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Prolonged lifetime of particulate-bound polycyclic aromatic hydrocarbons with coating of secondary aerosols during photochemical aging of biomass burning plumes

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Polycyclic aromatic hydrocarbons (PAHs), one class of most toxic compounds in atmosphere, showed much longer than predicted lifetimes in ambient air due to heterogeneous scavenging by ozone (O_3) according to previously studies. Here we show heterogeneous reactions with hydroxyl (OH) radical dominates far more over that with O_3 in the degradation of particle-bound PAHs based on chamber simulation on the evolution of plumes from biomass burning, the largest emitter of PAHs on a global scale. The evolution of crop straw burning fumes in a 30 m^3 smog chamber revealed that for heterogeneous reactions of PAHs with OH, their second order degradation rate constants were estimated to be $4.4\sim8.6\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at the initial stage of photo-oxidation, and they dropped 4-5 times to to $1.1\sim1.7\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} after $1\sim5\times10^{11}$ molecule cm^{-3} s OH radical exposure, corresponding to a decrease of uptake coefficients of OH (γ_{OH}) from 2.2±0.9 to 0.5±0.1. The decrease of second order rate constants and γ_{OH} were mainly caused by the reduction in secondary chemistry and the burial effect of coatings by secondary organic/inorganic aerosols during the atmospheric oxidation. Moreover, the OH oxidation pathway ($1.1\sim1.7\times10^{-6}$ s^{-1}) dominates over ozonolysis pathway ($1.7\sim12.7\times10^{-7}$ s^{-1}) in heterogeneous degradation of PAHs. The lifetimes of particulate PAHs were estimated to be 93.5~219 h, approximately 120 times that obtained previously by exposing pure PAHs to oxidants, implying their stronger long-range transport and more persistent health risks.