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# CHEMICAL AND PHYSICAL CHARACTERISATION OF LOW CLOUDS: RESULTS FROM THE FEBUKO GROUND-BASED CLOUD EXPERIMENT

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Clouds play an immense role in transport and transformation of atmospheric trace species. In the joint project FEBUKO (Field investigations of budgets and conversions of particle phase organics in tropospheric cloud processes) the microphysics and chemistry of different types of aerosols, the role of aerosol chemical composition for cloud formation as well as the chemical transformation in cloud processes have been investigated by means of ground-based cloud experiments at Mt. Schmücke in the Thuringian Forest (Germany). The groups involved used a wide range of measurements of trace gases, aerosol particles and cloud droplets at three sites to study their sources and sinks, especially those in cloud. Although kind and behaviour of organic substances were of special interest (e.g., organic acids, peroxides, organic carbon, soot) attention was paid to the role of inorganic soluble material being the main part of the cloud condensation nuclei. In this paper we present selected results from the first experiment in autumn 2001.

**KEY WORDS:** *aerosol-chamber, atmospheric aerosol, cloud base height, droplet size distribution, liquid water content, wet-denuder*

At any given time, about 60 % of the Earth's surface is covered by clouds and they occupy about 7 % of the troposphere's total volume (1). Even though the volume fraction of liquid water in clouds rarely exceeds $10^{-6}$ (1 mL in 1 $m^3$ air) the fundamental role of cloud droplets as a medium for chemical reaction has long been recognised. Clouds influence the photochemistry of the atmosphere, the radiation budget, and redistribute emitted trace compounds to other regions and from the boundary layer to the free troposphere. In the clouds chemical transformations are running that would otherwise not take place or would proceed at much slower rates. Cloud processes are responsible to more than 70 % for sulphate formation from gas-phase $SO_2$ (2-4). It has increasingly been accepted that clouds also influence the ozone budget regionally and even global between 10 and 30 % (5). Despite the short lifetime of single cloud droplets, cloud systems may persist for many hours or even days and may transport pollutants over distances of several hundreds of kilometres. Meanwhile evaporation and condensation (cloud cycling) can happen. Eventually, clouds can produce precipitation and finally trace components will be removed from the atmosphere via wet deposition. Precipitation can contribute to short-time very high deposition of species on the earth's surface and can cause ecological and material damages. On mountain sites, cloud water deposition is several times larger than rain water wet deposition (6-8) and can lead to environmental damage (9). On a regional and global scale, wet deposition contributes to 50-70 % to the total deposition. A cloud chemistry measurement program which started in 1991 at Mt. Brocken (Germany) revealed that 58 % of all low clouds up to 2500 m above sea level (a.s.l.) observed at this location have their cloud base below the Mt.

Brocken summit (1142 m a.s.l.) (10). Cloud droplets have sizes between 1 and 100 $\mu$m diameter, but the sizes between 1 and 20 $\mu$m are most frequent. Larger droplets (> 50 $\mu$m) can grow further to form rain droplets (mostly by colliding and coalescing with smaller droplets).

A cloudy atmosphere is a multiphase atmospheric system; gaseous species, atmospheric particulate and liquid droplets co-exists at one time. Soluble gases can dissolve and react to form new products, particles can be uptake by existing cloud droplets (gas and particle scavenging). Interactions between the different phases and the inhomogeneous nature of clouds must be taken into consideration when discussing physical and chemical processes in clouds. 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. Meteorology (temperature variation with height) and cloud dynamics are other factors influencing atmospheric chemistry. The explicit consideration of multiphase processes is still limited in transport and climate models. There are missing useful parameterisations for describing the presence of clouds, reservoir distribution of trace species, and chemical reactions in the condensed phase.

In the recent years several very complex international and national field campaigns have been carried out, which have resulted in many important findings (11, 12). With the emission abatement of key pollutants (dust, $SO_2$) the interest in cloud chemical processes in Europe and Northern U.S. is changing. Nowadays, a main focus is on organic substances and biogenic particles and their role to act as cloud condensation nuclei (13, 14). To improve the understanding of the multiphase processes in the troposphere investigations are done also in the research project FEBUKO (Field investigations of budgets and conversions of particle phase organics in tropospheric cloud processes). This project is one of the subprojects within the German Aerosol Research Program started in 2001 and fully synchronized with the project MODMEP ("Modeling of Tropospheric Multiphase Processes: Tools and Chemical Mechanisms"). Both projects are coordinated by the Institute for Tropospheric Research Leipzig (IfT). More details are given in (15) and (16). This paper gives selected results from the first ground based cloud experiment which was performed in autumn 2001 at a mountain site in the Thuringian Forest (Germany) to study the air flow over hills, cloud physics, air and cloud chemistry.

## METHODS

The ground based cloud experiment was performed in autumn 2001 at a mountain ridge in the Thuringian Forest (Germany). Air approaching the ridge is forced to rise up over it, cooling by adiabatic expansion, and forming orographic cloud in the boundary layer. This cloud is in contact with the ground at the summit of Mt. Schmücke and used as a flow through

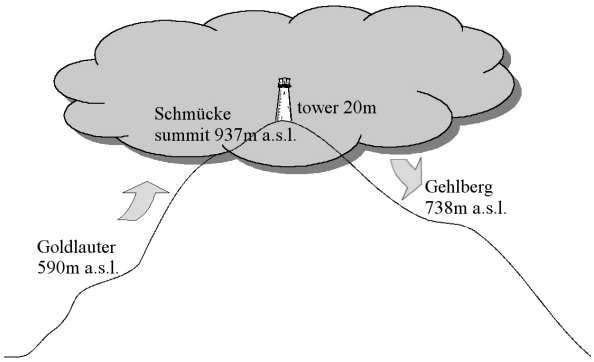



**Figure 1** *Schematic view of the FEBUKO experiment*

reactor. Figure 1 shows a cross-section through the location selected for studying cloud processes. In a south-westerly wind, the air characteristics are simultaneously determined in the Goldlauter valley before it enters the cloud, in the cloud at the summit and in Gehlberg after cloud processing. Data from ground based meteorological and trace gas (ozone) measurements and SF6 tracer experiments are used to define connected air flow conditions between the three measurement sites Goldlauter (windward), Schmücke summit and Gehlberg (leeward). The measuring location (50°39'N; 10°46'E) is surrounded by coniferous forests, the nearest town is Suhl (7 km NE). A period of six weeks in length was chosen for the experiment to meet the adequate experiment conditions. The ozone concentration measured at the three sites on 26-27 October 2001 indicated connected flow conditions (Figure 2).

On mountain top our measurements were focussed on cloud physical parameters (liquid water content, droplet spectra) as well as on collection and analysis of the cloud water. The equipment was installed on a measurement platform 20 m above ground (see Figure 1) to be above the surrounding coniferous forest. The liquid water content of the clouds covering the mountain top were measured every 10 s by an optical method using PVM100 (Gerber Scientific). This instrument is a forward

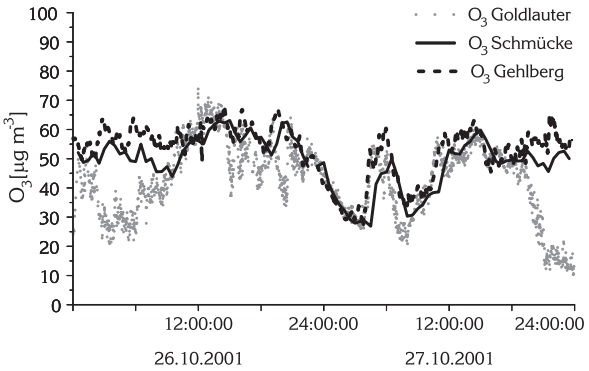



**Figure 2** *Ozone concentrations at the three experimental sites: before (Goldlauter), in (Mt. Schmücke) and after (Gehlberg) the cloud.*

scattering laser spectrometer for particulate volume measurements. A laser beam crosses the air over a length of 42 cm with an optical probing volume of 3 $cm^3$. A special receiver optics is used which guaranties linearity between scattering intensity and liquid water contents for droplet diameters from 3-45 $\mu$m (17). The droplet number size distribution was also measured with same frequency here using our Forward-Scattering Spectrometer Probe FSSP100 equipped for ground-based sampling. This is a single particle counting laser instrument and measures the droplet number in 16 channels with different size bins. From the droplet distribution, the total volume of liquid water can be calculated.

A single stage and a two stage cloud water collector [as described in (10)] were in operation at this platform to collect cloud water droplets greater than 5 $\mu$m or in the fraction 4-12 and >12 $\mu$m. The amount of solute components in the cloud water was detected by ion chromatography or by thermographic method. Simultaneously, a Counterflow Virtual Impactor (CVI) and particle counters were operated by IfT Leipzig to detect the number of cloud droplets > 5 $\mu$m and the particle concentration (also inside the cloud as interstitial aerosol).

At the valley station Goldlauter we operate a Vaisala CTK25 laser ceilometer (resolution in time 15 s, in space 30 m) for continuous determination of the cloud base height. There we also detected meteorological parameters, and trace gas mixing ratios of $O_3$ (Dasibi 1008), NO, $NO_2$, $NO_y$ (Ecophysics CLD 770 ppt/PLC 760) and $SO_2$ (TEI 42S) with high time resolution.

The partitioning of some water soluble inorganic compounds between the gas and aerosol phase was investigated using a denuder technique which allows the diffusion-based collection of reactive trace gases with a separation from their particulate counterparts. $HNO_2$ and $HNO_3$ measurements were performed using a wet effluent diffusion denuder (WEDD) coupled directly with an ion chromatography unit (18). The system was extended by a steam jet unit to determine aerosol components (nitrite, nitrate, chloride, sulfate) with a high time resolution. The airflow through the denuder / steam jet chamber is 10 L $min^{-1}$ and using 30 minutes sampling time concentrations of 0.010 $\mu g\ m^{-3}$ of $HNO_2$, $NO_2^-$, $HNO_3$ and $NO_3^-$ can be reliably recorded.

## RESULTS

Clouds develop in supersaturated air by condensation of water vapour onto a portion of pre-existing aerosol particles, called cloud condensation nuclei (CCN) and above continents probably mostly formed by anthropogenic emissions. In air with a relative humidity between 60 and 70 % aerosol particles become surrounded by a layer of water large enough to dissolve the soluble part of the particle. The growth of aerosol particles by water vapour condensation depends on the size and chemical composition of the particle and on the achieved supersaturation of water vapour. Particles growing above a critical droplet size are called activated particles. They can grow to larger droplets, whereas particles of unfavourable size and/or composition remain as interstitial aerosol between the cloud droplets. On average in *cumulus* or *stratus* clouds at a given supersaturation 50 to 1000 cloud droplets were found simultaneously with about 200 to 3000 not activated particles (19). The droplet number is highest at the cloud base. Above the cloud base the existing droplets consume all the water, and in rising air parcels of clouds, the supersaturation caused by the updraught leads to an increase in liquid water content (LWC) and droplet diameter with height above cloud base (20). It is known from many field measurements (21-23) and expected under wet adiabatic conditions, that the liquid water content (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 thus in cloud water composition are much smaller if the measurement position is more inside the cloud. Near cloud base and cloud top, entrainment processes (droplet evaporation by mixing with dryer air, aerosol and gas scavenging) disturb the adiabatic

conditions and let to high variation in LWC and chemical composition.

Measurements were made during discrete periods several hours in length when it was forecast that weather conditions would be suitable for the flow-through experiment (we call it cloud events). During the investigated cloud events (clouds only at Mt. Schmücke) medium or low polluted air masses moved from the Goldlauter valley to the mountain top. On average concentrations of $SO_2$ below 1 ppb and of $NO_2$ below 10 ppb were observed.

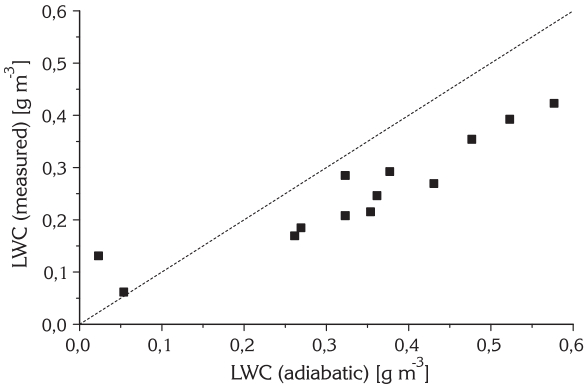



**Figure 3** *Comparison between measured and calculated (assuming adiabatic conditions) liquid water content (LWC) of clouds observed during the FEBUKO 2001 experiment*

For periods of the investigated cloud events observed during the FEBUKO 2001 experiment the really measured LWC was compared with the amount of liquid water expected in case of adiabatic cooling (adiabatic LWC), see Figure 3. On average a ratio of 0.7 was found and the differences may be caused by processes like droplet deposition and as already mentioned by entrainment of air not saturated with moisture. During the selected cloud event on October 26 and 27 the mountain top Schmücke was covered in the beginning by *stratocumulus* (Sc) and later by *stratocumulus fractus* clouds. A strong correlation between liquid water content and height above cloud base was found (Figure 4). A laser beam from our ceilometer operated in Goldlauter was scattered back after meeting cloud droplets and the registered signal gives us information about the height of cloud base above the valley station. Considering the different heights of the stations Goldlauter and Schmücke (see Figure 1) we can calculate how deep the mountain top is in cloud. Furthermore we derived from our FSSP measurements the cloud droplet number (Figure 5) and the effective droplet diameter (Figure 6) for the two days of the selected cloud event.

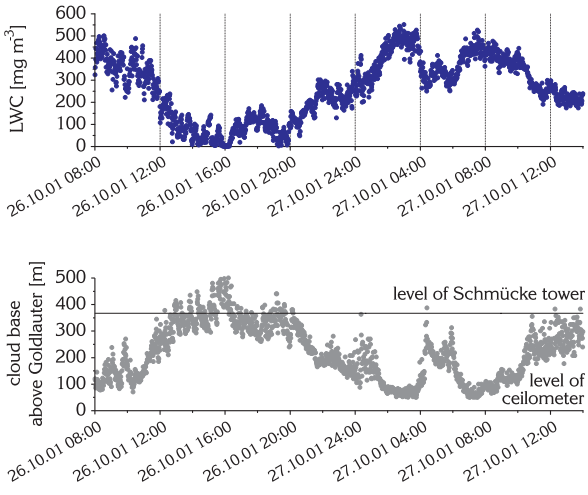



**Figure 4** *Relationship between liquid water content (LWC) and cloud base height during the 26-27 October cloud event (see also Figure 1)*

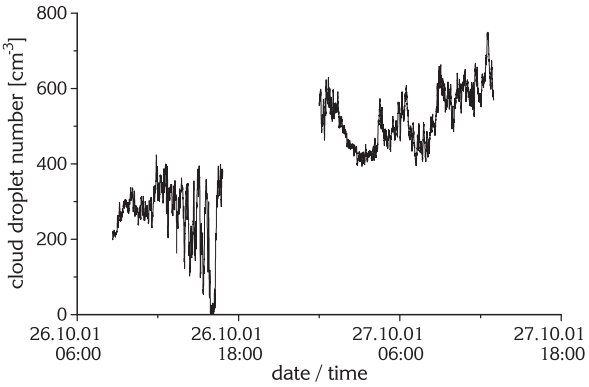



**Figure 5** *Variation in the number of cloud droplets during the cloud events on 26 and 27 October 2001.*

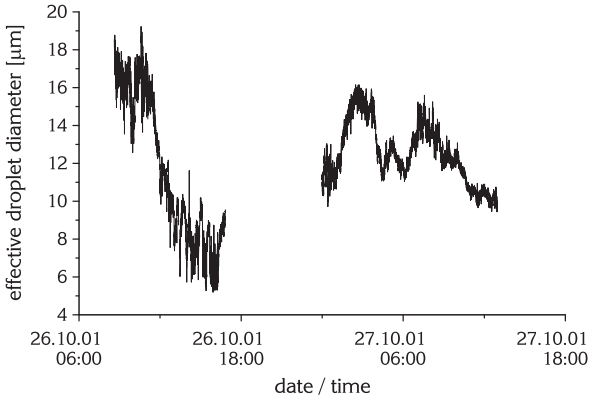



**Figure 6** *Variation in the effective droplet diameter during the cloud events on 26 and 27 October 2001*

The observations made on October 26 indicated that between 9-12 UTC more than 90 % of the liquid water was concentrated in droplets with diameters bigger than 10 $\mu$m (Figure 6). After 12:00 UTC a rapid

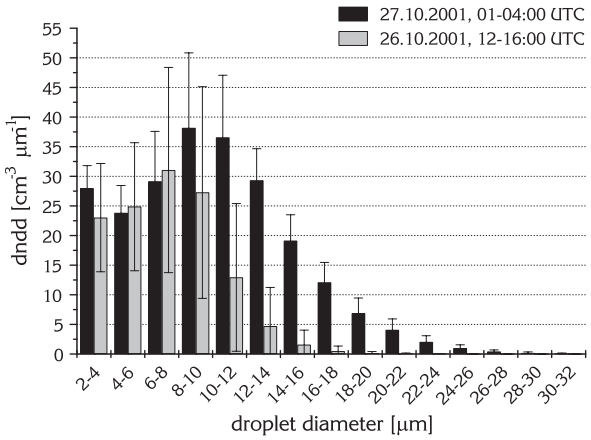
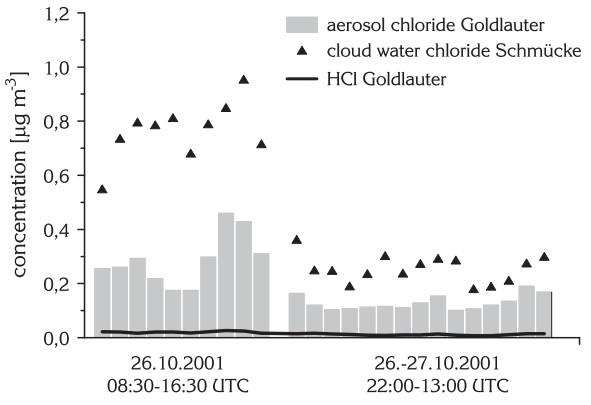



**Figure 7** *Size distribution of cloud droplets observed at Mt. Schmücke in the cloud on 26 and 27 October 2001 (given as number per µm diameter size detected in the different droplet spectra channels of the FSSP100)*

decrease of LWC was caused by a cloud lifting process and the Schmücke summit, and consequently the cloud water sampling position, were near the cloud base (Figure 4). Droplets evaporate and/or remaining droplets decrease in size, see Figs. 5 and 6. More smaller droplets were observed, mostly in the range between 2 and 10 $\mu$m (Figure 7). On October 27 the mountain top was often about 300 m inside the cloud (Figure 4) and the air masses from Goldlauter had to cross a long distance within clouds before reaching the leeward site. On average a LWC of 400 mg per $m^3$ was detected, mainly caused by the high number of big droplets (Figures 5 and 6). More than 80 % of the LWC were found in the droplets bigger than 10 $\mu$m diameter. The differences in the droplet size distribution, as shown in Figure 7, for two time intervals of Mt. Schmücke in cloud are mainly caused by different measurement / sampling position above the cloud base.

Figures 8a through 8d show the distribution of inorganic species between gas and aerosol phase at the upwind site Goldlauter for these special events. The gas and particle concentrations before cloud occurrence were compared with the content of the ions found in the Schmücke cloud water samples (time resolution 30 min). Nitrate and sulfate were the dominant anions in the aerosol phase during the FEBUKO 2001 experiment (Figures 8b and 8c),




**Figures 8a**

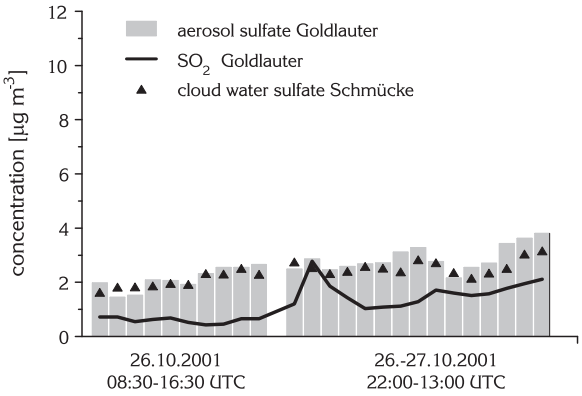



**Figure 8b**

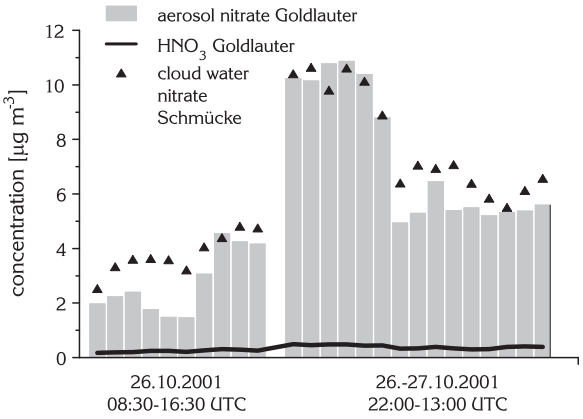



**Figure 8c**

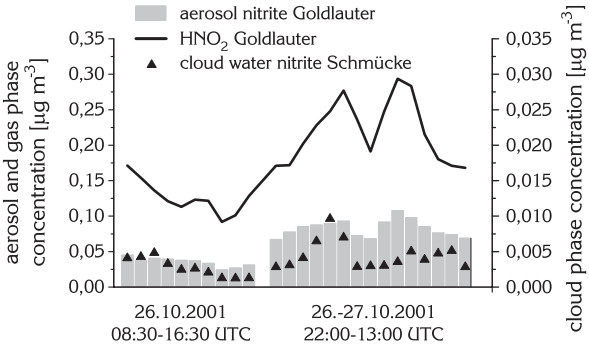



**Figure 8d**

**Figures 8a-8d** *Distribution of reactive components between gas and aerosol phase at the valley station Goldlauter before the air masses reached Mt. Schmücke during different cloud events. Cloud water was collected simultaneously using Winkler single stage sampler and analysed for the solute mass of these components*

whereas chloride played only a minor role (Figure 8a). The concentration changes in the Schmücke cloud water are very well correlated to the changes observed in the Goldlauter aerosol for nitrate, sulfate, chloride and nitrite. As expected, for the inorganic ions on average high scavenging coefficients were found. Beside heterogeneous nucleation also entrainment of particles and gases from the sub-cloud layer is assumed. The amount of water soluble organic compounds (WSOC) was found to be in the same range (see Figure 9) like the scavenged inorganic material, indicating the important role that organic particles play as part of cloud condensation nuclei.

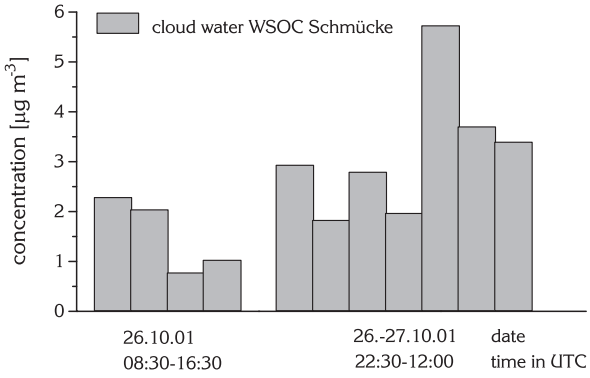



**Figure 9** *The amount of water soluble organic carbon (WSOC) observed in cloud water samples from 26 and 27 October 2001*

Nitrous acid ($HNO_2$) is produced via heterogeneous processes from $NO_2$ on adsorbed water on different surfaces. In Goldlauter a mean $HNO_2$ to $NO_2$ ratio of 0.015 was found, significantly higher than the contribution from direct emissions (on average 0.008) and an indication of additional formation of $HNO_2$ on ground and wet aerosols. About one fourth of the measured N(III) occurred in the aerosol phase (Figure 8d). The concentration of nitric acid ($HNO_3$) was very low because of nearly 100 % relative humidity and the high solubility of this gas. Up to 30 times more N(V) was found as inorganic nitrate in the aerosol phase (Figure 8c).

## CONCLUSIONS

For the evaluation of the chemical cloud water and aerosol data the description of the events by cloud physical data is essential. The aerosol particle number concentration measured at the three experimental sites simultaneously showed highest values at the valley station Goldlauter before the air masses entered the cloud. The sum of the cloud interstitial aerosol number and the cloud droplet number FSSP>5$\mu$m results exactly in the aerosol number at site Gehlberg after cloud. This behaviour was found for all FEBUKO 2001 cloud events indicating a particle loss by cloud processing and deposition processes during air mass transport over complex terrain. Nitrate was mostly the dominant anion in the aerosol and also in the cloud water phase. Similar observations, i.e. replacement of sulfate by nitrate, were made during many field experiments at other sites, e.g. at Mt. Brocken (10). After the drastic decrease in emissions of sulphur dioxide and dust the importance of nitrogen oxides being atmospheric pollutants increased markedly. Nitric acid and nitrate are now often the main input for acidification of ecosystems in Europe and North America. Beside inorganic material, water soluble organic compounds have been found to be important parts of cloud condensation nuclei.

### *Acknowledgements*

We would like to thank our colleagues from Institute for Tropospheric Research Leipzig, Zentrum für Umweltforschung Universität Frankfurt, Technical University Darmstadt as well as Deutscher Wetterdienst (station Schmücke) and Umweltbundesamt (station Schmücke) for excellent co-operation in the field measurements. This work was supported by the German BMBF (07ATF01; 07ATF40).

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***Sažetak***

KEMIJSKA I FIZIKALNA KARAKTERIZACIJA NISKIH OBLAKA: REZULTATI PRIZEMNO PROVEDENOG EKSPERIMENTA UNUTAR OBLAKA FEBUKO

Oblaci bitno utječu na prijenos i pretvorbe onečišćenja zraka. U sklopu projekta FEBUKO (Field investigations of budgets and conversions of particle phase organics in tropospheric clouds - Terenska istraživanja sadržaja organskih lebdećih čestica i njihovih pretvorbi u troposferskim oblacima) istražuju se fizika i kemija atmosferskih aerosola, uloga njihova kemijskog sastava pri stvaranju oblaka, kao i kemijske pretvorbe koje se dešavaju u oblacima. Navedena istraživanja se provode prizemnim eksperimentom u oblaku na mjernom mjestu smještenom na vrhu planine Schmuecke (Thuringian Forest, Njemačka). Istraživana su plinovita onečišćenja zraka, aerosoli, vodene kapi, te načini njihova nastajanja (izvori), odnosno njihova nestajanja (ponori) unutar oblaka. Iako su prvenstveno istraživane vrste i ponašanja organskih spojeva (tj. organske kiseline, peroksidi, organski ugljik, čađa), pažnja je također posvećena ulozi topljivih anorganskih tvari koje predstavljaju pretežiti dio jezgara kondenzacije. U ovome su radu prikazani rezultati prvog pokusa provedenog 2001. godine.

**KLJUČNE RIJEČI:** *aerosolna komora, atmosferski aerosol, razdioba kapljica po veličini, sadržaj vodene kapljevine, visina baze oblaka, vlažni difuzijski odvajač*

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