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Detailed heterogeneous chemistry in an urban plume box model: reversible co-adsorption of O_3, NO_2, and H_2O on soot coated with benzo[a]pyrene

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Abstract. This study assesses in detail the effects of heterogeneous chemistry on the particle surface and gas-phase composition by modeling the reversible co-adsorption of O_3, NO_2, and H_2O on soot coated with benzo[a]pyrene (BaP) for an urban plume scenario over a period of five days. By coupling the Pöschl-Rudich-Ammann (PRA) kinetic framework for aerosols (Pöschl et al., 2007) to a box model version of the gas phase mechanism RADM2, we are able to track individual concentrations of gas-phase and surface species over the course of several days. The flux-based PRA formulation takes into account changes in the uptake kinetics due to changes in the chemical gas-phase and particle surface compositions. This dynamic uptake coefficient approach is employed for the first time in a broader atmospheric context of an urban plume scenario. Our model scenarios include one to three adsorbents and three to five coupled surface reactions. The results show a variation of the O_3 and NO_2 uptake coefficients of more than five orders of magnitude over the course of the simulation time and a decrease in the uptake coefficients in the various scenarios by more than three orders of magnitude within the first six hours. Thereafter, periodic peaks of the uptake coefficients follow the diurnal cycle of gas-phase O_3-NO_x reactions. Physisorption of water vapor reduces the half-life of the coating substance BaP by up to a factor of seven by permanently occupying ~75% of the soot surface. Soot emissions modeled by replenishing reactive surface sites lead to maximum gas-phase O_3 depletions of 41 ppbv and 7.8 ppbv for an hourly and six-hourly replenishment cycle, respectively. This conceptual study highlights the interdependence of co-adsorbing species and their non-linear gas-phase feedback. It yields further insight into the atmospheric importance of the chemical oxidation of particles and emphasizes the necessity to implement detailed heterogeneous kinetics in future modeling studies.

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