

Interactive comment on “Measurements of OH and HO₂ concentrations during the MCMA-2006 field campaign – Part 1: Deployment of the Indiana University laser-induced fluorescence instrument” by S. Dusanter et al.

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This comment only refers to one equation in the manuscript. Open comments from non-reviewers on ACPD tend to be negative; I hope that this is viewed more as an open discussion on the important quantity P(O₃) rather than a critique of this manuscript. It is good to see what appears to be an excellent OH instrument being used for field measurements.

The definition of P(O₃) (Eq. 9) in this manuscript contains an erroneous term; the

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subtraction of the HNO₃ formation rate from the rate at which NO is oxidized to NO₂ by HO₂ and RO₂:

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

This term appeared earlier in Shirley et al (2006) and Sheehy et al (2008). (The RO₂ + NO term is not always considered as explained by the authors since they are calculating the portion of P(O₃) that is from HO₂ + NO only (since there are HO₂ measurements but not RO₂ measurements)).

The idea behind the subtracted term is to account for the NO₂ (formed from HO₂ + NO) that does not actually photolyze (producing O₃) and instead reacts with OH to form HNO₃. The problem with the subtraction is that it subtracts the rate at which all NO₂ react with OH, and not just the portion that was recently formed by HO₂ oxidation of NO.

If one wishes to account for the fraction of NO₂ (formed from R/HO₂ + NO) that react with OH instead of photolyze, then the $k[HO_2][NO]$ term should be *multiplied* by the fraction of NO₂ that undergo photolysis:

$$P(O_3) = k[HO_2][NO] * jNO_2[NO_2]/(jNO_2[NO_2] + k[OH][NO_2])$$

where jNO_2 is the photolysis rate constant and the RO₂ term has been ignored. This adjustment factor is equal to 0.995 for $jNO_2 = 9.6E-3 \text{ s}^{-1}$, $[OH] = 5E6 \text{ molec/cm}^3$, and $[NO_2] = 40 \text{ ppb}$ (noon-time values).

The value of the $k[OH][NO_2]$ term itself is $\sim 7 \text{ ppb/hr}$. Thus if $k[HO_2][NO]$ is 37 ppb/hr , subtracting $k[OH][NO_2]$ yields a value for P(O₃) from HO₂ + NO of $\sim 30 \text{ ppb/hr}$; over a 20% difference.

Even better would be to just consider the gross production rate of Ox (O₃ + NO₂) instead of O₃. Viewed in this context, OH + NO₂ is an Ox loss, just as O₃ dry deposition, O(1D) + H₂O, and HO₂ + O₃ are Ox losses.

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$$P(\text{Ox}) = k[\text{HO}_2][\text{NO}] + k[\text{RO}_2][\text{NO}]$$

which is equivalent to the definition of $P(\text{O}_3)$ most commonly used.

Formation/decomposition of PAN compounds has been ignored here but could be included as well.

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