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> Interactive Comment

Interactive comment on "Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in urban and suburban atmospheres of Beijing, China" by J. B. Zhang et al.

X. Xu

xuxb@cams.cma.gov.cn

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This is an interesting paper, but I feel some more attention should be paid to the derivation of equations that are used for your calculations. For example, the equation (5) may not be correct. Because the estimation of the termal decomposition of PAN and PPN is not limited to nighttime, the photochemical sources of the key radicals for PAN and PPN should be included in the derivation. For PAN, this source is the reaction: CH3CHO+OH+O2->CH3C(O)OO+H2O. Together with the reactions (1), (2) and (4) on page 8185 of the manuscript, the following equation can be obtained:

-d[PAN]/dt = k4[PAN]-k1(k4[PAN]+k5[CH3CHO][OH])[NO2]/(k1[NO2]+k2[NO]),





where, k5 is the reaction constant for CH3CHO+OH, and k1, k2, and k4 are the reaction constants for the reactions (1), (2), and (4), respectively (see page 8185 of the manuscript). This equation is different from your equation (5), but it can be simplified to obtain equation (5) if k4[PAN]»k5[CH3CHO][OH]. However, k5[CH3HO][OH] may not always be negligible. Taking your average PAN (1.41 ppb), the average CH3CHO for PKU (3.6 ppb, Shao et al., 2009), and the values of k4 (3.77x10⁻ 4 /s) and k5 (9.55x10¹2 cm³/mol/s) (298K, Atkinson et al., 1997), I obtained 2.17x10⁻17 mol/cm³/s for k4[PAN] and 2.33x10⁻18 to 2.33x10⁻17 mol/cm³/s for k5[CH3CHO][OH] for OH varying from 1x10⁶ to 1x10⁷ cm⁻3. Note that the conditions are close to the normal summer conditions in Beijing. Therefore, k4[PAN] and k5[CH3CHO][OH] should be comparable, at least for the daytime period, and omitting the later one may results in significant errors in your results.

Another point, you get loss rate of PAN using the thermal decomposition equation (say eq.(5)) but not the loss itself. You compare the absolute losses of PAN and PPN with their ambient concentrations in Fig. 9. However, it is not stated in the manuscript how are the absolute losses calculated. Integration over a certain period?

References

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