

A coupled field and modelling study on aerosol - cloud interaction

(AFO 2000 projects FEBUKO (FKZ 07ATF01) and MODMEP (FKZ 07ATF40))

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Introduction

The FEBUKO and MODMEP projects within AFO 2000 will improve the understanding of tropospheric multiphase processes and especially the interaction of aerosols and clouds with an emphasis on organic particle constituents. Field experiments on aerosol and cloud chemistry and physics, model development and model application are combined to investigate chemical and physical transformation of particles within a cloud passage.

A complex experimental data set was provided by two field campaigns. In MODMEP the development is directed towards a cloud module which combines a complex multiphase chemistry with detailed microphysics. The description of both is given with high size resolution of the drop spectrum. The influence of simplifications within single components and the kind of their coupling on the simulation results is investigated for different tropospheric situations. Furthermore, techniques are provided and tested which allow an effective implementation of multiphase processes in multidimensional cloud and chemistry-transport models.

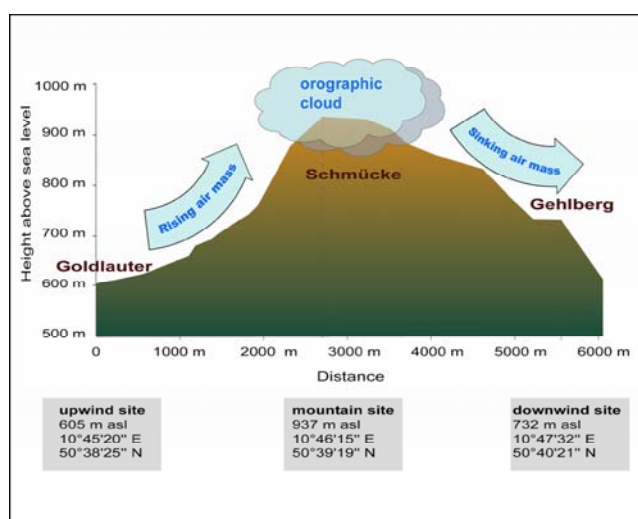


Figure 1: Investigation area

The FEBUKO experiments at the three research sites in the Thüringer Wald (Goldlauter, Schmücke and Gehlberg) were carried out in the autumn of 2001 and 2002, respectively, to characterize the aerosol and cloud water with respect to their chemical composition and their physical properties (Figure 1). The speciation of organic components was one of the most important tasks for the different size classes of the particle phase and in cloud water. The air masses encountered in the experimental region are of anthropogenically influenced origin and have then been exposed to biogenic emissions on their way from the Rhein-Main area to the Thüringer Wald.

Experimental

At the two valley measurement sites (Goldlauter (GL) – upwind site, 605 m asl, and Gehlberg (GB) – downwind site, 732 m asl) and at the mountain site (Schmücke (SM), 937 m asl) a complex set of meteorological parameters, trace gas components, cloud parameters and particle characteristics was determined. The sampling of particles using filter samplers and impactors for the chemical constitution measurements was carried out at the valley stations together with measurements of particle number concentrations, size distributions and hygroscopic properties. On top of a 20 m research tower a variety of different cloud water samplers were operated on the Schmücke. The interstitial aerosol and the cloud droplet residues were collected and physically characterized by mean of a counterflow virtual impactor (CVI) and an inlet to interstitial particles (INT) as well.

The flow connection between the three stations is an important prerequisite for the whole experiment. Hence, special tracer experiments, measurements of number and size distribution of particles as well as trace gas concentrations were performed. In addition, the synoptic experimental conditions were carefully investigated and flow simulations for the complex terrain area are currently in progress.

Results and discussion

In both campaigns in 2001 and 2002 a total set of 14 cloud events was identified for intensive measurements. The most important conditions of (i) a connected flow, (ii) an orographic cloud and (iii) good data coverage were best fulfilled during three events. The results within the present contribution refer to a 15 hours measurement period on 26/27-October 2001 (22:00 to 13:00 UTC).

On the modelling side, at the time of writing of this contribution simulations were made with an air parcel travelling from Goldlauter to the top of the mountain into the orographic cloud. The goal of the simulations was to investigate the multiphase chemistry occurring in orographic clouds and to understand the interaction of particle phase and gas phase of atmospheric trace constituents due to phase transfer and chemical transformation. Simulation results have been compared with cloud water measurements in order to interpret the experimental data and for validation of the multiphase chemistry model.

Physical aerosol characterization

Particle number concentration

Particle number size distributions were measured in GL and GB using a Differential Mobility Particle Sizer (DMPS) system. These measurements are complementary to the interstitial (INT) and Counter Flow Virtual Impactor (CVI) number size distribution measurements on the mountain station Schmücke (SM). In Figure 2, mean number size distributions at all sites are plotted for 27th of October 2001, 0:00 to 13:00 UTC. The black and green curves show the number size distribution measured in GL and GB while the red one represents the interstitial aerosol at the top of Schmücke in cloud. The peak number concentrations of the Aitken modes at GB and Schmücke are adjusted by a factor of 1.13 to the peak concentration at GL to recognize also small deviations. By this adjustment, the rising edge in the small particle size range between 25 and 60 nm of both curves are becoming identical not only qualitatively but also quantitatively. The mean number size distributions between GL and GB do not show a significant difference.

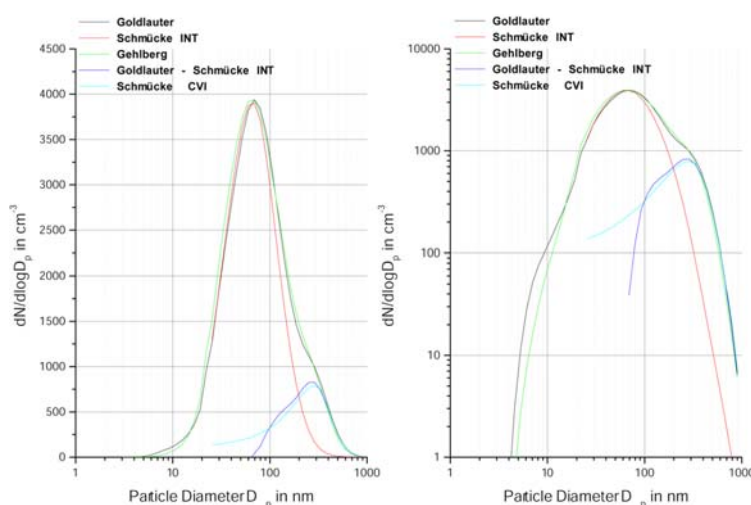


Figure 2: Particle number size distribution at Goldlauter (GL), Gehlberg (GB) and Schmücke (SM) on Oct. 27, 2001. The black and green curves show the mean size distribution at GL and GB, respectively, whereas the red and light blue curves represent the interstitial (INT) and CVI size distributions. The size distributions of SM INT and GB have been normalized the level of GL by a factor of 1.13. Finally the dark blue curve shows the deviation between the GL and SM INT size distribution.

Mean number size distributions of the droplet residues (light blue) and interstitial particles (red) are shown. They have been measured in-cloud at SM during the cloud event in the size range between 25 and 900 nm by two DMPS systems attached to the CVI and INT inlet system. Particles larger than a certain size are expected to become activated, which is demonstrated by the deviation of both distributions above 70 nm. Figure 2 shows this difference (dark blue) and represents the indirect

determination of the CCN number size distribution. This curve agrees well with the direct CVI measurement, which confirms that the phase partitioning due to the droplet activation is successfully observed during the connected flow between GL and SM.

Chemical aerosol characterization

In order to gain a deeper insight into budgets and conversions of specific organic compounds in tropospheric clouds and to have a realistic data set for the model initialisation, one of the aims of FEBUKO is a comprehensive organic speciation at all three measuring sites in addition to standard particle and cloudwater chemical analysis. Organics are usually trace compounds in different atmospheric phases which make their determination a challenging task. A variety of sampling devices was applied, some of them exclusively for organic speciation. With impactors, filters and spray collectors aerosol particles were sampled. Sorbent-filled cartridges were used for gas-phase measurements and four different types of cloud water samplers collected the liquid phase on the mountain. Most of the instruments give time-resolved information about organic concentration levels with a sampling time interval of 2 hours. Complementary to this the impactors allow insights into the size distribution of condensed organic material before and after cloud processing. After the campaign the samples were analysed using analytical equipment like gas chromatography/mass spectrometry (GC/MS), high performance liquid chromatography/mass spectrometry (HPLC/MS) or capillary electrophoresis (CE). With these field measurement equipment it was possible to create an extensive pool of data for dozens of organic substances in their respective most relevant atmospheric phases. Aliphatic and aromatic aldehydes and ketones as well as other volatile organic compounds (VOCs) like short-chain alkanes, alkenes, and volatile aromatics could be identified and quantified in the gas phase on a time-resolved basis. Depending on their polarity some of them can be scavenged by the cloud and therefore they were measured also in the liquid phase. The possible photooxidation products of carbonyls and VOCs such as higher oxygenated species like monocarboxylic acids in the gas phase and in cloud water and dicarboxylic acids in the particle phase and in cloud water were analysed in a time-resolved manner. Size distributions before and after the cloud passage as well as the corresponding liquid-phase concentrations are as well available for lower vapour pressure compounds such as long-chain alkanes, alcohols, sugars, fatty acids, dicarboxylic acids, and several biogenic compounds such as pinonaldehyde, squalene, and others. Bulk concentrations from filters for interstitial particles allow us to calculate directly the in-cloud scavenging for some of these compounds. More details of the organic analysis can be found under http://projects.tropos.de:8088/af02000g3/FEBUKO_dateien/febuko.html.

The complex data set obtained in the FEBUKO field experiments is of huge importance for the MODMEP model initialisation and validation. Besides, we can interpret it by comparing, correlating and balancing concentrations of selected species for different atmospheric phases, different times and different particle sizes. In combination with the model results we may now be able to achieve a better understanding of phase partitioning and chemical multiphase processes of tropospheric organic material.

Model initialization

The model developed within the course of the MODMEP project is initialized by means of the particle composition based on measurements with a five stage Berner impactor at the upwind site GL as described before. In the case of the cloud event on the 27th of October 2001, most of the mass was found on the third impactor stage, which collects aerosol particles with a diameter between 0.42 μm and 1.2 μm . Nitrate, sulfate, ammonium, organic and elementary carbon are the main components of the aerosol. In order to correct for losses encountered by the Berner impactor in the case of chloride and nitrate, data obtained with the Steam Jet sampler were used and distributed over the impactor stages according to the relative size distribution of each of these species derived with the Berner impactor. The alkaline and earth alkaline metal initial concentrations, i.e. sodium, magnesium, calcium and potassium, are taken from the Berner impactor. Other metal ion concentrations, i.e. manganese, iron, copper, aluminium and zinc, are initialised according to measurements made with a High-Volume-Sierra-Anderson (PM₁₀) sampler. These measure total contents are distributed over the

impactor stages as the mass determined by the impactors. The initialization of the dicarboxylic acids is based on impactor and spray collector measurements. To calculate the water mass of Goldlauter, aerosol growth factors were used. The used growth factors were measured during the ACE2 campaign, and are in a good agreement with the measured growth factors by a HTDMA analyzer within the FEBUKO field campaign.

In the gas phase NO, NO₂, O₃, and SO₂ were measured every 5 seconds with commercial instruments. For the measurement of HNO₂ and HNO₃ the wet effluent diffusion denuder technique was used. The measured organic species were implemented as stand-alone species or were lumped together into groups as used in the regional atmospheric chemistry mechanism RACM. Implemented stand-alone species are: formaldehyde, ethane, ethene, formic acid, glyoxal, methylglyoxal, and isoprene. Measured lumped gas phase species considered are aldehydes, ketones, unsaturated monoaldehydes, acetic acid and higher acids. For example 19 measured aldehydes were summed up to the lumped species 'ALD'. For some unmeasured species initial concentrations were adapted from the CAPRAM standard scenario 'urban' due to a reasonable agreement between measurements and the above-mentioned scenario.

Tracer experiments were carried out within the FEBUKO field campaign in order to verify the existence of a connected flow and to determine the transport time between the three sampling stations. Based on the experiments a realistic transport time between Goldlauter and Schmücke of 10-20 minutes resulted, depending on meteorological conditions. For the initial wind speed, data from the measurement site of the German weather service station located in Meiningen was used. For the cloud event on the 27th of October 2001 at 9.00 UTC an initial wind speed of 4 m s⁻¹ was applied, which led to a simulation time of about 11 minutes from the downwind site to the summit. For the simulations described here, a constant size-independent deposition velocity of 10⁻³ s⁻¹ was considered.

Coupled time-integration of detailed microphysics and complex multiphase chemistry in a size resolved cloud box model

To better understand the interaction, effects and evolution of the different physico-chemical processes taking place in the atmosphere their modelling requires a detailed description of all transformations with equal rigor. The most recently available models focus either on detailed microphysics or complex multiphase chemistry. In the framework of the joint AFO2000-project MODMEP the air parcel model SPACCIM ("Spectral Aerosol Cloud Chemistry Interaction Model") was developed for the description of cloud processes by coupling complex multiphase chemistry and detailed microphysics. The description of both process groups is given for a size-resolved particle/drop spectrum. Either the movement of the air parcel can follow a predefined trajectory (e.g., simulated by the regional model system LM-MUSCAT) or the vertical velocity is calculated for a buoyant parcel in prescribed environmental conditions. Entrainment and detrainment processes are included in a parametrized form. The model allows a detailed description of the transformation of gases and particles shortly before cloud formation, during the cloud life time and shortly after cloud evaporation.

Treatment of multiphase processes

The governing equations are the mass balance equations for a size-resolved particle/drop spectrum in a box model. The spectrum is described using a sectional approach. The prognostic microphysical variables for each bin are water mass, total and soluble particulate mass as well as particle number. The model considers growth/shrinking and impaction of aerosol particles as well as nucleation, condensation/evaporation and collision-coalescence of drops as most important physical processes. One important feature of the model is the description of the water phase transfer feedback on water vapour and air temperature (latent heat release) which is done in an iterative way to avoid overestimation of super-saturation (and, therefore, nucleation) especially at cloud base. The model accounts for the fact that larger aerosol particles do not have enough time to reach their equilibrium size at high relative humidities near 100% due to the faster changing environment.

The spectral multiphase chemistry model considers two types of chemical reactions:

- Forward reaction types in gas and aqueous phase including photolysis and temperature dependent reactions,

- Equilibrium reaction types, considered as forward and backward reaction.

The phase transfer is parametrized by the Schwartz approach with the hypothesis of well mixed droplets.

The applied mechanism (including phase transfer and kinetic constants) is given as an input file. Therefore, a high flexibility concerning changes in the chemical mechanism is ensured, and the replacement of the entire reaction system is also possible (Wolke et al., 2001). The performance of the model was shown for simple chemical test mechanisms (with only inorganic chemistry) as well as for very complex mechanisms of the CAPRAM family particle phase organic chemistry in a varying degree of complexity dependent of the CAPRAM version.

Coupling scheme and time integration

The model variables can be grouped into microphysical variables, chemical variables and mass fluxes between different particle/droplet classes caused by microphysical exchange processes (e.g., by aggregation, break up, condensation). These mass fluxes are schematically shown in Figure 3. When two particles coagulate, for instance, their masses are added to the resulting particle class assuming internally mixed aerosol in each class. The feedback of changes in the chemical composition by gas scavenging and chemical reactions on microphysical processes (e.g., water condensation growth rates via changes in surface tension and the Raoult term) is also implemented. The activation of droplets is explicitly described in the microphysical model.

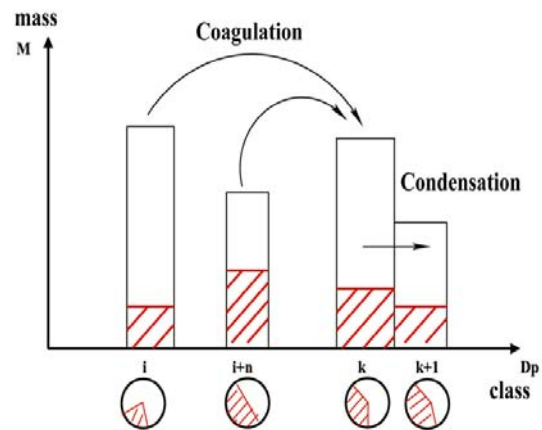


Figure 3: Schematic representation of mass transport between several sections due to microphysical processes. The red hatches part represents the mass fraction of one selected species in the corresponding section.

The time integration scheme for solving the multiphase problem is based on the multistep implicit method (Backward Differentiation Formula) widely used for the integration of stiff differential equations. In our approach, the resulting linear sparse systems are solved exploiting the properties of the Jacobian (sparsity, block structure, different types of coupling). An approximate matrix factorization to decouple the microphysical transport terms and the other parts of the Jacobian is possible. This is seen as an operator splitting at the linear algebra level and yields a computing gain (Wolke and Knoth, 2002). In addition to the higher order BDF scheme, the non-autonomous second order Rosenbrock method is implemented, presenting a low computing effort and showing a satisfactory accuracy. The model SPACCIM is evaluated with data from the FEBUKO field campaign and other case studies from literature. It offers several parameter setups allowing sensitivity studies to reach optimal runs for each studied case.

Microphysical model results

Figure 4 shows the cloud liquid water content (LWC, left) and drop number concentration (right) on Schmücke for the event 26/27th of October 2001. The model calculates the LWC adiabatically which leads to an overestimation of about 25% compared to the findings of the three different measurements carried out. The time dependent structures are represented rather well. In contrast to the LWC drop number depends on transport time from Goldlauter to Schmücke. Two model cases (red line: slow transport, green line: fast transport) are compared with measurement data. Drop number highly depends on the vertical velocity and, therefore, super-saturation especially at cloud base. The faster the transport and the higher the vertical velocity, the higher is the super-saturation and the more drops are activated.

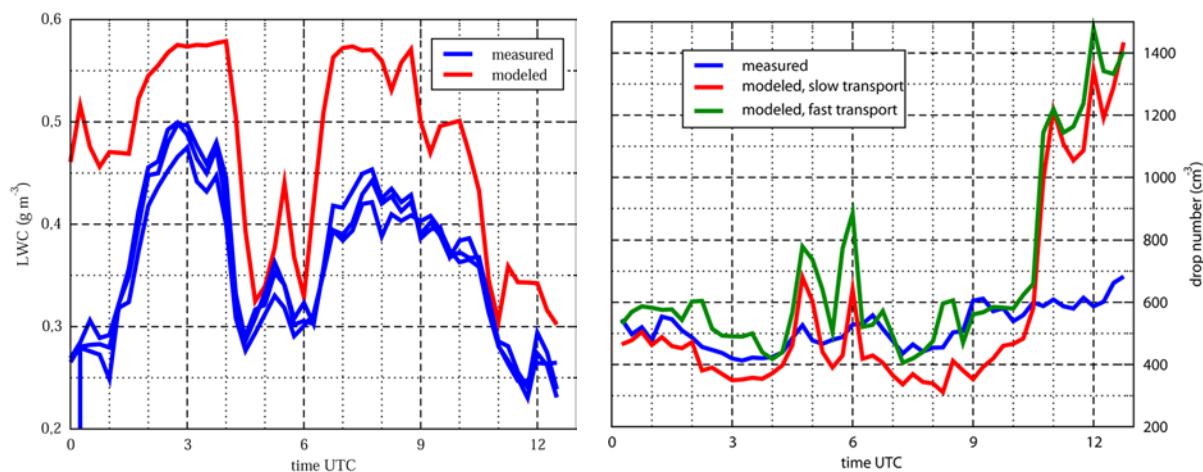


Figure 4: Cloud liquid water content (LWC, left) and drop number concentration (right) on Schmücke for 2001-10-26/27

High LWC corresponds to a low cloud base and a rather gentle terrain (compare Figure 1) connected with weak updrafts leading to the lowest drop numbers in the model (2-4 UTC, 7-9 UTC). The opposite is true for low LWC: steep orography with high velocities leads to (unrealistically) higher drop numbers in the model (4 UTC, 6 UTC, 11-13 UTC). These strong variations in the modelled drop numbers are not reflected by the experimental data where drop numbers are rather constant between 400 and 600 cm⁻³.

Generally, drop numbers fit very well with the experimental findings for LWCs above 0.4 g m⁻³, corresponding to a rather low cloud base. For lower LWCs the model seems to overestimate the vertical velocity and, therefore, super-saturation and activation.

Simulations with the coupled chemistry microphysics model SPACCIM and CAPRAM

By means of SPACCIM, simulations of the hill cap cloud passage experiment taken place on 27th of October 2001 were carried out. Calculations with an air parcel following a trajectory from the upwind site to the summit station Schmücke were performed. The simulation results have been compared to experimental data from the summit station.

The applied explicit aqueous phase radical mechanisms consist of CAPRAM 2.3 (Herrmann et al., 2000) and CAPRAM 2.4 (MODAC-mechanism, Ervens et al., 2003). The gas phase chemistry is described by the regional atmospheric mechanism RACM (Stockwell et al., 1997). Phase transfer processes are treated by means of the resistance model of Schwartz considering Henry's equilibrium, gas phase diffusion and mass accommodation. For the simulations a highly resolved particle spectrum is considered. A total number of 64 size bins ($2.3 \cdot 10^{-3} \mu\text{m} < d < 7.5 \cdot 10^3 \mu\text{m}$) is considered, where multiphase chemistry occurs in droplets where the LWC exceeds 10⁻⁹ g m⁻³. In the near future a feedback from the chemistry to the microphysics will also be implemented.

For the initial wind speed data from the measurement site of the German weather service station located in Meiningen was used. For the cloud event on 27th of October 2001 at 9:00 UTC an initial wind speed of 4 m s⁻¹ was applied, which led to a simulation time of about 11 minutes from the upwind station to the summit. For the simulations a constant deposition velocity of 10⁻³ s⁻¹ was considered.

Simulation results

For the respective cloud event on 27th of October 2001 the exact time for the simulations was fixed at 9:00 UTC due to a good agreement between the microphysical model and the measurement with regards to the total LWC and number concentration. At the upwind station a LWC of about 10⁻⁴ g m⁻³ exists. At the summit station the total LWC will reach a value of 4.9 · 10⁻¹ g m⁻³. At the end of the simulation, at the top of the mountain most of the LWC will be in the droplets with a diameter

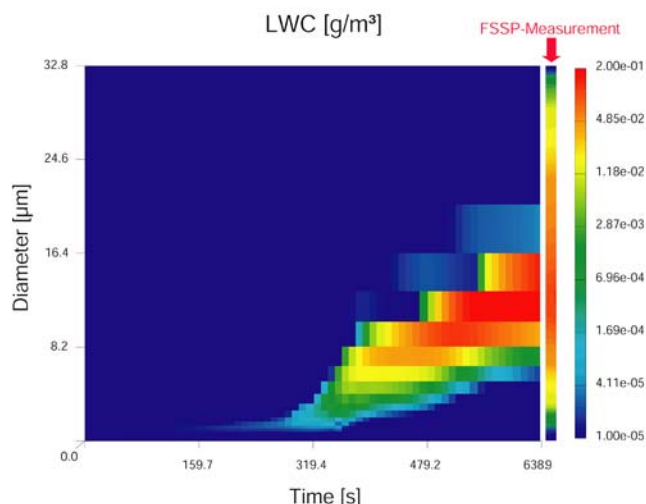
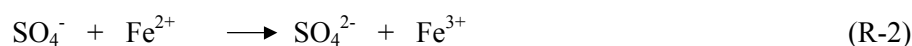


Figure 5: Size and time dependent evolution of the LWC between the luff and the summit station, comparison between measurement and simulation result at Schmücke

sampled cloud droplets with a diameter bigger than $3.5 \mu\text{m}$. At the summit the calculated SO_4^{2-} concentration reached a value of $4.1 \cdot 10^{-5} \text{ mol l}^{-1}$, HSO_4^- a value of $3.8 \cdot 10^{-7} \text{ mol l}^{-1}$ and H_2SO_4 a value of $1.6 \cdot 10^{-12} \text{ mol l}^{-1}$. As can be seen from the plot there is a good agreement between the calculated and measured value. As expected, due to uptake of liquid water the concentration decreases in time. At the summit, in the small droplets with less water content there will be a high sulfate concentration. In the small interstitial aerosol particles the sulfate concentration reaches values of about $2 \cdot 10^{-1} \text{ mol l}^{-1}$. In the size range where most of the liquid water can be found a sulfate concentration of circa $5 \cdot 10^{-5} \text{ mol l}^{-1}$ occurs. Analyzing the sources of sulfate, it can be said that sulfur oxidation proceeds mainly via the oxidation of bisulfite by hydrogen peroxide, i.e.



Before actually reaching cloud conditions or supersaturation and hence during the activation process, in the small droplets sulfur oxidation via aqueous phase radical chemistry involving transition metal ions plays a role and contributes to S(IV) to S(VI) conversion. At the final stage of this complex radical pathway sulfate is formed by the oxidation of Fe^{2+} by the so-called sulfate radical anion $\text{SO}_4^{\cdot -}$:



Sulfate production will be controlled by the SO_2 uptake from the gas phase, process significantly influenced by the pH value. The model exactly reproduces the measured H^+ concentration of $6.3 \cdot 10^{-5} \text{ mol l}^{-1}$ at Schmücke.

A further detailed analysis concerning the transformation of inorganic species, e.g. nitrate, chloride, the speciation of transition metal ions, e.g. iron, copper, manganese, and the aqueous oxidation of organic compounds, e.g. acetaldehyde, glyoxal, oxalate, is ongoing.

between 8 and $16 \mu\text{m}$. The maximum of the LWC distribution, as can be seen from Figure 5, occurs at droplets with a diameter of circa $12 \mu\text{m}$. In Figure 5 also the LWC spectra measured by an FSSP (Forward Scattering Spectrometer Probe) is plotted. It can be seen that the measured spectrum of the orographic cloud is broader than the calculated spectra. This discrepancy could be caused by a too broad spectra produced by the FSSP a too narrow spectrum resulted from the microphysical model or a combination of both. Activation of the aerosol particles will occur after a simulation time of about 300 s .

In Figure 6 the size-resolved sulfate concentration is represented. The concentration profile represents the sum of sulfate concentration over the size bins with a diameter bigger than $3.5 \mu\text{m}$. At the summit the concentration was measured with a cloud water bulk collector. The collector had

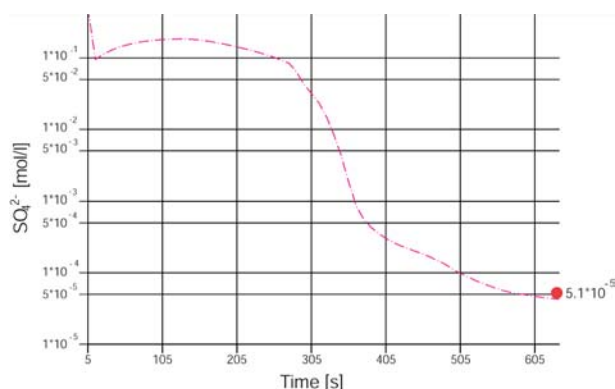


Figure 6: Size-resolved SO_4^{2-} concentration profile, comparison between measurement and simulation result at the summit, the red point representing the experimentally determined value

Summary and outlook

A coupled version of detailed microphysics and a complex multiphase chemistry in a box model is realized, allowing a high flexibility concerning the use of chemical mechanisms and the simulation of case studies like the FEBUKO field experiment. In the simulations of the latter experiments using SPACCIM and CAPRAM for some species there is a quite good agreement between the measurements and model results, with deviations below a factor of two, e.g., NO_3^- , SO_4^{2-} , K^+ , HCOOH , CH_3COOH . For other species, e.g. Fe(II)-Fe(III), HCHO , bigger differences were encountered. It has to be noted that some of the negative deviations are due to the fact that for the current model results the input aerosol size distribution is only considered for up to $D_p = 900$ nm. A coarse mode treatment is under development and may lead to better agreement for species such as most of the cations. For a better description of organic chemistry, simulations with the CAPRAM 2.5 mechanism will be conducted. The CAPRAM 2.5 mechanism consisting of the CAPRAM 2.4 (MODAC mechanism) reduced, coupled to the CAPRAM organic extension considers the oxidation of organic compounds with up to four carbon atoms. Also in the near future simulations with an air parcel travelling from the upwind site, passing through a hill cap cloud, and then transported to the downwind site will be carried out to better chemical modifications of the particle ensemble after a single cloud process under real field conditions. The SPACCIM model development initiated after MODMEP will continue to further refine the available model framework. The CAPRAM mechanism will be continuously updated and last, but not least, the Schmücke hill-capped cloud experimental site is ready for further focussed ground based aerosol-cloud-interaction experiments with emphasis on organics under real conditions and hence complementary to more specialized laboratory experiments.

Acknowledgements

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