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Case study of cloud physical and chemical processes in low clouds at Mt. Brocken

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Abstract

Frequency distributions of cloud base height and cloud type of low clouds observed between May and October 1998 at Mt. Brocken (Germany) have been derived from ceilometer measurements and synoptic observations. The summit at 1142 m a.s.l. was about 50% of that time in cloud. During daytime, Stratus clouds were the dominant cloud type (65%), whereas Cumulus clouds amounted to 27% and Stratocumulus clouds to 8%. Evidence was found that the increase of the cloud base height observed at Mt. Brocken continues since the end of the 1980s. An example for a clear anticorrelation between the liquid water content (LWC) of the cloud and the height above cloud base is shown. Other results of this detailed case study of a cloud event on October 8, 1998 concerning phase partitioning of water-soluble inorganic compounds, black carbon (BC) and organic carbon (OC) between the liquid and the interstitial phase will also be presented. The observed ion-specific increase in the solute mass per cubic meter of air with decrease of the distance between sampling position and cloud base was caused mainly by entrainment of air from the below-cloud layer. As expected, for sulfate, ammonia and nitrate, high scavenging coefficients (>0.8) were found. OC exhibits a high scavenging fraction of between 0.4 and 0.7; the value for black carbon (0.2–0.4) implies that soot was possibly to some extent internally mixed in the cloud condensation nuclei (CCN). Simultaneous measurements during a cloud event of HNO_2 and HNO_3 in the gas phase and N(III) and N(V) in the liquid phase were made for the first time.

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1. Introduction

During the last decades, numerous studies of the interactions of low clouds with aerosol particles were completed at many sites to investigate the influence of multiphase chemical, transport and removal processes on the budget of acid components, photo-oxidants and aerosols. Since 1991, an excellent platform for air and cloud chemical measurements has been provided at Mt. Brocken (51.80°N, 10.67°E) in Germany, with 1142 m a.s.l., the highest peak of the Harz Mountains. Among the long-term monitoring program (BROCC-MON), we studied several processes, e.g. the influence of clouds on the regional ozone budget (Acker et al., 1995), the relationship between liquid water content (LWC) of low clouds, cloud type, height above cloud base and cloud water ionic content (Möller et al., 1996a), the influence of changing emission patterns on ambient concentrations (Acker et al., 1998b) and the distribution of phenols and nitrated phenols (Lüttke et al., 1999) and metal ions (Plessow et al., 2001) in the clouds approaching Mt. Brocken.

2. Experimental

Detailed description of the measurement site, the methods used within the cloud chemistry program (most of them operated only during the frost-free periods because of extreme winter weather conditions), the detailed air mass transport analysis program and the quality assurance activities have been presented by Acker et al. (1998a). The liquid water content (LWC) of the clouds is measured by Particle Volume Monitor PVM-100 (Gerber Scientific) every 5 s. The Forward-Scattering Spectrometer Probe FSSP-100 (PMS), equipped for ground-based sampling, measures droplet number size distributions with similar frequency. Cloud base height is determined using a Vaisala CT25K Laser ceilometer (resolution in time 15 s, in space 30 m) which is installed at 612 m a.s.l. at Schierke, 4.5 km in horizontal direction south/east at the foot of Mt. Brocken. In addition, parallel observations of the local synoptic conditions at the Schierke site were also carried out by eye at hourly intervals by an experienced observer. Separation and sampling of droplets and interstitial aerosol particles is done using different types of impactors. At an operational sample flow rate of $120 \text{ m}^3 \text{ h}^{-1}$, drops greater than $5 \mu\text{m}$ (50% cutoff diameter) will be collected with an efficiency between 55% and 97% using a single-stage active cloud water collector (Winkler, 1992). This Winkler collector is combined with a filter sampling unit for collection of interstitial aerosol particles on Nuclepore filters (time resolution for cloud water 1 h, for particles, 4 h). These samples were analysed for inorganic ions and pH and these data are used for phase partitioning calculations. A two-stage cloud water collector (Enviroscope) was also in operation to investigate the distribution of solute inorganic components between two droplet size ranges. The 50% cutoff diameter of the first stage is $10 \mu\text{m}$ and of the second one $5 \mu\text{m}$, calculated for a flow rate of $150 \text{ m}^3 \text{ h}^{-1}$ where the instrument achieves isokinetic sampling conditions (Schell et al., 1997). All inorganic ions were determined by ion chromatographic methods. Simultaneously, droplets were collected by a Counterflow Virtual Impactor (CVI) and interstitial aerosol particles by a droplet segregating inertial impactor (INT) detailed in Schwarzenböck et al. (2000) and references therein. Behind these impactors, filter sampling units (Nuclepore,

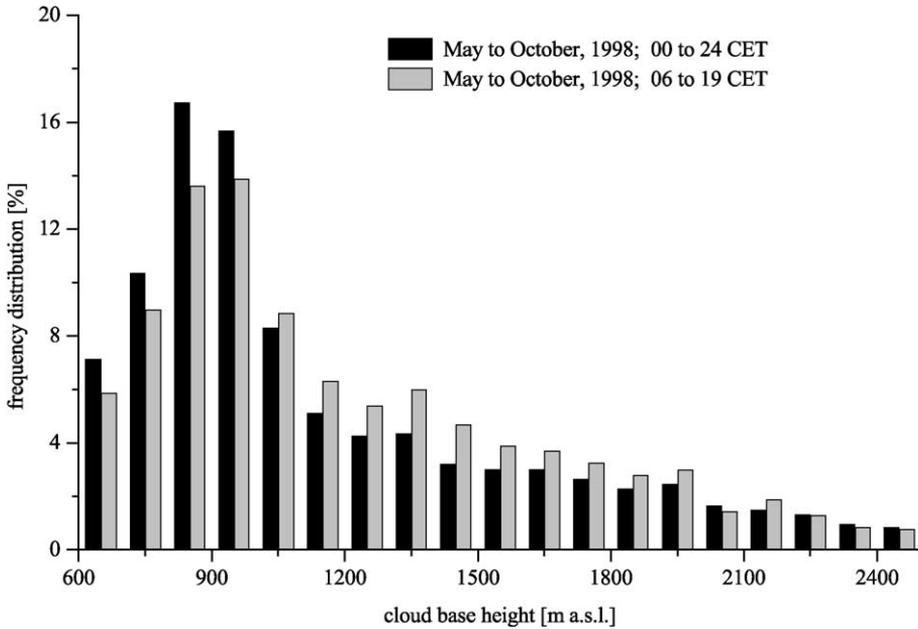


Fig. 1. Cloud base height of low clouds observed above 612 m a.s.l. (ceilometer location, near Mt. Brocken).

Pallflex) were attached. The number of the interstitial particles was determined with a Condensation Particle Counter (CPC-3760A, TSI). Black carbon (BC) content was measured using a Particle Soot Absorption Photometer (PSAP, Radiance Research). The organic carbon (OC) content in the residual and interstitial particles was calculated by subtracting the amount of BC from the amount of total carbon (TC) derived from a thermographic determination (Schmid et al., 2001) of the filter samples (time resolution 2 h). All sampling devices were oriented into the direction of the wind during the cloud event. Commercial instruments and analysers were used to measure meteorological standard parameters (Thies, Metek) and trace components (Dasibi for O_3 , Ecophysics for NO_x , TEI for SO_2 , Aerolaser for $H_2O_{2(liquid)}$, Umweltdata for $S(IV)_{(liquid)}$). Diffusion-based collection with separation of the gaseous species from their particulate counterparts was performed continuously using a wet effluent diffusion denuder in combination with an

Table 1

Percentage contribution of different cloud classes to low clouds observed during daytime above Schierke (612 m a.s.l.)

Class	CL1	CL2	CL3	CL4	CL5	CL6	CL7	CL8	CL9
Cloud type	Cu hum, Fra	Cu med, con	Cb cal	Sc (cugen)	Sc	St neb, fra	St fra, Cu fra	Cu, Sc	Cb cap
612–1150 m a.s.l.	3.2	12.1	11	0	1.3	30.8	33.9	6.5	1.1
600–2500 m a.s.l.	6.2	25.3	10.8	0.7	6.7	15.9	17.3	13.6	3.5

ion chromatography unit (WEDD-IC) to determine nitrous and nitric acid inside and outside of clouds (Acker et al., 2001). At a sample flow rate of $0.6 \text{ m}^3 \text{ h}^{-1}$ through the denuder and 15 min time resolution, the detection limit for both species is 5 ng m^{-3} and the uncertainty is no greater than 20 ng m^{-3} . Separation of the interstitial air from the cloud droplets was done using an active single-stage Winkler collector in front of the denuder. Nitrite, nitrate and $[\text{H}^+]$ in cloud water were analysed within 15 min after sampling at the field site.

3. Results and discussion

3.1. Characterization of low clouds observed at Mt. Brocken

Based on LWC measurements (the average uncertainty was no greater than 9 mg m^{-3}) made in 1998 at Mt. Brocken between May 1 and October 31 (data completeness 88%), a mean value for the liquid water content of the clouds reaching this site was determined to be $327 \pm 205 \text{ mg m}^{-3}$. For this calculation, 10-min averages of the original LWC data set were used; they varied between 10 and 1370 mg m^{-3} . The summit was in cloud nearly half of the period (May, 30%; June, 33%; July, 51%; August, 38%; September, 47%; October, 84%).

In an undisturbed cloud, generally wet adiabatic condensation can be assumed (Kraus, 2000). Therefore, LWC increases almost linearly with height above cloud base,

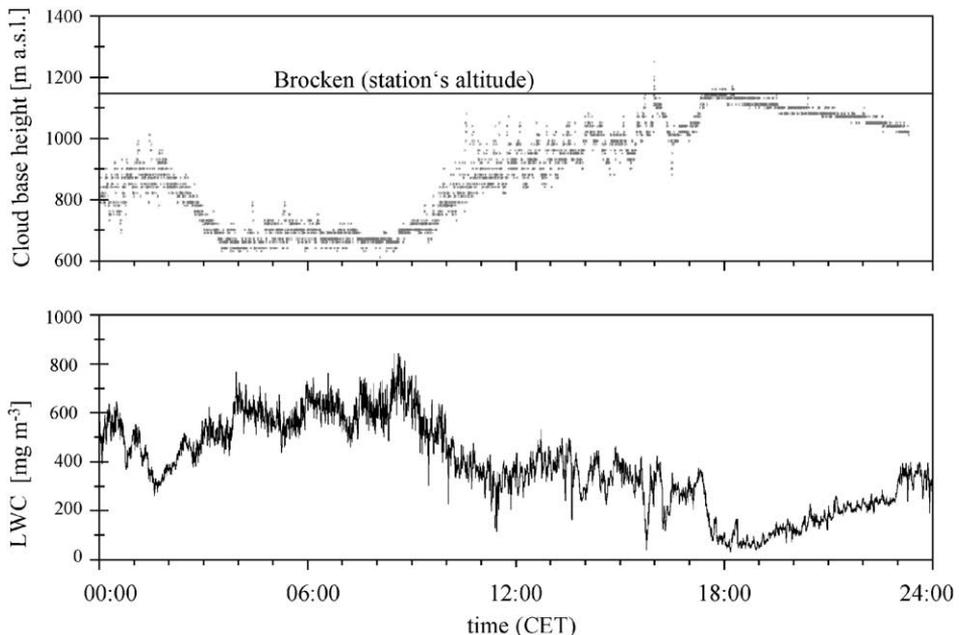


Fig. 2. Relationship between liquid water content and the position inside the cloud.

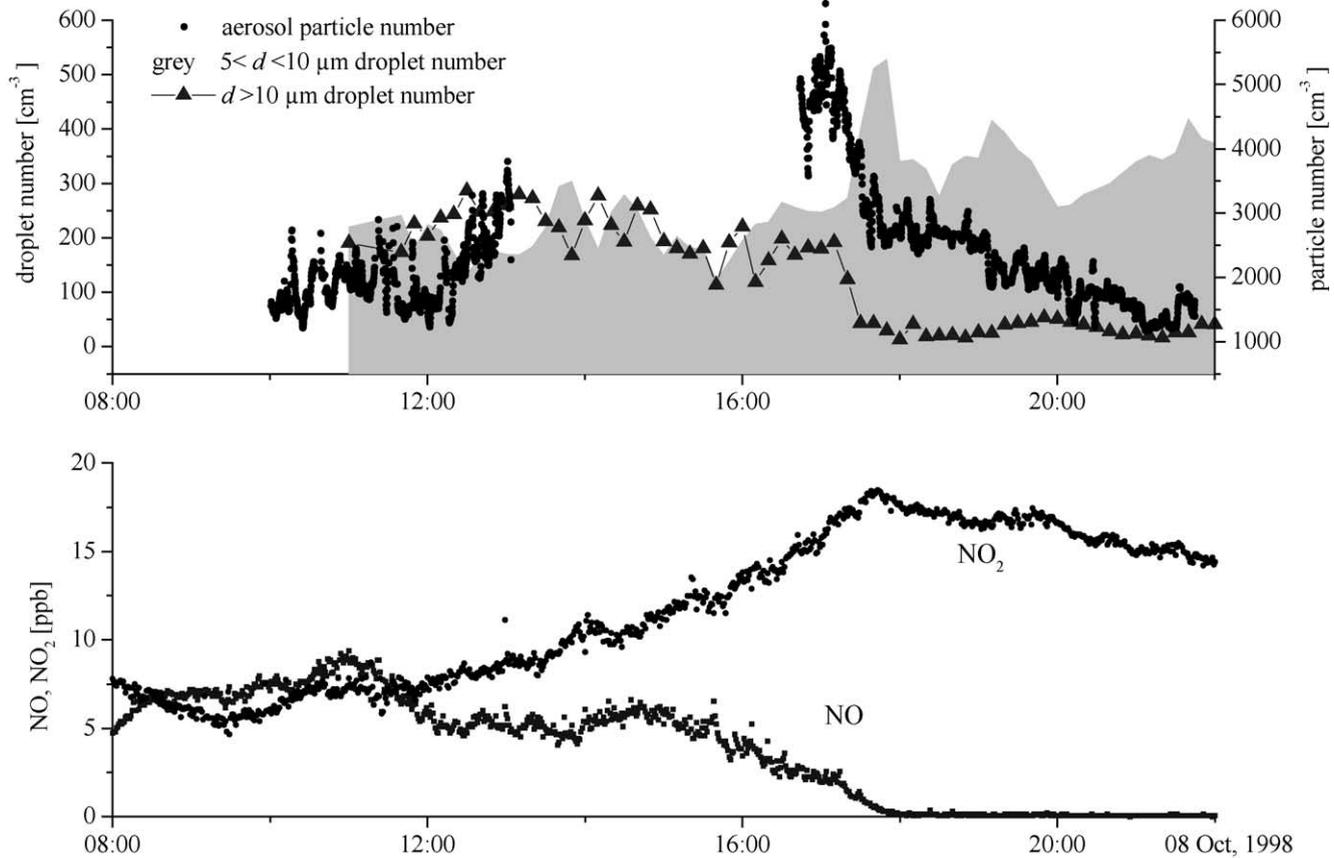


Fig. 3. Variation of droplet number, aerosol particle number, NO and NO₂ during the cloud event observed at Mt. Brocken on 8 October 1998.

reaching a maximum at about 80–90% of the cloud thickness. After that point, LWC strongly decreases up to the cloud top. Such profiles were measured at Mt. Grönten (Germany) using a cable car being the measurement platform (Wieprecht et al., 1995). The knowledge of the distance between Brocken summit (sampling position) and cloud base is therefore essential for any physico-chemical interpretation of cloud data. Ceilometer measurements from a point 530 m below the Mt. Brocken summit were done continuously (data completeness 80%). Fig. 1 shows the frequency distribution of the cloud base heights for all low clouds (these are clouds observed up to 2500 m above sea level) observed between May 1 and October 31, 1998 at Schierke. For this presentation, 1-h averages of cloud base height (uncertainty ± 30 m) were used. It was found that 58% of all low clouds have their cloud base below the Mt. Brocken summit (1142 m a.s.l.). This value is in very good agreement with the observation “station in cloud” (50%) obtained by LWC measurements during the time period. The distribution in Fig. 1 shifts a little to higher cloud base levels if only ceilometer data between 6:00 and 19:00 (Central European Time, CET) are used. For that daytime between May 1 and October 31, 1998, hourly operator observations (data completeness 98%) of the cloud base height and the cloud type are also available (location like ceilometer). These data confirm the high occurrence of clouds which cover the Mt. Brocken summit also during daytime (49%). A classification of the observed low clouds into nine classes from CL1 to CL9 (de Bont, 1987) was done in accordance with the meteorological code and the definitions from the World Meteorological Organization. In Table 1, the frequency distributions of these different cloud types are given for all low clouds observed up to about 2000 m above Schierke (612 m a.s.l.) and for clouds with a base level 0–500 m above Schierke. For this latter case implying “Brocken station in cloud”, Stratus clouds (CL6, CL7) were the dominant cloud type (65%), dominantly with a cloud base height between 900 and 1000 m a.s.l., whereas Cumulus clouds amounted to 27% of the cases. Below 900 m a.s.l., Stratus clouds were nearly exclusively observed. Compared with earlier synoptic observations at Mt. Brocken, the 1998 data confirm a continuing increase of the cloud base height, a phenomena established since the end of the 1980s, more or less for all types of low clouds. During a comparable time period in 1993, only 39% of all clouds covering Mt. Brocken were classified as Stratus, mostly with a cloud base of between 700 and 900 m a.s.l. (Möller et al., 1996b). The properties of Stratus, Cumulus and Stratocumulus clouds are different when considering their droplet spectra, LWC, vertical movement, precipitation probability and lifetime, which influence the cloud chemistry. Therefore, a detailed climatological study of these issues is in preparation and will be presented later elsewhere.

Table 2

Organic and black carbon concentrations during a cloud event at Mt. Brocken

Time on October 8, 1998	10:00–12:00	13:00–17:00	17:30–19:30	20:00–21:30	22:00–23:30
OC liquid phase ($\mu\text{g m}^{-3}$)	3.3	1.4	2.2	2.5	1.6
OC aerosol phase ($\mu\text{g m}^{-3}$)	2.1	0.8	1.4	–	2.2
BC liquid phase ($\mu\text{g m}^{-3}$)	0.04	0.05	0.06	0.1	0.08
BC aerosol phase ($\mu\text{g m}^{-3}$)	0.36	0.33	0.25	0.18	0.16

3.2. Detailed characterization of a single cloud event

On October 8, 1998, air masses arrived at Mt. Brocken from the South. The air was slowly transported wholly within clouds over the previous 72 h, the wind speed at Mt. Brocken was

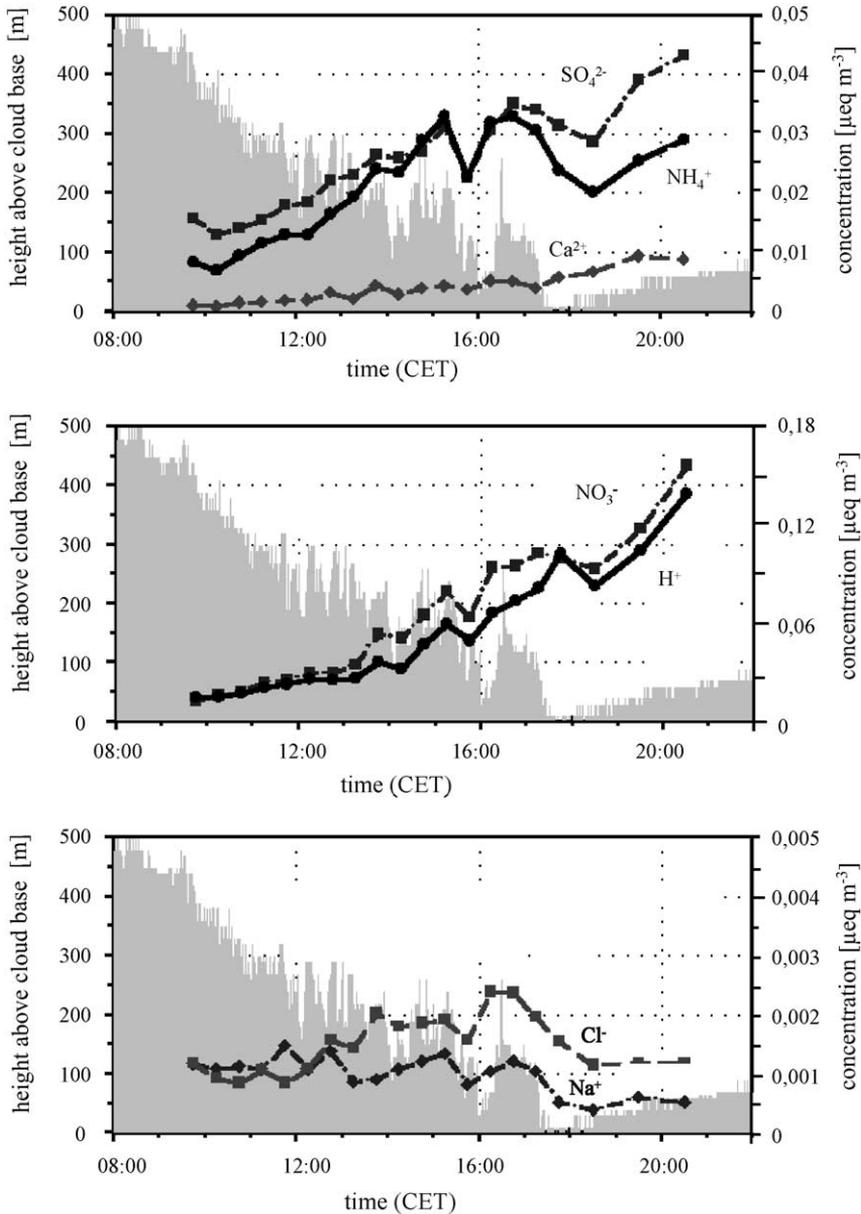


Fig. 4. Ion-specific changes in the solute mass during a cloud lifting process.

2–5 m s⁻¹. Due to wet removal in the alpine area, the aerosol and trace gas loading of the approaching air mass was low. The observed cloud type was Cumulus mixed with Stratus fractus, later Stratocumulus. After 10:00, a lifting process caused a strong decrease in the liquid water content of about 130 mg m⁻³ per 100 m (see Fig. 2). This value is consistent with earlier investigation results from Mt. Brocken (Wieprecht et al., 1995) in which for low clouds a change of LWC greater than 1 mg m⁻³ per meter height above cloud base was found indicating sub-adiabatic conditions (Kraus, 2000). The observed decrease in LWC was connected with a shift of the droplet size distribution (measured by FSSP) to smaller droplets (see Fig. 3). The concentrations of organic carbon (OC) and black carbon (BC) in the liquid and aerosol phases are given in Table 2. The partitioning of species between liquid and interstitial phase is expressed by the scavenging coefficient $\varepsilon = [x]_{\text{drop}} / ([x]_{\text{drop}} + [x]_{\text{int}})$, where $[x]$ denotes the mass concentration of interest per air volume. Organic carbon exhibits a high ε of between 0.4 and 0.65; the high amount of soluble organic material seems to be consistent with the important role that organic particles play as part of cloud condensation nuclei (CCN). The scavenging coefficient of black carbon varied between 0.1 and 0.4. According to sensitivity calculations (e.g. Twohy et al., 1989), the observed BC “liquid phase concentration” between 200 and 800 μg per liter of cloud water is not sufficient to reduce the cloud albedo significantly. The partitioning of water-soluble ions in the cloud water and in the interstitial aerosol during the whole event showed that about 80% of the sulfate and ammonium and nearly all of the nitrate were dissolved in the cloud water. For sodium and chloride, scavenging coefficients ε of about 0.5 were determined. During the period where cloud base was changing, an approximately linear increase of the solute mass (calculated from a liquid phase concentration multiplied by the LWC) of sulfate, ammonium, nitrate and calcium was found (see Fig. 4), whereas for sodium and chloride only slight changes were observed. The ascent for sulfate and ammonium is absolutely identical and that for nitrate much steeper. Therefore, entrainment of aerosol particles from the sub-cloud layer, mostly consisting in this case of highly soluble ammonium sulfate and nitrate, is assumed. An increase in the aerosol number concentration and in the number of small cloud droplets was observed (see Fig. 3). Most of the solute mass of nitrate, sulfate and ammonium was now found in the small droplet fraction (5–10 μm diameter) of the two-stage cloud water impactor (see Fig. 5).

The gas phase concentrations of SO₂ ($\sim 3 \mu\text{g m}^{-3}$) and that of S(IV) ($< 10 \text{ ng m}^{-3}$ air volume) were low during the event. Consequently, S(IV) to S(VI) transformation seems not to be responsible for the observed increase in cloud water sulfate. An indication for that is also the measured increase of the H₂O₂ liquid phase concentration from 30 to 280 ng m^{-3} air volume between 12:00 and 19:00. Highly soluble gases can be transported by entrainment of undersaturated air into the cloud. The much stronger increase of the dissolved NO₃⁻ compared with SO₄²⁻ may be caused also by an uptake of nitric acid (which may be also adsorbed on aerosol particles) entrained into the cloud, causing an increasing NO₃⁻/SO₄²⁻ ratio from about 1 within the main body of the cloud to 3.5 near cloud base. The cloud water pH decreased from about 4 at 12:00 to 2.9 at 18:00. Because of its high solubility, only low concentrations of nitric acid were observed in the interstitial gas phase (50–300 ng m^{-3}). The more acidic character of the aerosol particles could be the reason for the higher scavenging coefficient of black carbon observed after 18:00. The increase in NO₂ concentration (Fig. 3) may support the given explanation of entrainment

of air masses from the layer below cloud. The increase of the NO_2 to NO ratio and the accumulation of solute hydrogen peroxide in cloud water show that with changing cloud base a more aged air mass is arriving at Mt. Brocken.

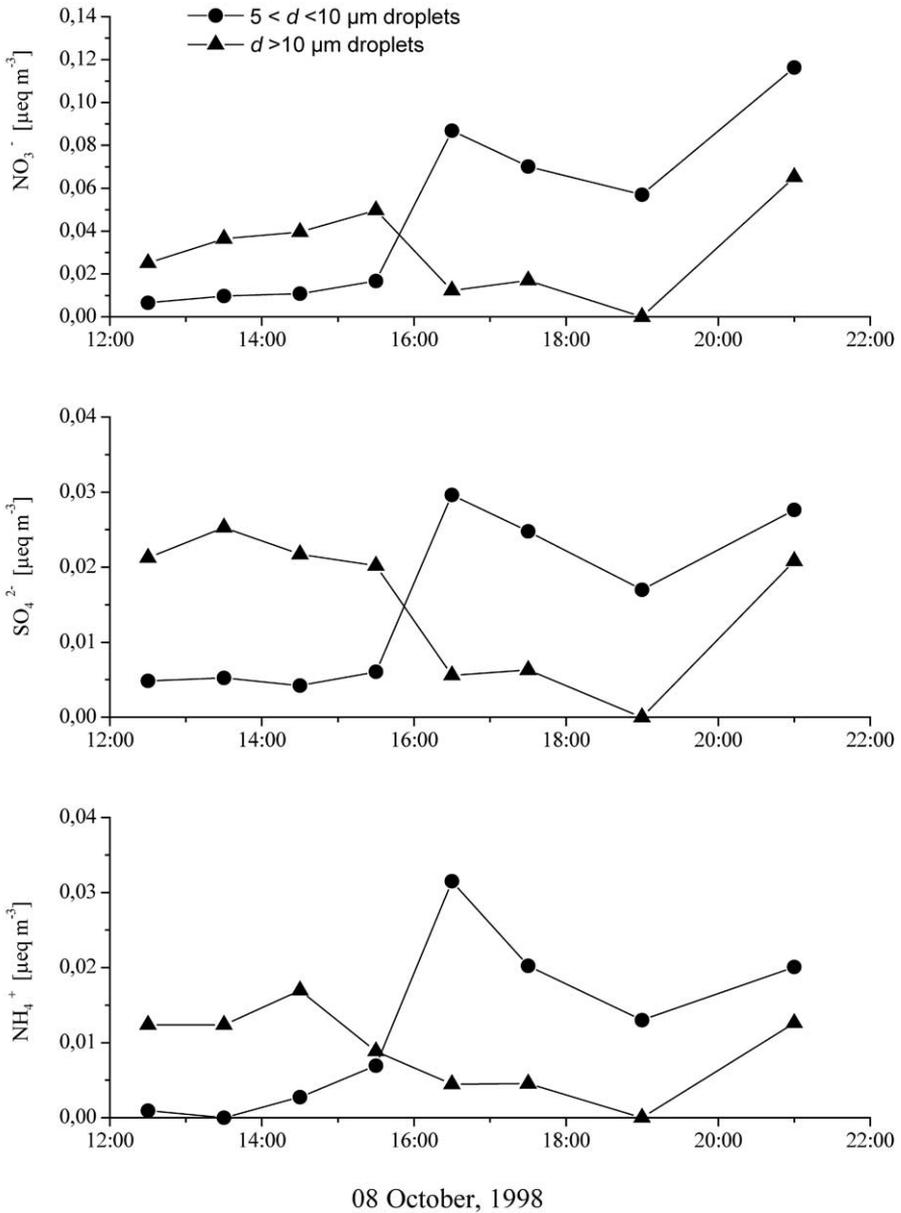


Fig. 5. Concentrations of sulfate, ammonium and nitrate in two different cloud droplet fractions, collected by the two-stage cloud water collector.

A wet denuder technique was used to measure nitrous acid inside and outside of clouds during field campaigns at Mt. Brocken in 1998 and 1999. The concentrations of HNO_2 were found to be highly correlated with those of NO_2 . A HNO_2 to NO_2 ratio of $(3.1 \pm 1.7) \times 10^{-2}$ was observed. Heterogeneous formation on the surface of droplets and wet aerosols and accumulation processes led to the observed maximum HNO_2 (up to 320 ng m^{-3}) between midnight and morning. For the first time, measurements of nitrous acid in the gas phase and nitrite in the liquid phase were done simultaneously during cloud events. Aqueous-phase nitrite concentrations between 5 and $300 \mu\text{g l}^{-1}$ (according to $1\text{--}30 \text{ ng m}^{-3}$ air volume) were observed. The higher values were measured in the case of low acidity ($\text{pH} > 5.5$). Under more acidic conditions ($\text{pH} 4.7\text{--}2.9$), most of the HNO_2 was found in the gas phase, the calculated HNO_2 to nitrite ratio varied then between 25 and 125. Large discrepancies (up to two orders of magnitude) with respect to Henry's law were found. The observed supersaturation of N(III) in the liquid phase is higher at lower pH. Only in a few cases at pH values > 5 was subsaturation (up to one order of magnitude) found.

4. Conclusions

Distributions of cloud base height and cloud type of low clouds at Mt. Brocken between May and October 1998 were presented. Evidence was found that the increase of the cloud base height observed since the end of the 1980s continues. The concentration range and the low aerosol particle concentration during the detailed case study verify rural environmental conditions during this period. Ammonium sulfate was the dominant species present in the CCN. Organic carbon (OC) was found to be an important part of CCN. In contrast to OC, BC remained mostly in the interstitial phase. To our knowledge, the first HNO_2 measurements have been carried out within clouds. Some large deviations from Henry's law for N(III) were found. The data indicate that it is not possible to extrapolate HNO_2 interstitial gas phase concentrations simply from measured bulk nitrite liquid phase concentrations of a cloud.

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