

# SPACCIM SIMULATIONS OF THE MULTIPHASE CHEMISTRY OCCURRING IN OROGRAPHIC HILL CAP CLOUDS

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## Introduction and model outline

The parcel model SPACCIM (Spectral Aerosol Cloud Chemistry Interaction Model) has been applied to investigate the effect of multiphase cloud processing on tropospheric aerosol particles and trace gases resulting from a passage through an orographic cloud at Mt. Schmücke (Thuringia, Germany) during the joint research project FEBUKO (field investigation of budgets and conversions of particle phase organics in tropospheric cloud processes) in October 2001 and 2002 (Herrmann et al., 2005a). Measurements were made at three sampling stations (upwind site / summit site Schmücke / downwind site). Simulations were made with an air parcel traveling along a trajectory from Goldlauter across the orographic cloud to Gehlberg. The central objective of the simulations was to investigate the multiphase processing of the aerosol occurring in orographic clouds and to understand the incorporation and transformation of inorganic as well as in particular organic atmospheric trace constituents. Model results have been compared with in-cloud observations at the summit and measurements at the downwind station in order to interpret the experimental data and for validation of the multiphase chemistry model. In total, 14 cloud events were investigated. Out of these, three events (E I, E II; E III) were selected based on detailed analysis of meteorological conditions.

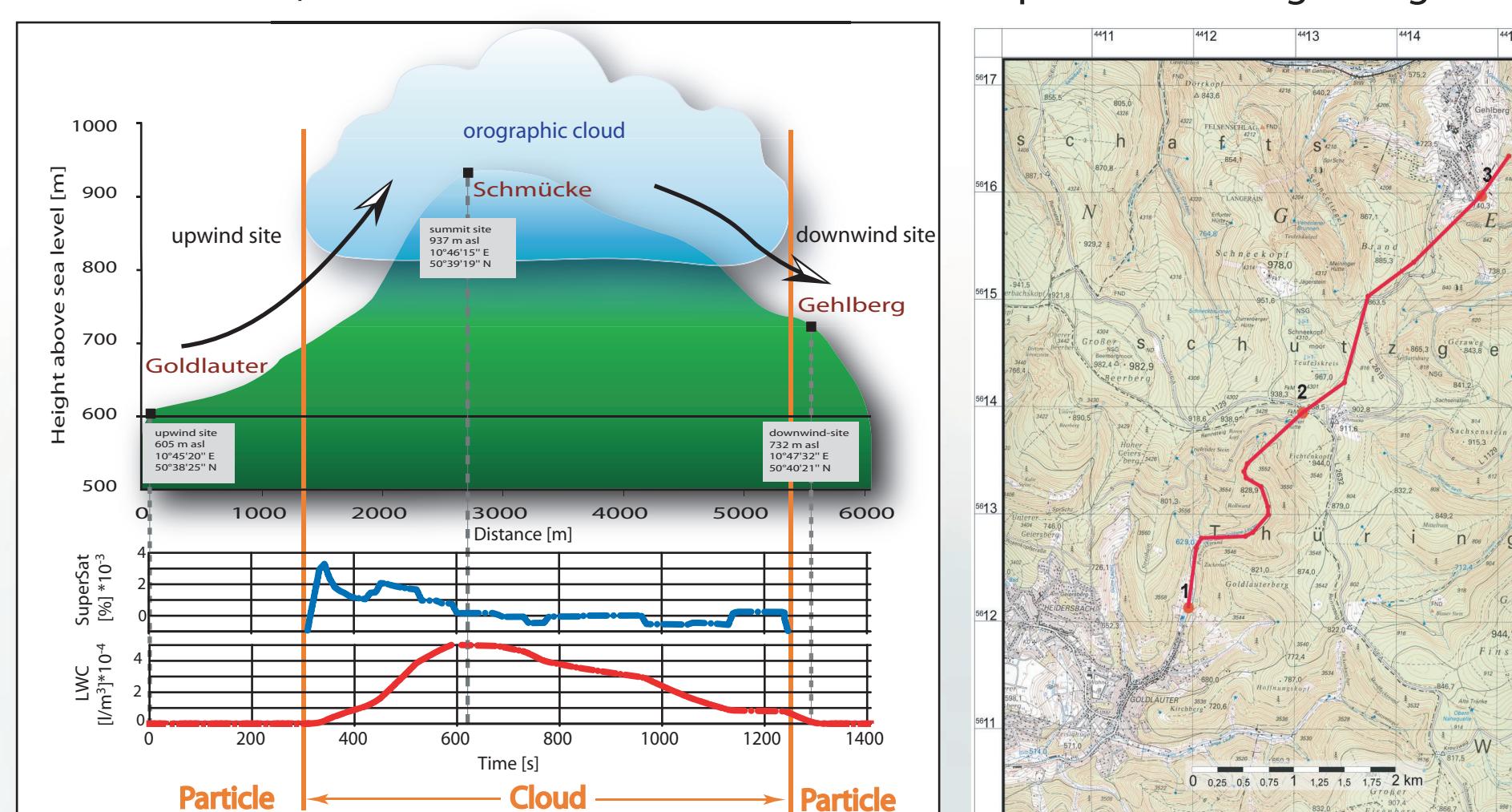


Figure 1: Investigation area: topographic profile and region map with the trajectory (red line).

The air parcel model SPACCIM (Wolke et al., 2005) was developed for the description of cloud processes combining a complex multiphase chemistry with detailed microphysics. The description of both separate processes is performed for a highly size-resolved particle and droplet spectrum. The model allows a detailed description of the processing of gases and deliquescent particles before the cloud formation, under cloud conditions and after cloud evaporation. All microphysical parameters required by the multiphase chemistry model are taken over from the microphysical model. The adiabatic air parcel model contains a detailed description of microphysical processes of deliquescent aerosol particles and droplets, see Simmel et al. (2005). The applied explicit multiphase mechanisms consists of CAPRAM 3.0 (Herrmann et al., 2005b) and the gas phase 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 coefficients. For the simulations a fine resolved particle spectrum is considered. CAPRAM 3.0 contains a complex implementation of aqueous phase inorganic as well as organic chemistry including organic species with up to mainly four carbon atoms. The chemistry mechanism was initialised with physical and chemical data based mainly on the measurements of the upwind site (cp. Tilgner et al. 2005). The initialisation of the particle phase based mainly on measurements with a five stage Berner impactor (see Figure 2) and a DMPS (Differential Mobility Particle Sizer).

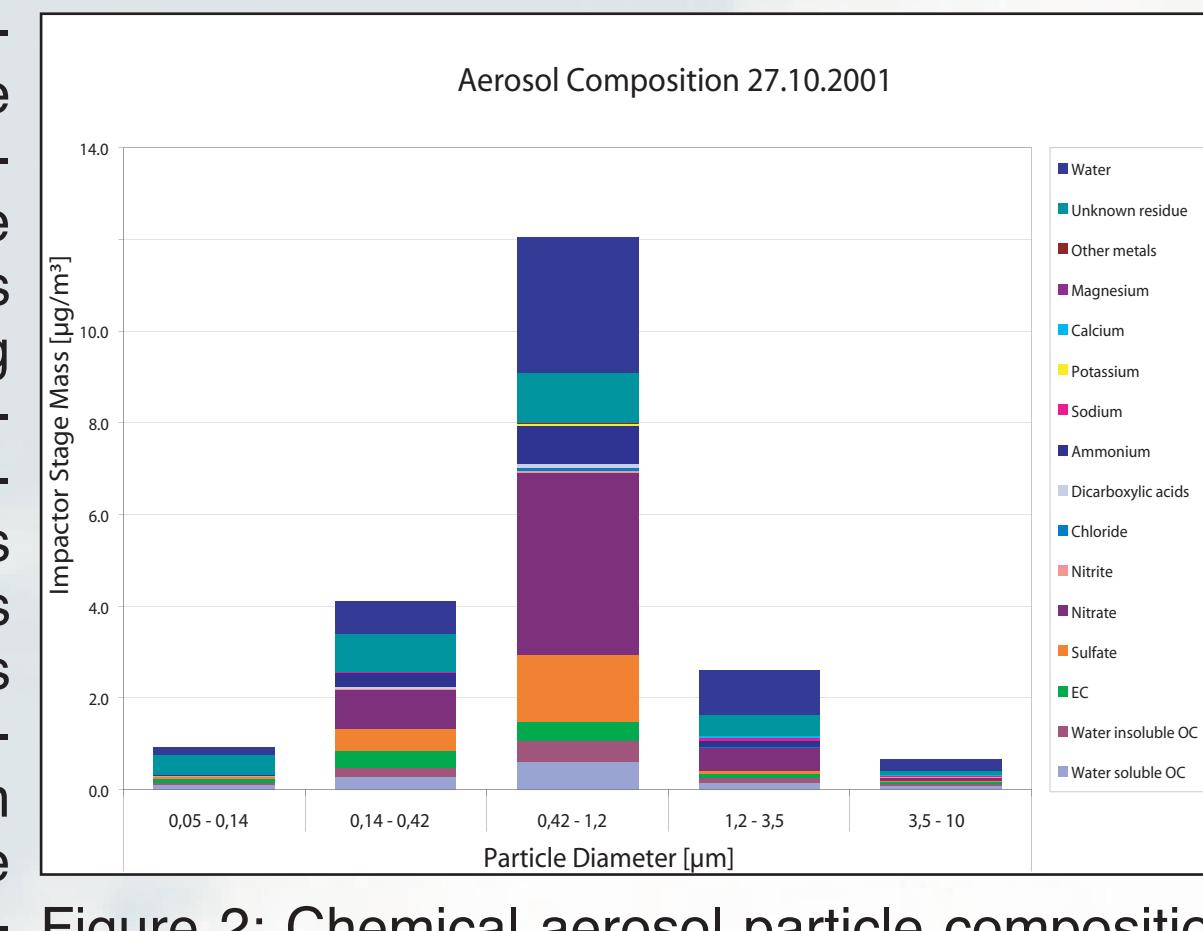


Figure 2: Chemical aerosol particle composition for the cloud event E I (27-10-2001 09 UTC).

## Simulation results and discussion

### Micophysical conditions

As can be seen from Figure 3 the transport of the air parcel takes about 23 minutes from upwind to downwind site. The droplet activation occurs at about 325 s (E I). Consequently, droplets larger than the activation diameter of about 180 nm are activated to cloud droplets with a huge increase of the mean diameter especially within the first 100 s due to the peak of the supersaturation. Therefore, an interstitial aerosol spectrum as well as a cloud droplet spectrum arises from the relatively uniform deliquescent aerosol spectra. The LWC predicted by the model follows the mean diameter as well the corresponding number concentration and reach the total maximum value of about 0.52 g m<sup>-3</sup> at the summit.

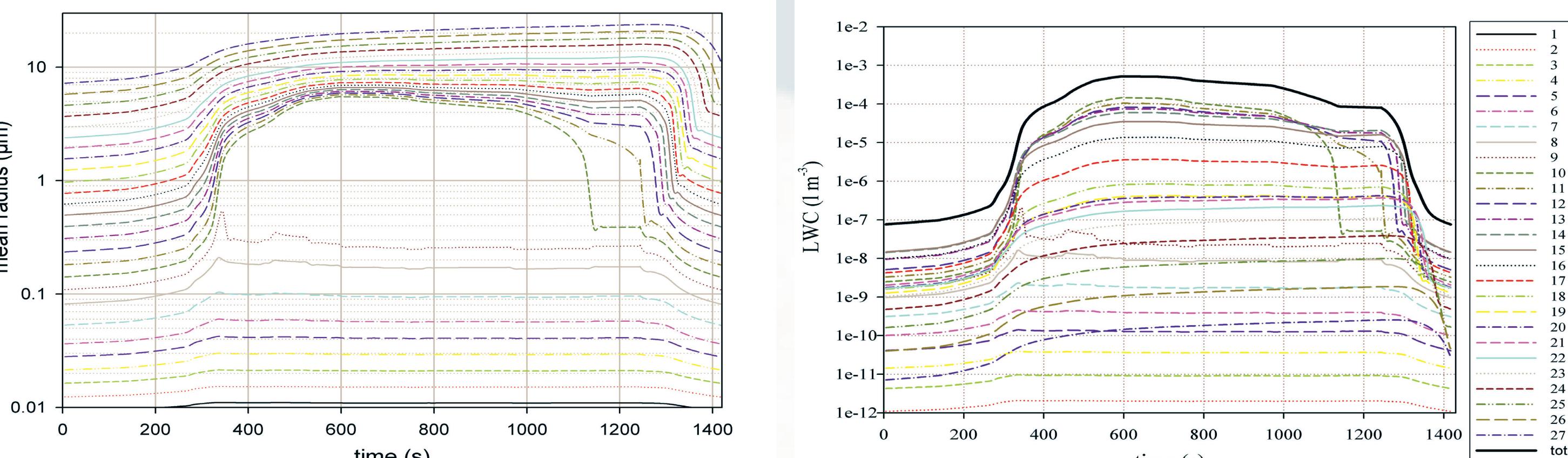


Figure 3: Temporal evolution of mean radius and LWC of all size bins of the particle/droplet spectra for the cloud event E I.

### Radical oxidants

According to the simulation times, the cloud event E I shows a mixed radical regime of typical day and night conditions. However, the event appears to be mainly characterised by a nighttime chemistry regime because of the low available actinic radiation due to the occurrence of high clouds shielding the experimental sites. The gas phase concentrations of the radicals become significantly reduced when the hill-capped cloud forms (Figure 4). In the case of OH, the decrease of the gas phase concentration of about 44 % in the cloud is mainly caused by the efficient uptake of the precursor HO<sub>2</sub> into the cloud and not by the direct phase transfer into the droplets. Compared to the relatively low concentrations of OH and NO<sub>3</sub> in the aqueous phase, HO<sub>2</sub>/O<sub>2</sub> reaches concentrations at the summit of about 2.0·10<sup>-13</sup>. These levels are very small for the hydroperoxy radical which is generally regarded as the most abundant tropospheric aqueous phase radical the concentration level of which was reported to be in the order of 3·10<sup>-12</sup> to 3·10<sup>-13</sup> mol m<sup>-3</sup> in box model calculations (Herrmann et al., 2005b). The strong reduction in the HO<sub>2</sub> aqueous phase concentration is caused by a predominant TMI (transitional metal ion) nighttime chemistry in all three events.

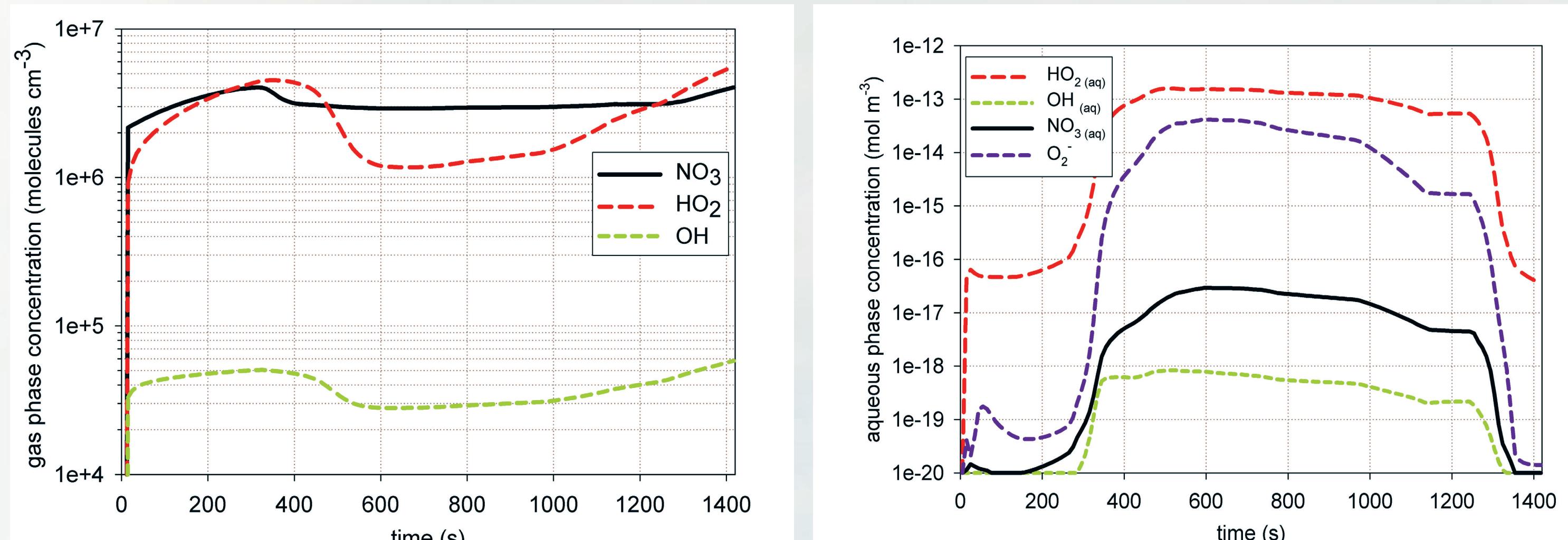


Figure 4: Gas and aqueous phase radical concentrations vs. travelling time for the cloud event E I

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### Organic chemistry

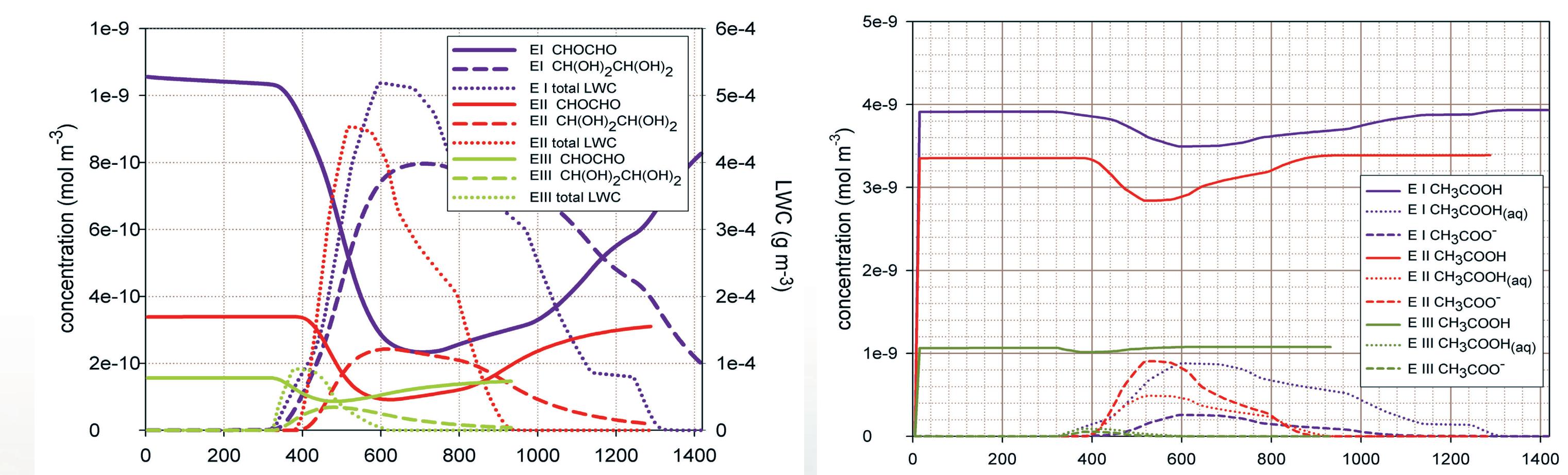


Figure 5: Multiphase concentrations of glyoxal and acetic acid vs. travelling time for the cloud events E I, E II and E III.

Because of the limited cloud passage duration and the low or not available actinic radiation during the events, the radical oxidation of organic compounds is generally quite restricted. Therefore, production of acetic acid which is increased after the cloud passage with approximately 0.6, 1.1 and 1.3 % for E I, E II and E III, respectively, is not dominated by the direct aqueous oxidation of acetaldehyde. The concentration increase is almost solely caused by the aqueous oxidation pathway of the acetylperoxy radical which is efficiently transferred into the cloud droplets (Figure 5). At the summit the gas phase concentrations of glyoxal are decreased of about 72, 56 and 18 % for E I, E II and E III, respectively. Furthermore, hydrated carbonyls such as glyoxal reach their maximum concentrations in the aqueous phase at the highest LWC level (summit) but rather about 100 s later due to the duration of the hydration process.

## Comparison model results vs. measurements

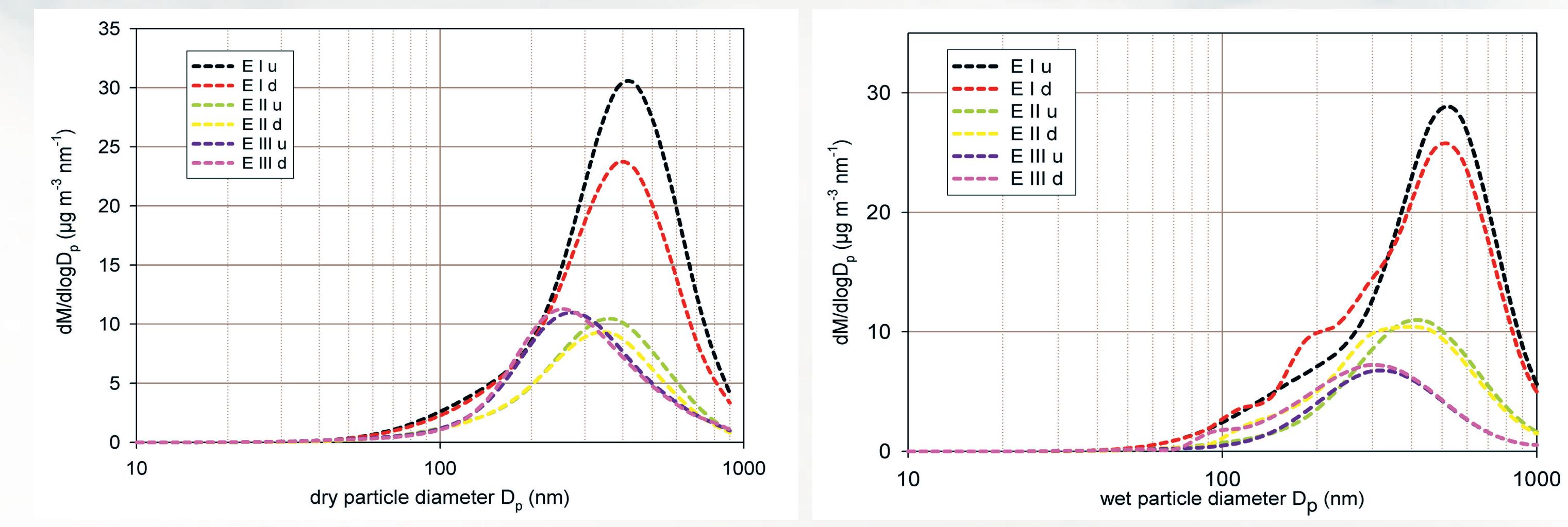


Figure 6: Measured (average of all measured) and calculated [right] spectral distribution of the dry particle mass at the two valley stations (u: upwind site, d: downwind site) for the all treated cloud events.

The dry mass increases slightly before and extensively during the cloud formation as well as decreases with the cloud evaporation due to the uptake of soluble gas phase species followed by back-transfer of such species upon cloud water evaporation (Figure 7). At the end of the simulation the total mass has increased by 0.7  $\mu\text{g m}^{-3}$  or 14 % for event E III. The comparison between the valley stations spectrum shows that the mass increase is limited to a size interval between the activation diameter and about 400 nm (cp. Figure 6). Furthermore the results of the impactor measurements such as the mass increase predominantly within the second impactor stage and the according concentrations are well reproduced by the model.

In general measured and modelled chemical data on both sites correlate relatively well (Figure 8-9). In particular, the best congruencies are observed in the case of compounds with high concentrations such as nitrate with relative difference of just about 5 %. In addition to compounds mainly originating from particles also substances being transferred from the gas phase like H<sub>2</sub>O<sub>2</sub> and organic mono carboxylic acids are in a good agreement with the measurements. Larger discrepancies between the measurements and simulation results exist for the higher carbonyls. The cloud water concentrations of the model are partly more than two orders of magnitude lower than the measured ones. The measured concentrations of the carbonyls are significantly dissimilar from the value which can be derived from Henry solubility calculations, see van Pinxteren et al. (2005). The model is not able to explain these high cloud water concentrations. Other previous field measurements showed similar observation also for other hydrophobic organic compounds such as pesticides (Glotfelty et al., 1987). Possible explanations for these findings discussed in the literature are the adsorption on cloud droplet surfaces (Valsaraj et al., 1993) as well as chemical productions from higher concentrated and soluble carbonyl precursors.

Figure 7: Total dry condensed non-water mass as function of the travelling time for the cloud event E III.

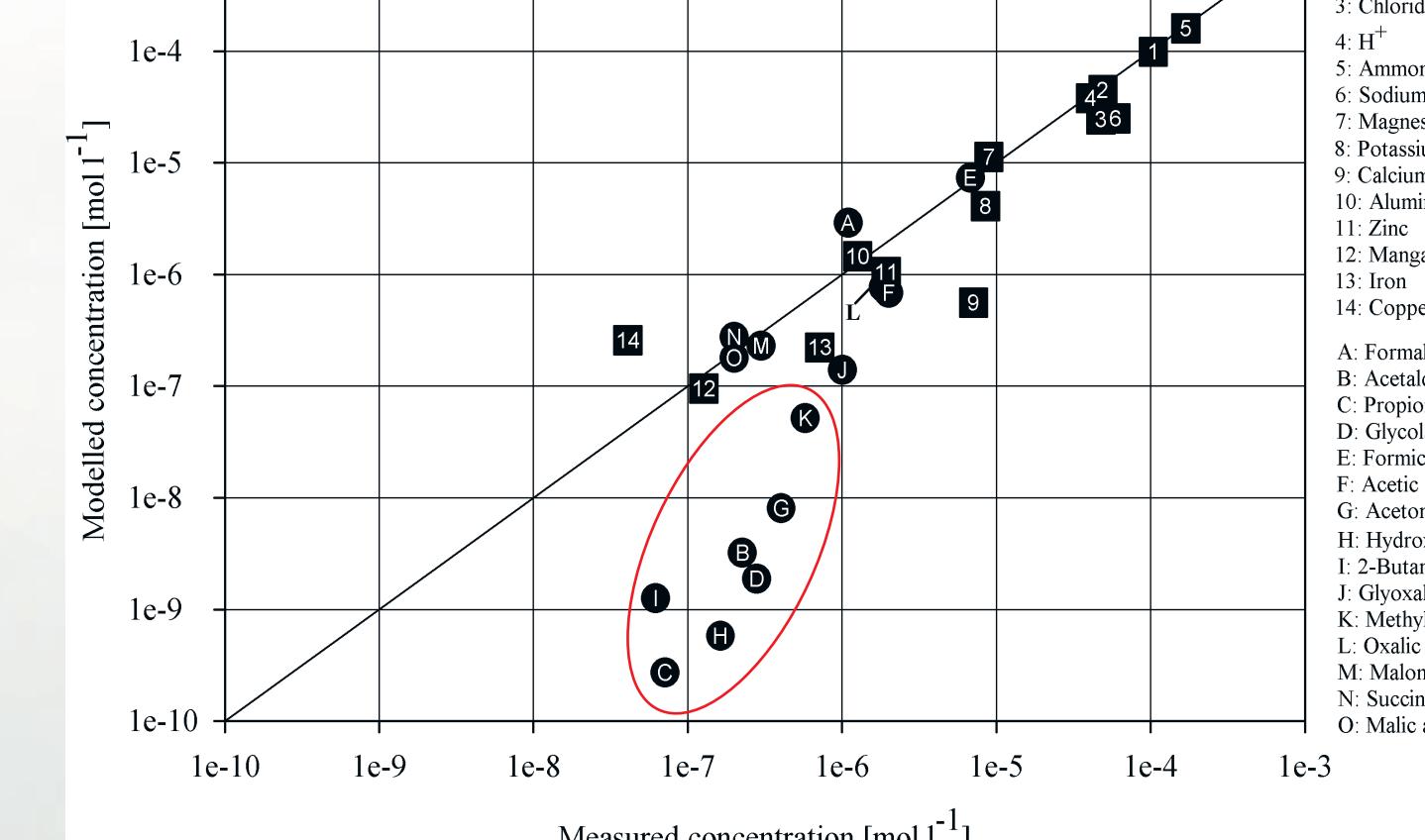


Figure 7: Total dry condensed non-water mass as function of the travelling time for the cloud event E III.

Figure 8 compares measured and modelled cloud water concentrations (mol l<sup>-1</sup>) at the summit for the cloud event E III. The y-axis is 'Modelled concentration [mol l<sup>-1</sup>]'. The x-axis is 'Measured concentration [mol l<sup>-1</sup>]'. Data points are plotted with numerical labels 1-27. A legend lists various chemical species: 1. Nitrate, 2. Sulfate, 3. Chloride, 4. H<sup>+</sup>, 5. Ammonium, 6. Sodium, 7. Magnesium, 8. Calcium, 9. Zinc, 10. Aluminum, 11. Iron, 12. Manganese, 13. Copper, 14. Zinc, 15. Formaldehyde, 16. Acetaldehyde, 17. Propionaldehyde, 18. D-Glycolaldehyde, 19. Ethanal, 20. Acetic acid, 21. 2-Butanone, 22. K-Methylglyoxal, 23. Malic acid, 24. Succinic acid, 25. Oxalic acid, 26. Glyoxal, 27. total.

Figure 8: Comparison between the measured and modelled cloud water concentrations (mol l<sup>-1</sup>) at summit for the cloud event E III.

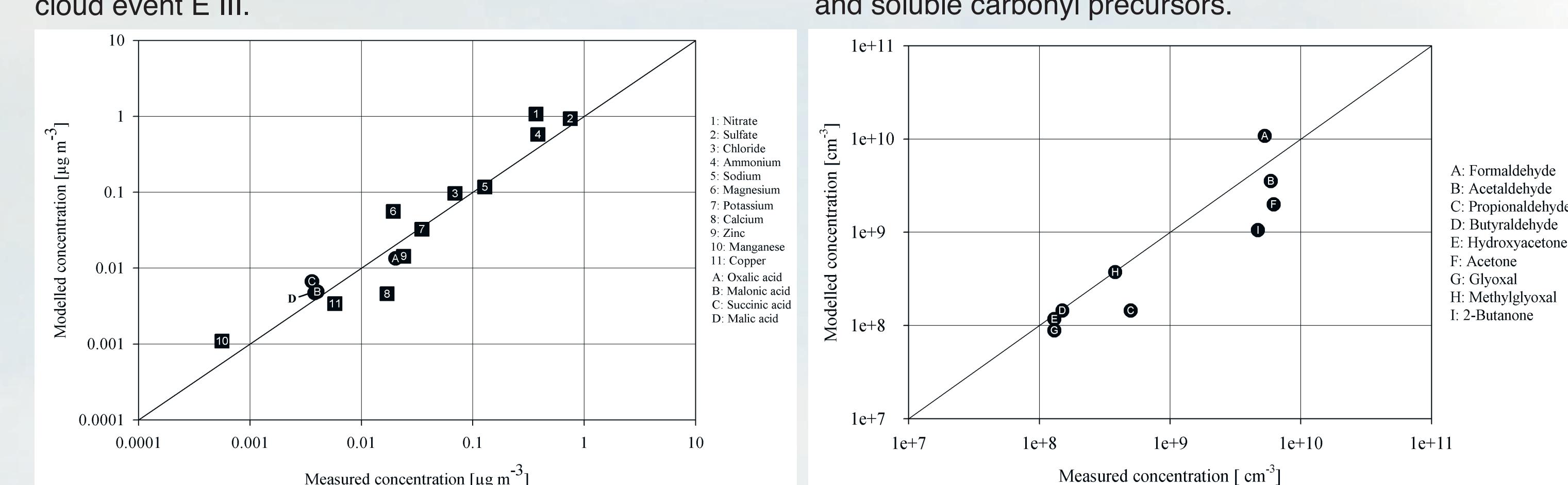


Figure 9: Comparison between measured and modelled particulate matter concentrations ( $\mu\text{g m}^{-3}$ ) [left] as well as gas phase concentrations ( $\text{molecules cm}^{-3}$ ) of organic compounds [right] at downwind site for the E III.

## Summary

SPACCIM simulations of a hill capped cloud experiment were carried out considering detailed microphysics and complex multiphase chemistry (RACM/CAPRAM 3.0). Significant cloud condensation nuclei (CCN) modification with sizes up to about 400 nm, mass productions up to about 0.7  $\mu\text{g m}^{-3}$  and acidification caused by cloud processing was identified in the model in agreement with the experimental findings. The applied model reproduces well the measured data at both sites. However, for organic compounds with low solubilities the cloud water measurements show considerably higher concentrations as expected from both (i) their Henry solubilities and (ii) the complex multiphase modelling as performed here.