

Determination of Organic Compounds during the FEBUKO Hill Cap Cloud Experiments

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The interaction of atmospheric aerosol particles with clouds has been addressed by a number of ground based field experiments during the last decades (Fuzzi, 1994, Fuzzi, 1997, Gallagher, 1999, Bower et al., 2000). In terms of chemical measurements all of them focus on the inorganic speciation of aerosol particles and cloud water and include only few contributions to the multiphase chemistry of organic compounds. An extensive speciation of organic compounds was conducted during the FEBUKO cloud experiments in autumn 2001 and 2002. Three measurement sites were chosen at the Schmücke mountain in the Thüringer Wald region, Germany, which allowed to characterise air masses chemically before, during, and after their passage of a hill-capped cloud. Concentrations of 33 organic carbonyl compounds, 5 monocarboxylic acids, and 10 dicarboxylic acids are reported for different atmospheric phases at the three sites. Some of them were determined for the first time in cloud water. The concentration levels of the compounds were usually low, consistent with the rural sampling region. The identified fraction of dissolved organic carbon in the cloud water was 17.3%, 14.7%, and 10.1%, on average, for three independent cloud events. For the gas phase compounds the phase partitioning between liquid phase and interstitial gas phase inside of the cloud was determined and compared to the theoretically expected values considering thermodynamic equilibrium conditions (Henry's law). The results of this comparison are given in Figure 1. Data was averaged over all three cloud events.

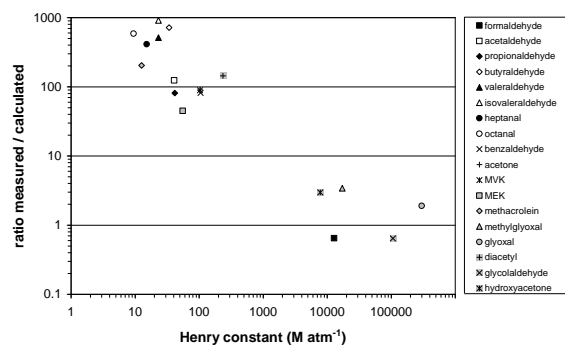


Figure 1: Average liquid phase fraction ratio (measured/calculated) as a function of the Henry constant for all determined organic carbonyl compounds during E I - E III.

For relatively polar organic carbonyl compounds (with a high Henry constant and a high effective water solubility), the ratio of measured to calculated liquid phase fractions was close to 1 (0.6 – 3.4). For the more hydrophobic compounds, however, a significant liquid phase supersaturation with respect to the gas phase concentrations was observed (ratios of 45 – 912). For the monocarboxylic acids, only small deviations from Henry's law were determined, comparable to the ones of the polar organic carbonyl compounds. The scavenging efficiency of the particulate dicarboxylic acids inside of the cloud was close to 100%.

Concentrations at the downwind site of both particulate and gas phase organic compounds were usually lower than at the upwind site, most likely due to physical sink processes during the passage of the air parcel over the forested Schmücke mountain.

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