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Atmospheric
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Discussions

Interactive comment on "Measurements of OH and HO_2 concentrations during the MCMA-2006 field campaign – Part 1: Deployment of the Indiana University laser-induced fluorescence instrument" *by* S. Dusanter et al.

S. Dusanter et al.

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We are grateful to Dr. Ezra Wood for his short comment which helped us to improve the manuscript. For clarity, the comment is reproduced below with a bold font, followed by our reply.

The definition of P(O_3) (Eq. 9) in this manuscript contains an erroneous term; the subtraction of the HNO_3 formation rate from the rate at which NO is oxidized to NO_2 by HO_2 and RO_2:

$P(O_3) = k[HO_2][NO] + k[RO_2][NO] - k[OH][NO_2]$.

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This term appeared earlier in Shirley et al (2006) and Sheehy et al (2008). (The RO_2 + NO term is not always considered as explained by the authors since they are calculating the portion of P(O_3) that is from HO_2 + NO only (since there are HO_2 measurements but not RO_2 measurements)). The idea behind the subtracted term is to account for the NO_2 (formed from HO_2 + NO) that does not actually photolyze (producing O_3) and instead reacts with OH to form HNO_3. The problem with the subtraction is that it subtracts the rate at which all NO_2 react with OH, and not just the portion that was recently formed by HO_2 oxidation of NO. If one wishes to account for the fraction of NO_2 (formed from R/HO_2 + NO) that react with OH instead of photolyze, then the k[HO_2][NO] term should be *multiplied* by the fraction of NO_2 that undergo photolysis:

P(O_3) = k[HO_2][NO] * j_{NO2}[NO_2]/(j_{NO2}[NO_2] + k[OH][NO_2])

where j_{NO2} is the photolysis rate constant and the RO_2 term has been ignored. This adjustment factor is equal to 0.995 for j_{NO2} = 9.6E-3 s^{-1}, [OH] = 5E6 molec/cm^3, and [NO_2] = 40 ppb (noon-time values). The value of the k[OH][NO_2] term itself is ∼7 ppb/hr. Thus if k[HO_2][NO] is 37 ppb/hr, subtracting k[OH][NO_2] yields a value for P(O_3) from HO_2 + NO of ∼30 ppb/hr; over a 20% difference.

Even better would be to just consider the gross production rate of O_x (O_3 + NO_2) instead of O_3. Viewed in this context, OH + NO_2 is an O_x loss, just as O_3 dry deposition, O(^{1}D) + H_2O, and HO_2 + O_3 are O_x losses.

P(O_x) = k[HO_2][NO] + k[RO_2][NO]

which is equivalent to the definition of P(O_3) most commonly used. Formation/decomposition of PAN compounds has been ignored here but could be included as well.

The formalism adopted in this paper for the calculation of P(O_3) is similar to that developed in Shirley et al. (Shirley et al., 2006). This was done in an attempt to compare net instantaneous rates of O_3 production from HO_2 only observed during the MCMA-2003 and 2006 field campaigns. We agree with Dr. Wood that subtracting the rate of HNO_3 formation from the chemical reaction rate of HO_2+NO leads to an underestimation of P(O_3) that can be attributed to HO_2. As suggested by Dr. Wood, we revised the manuscript to include P(O_x) calculations from the following equation:

$$P(O_x) = k_{HO2+NO}[HO_2][NO] + \Sigma k_{RO2+NO}\Phi_{RO+NO2}[RO_2][NO]$$

where Φ_{RO+NO2} represents the production yield of RO+NO_2 from RO_2+NO. HO_2 and NO measurements were used to calculate the gross production of oxidants (O_3 + NO_2) formed from the NO-to-NO_2 conversion due to HO_2. For the sake of the comparison with MCMA-2003, we still present P(O_3) calculations as defined in Shirley et al. (2006):

$$P(O_3) = k_{HO2+NO}[HO_2][NO] + \Sigma k_{RO2+NO}\Phi_{RO+NO2}[RO_2][NO] - k_{OH+NO2}[OH][NO_2]$$

The difference between P(O_x) and P(O_3) represents the rate of HNO_3 formation from OH + NO_2.

References

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 13689, 2008.

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