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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Importance of Biogenic Volatile Organic Compounds to Peroxyacyl Nitrates (PANs) Production in the Southeastern U.S. during SOAS 2013" *by* Shino Toma et al.

Anonymous Referee #1

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Toma et al. present measurements of PAN, PPN, and MPAN utilizing the GC-ECD technique during SOAS. Measurements of these 3 compounds by the same technique have been made in various parts of the world over the past decades. As such, analytical approaches (i.e. to attribute PAN to anthropogenic and biogenic sources using PPN and MPAN, respectiely) are also well established. Toma et al. do well to follow in those footsteps and present their work in a succint, clearly written manuscript. The authors, however, missed an opportunity to clearly deliver a more impactful (in my opinion) message, that is, on the changes in atmopsheric composition (in this case, PANs) in the backdrop of decreasing NOx emissions over the last few decades. The sections discussing the correlation between isoprene nitrate and MACR, and the correlation be-

tween MPAN and OA, sound painfully stretched to suggest the potential of something important but lack convincing evidence. The focus, in my opionion, should be on presenting the high quality of the measurements and how atmospheric composition (PANs in this instance) have changed over time, and why. The manuscript has a lot of potential and deserves consideration for publication, but after significant improvements.

Results shown on figure 3 (PAN behavior with NOx) are intruiging. But how would you discount the possibility that the plateauing/leveling-off of PAN with NOx above 3.5 ppb is not due to lack of VOC or that measurements were made so close to NOx emission sources (since the NOx levels are so high) that the VOCs did not have time to react to form PAN? Possible to utilize your 0-D model accounting for as much of observations (VOCs, NO, NO2, etc.) to detrermine the chemical scenarios under which this PAN vs NOx behavior can be reproduced? By presenting PAN versus NOx for all the campaigns (figure 3), authors are implying that NOx level is all you need to know to get PAN levels. This needs to be justified.

Results shown on figure 4 is fascinating. I think a more thorough discussion of this PAN source attribution comparison between Dickson and SOAS is merited. (Side note, making this into 2 pie charts using the same red and blue color scheme for SOAS and Dickson as in figure 3 would be nice, not critical though). For instance, WHY is anthropogenic a much bigger contributor to PAN during Dickson than SOAS? Can you look into biogenic and anthropogenic VOC emissions inventories for the two regions during the appropriate time periods to determine how they have changed? The NOx level during Dickson (figure 3) would suggest it is well below the 3.5 ppb threshold. As such, Dickson is still clearly in the "NOx limited" regime. So why would PAN attribution (anthro vs biogenic) be so different between SOAS and Dickson? There are obviously many variables that affect PAN ambient levels (boundary layer height, transport time from main regional NOx source, etc.). But at minimum presenting the approximate VOC (anthro and biogenic) precursor levels that affect PAN production and temperature that affect PAN lifetimes for the two campaigns would be helpful.

I would like to see (in the SI or main) the diurnal plot of the PAN/NOy ratio (like figure 2 of Roberts 2002) for the Dickson and SOAS campaigns. That ratio can tell you amongst other things how efficiently PANs are being produced. How have the ratios changed over time? Why?

I would like to see (in the SI) the MPAN vs PAN and PPN vs PAN scatter plots. Are the slopes comparable to obserations from other studies? Can these slopes be used as characteristic signatures of anthropogenic and biogenic influences? Roberts used a range of MPAN vs PAN depending on time of day. Did the authors have to do that as well or were the slopes constant throughout SOAS?

I would like to see (possibly appended to figure 1) a diurnal plot of the MLR calculated PAN next to the observed PAN. The MLR model explains 60% of the variance. On average, when is the agreement good and bad. I am skeptical how robust the anthro vs biogenic attribution is for SOAS given how PAN, PPN and MPAN appear all well correlated in time (figure 1).

Section on attribution of BHC derived PAN to isoprene. For the ODR approach, your only input was from chamber oxidation of isoprene. Were you able to test MPAN production rates from MBO oxidation? Monoterpenes oxidation? I am concerned that your answer came out to be isoprene only because your input to the ODR was isoprene.

I question the relevance/validity of discussion section 4.1. Authors used MPAN vs PAN to establish that 50-70% of SOAS PAN is biogenic. You determined that biogenic PAN is mostly from isoprene. So why is it surprising that MPAN and isoprene hydroxy nitrates are well correlated?

The statement that "...MPAN shows significant contribution to OA growth...", based entirely on correlation, is unconvincing. The contribution to OA from MPAN can be estimated knowing the volatility (or C*) and its abundance in the gas phase or its SOA yield along with its lifetime. More data (calculations, model runs, etc.), not citations to other papers that merely suggest the possibility, is needed.

Need citations for sentence on lines 16-18, page 10.

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