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Interactive comment on “Low temperatures enhance organic nitrate formation: evidence from observations in the 2012 Uintah Basin Winter Ozone Study” by L. Lee et al.

L. Lee et al.

ottawanrc@gmail.com

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We thank referee #2 for his/her comments.

The comments are addressed as follows:

My only major comment is that I would like to see a more thorough error analysis. The calculations are based on measurement data that is at times subject to corrections in excess of 50%. Assumptions are made about background mixing ratios to estimate dilution. OH production rates are estimated using filter radiometer measurements (see below). In addition, the alkyl nitrate yields for the larger, and branched alkanes were

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calculated to take into account secondary AN production down-chain and from secondary oxygenates. It would be nice to see an attempt to carry all these errors and uncertainties through to the final numbers in tables 2 and 3. This would allow the reader to put the significance of the difference between 57 and 64 ppb of ozone into perspective.

Author reply: An error estimate was not given for the nitrate branching ratio estimation method given by Carter and Atkinson, 1989. A simple estimation from comparisons between predicted and experimental values listed in Table 1 of the said paper suggests a margin of \sim 15% near ambient conditions. The current uncertainty estimate of the O₃ pyrolysis correction is up to 15% of the reported Σ AN concentration, as estimated from the absolute errors associated with the empirical fit to the laboratory data. The uncertainty in estimated OH concentration is in general 22%, proportional to the uncertainty in J values and OH reactivity data. This results in an uncertainty of ensemble averaged nitrate yield of 28% (oxidation-production method, section 3.2.2), as a result of uncertainties in alkyl nitrate production rate (18%) and dilution rate (26%). We have therefore added uncertainties for the expected maximum Ox concentration under 273K in Table 3 (57 \pm 8 ppb; 140 \pm 33 ppb), but not for values under 300K since the uncertainties are fully correlated under this scenario calculation.

Minor comments

OH production rates are calculated using measurements of O₁D and JNO₂. Are those filter radiometer measurements? If yes, how were the photolysis rates of the other OH sources calculated and what is the uncertainty of these calculations?

Author reply: The photolysis rates are based on 3 individual filter radiometer measurements, of O₃ (O₁D), NO₂ and NO₃. They are manufactured by Metcon Inc. with a cited uncertainty of 20%. Photolysis rates of organic species such as formaldehyde are calculated using linear combination of J(O₃) and J(NO₂) values, according to the method of (Stark et al., 2007).

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While I like the analysis done here and appreciate the idea behind this paper, I think that the importance for including temperature dependent production rates for ANs into regional models is probably limited to unique environments like this one. In most other parts of the world the ozone production from alkanes (for which there is sufficient kinetic data available to include in models) is very small to negligible. The authors might consider pointing this out in the conclusions.

Author reply: It is true that reactions of biogenic alkenes dominate the greater part of the global tropospheric environment. However, we expect similar temperature dependence of organic nitrate yield from the associated peroxy radicals since the underlying requirement of collisional stabilization remains the same. We agree with the referee that better characterizing the temperature dependence of organic nitrate formation from isoprene and monoterpenes is the crucial step in generalizing this correction to a global scale.

Stark, H., Lerner, B. M., Schmitt, R., Jakoubek, R., Williams, E. J., Ryerson, T. B., Sueper, D. T., Parrish, D. D., and Fehsenfeld, F. C.: Atmospheric in situ measurement of nitrate radical (NO₃) and other photolysis rates using spectroradiometry and filter radiometry, *J. Geophys. Res.-Atmos.*, 112, 11, 10.1029/2006jd007578, 2007.

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