

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 #2

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Toma et al. present measurement of PAN, PPN and MPAN obtained during a ground based field campaign in 2013 in Southeastern U.S. The measurements were done using GC-ECD which is a well-established technique. The way the compounds were measured and the instruments deployed and calibrated are well presented. The general behavior of the measured compounds is briefly described and compared with older measurements in this region.

The results and discussion sections are focused on two major points:

- The analysis of historical and recent PAN and NO_x datasets which tend to show that the recent measurements correspond to a regime where PAN production is limited by

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the availability of NO_x.

- The comparison of different methods to identify PAN organic precursors and the use of those methods on two datasets obtained in similar environment but 20 years apart. The more recent measurements had PAN production dominated by biogenic volatile organic compounds while the old measurements had PAN production dominated by anthropogenic volatile organic compounds.

The writing style is satisfying, the paper well referenced. The introduction part should be improved as it is in its current state lacunar. While the results are very interesting, the conclusions drawn could be made more solid if the authors were exploring further the different datasets and more exhaustive in their way to discuss the results.

I recommend publication after the following comments are addressed:

General comments:

Section 1: The first paragraph of the introduction should be placed in the experimental section as it is related to the measurements site and context. It would be useful to give typical mixing ratios (or ranges) of PANs expected in urban/rural/forested environments with information on seasonal variations and global trends over the last decades. The different sinks of PANs should be described. The introduction should better underline the importance of understanding PANs chemistry (NO_x removal/ transport, aerosol aging).

Section 2: The experimental section should contain a brief description of the meteorological conditions at the site during the campaign (temperature, humidity ...). Were those conditions expected at this location or were there different from classically encountered conditions? A citation could be placed if other papers describe the campaign in more details. I don't understand the point of discussing in such details the sum of PANs measurements by thermal dissociation as those data are used marginally in the paper. The authors should precise what they mean by NO_y and NO_y measurements.

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This last comment apply to the whole manuscript.

Section 3.1: The time series of PANs (figure 1) should be accompanied by temperature, NO_x and O₃ as correlations are strongly expected and this would help to see anthropogenic influence. The profiles of PANs could be discussed further. To what is due the morning peak, is it advection? Mixing with residual layer? It would be useful to add a profile for global radiation to figure 2. Since the sum of PANs have been measured, it would be interesting to know what fractions of total PANs represent PAN, PPN and MPAN. This would justify the big paragraph of total PANs measurements comparison in the experimental section.

Section 3.2: Figure 3 is very interesting and show well that the 2013 measurements might correspond to a shift to a NO_x limited regime, however, the authors should discuss further the possibility that the observations on the 2013 can be explained by a lower PHO_x (due to lower photolysis rates or OH pre-cursors) as mentioned very/too briefly and explained in Thornton et al. 2002. The authors should also discuss the possibility that observations correspond to older air masses or higher NO_x/PANs loss rates compared to the other measurements which would explain the lower PAN and NO_x data.

Section 3.3: The authors should describe briefly the hypothesis that are necessary to apply the MLR (and not only cite references) and the validity limits. Especially, this method imply that all PANs are only lost by thermal decomposition, however, the authors state in Section 4 that the reaction MPAN + OH represent a non-negligible sink of MPAN. Doesn't it invalidate/limit the MLR analysis? LaFranchi et al. 2009, using a steady state method for PAN sources attribution, show that the results (relative parts of BHC and AHC) are strongly dependent on temperature, because this factor affects the emissions of isoprene (Worton et al. 2013). This could maybe explain the differences between the 2013 and 1999 results (if temperature was much higher in 2013). The authors should comment on this. Why not apply all 3 methods to all the historical measurements? This would allow to make the conclusions more ro-bust if for all rural

measurements in the 90s, the BHC role as PAN precursors was higher than for urban measurements, and if all rural measurements in the 90s were all more oriented toward AHC than the 2013 results. This would maybe allow to conclude on the decrease of AHC role in PANs production.

Section 4: As stated by the authors, the relationship between IN and MPAN should be depending on the NO/NO₂ ratio. This fact could be well visualized by a plot of IN vs MPAN color coded with the NO/NO₂ ratio. The authors cite Worton et al. 2013 but do not mention that in this reference, the authors state that MPAN uptake on aerosols results in the formation in organo-sulfates in the aerosol phase, which is a likely explanation for the weak dependence of pONs on MPAN.

Section 3 and 4: Isoprene has a central role in all results and discussions but nothing is said about its mixing ratios which were measured in 2013 and 1999 together with the PANs.

Specific comments

page 1 line 31 : sensitive could be replaced by "controlled by NO_x"

page 2 line 1 & 2 : the last sentence is not really necessary

page 2 line 9 : also give official IUPAC name

page 2 line 11 : The role and importance of PANs could be placed in a global context instead of being reduced to the Eastern U.S.

page 2 line 13 : phytotoxic

page 2 line 14 : how abundant in terms of fraction of PANs ?

page 2 line 25 & 26 & 27 : this sentence is confusing, maybe removing the because would help. aerosol radiative forcing could be replaced by secondary organic aerosol formation.

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page 3 line 6 : "was" should be replaced by "is" ; which type of vegetation does "forested" correspond to ?

page 3 line 10 : what about BHC sources at the Dickson site

page 3 line 15 : what about air mass origins during the measurements ?

page 4 line 3 : what is NO_y, is it total NO_y by catalytic conversion ?

page 4 line 15 : what does WMU stands for ?

page 4 line 18 : Where are those WMU measurement described ? With which type of instrument ?

page 4 line 27 & 28 : the correlation allows for the investigation of PANs behavior but those values are never used in this paper, why compare the 3 instruments then ?

page 5 line 7 : add "(see Sect.3.2)" after "the last 20 years"

page 5 line 9 : what about the 2 others peaks near 1 ppbv

page 5 line 11 : what is the ratio between PAN and sum of PNs ?

page 5 line 14 : define NO_y

page 5 line 20 : replace "surface air" by "air masses" or "sampled air" ; they seems to be a net difference between air masses from the south and air masses from the north. Would the MLR for PAN pre-cursors identification reveal a difference as well between south and north.

page 5 line 24 & 25 : it would be nice to be able to see NO_x and O₃ somewhere. And what about differences in terms of VOCs mixing ratios between North and South, some BHC and AHC were measured during SOAS 2013. They could be described somewhere in the paper.

page 5 line 29 : to solve that a different scale could be used on figure 2 for the North and the South data

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page 5 line 31 : maybe an equation would be helpful for the decomposition lifetime calculation.

page 6 line 11 : replace "higher PAN concentration with higher NO_x" with "higher PAN and NO_x concentrations"

page 6 line 12 : what does "revisited" means ?

page 6 line 13 : "hence, the PAN concentrations can vary depending on place and year" could be re-placed by "Overall, the PAN concentrations were strongly variable between sites and years" ; which type of curve fit ?

page 6 line 17 : "and the peak was at around" should be replaced with "with a maximum around"

page 6 line 30 : yes covariance has been observed but that is because they are both produced by photo-oxidation of VOCs in the presence of NO_x, this is the reason why PAN vs NO_x looks similar to O₃ vs NO_x : their production pathways are the same.

page 7 line 2 & 3 : the sentence "and most PAN concentration at rural sites were dependent on NO_x concentrations" is confusing and does not bring any information. It seems to say that only in rural areas are PAN concentrations correlated with NO_x concentrations which is not the case.

page 7 line 7 : references ?

page 7 line 11 : "sources" should be replaced with "precursors"

page 7 line 18 : it should be mentioned somewhere that the A factor correspond to background PAN

page 8 line 16 : replace "Also, in Dickson 1999 . . . higher" with : "while NO_x levels were seven times higher".

page 8 line 19 : "(mostly isoprene)" could be added behind "Biogenic influence"

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page 9 line 8 : describe the 0D model method in more details. What are the hypothesis ?

page 10 line 25,26,27 : the fact that IN is high during the day does not mean that its production is high during the day, it could be produced by NO₃ oxidation of isoprene and have a long lifetime enough to be observed during the day, which is why talking about daytime in line 26 is not very accurate. Moreover, saying that IN is the dominant sink is as well not accurate. IN is a sink of NO_x if IN removal leads to a net loss of NO_x, but what happens if IN releases NO_x due to oxidation or due to uptake to the aerosol phase and subsequent release of NO_x. How does the general context of those measurements compare to Romer et al. ?

page 11 line 4 : Worton et al. 2013 suggest that uptake of organics following MPAN + OH reaction occurs through the formation and subsequent uptake of methacrylic acid epoxide (MAE).

page 12 line 5 : remove "data"

page 12 line 6 : you showed that PAN production is limited by NO_x availability,

page 12 line 8 : what is seen is that lower NO_x emissions seem to result in lower ambient PAN concentrations.

page 12 line 11, 12, 13 : the first part of the sentence just repeats line 6 and 7, the second part of the sentence is confusing, where is MPAN production rate as a function of NO_x discussed ?

page 12 line 16 : same remark as for line 25, 26, 27 page 10, it is not clear that IN is a net sink, since the removal pathway that is discussed in this paper, aerosol uptake, does not seem to trap NO_x in the aerosol phase.

page 12 line 17 : is 66% an average of the three methods ? The sentence "twice as much as anthropogenic influence during the overall campaign" is redundant. If biogenic influence is 66%, then the rest is obviously anthropogenic influence and logically

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33% which is ... twice less.

Additional references :

LaFranchi, B. W., Wolfe, G. M., Thornton, J. A., Harrold, S. A., Browne, E. C., Min, K. E., Wooldridge, P. J., Gilman, J. B., Kuster, W. C., Goldan, P. D., de Gouw, J. A., McKay, M., Goldstein, A. H., Ren, X., Mao, J., and Cohen, R. C.: Closing the peroxy acetyl nitrate budget: observations of acyl peroxy nitrates (PAN, PPN, and MPAN) during BEARPEX 2007, *Atmos. Chem. Phys.*, 9, 7623-7641, <https://doi.org/10.5194/acp-9-7623-2009>, 2009.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-418>, 2018.

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