Influence of Cloud Chemistry on 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 describe gas phase chemistry (e.g. Stockwell et al. 1997), detailed cloud chemistry is considered only in few mechanisms. Currently CAPRAM 2.4(MODAC-mechanism) represents one of the most extended mechanisms (Ervens et al., 2001). On the one hand in an extended version of CAPRAM organics with up to four carbon atoms are considered exceeding by far other aqueous phase mechanisms. Furthermore, an additional module was developed describing halogen activation from tropospheric clouds both in continental and maritime scenarios (HALOGEN 2.1).

It will be clarified that chemical processes in clouds can change essentially the composition of the gas phase, because not only soluble species are dissolved effectively but also gas phase concentration levels for less soluble species such as OH and NO_3 are decreased in a cloudy environment. However, in other cases the oxidation capacity of the gas phase can be increased by cloud processing. An example for this effect is halogen activation from the particle phase leading to enhanced concentrations of chlorine and bromine atoms in the gas phase. In the present study different pathways of halogen activation in clouds were identified for clean and polluted conditions. It will be shown that in cloud droplets the importance of radical chemistry will increase comparing to known reaction patterns in sea salt particles because of different conditions (higher pH values and lower ionic strength).

Furthermore, it will be clarified whether cloud processing can act as link between gas phase chemistry and the composition of solid aerosol particles. Possible formation pathways of low volatile organic compounds (dicarboxylic and keto acids) as found in aerosol particles will be discussed. To this end, it will be demonstrated that cloud chemistry influences not only the composition of the gas phase but also the composition (inorganic and organic) of the solid particle phase.

In general the interactions of the gas and aqueous phase are dependent on the surface area between the phases. Assuming different droplet radii (or a polydisperse droplet distribution) some reaction patterns change in the multiphase system because the phase transfer is often controlled by transport processes (mass accommodation, gas phase diffusion). This effect will be demonstrated with regards to some selected species in the multiphase system. With regards to halogen activation, the influence of the direct phase transfer of chlorine and bromine atoms will be discussed as a possibly important source of these radicals in the gas phase.

References

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