Influence of Cloud Chemistry to the Composition of the Tropospheric Gas and Particle Phase: A Modeling Study

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The troposphere is a complex system with liquid and solid particles in the gas phase. Whereas several models exist describing the gas phase chemistry (e.g. Stockwell et al. 1997) detailed cloud chemistry is considered in only few mechanisms. Currently one of the most extended mechanism is CAPRAM 2.4(MODAC-mechanism) (Ervens et al., 2001). Beside of the inorganic chemistry (e.g. detailed sulphur oxidation, redox cycling of transition metal ions) organic chemistry with up to two carbon atoms - in an additional extension even to four carbon atoms - is considered in this aqueous phase mechanism.

In several model studies it was shown that in presence of clouds concentration levels in the gas phase can change essentially (Herrmann et al. 2000). Not only soluble species such as hydrogen peroxide are dissolved effectively in the aqueous phase but also the gas phase concentration levels for less soluble species such as OH and NO_3 are decreased in a cloudy environment. On the one hand this effect is due to the fast consumption of these species in the cloud droplets and on the other hand reaction patterns in the gas phase are changed because important precursors or reservoir species such as HO_2 and N_2O_5, respectively, are removed from the gas phase.

In analytical studies it was found that in tropospheric aerosol particles the main contributors of the organic carbon are dicarboxylic acids and keto acids (Neusüß et al. 2000). The formation processes of these compounds are not clarified up to now. The present study will show that cloud processing represents the link between gas phase chemistry and the existence of these compounds in the aerosol particles. Therefore, it will be clarified that not only the composition of the inorganic fraction in solid aerosol particles is caused by cloud processes but also the organic fraction.

The interactions between the gas and aqueous phase is mostly controlled by the surface area between the phases. Therefore, some reaction patterns change if not a simplified monodisperse droplet distribution but a size resolved distribution is considered in model calculations. It will be shown that the uptake into the droplet for several species is controlled clearly by transport processes (mass accommodation, gas phase diffusion) and not exclusively by the physical solubility leading to thermodynamic equilibrium. The highly dynamical behaviour of the tropospheric multiphase system leads to different phase transfer fluxes if droplets of different size are considered. The influence of the size resolved droplet distribution to the chemical composition of the multiphase system will be discussed.

References

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