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Peroxyacetic acid in urban and rural atmosphere: concentration, feedback on PAN-NO_x cycle and implication on radical chemistry

X. Zhang, Z. M. Chen, S. Z. He, W. Hua, Y. Zhao, and J. L. Li
State Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

Abstract. Peroxyacetic acid (PAA) is one of the most important atmospheric organic peroxides, which have received increasing attention for their potential contribution to the oxidation capacity of the troposphere and the formation of secondary aerosols. We report here, for the first time, a series of data for atmospheric PAA concentrations at urban and rural sites, from five field campaigns carried out in China in summer 2006, 2007 and 2008. For these five measurements, daytime mean (08:00–20:00 LT) PAA concentrations on sunlit days were 21.4–148.0 pptv with a maximum level of ~1 ppbv. The various meteorological and chemical parameters influencing PAA concentrations were examined using Principal Factor Analysis. This statistical analysis shows that the local photochemical production was the major source of PAA, and its concentration increased with increasing temperature, solar radiation and ozone but decreased with increasing NO_x (NO and NO_2), CO, SO_2, and relative humidity. Based on the dataset, several issues are highlighted in this study: (i) Because PAA is a product from the photochemical oxidation of some specific volatile organic compounds (VOCs) that lead to acetyl peroxy radicals, the importance of various VOCs with respect to the PAA formation is therefore ranked using the incremental reactivity method. (ii) The contribution of PAN thermal degradation to PAA formation under conditions of different NO_x concentrations is estimated based on the chemical kinetics analysis. The result shows that PAN seems to play an important role in the formation of PAA when the NO/NO_2 concentration ratio was less than 0.2 and PAA would correspondingly have feedback on the PAN-NO_x cycle. (iii) PAA and other peroxides, such as methyl hydroperoxide (MHP) and H_2O_2, usually exhibited a similar asymmetric shape typically shifted to the afternoon. However, under some conditions, H_2O_2 diurnal cycle was out of phase with MHP and PAA. The combination of linear regression and kinetics analysis indicate that the formation and removal processes of H_2O_2 may be different from those of MHP and PAA. (iv) Considering that PAA is the reservior of free radicals, its fate is expected to have an effect on the free radical budget in the atmosphere. A box model based on the CBM-IV mechanism has been performed to access its influence on the radical budget. We suggest that the detailed information on PAA in the atmosphere is of importance to better understand the free radical chemistry.

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