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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observation of isoprene hydroxynitrates in the Southeastern United States and implications for the fate of NO_x" *by* F. Xiong et al.

Anonymous Referee #2

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The authors present a combination of laboratory and field measurements of isoprene nitrates plus related compounds. They use a 0-D chemical model to interpret the data in terms of constraints on isoprene nitrate formation and fate in the atmosphere. This paper is well written and makes a valuable contribution to our developing understanding of isoprene nitrate chemistry in the atmosphere. It should be published. Comments and suggestions are listed below, and are generally minor.

17857, 25: You could still have some IN production from NO3 + isoprene in the NBL. NO is not so high at night that it would dominate NO3 loss. The ratio of the rate coefficients k(NO3+NO)/k(NO3+isoprene) is about 37. Fig 6 shows that NOx at midnight

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was around 0.6 ppb, but this is almost all NO2, NO at midnight averaged <10 ppt. On the other hand isoprene was >2ppb at midnight. Based on that, isoprene + NO3 would be 5-6 times faster than NO + NO3 at that time.

Would this affect your interpretation of the diurnal IN cycle? Would the CIMS detect any of the NO3 + isoprene nitrates with the daytime products, or no?

17848, 15-28. Please discuss why you believe it is reasonable to use the sensitivity for 4,3-IN as a surrogate for all other beta INs (aside from 1,2). And likewise using cis/trans-1,4 for cis/trans-4,1.

17854, 5. Some significant assumptions had to be made for the instrumental sensitivities for the various IN isomers. Only a couple isomers were actually synthesized and calibrated directly, and the derived sensitivities for those range over a factor of 7. These were then used to estimate the sensitivity for other IN isomers. Given that, I find it hard to believe that the reported 15% uncertainty for IN measurements is even close to realistic.

17849, 20-25. Do we know that 1,2-IN is the only isomer affected by humidity in this way? If that's not the case would that affect your interpretation of the field data? Likewise (17854, 13) do we know that 1,2 is the only isomer affected by inlet loss?

17851, 16-28. Was the sample stream humidified for the field measurements as it was for the lab data? If not, how do you correct for humidity-dependent losses of the various isomers?

Fig. 7 is well done. The diurnal trend in gamma shows nicely how the fractional importance of RO2 + NO versus other RO2 sinks varies during the day. It may also be worth pointing out that the calculated IN production rate (Fig 7b) is not as peaked in the morning as the RO2 loss rate to RO2 + NO (Fig 7a) or gamma. And that this is because the RO2 concentrations are still quite low at that time. Right?

Fig 8, 17859-17860. You consider the possibility of fast photolysis to explain the day-

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15, C6063–C6065, 2015

time IN decrease. Could heterogeneous losses / deposition be playing a role?

17849, 1-8. It seems this method could be used as a check on the relative sensitivities for all IN isomers. Is it just that 4,3 and 1,2 are the only ones detected with enough signal for the purpose?

17853, 5. Should say “partially cancel the influence of dilution” or “reduce the influence”. Transport could easily affect MVK+MACR differently than INs, just based on differing lifetimes and concentrations in the residual layer, advected air masses, etc.

17853, 11-18. Need a description or at least a mention and citation for the other measurements used (PTR, GC).

17854, 13-18. Reported 9% IN yield is “in the 4-14% range of IN yields determined from previous experiments (. . .) but is more consistent with determinations from the higher end of the range”. Actually it seems to be exactly in the middle.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 17843, 2015.