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The influence of clouds on the oxidising capacity of the troposphere

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Previous model simulations have demonstrated the potential impact of clouds on gas-phase radical chemistry[1]. The lack of direct observations and uncertainty in gas-phase cloud-phase interactions, however, has led to this area of atmospheric chemistry being largely overlooked in global models for over two decades. Here we present measurements of OH and HO_2 radicals made during the HCCT (Hill Cap Cloud Thuringia) campaign that took place on Mt. Schmücke, Thuringia in Germany during September/October 2010. The University of Leeds Fluorescence Assay by Gas Expansion (FAGE) instrument was located near the summit of Mt. Schmücke (982 m) and made near-continuous measurements of the radicals at the top of a 22 m tower. The site was regularly influenced by orographic clouds throughout the measurement period. On average, the photolysis rate of O_3 to form $O(^1D)$, $J(O^1D)$, the most common primary initiator of HO_x radicals, was $\sim$ 30 % of its value out of cloud. The HO_2 concentrations were significantly depleted in cloud, with concentrations only $\sim$10 % of the value out of cloud, with OH not observed above the instrument detection limit during cloud events. These results suggest that heterogeneous processes in clouds do perturb the gas-phase radical chemistry. Using an analytical expression to simulate the HO_2 in-cloud observations, a first order loss rate of HO_2 to clouds of ~ 0.1 s^{-1} is needed to enable agreement between the simulation and measured values, suggesting a reactive uptake coefficient, γ_{HO_2}= 0.005, at the observed mean cloud droplet surface area of 1.2 x 10^{-3} cm^2cm^{-3}. This value is in good agreement with very recent recommendations based of laboratory studies of heterogeneous uptake of HO_2 on aqueous aerosols[2]. The rate of loss of HO_2 is strongly correlated with both cloud droplet surface area and pH, demonstrating clear dependencies of γ_{HO_2} on these parameters. The functional form of γ_{HO_2} observed over the pH range encountered during the project can be well replicated using the mechanism outlined by Thornton et al.[3] for HO_2 loss in aqueous aerosol without the presence of significant levels of transition metal ions. This work provides experimental evidence that clouds can alter gas-phase concentrations of HO_2 through heterogeneous reactions, and facilitates the correct parameterisation within models. Global model simulations were run and have demonstrated the impact that this neglected aqueous phase chemistry has on the oxidising capacity, with surface OH concentrations significantly reduced by clouds around the Equator, a region where the removal of methane is most efficient.

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