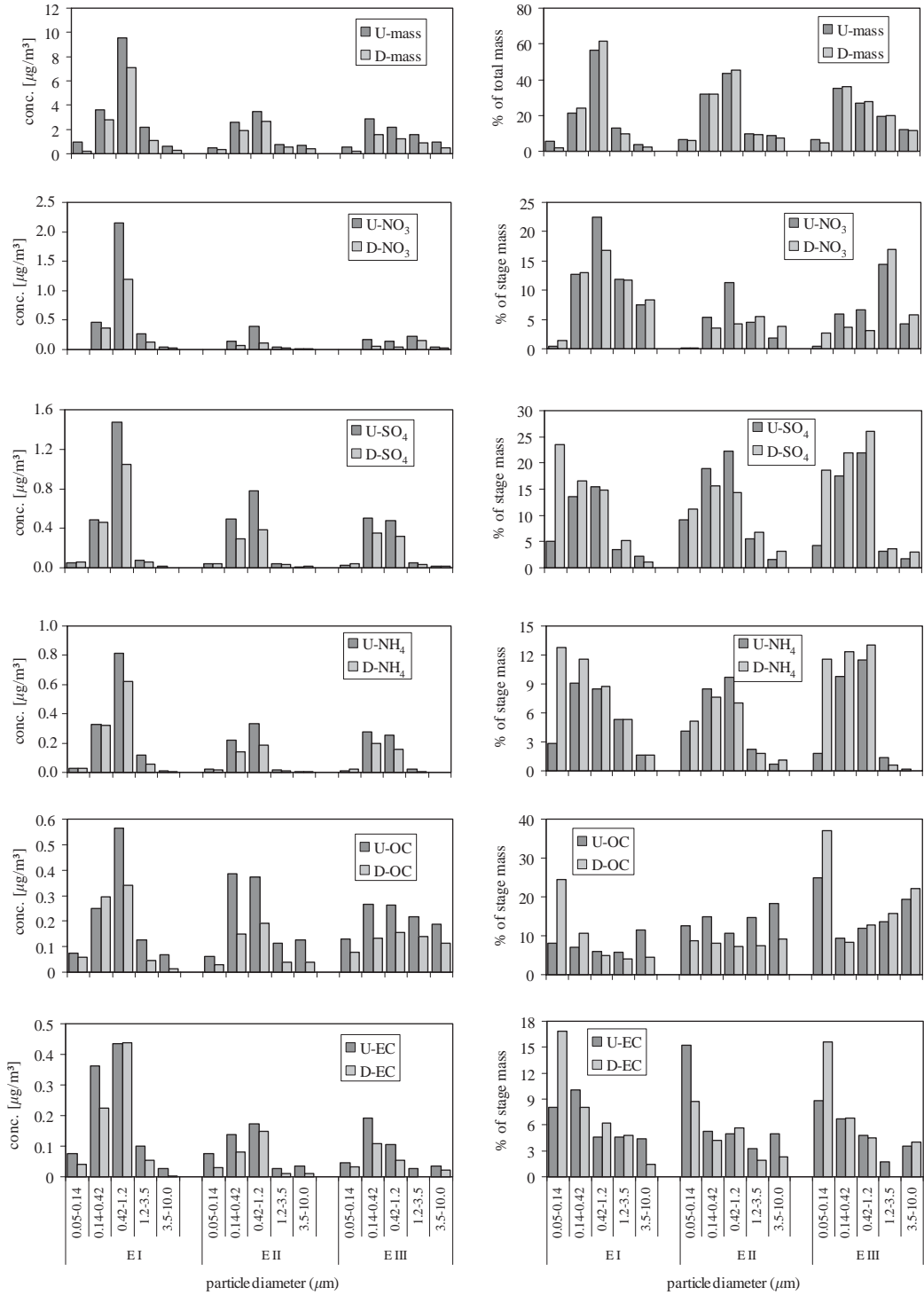
Fig. 4. Size-segregated mass, nitrate, sulphate, ammonium, OC, and EC concentration and part of total (for mass) and stage mass concentration for events I, II, and III at U and D sites.

autumn 2001 and 2002. Cloud and particulate components were measured by different sampling techniques. Additionally, trace gas mixing ratios and meteorological parameters were measured. Three out of 14 events fulfilling the connected flow between the sites were discussed.

Particle mass concentration losses were observed from upwind to downwind sites (in total about 30–40%) caused by physical sink processes. In addition to the changes in concentration, the changes of mass parts of the components were considered.

During event I LWC, pH, and nitrate decreases and an OC increase in cloud water were found. During events II and III only minor variations were observed.

The concentrations of ionic components and TOC sampled by different collectors roughly agree for the three events. Non-volatile species (in E I, II, III for sulphate and in E I, III for EC) were found to be in agreement in cloud water and particulate component concentration at upwind site, whereas volatile components (nitrate, ammonium, and OC) in general were lower at the U site due to losses by some of the collecting techniques applied. Losses found between cloud water and particle concentration at the D site are additionally caused by deposition and dilution during transport. For Fe and Zn higher concentrations in cloud water (more acidic) were measured than in aqueous particle extracts. Particulate Cu was higher after the cloud passage probably due to local traffic emissions from the road nearby.

Concentration increases occur only in the smallest range (0.05–0.14 μm) representing for sulphate about 20% (E I) and 70% (E III), ammonium about 17% (E I) and 150% (E III as well as for OC in the 0.14–0.42 μm range about 20% (E I). Considering the fraction of stage mass the same components were increased and some others too. In several cases consistency between experimental and modelled results could be found. The observed mass increases are possibly related to acid formation (sulphuric and nitric acid) and neutralisation (ammonia) processes as well as SOA formation.

Acknowledgements

Appendix A. Supplementary Materials

The online version of this article contains additional supplementary data. Please visit doi:10.1016/j.atmosenv.2005.02.013.

References

Acker, K., Mertes, S., Möller, D., Wieprecht, W., Auel, R., Kalaß, D., 2002. Case study of cloud physical and chemical processes in low clouds at Mt. Brocken. Atmospheric Research 64, 41–51.

Acker, K., Wieprecht, W., Möller, D., 2003. Distribution of reactive nitrogen compounds between atmospheric gas and aerosol phase. In: ten Brink, H., Baltensberger, U. (Eds.), Composition and Size Evolution of the Secondary Aerosol. EUROTRAC-2 subproject AEROSOL Final Report, GSF Munich, pp. 197–203.

Baltensperger, U., Schwikowski, M., Jost, D.T., Nyeki, S., Gäggeler, H.W., Poulida, O., 1998. Scavenging of atmospheric constituents in mixed phase clouds at the high-alpine site Jungfraujoch, Part I: basic concept and aerosol scavenging by clouds. Atmospheric Environment 32, 3975–3983.

Birmili, W., Stratmann, F., Wiedensohler, A., 1999. Design of a DMA-based size spectrometer for a large particle size range and stable operation. Journal of Aerosol Science 30, 549–553.

Brüggemann, E., Rolle, W., 1998. Changes of some components of precipitation in East Germany after the unification. Water, Air, and Soil Pollution 107, 1–23.

Chemnitzer, R., 2002. Bestimmung von Metallen in troposphärischen Partikeln und Wolkentröpfchen mittels Atom-Absorptionsspektrometrie. Diplomarbeit Technische Universität Bergakademie Freiberg.

Demoz, B.B., Collett Jr., J.L., Daube Jr., B.C., 1996. On the caltech active strand cloudwater collectors. Atmospheric Research 41, 47–62.

Deutsch, F., Hoffmann, P., Ortner, H.M., 2001. Field experimental investigations on the Fe(II)- and Fe(III) content in cloud water samples. Journal of Atmospheric Chemistry 40, 87–105.

Dore, A.J., Choularton, T.W., Inglis, D.W.F., 2001. Monitoring studies of precipitation and cap cloud chemistry at Holme Moss in the Southern Pennines. Water, Air, and Soil Pollution: Focus 1, 381–390.

Electronic supplemental material: ⟨http://www.projects.tropos.de:8088/afo2000g3/FEBUKO_dateien/febuko.html⟩.

Facchini, M.C., Fuzzi, S., Zappoli, S., Andracchio, A., Gelencser, A., Kiss, G., Krivacsy, Z., Meszaros, E., Hansson, H.-C., Alsberg, T., Zebühr, Y., 1999. Partitioning of the organic aerosol component between fog droplets and interstitial air. Journal of Geophysical Research 104, 26,821–26,832.

Faust, B.C., Zepp, R.G., 1993. Photochemistry of aqueous iron(III)-polycarboxylate complexes: roles in the chemistry of atmospheric and surface water. Environmental Science and Technology 27, 2517–2522.

Finnlayson- Pitts, B.J., Pitts Jr., J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, San Diego, USA Chapter 8, p. 310.

Gieray, R., Wieser, P., Engelhardt, T., Swietlicki, E., Hansson, H.-C., Mentes, B., Orsini, D., Martinsson, B., Svenningsson, B., Noone, K.J., Heintzenberg, J., 1997. Phase partitioning of aerosol constituents in cloud based on single-particle and bulk analysis. Atmospheric Environment 31, 2491–2502.

Gnauk, T., Brüggemann, E., Müller, K., Chemnitzer, R., Rüd, C., Galgon, D., Nowak, A., Wiedensohler, A., Acker, K., Auel, R., Wieprecht, W., Möller, D., Jaeschke, W., Herrmann, H., 2005. Aerosol characterisation at the FEBUKO upwind station Goldlauter (I): Particle mass, main ionic components, OC/EC, and mass closure. Atmospheric Environment (this issue).

Heinold, B., Tilgner, A., Jaeschke, W., Haunold, W., Knoth, O., Wolke, R., Herrmann, H., 2005. Meteorological characterisation of the FEBUKO hill cap cloud experiments, Part II: Tracer experiments and flow characterisation with nested non-hydrostatic atmospheric models. Atmospheric Environment (this issue).

Herrmann, H., Wolke, R., Müller, K., Brüggemann, E., Gnauk, T., Barzaghi, P., Mertes, S., Lehmann, K., Massling, A., Birmili, W.A., Wiedensohler, A., Wieprecht, W., Acker, K., Jaeschke, W., Kramberger, H., Svrcina, B., Bächmann, K., Collett Jr., J.L., Galgon, D., Schwirn, K., Nowak, A., vanPinxteren, A., Plewka, A., Chemnitzer, R., Rüd, C., Hofmann, D., Tilgner, A., Diehl, K., Heinold, B., Hinneburg, D., Knoth, O., Sehili, A.M., Simmel, M., Wurzler, S., Mauersberger, G., Majdik, Z., Müller, F., 2005. FEBUKO and MODMEP: Field measurements and modelling of aerosol and cloud multiphase processes. Atmospheric Environment (this issue).

Hitzenberger, R., Berner, A., Kromp, R., Kasper-Giebl, A., Limbeck, A., Tscherwnka, W., Puxbaum, H., 2000. Black carbon and other species at a high-elevation European site (Mount Sonnblick, 3106 m, Austria): concentrations and scavenging efficiencies. Journal of Geophysical Research 105, 637–645.

Hitzenberger, R., Berner, A., Galambos, Z., Maenhaut, W., Cafmeyer, J., Schwarz, J., Mueller, K., Spindler, G., Wieprecht, W., Acker, K., Hillamo, R., Mäkelä, T., 2004. Intercomparison of methods to measure the mass concentration of the atmospheric aerosol during INTERCOMP 2000—influence of instrumentation and size cuts. Atmospheric Environment 38, 6467–6476.

Kasper, A., Puxbaum, H., Brantner, B., Paleczek, S., 1998. Scavenging efficiency of lead and sulfate in supercooled clouds at Sonnblick, 3106 m a.s.l., Austria. Atmospheric Environment 32, 3967–3974.

Laj, P., Fuzzi, S., Facchini, M.C., Orsi, G., Berner, A., Kruisz, C., Wobrock, W., Hallberg, A., Bower, K.N., Gallagher, M.W., Beswick, K.M., Colvile, R.N., Choularton, T.W., Nason, P., Jones, B., 1997. Experimental evidence for in-cloud production of aerosol sulphate. Atmospheric Environment 31, 2503–2514.

Mertes, S., Galgon, D., Schwirn, K., Nowak, A., Lehmann, K., Massling, A., Wiedensohler, A., Wieprecht, W., 2005. Evolution of particle concentration and size distribution observed upwind, inside and downwind hill cap clouds at connected flow conditions during FEBUKO. Atmospheric Environment (this issue).

Müller, K., Spindler, G., Maenhaut, W., Hitzenberger, R., Wieprecht, W., Baltensperger, U., ten Brink, H., 2004. INTERCOMP 2000, a campaign to assess the comparability of methods in use in Europe for measuring aerosol composition. Atmospheric Environment 38, 6459–6466.

Neusüß, C., Pelzing, M., Plewka, A., Herrmann, H., 2000a. A new analytical approach for size-resolved speciation of organic compounds in atmospheric aerosol particles: methods and first results. Journal of Geophysical Research 105, 4513–4527.

Neusüß, C., Weise, D., Birmili, W., Wex, H., Wiedensohler, A., Covert, D.S., 2000b. Size-segregated chemical, gravimetric, and number distribution-derived mass closure of the aerosol in Sagres, Portugal during ACE-2. Tellus 52B, 169–184.

Oberholzer, B., Collett Jr., J.L., Staehelin, J., Waldvogel, A., 1992. In-cloud scavenging of gases and aerosols at a mountain site in Central Switzerland. Journal of Atmospheric Chemistry 14, 61–71.

Pehkonen, S.O., Siefert, R., Erel, Y., Webb, S., Hoffmann, M.R., 1993. Photoreduction of iron oxyhydroxides in the presence of important atmospheric organic compounds. Environmental Science and Technology 27, 2056–2062.

Plessow, K., Acker, K., Heinrichs, H., Möller, D., 2001. Time study of trace elements and major ions during two cloud events at the Mt. Brocken. Atmospheric Environment 35, 367–378.

Plewka, A., Gnauk, T., Brüggemann, E., Neusüß, C., Herrmann, H., 2004. Size-resolved aerosol characterisation for a polluted episode at the IfT research station Melpitz in Autumn 1997. Journal of Atmospheric Chemistry 48, 131–156.

Rüd, C., 2003. Bestimmung von Metallen in Aerosolpartikeln und Wolkenwasser mittels Atom-Absorptionsspektrometrie. Diplomarbeit Universität Leipzig.

Sedlak, D.L., Hoigné, J., David, M.M., Colvile, R.N., Seyffer, E., Acker, K., Wieprecht, W., Lind, J.A., Fuzzi, S., 1997. The cloud water chemistry of iron and copper at Great Dun Fell, UK. Atmospheric Environment 31, 2515–2526.

Schmid, H., Laskus, L., Abraham, H.J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H.M., Giesen, K.-P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.-P., Toom-Sauntry, D., Puxbaum, H., 2001. Results of the "carbon conference" international aerosol carbon round robin test stage I. Atmospheric Environment 35, 2111–2121.

Schwarzenböck, A., Heintzenberg, J., Mertes, S., 2000. Incorporation of aerosol particles between 25 and 850 nanometers into cloud elements: measurement with a new complementary sampling system. Atmospheric Research 54, 241–260.

Strader, R., Lurmann, F., Pandis, S.N., 1999. Evaluation of secondary organic aerosol formation in winter. Atmospheric Environment 33, 4849–4863.

Tilgner, A., Heinold, B., Nowak, A., Herrmann, H., 2005a. Meteorological characterisation of the FEBUKO hill cap cloud experiments, Part I: Synoptic characterisation of measurement periods. Atmospheric Environment (this issue).

Tilgner, A., Majdik, Z., Sehili, A.M., Simmel, M., Wolke, R., Herrmann, H., 2005b. SPACCIM: Simulations of the multiphase chemistry occurring in the FEBUKO hill cap cloud experiments. Atmospheric Environment (this issue).

Voisin, D., Legrand, M., 2000. Scavenging of acidic gases (HCOOH, CH$_3$COOH, HNO$_3$, HCl, and SO$_2$) and ammonia in mixed liquid–solid water clouds at the Puy de Dome

mountain (France). Journal of Geophysical Research 105, 6817–6835.

Wieprecht, W., Acker, K., Mertes, S., Collett Jr., J.L., Jaeschke, W., Brüggemann, E., Möller, D., Herrmann, H., 2005. Cloud physics and cloud water sampler comparison during FEBUKO. Atmospheric Environment 0 (this issue).

Winkler, P., 1992. Design and calibration of a fog water collector. Instruments and observing methods. WMO/TD-No 462, 17–21.