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Nighttime HO_x chemistry in the Pearl River Delta and Beijing in summer 2006: intense oxidation without sunlight

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Due to the absence of sunlight, unexpected high nighttime OH concentrations reported in previous field studies are of high interest for in-depth understanding of trace gas removal and reaction kinetics. In summer 2006, within the framework of PRIDE-PRD2006 and CAREBEIJING2006, we performed intensive in-situ measurements for HO_x radicals and ancillary parameters at two non-urban sites in Pearl River Delta and Beijing, respectively. During nighttime, quite similar features for both campaigns were observed. Measured nighttime OH and HO_2 concentrations were about $0.5 – 3 \times 10^6 cm^{-3}$ and $0.2 – 5 \times 10^8 cm^{-3}$, respectively. A box model with the established chemical mechanism (RACM-MIM-GK) underestimated these observed OH concentrations by an order of magnitude while reproduced the observed HO_2 taking into account the known interference from ambient RO_2 radicals (Fuchs et al. 2011). By testing the recently proposed recycling mechanisms applied for daytime chemistry, we found both a small primary source and a secondary source of OH radicals, the last one comparable to daytime observations (Lu et al., 2011, Hofzumahaus et al., 2009). Interestingly, the widely applied LIM0 and $MIM2^+$ showed marginal impacts on the modeled nighttime OH concentrations under high isoprene concentrations. With the help of a simple 1 d simulation, we found that direct input of ROx radicals by vertical transport was negligible while the input of PAN and MPAN could be of significance. Averaged nighttime pollutant turnover rates by OH were as high as 8 ppb/h and 4 ppb/h for PRD and Beijing, respectively, dominating nighttime oxidation processes.

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