Model studies on multiphase chemistry interactions under polluted environmental conditions with MCM/CAPRAM

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Polluted urban regions are characterized by both high emissions of volatile organic compounds, such as aromatic compounds, and high oxidant concentration levels impacting atmospheric chemistry and, hence, the air quality. Thus, detailed multiphase chemistry modelling studies are performed to gain a better knowledge of the interactions of air pollutants and oxidants, and their linked processing.
In the first part of the contribution, results of model investigations will be presented and discussed focusing on the oxidation of substituted aromatic hydrocarbons in the tropospheric aqueous phase. Here, the development of the new aqueous-phase oxidation mechanism for monocyclic aromatic compounds (CAPRAM AM1.0) and selected model results for different urban environmental conditions are presented. Results show that the aqueous-phase chemistry of aromatic compounds, particularly in clouds, contributes to the secondary organic aerosol mass. Moreover, the aqueous-phase oxidations of aromatic compounds are shown to be important for both the degradation and the formation of nitrated aromatic compounds. In-cloud chemistry contributes up to 54% to the nitrocatechol oxidation and up to 37% to its formation under polluted tropospheric conditions. Furthermore, the model simulations indicate that besides OH radical oxidations, aromatic compounds with two hydroxyl groups are also strongly oxidized by O_3 and HO_2.
In the second part of the contribution, results of detailed multiphase chemistry model studies are presented investigating the effect of air pollution on activation of halogen radicals in polluted coastal regions. The studies reveal that not only the photolysis of $ClNO_2$ but also the photolysis of ICl represents an important process for formation/cycling of the gaseous Cl radicals. The model runs shows larger contributions of the $ClNO_2$ photolysis in the forenoon and higher of the ICl photolysis in the afternoon. Throughout the simulation time the $ClNO_2$ photolysis contributes 42% and 62% and ICl photolysis 35% and 28% to Cl activation in the cloud and cloud-free scenario, respectively. ICl is formed by aqueous-phase reaction of HOI with chloride and HOI is formed from INO_3 hydrolysis. Overall, the simulations reveal that INO_3 hydrolysis is a crucial reaction pathway influencing the activation of Cl and Br radicals in polluted coastlines and potentially other urban environments with high halogen loadings, e.g. from coal combustion or biomass burning.