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

We are so grateful to both reviewers for their time and insightful comments. Both reviewers were very thorough in their reading of the submitted manuscript. They made thoughtful comments and some excellent suggestions to improve the document and pushed us to think about aspects in different ways. The paper is significantly better as a result of their very careful review. Most of their suggestions have been incorporated in a revised manuscript as described below. Additions, revisions, and other changes made in the document are highlighted in the Word file for easy reference.

Suggestions from and responses to Anonymous Referee #1

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.

The reviewer is right; there are many possible inputs such as loss rates or photochemical aging or HOx production rates that could be responsible (likely a combination) for the behavior. In all these examples NOx chemistry and lifetime are key. The Figure is not intended to be seen as a mechanistic explanation but more an observation of a trend seen in a range of sites in the region. We have tried to revise the section of the text to tone down the impression that NOx level can be predictive of PAN levels on its own.

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.

NO$_x$ levels continue to decrease in the country (Blanchard et al., 2012; Russell et al., 2012; USEPA). Emission inventories for anthropogenic VOC emissions have steadily decreased in the southeast over the last 15 years (USEPA) This is consistent with anthropogenic VOC measurements made at various SEARCH sites (including Centreville) in the SE over the same time period. In contrast, the more limited BVOC measurements made at SEARCH sites show consistent BVOC levels over the same time (Hagerman et al., 1997; Hidy et al., 2014). Table 1 now shows that mean levels of O$_3$ and NOx were substantially higher at Dickson than at Centreville, while isoprene levels are a factor of 2 higher at Centreville during the daytime. We have added a diurnal plot of isoprene concentrations from both sites in Figure S4b.

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?

We plotted the hourly mean diurnal profiles of PANs/NO$_y$ from the Dickson 1999 and SOAS 2013 campaigns in Figure S4a. This figure shows similar behavior at both sites with similar mean values (0.136 for Dickson and 0.155 for SOAS 2013, see Table 1 in the manuscript) that peak during the daytime. Roberts et al. (2002) reported similar diurnal profiles for the Cornelia Fort Airpark in 1999.

I would like to see (in the SI) the MPAN vs PAN and PPN vs PAN scatter plots. Are the slopes comparable to observations 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?

We added the MPAN vs PAN and PPN vs PAN scatter plots in Figure S5 of the Supplementary Information. While slopes from a single linear regression (SLR) may be similar to the mean ratio, in the multiple linear regression (MLR), the t-value, which is obtained by partial slope/standard error, or β-value (standardized partial regression coefficient) is used to compare the influence of each independent variable instead of slopes, because slope calculations are different in MLR and SLR. In this study we used the determination of coefficients to determine anthropogenic and biogenic sources based on the β-value and correlation coefficient. In general, MLR is more accurate than SLR to predict dependent variable: the coefficient of determination, R^2 in MLR is higher than in SLR.

We limited the analysis in this manuscript to daytime data only, and similar to Roberts et al, 2002, we did find different slopes of the regression of MPAN on PAN on different days. The overall slopes of MPAN/PAN are in the same range as previous results, although SOAS has a greater slope overall than Dickson. The observed levels of PPN and MPAN were lower than seen in sites in the 1990s in the southeast such as, Nashville, Dickson, and Youth In., and limited number of data above detection limit made it challenging to compare the behavior at specific times. Since we used measurements from the entire campaign, the data has wider variance. The statistics should be able to assess each partial slope based on calculated probability (p-value). The p-values in Table S2 support the calculated values as signatures of anthropogenic and

biogenic influences. Hence, we think the results from MLR statistic are appropriate to discuss in this study.

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).

We added the plot for measured PAN versus predicted PAN using MLR in Figure S6. The diurnal plot of predicted and measured PAN was added in Figure S7. On average, predicted PAN correlated well with measured PAN, especially in the afternoon. However, the standard deviation of both measured and predicted data are similar (that is why p-value from ANOVA test in Table S1 showed less than significant level). This gives us confidence that the coefficient values for PPN and MPAN in MLR are representative (or robust) values for overall campaign.

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.

As the reviewer points out, the ODR approach in this study is limited, since we used isoprene as a proxy for biogenics. This is not completely unreasonable. Isoprene accounted for the majority of OH reactivity at SOAS (Kaiser et al., 2016), MBO has not been shown to produce MACR, at least from OH and O_3 chemistry (e.g. Alvarado et al., 1999; Spaulding et al., 2003) and some monoterpenes can form PAN as a secondary product, but not MACR. The ODR method compared a smog-chamber derived ratio of MPAN/PAN from isoprene to a modeled ratio and used that ratio to get an approximation of isoprene attribution, which is a lower limit of total BVOC attribution.

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?

We expected that primary products from isoprene oxidation (MACR and IN) would be more tightly correlated than a primary and a secondary (MPAN and IN). So maybe "surprising" is too strong of a word, but it is noteworthy that. Also we added a figure of the ratio of IN/MPAN as a function of NOx that shows that the variability of the relationship is different under different NOx conditions. In the range of NOx that Thornton et al. (2002) found for high P(HOx) the ratio spans a large range. At higher NOx values the ratio is relatively constant.

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.

The word "significant" in this phrase simply refers to the statistical test of the correlation and does not mean to imply a specific contribution to aerosol growth. We agree that the data are too limited to draw strong conclusions, but they do support the hypothesis that there is a contribution to aerosol growth without inclusion of nitrogen. We have re-worded this statement to remove the word significant.

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

Three representative citations were added: Paulot et al. (2009), Mao et al. (2013), and Liu et al. (2013).

Suggestions from and responses to Anonymous Referee #2

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 (NOx removal/ transport, aerosol aging).

This first paragraph was moved to Section 2, as suggested. The introduction was enhanced to give a more detailed evaluation of the importance of PAN in the global atmosphere and to outline the loss mechanisms for PAN compounds as suggested by the reviewer.

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 lo-cation 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 NOy and NOy measurements. This last comment apply to the whole manuscript.

The meteorological conditions of the ground site have been described in detail in Carlton et al, 2018 and Hidy et al., 2014. We have indicated this in the revised version. The point of discussing the comparison of measurements is for due diligence of somewhat co-located measurements at the site, although there was no formal inter-comparison between the measurements during the campaign. This gives us limits on the confidence we have for the speciated measurements. We agree that having this section in the main paper can be distracting and we have moved it to the supplemental materials. NOy is defined as gas-phase oxidized nitrogen now in the experimental section where it is introduced.

Section 3.1: The time series of PANs (figure 1) should be accompanied by temperature, NOx 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.

We have added timeseries for NOx, O₃, and Temperature to Figure 1. The diurnal morning increase observed for PANs is also observed in ozone, NOx, and isoprene is a result of morning breakup of a nocturnal inversion that was commonly observed at the site. It is very similar to variations observed at other ground sites (Nashville, Dickson, BEARPEX, PROPHET). We have also included in Table 1 additional information regarding the relative concentrations of various parameters, as suggested by the reviewer, for the SOAS site as well as for the other historical sites where PANs were measured. This was made more clear in the text.

Section 3.2: Figure 3 is very interesting and show well that the 2013 measurements might correspond to a shift to a NOx limited regime, however, the authors should discuss further the possibility that the observations on the 2013 can be explained by a lower PHOx (due to lower photolysis rates or OH precursors) 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 NOx/PANs loss rates compared to the other measurements which would explain the lower PAN and NOx data.

This is a good point. As seen in Figure 1, and explained in Hidy et al., ozone, NOx, and photolysis rates were all lower at this ground site than in previous years, which likely results in lower overall oxidation rates due to lower radical production rate (PHOx). This paragraph has been revised.

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 robust 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.

The MLR is a purely observational model that necessarily incorporates all loss processes for PANs active at the time and place of the measurements. Because OH reactions with MPAN is more important than with PAN or PPN the biogenic (MPAN) contribution might be conservative in our analysis. As pointed out, it appears that P(HOx) was low at SOAS 2013, so this factor may be smaller than at other sites. Additional modeling is beyond the intention of this work, and application of other models at Dickson is hampered by the more limited dataset available for Dickson and other sites.

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 pahse, which is a likely explanation for the weak dependence of pONs on MPAN.

As recommended by the reviewer, a graph of the ration IN/MPAN vs NOx has been included as Figure 6 in the manuscript. The figure shows two modes. The IN/MPAN ratio varies over a large range when NOx <1ppb, corresponding to the range of high P(HOx) described by Thornthon et al., (2002). At higher NOx levels, the ratio remains fairly constant around 2.5-3. At lower NOx levels, NOx is more efficiently tied up in IN than in MPAN) and the MPAN+OH loss rate at low NOx? We have edited the paragraph to explain this. Reference to the organosulfate mechanism has been added to this section. Thanks.

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.

In the supplemental materials we have added figures illustrating isoprene levels at SOAS and Dickson in Figure S4b. Emissions at both sites were significant, but with lower photolysis rates and the lower levels of radical precursors (mainly O_3) the lifetime of isoprene was likely greater at SOAS leading to higher average daytime values.

Most of the "Specific Comments" made by reviewer #2 listed below were incorporated in the revised manuscript exactly as suggested.

Specific comments

page 1 line 31 : sensitive could be replace by "controled by NOx"

Replaced.

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

Deleted.

page 2 line 9 : also give official IUPAC name

Added.

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

Added several sentences to expand the context.

page 2 line 13 : phytotoxic

This sentence was revised to read "they are significant health hazards for both humans and plants."

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

Added the approximate range of PAN/NOy values that have been observed.

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.

Revised as suggested.

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

Clarified. A more detailed description of the forest type is given with reference.

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

Information about mean isoprene values for Dickson have been included in Table 1.

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

Air mass origins have been discussed in Hidy et al. (2014) and Carleton et al. (2018).

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

NOy was defined explicity as described in Hidy et al., 2014..

page 4 line 15 : what does WMU stands for ?

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

These two comments refer to the comparison between measurements that was moved to the supplemental materials. WMU stands for Western Michigan University, where the primary author did the work.

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 ?

As described above, the point of discussing the comparison of measurements is for due diligence of somewhat co-located measurements at the site, although there was no formal inter-comparison between the measurements during the campaign.

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

Added.

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

The other peaks could not be attributed to extremely local biomass burning.

page 5 line 11 : what is the ratio between PAN and sum of PNs ? page 5 line 14 : define NOy

Details for all sites can now be seen in Table 1. We also included a line in the text that reads "PAN was consistently the most abundant peroxyacyl nitrate compound, the mean daytime levels accounting for approximately 90% of total PANs."

page 5 line 20 : replace "surface air" by "air masses" or "sampled air" ; they seems to be a net differ-ence 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.

Surface air was replaced. We also included a polar plot of isoprene concentrations in the supplemental materials that shows the biogenic precursors are not as directionally dependent.

page 5 line 24 & 25 : it would be nice to be able to see NOx 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.

These have been added to Figure 1..

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

This sentence was revied to rea" The diurnal cycle for PPN was less pronounced because of the low concentrations observed over the campaign".

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

An equation has been added to the Introduction section to describe PAN loss dependence on NOx.

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

Replaced.

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

The phrase was modified to read "The only site sampled in more than one year was ROSE…".

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

The sentence was revised. A log-normal curve fit function is now indicated.

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

Replaced.

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

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

We thank the reviewer for pointing out the oversimplification of the last 2 comments. We have revised the text to read "The covariance between PAN and O_3 (Bottenheim et al., 1994) due to their common photochemical pathway in the atmosphere suggests that the steep increase of PAN concentrations with NO_x at low NO_x in Figure 3a could result from NO_x-limited chemistry. Most rural sites showed PAN levels more sensitive to NO_x concentrations."

page 7 line 7 : references ?

References to decreases in NOx concentrations and emissions have been added.

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

Replaced.

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

A parenthetical phrase was added.

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

Replaced.

page 8 line 19 : "(mostly isoprene)" could be added behind "Biogenic influence" C6

Added.

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

The 0D model was based on the Master Chemical Mechanism v3.3. Explicit isoprene chemistry together with the inorganic mechanisms was used included chemical mechanisms for some monoterpenes (a-pinene, b-pinene,and limonene) was used to evaluate ambient field data. PANs were the main focus, so the model was constrained with a subset of parameters (NO_2, NO, OH, HO_2, CO, H_2O, ozone, acetaldehyde, and acetone). In addition to thermal and OH loss processes, the model included PAN loss by deposition.

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 NOx if IN removal leads to a net loss of NOx, but what happens if IN releases NOx due to oxidation or due to uptake to the aerosol phase and subsequent release of NOx. How does the general context of those measurements compare to Romer et al. ?

We agree this section was overstated, and again thank the reviewer for calling it out. We have toned down the text by removing the last sentence. We discuss the NOx dependence in more detail, as described earlier, with a new figure. Romer et al. do find that the production and loss of organic nitrates strongly affect NOx at SOAS and that daytime production is significant.

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).

A reference to Worton et al. 2013 was included in this sentence.

page 12 line 5 : remove "data"

Removed.

page 12 line 6 : you showed than PAN production is limited by NOx availability,

The sentence was revised as suggested.

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

The sentence was revised as suggested.

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 NOx discussed ?

The sentence was removed to avoid redundancy.

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 NOx in the aerosol phase.

The last part of this sentence suggesting that IN is a net sink was removed.

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 33% which is ... twice less.

Redundancy was removed.

Importance of Biogenic Volatile Organic Compounds to Peroxyacyl Nitrates (PANs) Production in the Southeastern U.S. during SOAS 2013

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Abstract

Gas-phase atmospheric concentrations of PAN, PPN, and MPAN were measured at the ground using GC-ECD during the SOAS 2013 campaign (1 June to 15 July 2013) in Centerville, Alabama in order to study biosphere-atmosphere interactions. Average levels of PAN, PPN and MPAN were 169, 5, and 9 pptv respectively, and the sum accounts for an average of 16% of NO_y during the daytime (10 am to 4 pm local time). Higher concentrations were seen on average in air that came to the site from the urban NO_x sources to the north. PAN levels were the lowest observed in ground measurements over the past two decades in the Southeastern U.S. A multiple regression analysis indicates that biogenic VOCs account for 66% of PAN formation during this study. Comparison of this value with a 0-D model simulation of peroxyacetyl radical production indicates that at least 50% of PAN formation is due to isoprene oxidation. MPAN has a statistical correlation with isoprene hydroxynitrates (IN). Organic aerosol mass increases with gas-phase MPAN and IN concentrations, but the mass of organic nitrates in particles is largely unrelated to MPAN.

1. Introduction

Peroxyacyl nitrates (carboxylic nitric anhydrides) (PANs, RC(O)OONO₂), products of the photooxidation of VOCs in the presence of nitrogen oxides (NOₓ), play an important role in the chemistry of both gases and particles in the troposphere. Measurements around the world have shown that PANs can comprise 15-40% of total gas-phase oxidized nitrogen in rural and forested areas, including the Eastern United States depending on how aged the air sampled at the site (e.g. Trainer et al., 1993, Nouaime et al., 1998). The fraction depends on air mass history and conditions. Gas-phase nitric acid, the other major component is more easily lost than PAN so HNO₃ deposition rate is also a factor. PANs are ubiquitous reservoir species for NOₓ and radicals in the atmosphere that affect the lifetime of NOₓ and enhance tropospheric O₃ formation (Carter et al., 1981). In addition, they are significant health hazards for both humans and plants (Finlayson-Pitts and Pitts, 2000; Kleindienst et al., 1990).

The peroxyacyl (PA) radicals that are the immediate precursors of PANs can form directly from aldehydes via hydrogen abstraction or from intermediate fragmentation of larger organic compounds and hence can have both anthropogenic and biogenic origins. Scission of the thermally weak bond to NO₂ regenerates the PA radical. Permanent loss of PANs occurs when the PA radical is lost. With sufficient NOₓ, this occurs via reduction of NO, and gas-phase PAN thermal lifetime, assuming steady-state for PA, depends on the ratio NO/NO₂ as described below. NO competes with peroxy radicals for reaction with PA at low NOₓ.

$$\text{PAN} \underset{k_{-1}}{\overset{-NO_2,\ k_1}{\rightleftarrows}} \text{PA} \xrightarrow{NO,\ k_2} \text{Products}$$

$$-d[PAN]/dt = k_1[PAN]\left(1 - \left(\frac{1}{1+\left(\frac{k_2[NO]}{k_{-1}[NO2]}\right)}\right)\right)$$

Peroxyacetyl nitrate (PAN) is the simplest and most abundant of the PANs, typically accounting for more than three quarters of the total PANs concentration. Peroxypropionyl nitrate (PPN) and peroxymethacryloyl nitrate (MPAN) also are observed in the field (e.g. Nouaime et al., 1998; Pippin et al., 2001; Roberts, 2002). PAN is formed from both anthropogenic and biogenic hydrocarbon precursors. PPN, on the other hand, is formed primarily from anthropogenic hydrocarbons (AHCs) (e.g. propanal, propane, 1-butene) while MPAN is derived from methacrolein (MACR), an oxidation product of the mostly biogenic hydrocarbon (BHC), isoprene (e.g. Biesenthal and Shepson, 1997; Carter and Atkinson, 1996).

Recent laboratory experiments have suggested that OH reaction with the double bond of MPAN could be involved in the formation of secondary organic aerosol (SOA) (Chan et al., 2010; Kjaergaard et al., 2012; Lin et al., 2013; Nguyen et al., 2015; Surratt et al., 2010; Worton et al., 2013). This pathway is currently treated in a few models that include isoprene (e.g. Pye et al., 2013; Pye et al., 2015; Jenkin et al., 2015; Wennberg et al., 2018), although isoprene is the biogenic non-methane hydrocarbon with the greatest global

emission rate (Guenther et al., 1995), the contribution of isoprene photooxidation to secondary organic aerosol formation may be underestimated.

We measured PANs concentration during the SOAS 2013 campaign to characterize the systematic behavior and levels of individual PAN species at an urban-impacted forest and to assess the current state of the attribution of PANs formation to biogenic and anthropogenic precursors quantitatively using several statistical methods. Finally, we compared MPAN with another nitrogen compounds in the gas phase, total isoprene hydroxynitrates (IN) and with organic nitrates or total organic aerosol (OA) in the particle phase to investigate relationships that might explain their influence on SOA formation.

2. Experimental

Ground-based measurements were conducted from 1 June to 15 July 2013 at the Southeastern Aerosol Research and Characterization (SEARCH) Centreville (CTR) site, which is located in mixed deciduous–evergreen forest in the Talladega National Forest near Brent, Alabama, (lat: +32°54′11.81″, long: -87°14′59.79). The major anthropogenic influence at this site comes from the cities of Tuscaloosa and Birmingham, which are located 50 km northwest and 80 km northeast respectively. The meteorological conditions of the ground site have been described in detail in Carlton et al (2018) and Hidy et al. (2014).

Measurements of PANs using similar methods to those described below were made in Dickson, TN from 15 June to 14 July, 1999 as part of the Southern Oxidants Study (SOS) (Cowling et al., 1998) and are referred to in the text. The site is in an area of mixed deciduous forest and pastureland located near Montgomery Bell State Park about 60 km west-southwest (upwind) of downtown Nashville, TN (Chen, 2001). While in a different part of the southeast, we believe that the distance from major urban areas makes this site a good comparison.

PANs were quantified using a custom gas chromatograph (GC) equipped with a Shimadzu GC-Mini-2 ^{63}Ni electron capture detector (ECD) maintained at 55 °C (described by (Nouaime et al., 1998)). A polar column (RESTEK, Rtx-200, 15 m x 0.53 mm ID x 1 μm) was kept at 15 C° to minimize thermal decomposition of PAN compounds. Helium was used as carrier (8 cm^3 min^{-1}) with N$_2$ make-up gas (3 cm^3 min^{-1}). Ambient air was drawn through a ¼″ OD PFA Teflon tube from 8.2 m height above the ground at 1 SLPM and a sub-sample of this air was drawn through a 1 cm^3 sample loop at 50 sccm. The residence time was approximately 9 sec. The sample loop contents were injected into the column at 20 min intervals via a 6-port Teflon valve (Hamilton). The baseline and sensitivity of the GC-ECD were checked every day during the campaign using standard addition of gas streams from liquid standards added to ambient air scrubbed

through a charcoal trap at the beginning of the sampling line. In this way, the impact of the inlet line was accounted for in the calibration. Separate calibrations were performed with synthetic PAN, PPN, and MPAN samples in dodecane or tridecane maintained at ice water temperature in diffusion cells. The level of PAN in each synthetic compound was determined with a chemiluminescence NO_x analyzer (Themo Environmental Instruments, Inc., Model 42S) equipped with a Mo converter held at 325°C. The converter efficiency was tested by O_3 titration of NO to NO_2. Calibration of the NO_x analyzer was done against a NIST-traceable cylinder of 2ppmv NO in N_2 (SCOTT-MARRIN, INC). Based on sensitivity and background measurements, the detection limits (S/N=2) for PAN, PPN and MPAN were estimated as 2.5 pptv, 3.6 pptv and 3.9 pptv, respectively. Uncertainty determined by error propagation, most of which came from the chemiluminescence NO_x analyzer, was estimated to be 20% RSD.

Measurements of other trace gases, such as NO_y (total reactive nitrogen measured by catalytic conversion), NO_x, and O_3, wind direction, temperature, and boundary layer height were made by Atmospheric Research & Analysis, Inc. (ARA) as described by Hidy et al. (2014). Boundary layer heights were calculated by ARA using LIDAR back-scatter measurements from a Lufft CHM 15k ceilometer. Total isoprene hydroxynitrate (IN) concentrations were determined by Purdue University using a chemical ionization mass spectrometer (CIMS) with operating conditions described by Xiong et al. (2015). VOC measurements, including isobutane, isopentane, MACR and isoprene were measured by NOAA ESRL Chemical Sciences Division and University of California, Berkeley (Goldstein group) using a GC-MS. Particle-phase organic nitrates (pONs) were measured by University of California, Berkeley (Cohen group) using thermal dissociation laser-induced fluorescence (TD-LIF), described by Rollins et al. (2010), and by University of Colorado with a high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) described by DeCarlo et al. (2006) and Hu et al. (2015). A comparison in Lee et al. (2016) found that the pONs-TD-LIF was generally higher by factor ~5 than pONs-HR-ToF-AMS. Both sets of data provide a reasonable range of pONs concentration. Total OA mass was measured using HR-ToF-AMS.

3. Results

3.1 General behavior of PANs in 2013

Figure 1 shows a time series of PAN, PPN, and MPAN throughout the campaign. Data that were below detection limit (BDL) are plotted at half of the reported detection limit for that compound. This was done to distinguish the BDL points from missing data due to tests, calibrations, and the periodic existence of a noise interference that often appeared during this campaign and could not be eliminated, and to not lose the low concentration information content. Relatively high levels of PAN were observed as periodic spikes

during the campaign, but overall PAN levels were lower than most other measurements in the southeast made over the last 20 years (see Sect. 3.2). A local biomass burning event was observed on June 4th (Washenfelder et al., 2015), which resulted in an unusually high level of PAN of around 1600 pptv and an extreme deviation from the median. Hence, the data on June 4th was removed from statistical analyses.

General descriptive statistics for all daytime data are summarized in Table 1. Daytime was defined as 10 am to 4 pm local time (CDT). PAN was consistently the most abundant peroxyacyl nitrate compound, the mean daytime levels accounting for approximately 90% of total PANs. In Table 1, "PANs" describes the sum of individual PAN, PPN, and MPAN values. The average of the ratio of PANs/NO_y during daytime was 0.16. Peroxyacryloyl nitrate (APAN) was also observed occasionally during the campaign. APAN has been proposed to arise from 1,3-butadiene, either from anthropogenic sources or biomass burning, and from direct emission of acrolein (Roberts et al., 2001; Tanimoto and Akimoto, 2001). Our data did not show a strong relationship to biomass burning events, as identified by Washenfelder et al. (2015), although an instrument interference problem limited the amount of reportable APAN data, so no clear conclusion can be drawn.

Although sampled air most frequently came from the south during the SOAS 2013 campaign, air from the north contained levels of PANs that were twice as large as from south. The averages of PAN, PPN, and MPAN with air from the north were 182, 5.3, and 8.4 pptv respectively, while averages of air from south showed 94.6, 2.8, and 3.6 pptv. Polar plots of PAN, PPN and MPAN as a function of surface wind direction are shown in Figure S3 with wind frequency. This elevated northern distribution is also seen with NO_x and O_3 reflecting the influence of anthropogenic pollution sources from Tuscaloosa, Birmingham, and Atlanta.

Plots of diurnal mean separated by surface wind direction (Figure 2) indicate a noticeable pattern in PAN, PPN, and MPAN from the north and a much weaker pattern in southerly air. Levels of all three PANs were highest (also with greatest variance) during the daytime on average. The diurnal cycle for PPN was less pronounced because of the low concentrations observed over the campaign. The PAN diurnal pattern was generally similar to those reported for Nashville in 1995 and 1999 (Nouaime et al., 1998; Roberts, 2002) resulting from early morning breakup of a nocturnal inversion that was commonly observed at the site. Similar behavior is observed at SOAS in ozone, NO_x, and isoprene. The diurnal behavior and mid-day means of PAN/NO_y are very similar between the Dickson site and the SOAS site (Figure S4a).

A calculation of PAN thermal decomposition lifetime using ambient temperature and [NO]/[NO_2] shows that the effective lifetime changes little over the course of the afternoon, which suggests that PAN levels fluctuate during early afternoon mostly due to dilution by boundary layer growth. Boundary layer height increased by a factor of 2-3 from 9am to 3pm on average based on LIDAR measurements.

3.2 Historical PANs measurements in the Southeastern US over last 23 years

PAN compounds have been measured at various rural and urban locations within the Southeastern U.S. over the last 23 years. Observations from six sites, Elberton (GA) 1990; ROSE (AL) 1990 and 1992; New Hendersonville (TN) 1994; Youth Inc. (TN) 1995; Dickson (TN) 1999; Cornelia Fort Airpark (TN) 1999 are compared here with SOAS 2013 data (a map of the locations is shown in Figure S2 and descriptive statistics of PANs and other trace gases are summarized in Table 1).

Binned PAN concentrations during the daytime (10 am – 4 pm) are plotted as a function of the concentration of NO_x (grouped into deciles) in Figure 3a. Urban areas have higher PAN and NO_x concentrations than rural areas. The only site sampled in more than one year was ROSE, where PAN levels in 1990 were more than twice as high as in 1992. Overall, the PAN concentrations were variable between sites and years. A log-normal curve fit of the data in Figure 3a shows an asymmetric peak in the concentration at around 3.5 ppb NO_x. PAN concentration increases approximately linearly with NO_x up to 2 ppb and beyond the peak it decreases slowly with further increases in NO_x. Similar behavior was observed in the relationship between O_3 and NO_x concentration in Figure 3b with a maximum around 1.5 ppb NO_x.

The relationship of O_3 production with NO_x and VOC concentrations is typically discussed in terms of "NO_x-limited" and "VOC-limited" regimes, (Finlayson-Pitts and Pitts, 2000; Milford et al., 1994; Chemeides et al., 1992), although there has been less discussion of the sensitivity of PAN production to these reactants. This curve is reminiscent of the modeled O_3 production rate as a function of NO_x and HO_x in Thornton et al. (2002) from OH oxidation of VOC based on measurements from Cornelia Fort Airpark in 1999. At low NO concentration, O_3 production rate increases with NO, since OH is regenerated via HO_2+NO and the primary chain termination are HO_x+HO_x reactions. On the other hand, O_3 production rate slows at higher NO concentrations when OH is consumed, because HO_x+NO_x and RO_2 + NO reactions (Romer et al., 2016) become faster than HO_x+HO_x reactions. The peak in Figure 3 is related to the crossover point between NO_x-limited and NO_x-saturated. A high HO_x production rate enhances the O_3 production rate with NO for low NO and the crossover point shifts to higher NO. The relationship based on field data in Figure 3 is phenomenological and reflects a complex combination of production and loss processes. Untangling the exact mechanisms that contribute to the observed behavior were not investigated, although several mechanisms could contribute. For instance, older air masses would reflect different PAN/NO_x ratios. Based on average PAN/NO_y ratios (Figure S4a), the air masses experienced at Dickson and SOAS were of similar ages. Differential loss rates for PAN and NO_x or overall shorter lifetimes could yield lower absolute values and could also influence this ratio. As seen in Figure 1, and explained in Hidy et al. (2014), ozone, NO_x, and photolysis rates were all lower at this ground site than in previous years, which likely results in

lower overall oxidation rates due to lower radical production rate. Lower radical production rate also increases the isoprene lifetime and leads to larger mid-day average levels of isoprene than seen in other SE ground sites (Table 1).

The covariance between PAN and O_3 (Bottenheim et al., 1994) due to their common photochemical pathway in the atmosphere suggests that the steep increase of PAN concentrations with NO_x at low NO_x in Figure 3a could result from NO_x-limited chemistry. Most rural sites showed PAN levels more sensitive to NO_x concentrations. The slow decrease of PAN concentration at higher NO_x levels such as those seen at more urban sites could result from faster radical termination rates, and thus slower VOC oxidation rates. This empirically-derived distinction is likely related to differences in reaction rates with peroxy radicals that could be investigated computationally. PAN, O_3 and NO_x levels in the Southeast were all lowest at SOAS 2013. As NO_x levels continue to decrease in the country (Blanchard et al., 2012; Russell et al., 2012; USEPA), PAN production rates might become more widely sensitive to NO_x. Emission inventories for anthropogenic VOC emissions has steadily decreased in the southeast over the last few decades. Mean isobutane and isopentane levels measured at the Centreville site were 70% lower in 2013 than in 1993. (Hagerman et al., 1997) VOC measurements at SEARCH sites show more consistent BVOC levels over the same time (Hagerman et al., 1997; Hidy et al., 2014; USEPA; E. Edgerton unpublished data).

3.3 Anthropogenic vs Biogenic contribution to PAN production

3.3.1 Description of MLR and its Statistical Meaning

A multiple linear regression (MLR) has been used to quantify PAN precursors (Roberts, 2002; Roberts et al., 1998; Williams et al., 1997). Since the thermal decomposition rates of PANs are similar (Roberts and Bertman, 1992), and MPAN and PPN are formed from BHC and AHC respectively and PAN is formed from both, [PAN] can be approximately represented as a weighted linear combination of [MPAN] and [PPN]. The combination of BHC and AHC chemistry is indicated by MPAN and PPN. The linear model is applied as in equation 1.

$$[PAN] = A + B_1[MPAN] + B_2[PPN] \tag{1}$$

Here, A is the intercept (describing background PAN levels) and B_1 and B_2 are partial regression coefficients, estimated using a computer software program based on field observations. The MLR statistical analysis includes estimation of A, B_1 and B_2, overall F-test and a t-test, and diagnostic procedures (e.g. Mendenhall et al., 2008). The F-test is used to investigate the statistical significance of the model in Equation (1) using an analysis of variance (ANOVA) table. The strength of the model is evaluated using the coefficient of determination R^2 between predicted and measured [PAN] (also provided through this statistical analysis).

1 The individual *t*-test, which is based on the Student's t statistic, is used to investigate the statistical

2 significance of the individual B_1 and B_2. In a MLR statistical analysis, the magnitude of the standardized

3 partial regression coefficients, β_i, which is calculated as a product of partial regression coefficient and the

4 ratio between the standard deviation of the respective independent variable (MPAN or PPN) and the

5 standard deviation of the dependent variable (PAN), is frequently used to compare the relative contribution

6 of independent variables. The results of MLR statistical analysis are summarized in Tables S1 and S2.

7   Tatsuoka (1971) showed that R^2 from the MLR is equal to the sum of the product of the β_i and the zero-

8 order (simple bivariate) correlation, r_i, which are obtained as results of MLR (see Table S2). That is, $R^2 =$

9 $\Sigma \beta_i r_i$. Therefore, we used the fraction of R^2 based on the strength of relationship in each [MPAN] and

10 [PPN] to [PAN] to describe the relative importance of BHC and AHC. Each partial R^2 is obtained as shown

11 in equations 2 and 3.

12 $R^2_{BHC} = \beta_1 r_{MPANvs.PAN}$ (2)

13 $R^2_{AHC} = \beta_2 r_{PPNvs.PAN}$ (3)

14 This approach allows us to directly treat the R^2 in the MLR to assess the relative importance of BHC and

15 AHC, including the strength of correlation with PAN.

16 Results from SOAS were compared with similar PAN data collected from Dickson, TN in 1999, another

17 rural southeastern site, which show that the MLR model and regression coefficients for both MPAN and

18 PPN at both sites were statistically significant (see Tables S1 and S2). During SOAS 2013, 60% of the

19 variance in the measurements was explained by the MLR model. At the Dickson site in 1999, 77% of the

20 variance was explained by the MLR model. The R^2 of MLR in the SOAS 2013 data was lower than that in

21 Dickson 1999, which might result from the lower absolute PANs levels during SOAS 2013. In particular,

22 SOAS MPAN and PPN data included a large number of below detection limit measurements, while Dickson

23 1999 data did not. The means of PAN, MPAN, and PPN in Dickson 1999 were three times higher than the

24 mean for SOAS 2013, while NO_x levels were five times higher (see Table 1). In Figure 4, the relative

25 importance of BHC and AHC was standardized to compare SOAS 2013 and Dickson 1999. Standardized

26 relative percentiles were calculated as $R^2_{BHC}/R^2 \times 100$ for BHC and $R^2_{AHC}/R^2 \times 100$ for AHC. Biogenic

27 influence accounted for 66% of PAN during SOAS 2013 and was two times larger than the anthropogenic

28 influence. This is the opposite of results from Dickson where the biogenic influence (mostly isoprene)

29 accounted for only 25% of PAN. Although both sampling locations were located in rural areas in similar

30 environments, the results using MLR indicate that the HC precursors were different.

31 **3.3.2   Comparison of contribution of isoprene oxidation with computational modeling**

1   We used two computational approaches to assess the contribution of isoprene oxidation to PAN formation

2   by 1) orthogonal distance regression (ODR) between field measurements of MPAN and PAN and 2)

3   simulation of the production of peroxyacetyl (PA) radicals, precursors of PAN, using an ambient 0-D

4   photochemical model.

5   In ODR, the fraction of PAN production from isoprene oxidation can be expressed as

6   $(d[PAN]_{isoprene}/dt)/(d[PAN]_{all}/dt)$. Assuming that MPAN is solely derived from isoprene oxidation, the

7   relative yield of $(d[MPAN]/dt)/(d[PAN]_{isoprene}/dt)$ was obtained from an isoprene oxidation chamber

8   experiment as 0.15 ± 0.03 RSD. The reaction was initiated with 1.37 ppm isoprene, 268 ppb NO, and 206

9   ppb NO_2 under 5% RH in a 5.5 m^3 Teflon cylindrical bag. The OH radical was produced by photolysis of

10 HONO. The fraction of PAN production from isoprene oxidation to total PAN formation in the field was

11 rearranged as the following equation.

12 $$\frac{d[PAN]_{isoprene}/dt}{d[PAN]_{all}/dt} = 6.7 \times \frac{d[MPAN]/dt}{d[PAN]_{all}/dt} \qquad (4)$$

13 The $(d[MPAN]/dt)/(d[PAN]_{all}/dt)$ was obtained from measurements in SOAS 2013 as the slope of the linear

14 regression line of [MPAN] to [PAN].

15 In the 0-D photochemical model simulation, the relative contribution to peroxyacetyl (PA) radicals from

16 VOCs present at the field site is based on the Master Chemical Mechanism (MCM) v3.3. The ambient

17 model included not only isoprene and its oxidation products (including $CH_3C(O)CHO$) but also acetone,

18 acetaldehyde, and some mono-terpenes as precursors. The detail of the parameters for MCM set are

19 described in Groff (2015).

20 These two methods were compared with the relative importance of BHC, $\beta_1 r_{MPANvs.PAN}$, from the MLR

21 model in this work. Four days (Jun 3rd 12:30 – 18:00, Jun 14th 11:30 – 18:00, Jun 26th 11:00 – 18:00, and

22 Jul 12th 13:00 – 18:00) of data from SOAS 2013 were selected to run the 0-D model because the production

23 ratio using ODR can only be used when PAN, MPAN and NO_x concentrations were appropriately high.

24 The time ranges were chosen so that the boundary layer height would be stable and any dilution effect

25 would be minimal. Results of the comparison are plotted in Figure 5. Although the relative importance of

26 BHC in the MLR model was less than 40% on June 3rd, it was statistically dominant on the other three days

27 accounting for more than 68%. (Note: PPN on June 3rd did not have a significant level to predict PAN in

28 MLR analysis, p=0.600.) By comparison, the estimated contribution of isoprene oxidation using ODR on

29 June 3rd had the steepest slope, however, the range of the 95% confidence interval (C.I.) on this day was

30 large. On the other three days, the relative contributions of isoprene oxidation using ODR were estimated

31 at $23 - 49\%$, lower than the results derived from the other two methods. This might be due to the differences

1 between the chamber experiment and ambient conditions. Specifically, the ratio of secondary to primary

2 oxidation products varies between chamber and ambient conditions, with likely relatively greater primary

3 products under chamber conditions. Since PAN is formed via the oxidation of secondary products of

4 isoprene, the [MPAN]/[PAN]$_{isoprene}$ ratio would be higher in the chamber experiment than in ambient

5 environment. This ratio is expected to derive results that are biased low, when used to estimate the ambient

6 isoprene-derived PAN concentration. In addition, photolysis rates also are significantly different between

7 the chamber and the field conditions. The results of the 0-D model suggest that isoprene oxidation

8 significantly contributed to PAN formation with a mean range of 55–73% over all selected days. Hence,

9 both methods, the MLR and the 0-D model, indicate that isoprene oxidation was the main source when high

10 levels of PAN were observed during SOAS 2013.

11 **4. Discussion**

12 **4.1   Comparison among MACR, IN, and MPAN**

13 MACR is a first generation product of isoprene photooxidation mechanisms, and MPAN is derived from

14 MACR oxidation (Bertman and Roberts, 1991; Kjaergaard et al., 2012). With enough NO$_x$, the OH adduct

15 of isoprene that is the precursor to MACR in these mechanisms is also a precursor of gas-phase isomers of

16 isoprene hydroxynitrates (IN) (Shepson, 2007; Grossenbacher et al., 2001, 2004; Barker et al., 2003; Paulot

17 et al., 2009; Lockwood et al., 2010). Xiong et al. (2015) reported IN at SOAS, which affords the opportunity

18 to study this aspect of NO$_x$ sensitivity of isoprene oxidation. In this work, the daytime (10 am – 4 pm)

19 relationships among MPAN, MACR and IN at SOAS was investigated using the Pearson's correlation

20 statistical test. Missing data was treated as pairwise deletion (not listwise deletion). The correlation

21 coefficient between the first generation products of isoprene, MACR and IN was 0.528 (p < 0.001) and

22 indicated a statistically significant positive correlation, as would be expected. According to the known

23 chemical pathways, a strong relationship is expected between MACR and MPAN, while a weak relationship

24 is expected between IN and MPAN given that IN is a primary product, while MPAN is secondary. The

25 results show, however, that daytime data over the whole campaign did not show a statistically significant

26 correlation between MACR and MPAN ($r = 0.148$, p $= 0.104$). In contrast, IN has a statistically significant

27 positive correlation with MPAN ($r = 0.499$, p < 0.001). Likely this relationship is a result of the NO$_x$

28 dependence of both organic nitrate products. Because MACR can be produced in the absence of NO$_x$ (Paulot

29 et al., 2009b; Liu et al., 2013; Mao et al., 2013), MPAN is more dependent on NO$_x$ than on MACR at this

30 site, and isoprene nitrates constitute a larger fraction of gas-phase organic nitrates from BVOC than MPAN

31 does, consistent with Romer et al. (2016). Figure 6 shows that the IN/MPAN ratio varies over a large range

4.2 Gas-phase MPAN vs. organic aerosol mass

During SOAS 2013, Lee et al. (2016) estimated that the particle-phase organic nitrates (pONs) accounted for 3% of total organic aerosol (OA) mass, on average, during the day (12 pm – 4 pm) and BVOC precursors strongly impacted the diel trends of pONs. Laboratory experiments suggest that MPAN can play a key role in SOA formation under high NO_x conditions. C4-hydroxynitrate-PAN or hydroxymethyl-methyl-α-lactone (HMML) (Kjaergaard et al., 2012; Nguyen et al., 2015; Wennberg et al., 2018) and methacrylic acid epoxide (MAE) (Worton et al., 2013) have been proposed as precursors for uptake into the particle-phase from MPAN oxidation. Nguyen and co-workers (2015) estimated the SOA yield as approximately ~60 % by mole from MPAN + OH reaction in the absence of NO_x. IN is also expected to contribute to SOA formation (Jacobs et al., 2014). Organic nitrate involvement in SOA formation suggests as relationship between gas-phase MPAN and IN with particle mass, although the nitrogen could be unretained in the particle. Figure 7a&b shows the relationship of gas-phase MPAN and IN with daytime particle measurements. As MPAN and IN concentrations increase, Figures 7a&b show that OA mass increases, while pONs mass increases very little (measured by both HR-ToF-AMS and TD-LIF), although the slopes of MPAN and IN vs. pONs are statistically different from zero. The relative magnitude of the response of OA and pONs to increases in MPAN and IN suggests that they may contribute to OA growth more than to pONs growth. Although this may suggest that if MPAN oxidation by OH is involved in particle growth, the nitrogen from MPAN is not represented in aerosol organic nitrate. Oxidation of MPAN modeled from MACR + OH results at FIXCIT (Nguyen et al., 2014) using measured total peroxynitrates and kinetics of the isoprene mechanism in MCM v3.3.1 (Jenkin et al., 2015) showed a positive relationship between MPAN oxidation and pONs formation, although with a yield <3% (P. Romer, personal communication). Results of direct reaction of MPAN + OH suggest that it is unlikely that pONs formation is mainly derived from MPAN+OH reaction, even in the presence of NO_x (Nguyen and Wennberg, personal communication). This small contribution of isoprene oxidation compounds to pONs formation is consistent with reported modelling of pONs formation (Xu et al., 2015; Ayres et al., 2015; Pye et al., 2015). Ayres et al. (2015) suggest that pONs formation at SOAS was dominated by nighttime reactions of NO_3 radicals with BVOCs

rather than daytime reactions, and more from monoterpene oxidation than isoprene oxidation. MPAN uptake on aerosols results in the formation of aerosol-phase organo-sulfates (Worton et al., 2013), which also contributes to the weak dependence of pONs on MPAN.

Rather, MPAN is likely a precursor of low vapor pressure products that undergo aerosol uptake. The correlation between INs and MPAN with OA may reflect that much of the OA derives from BVOC oxidation, and the conditions that lead to large rates of BVOC emission and oxidation (high T and radiation) simultaneously produce OA, along with INs and MPAN. That OA does not correlate well with condensed phase organic nitrate reflects the fast hydrolysis of organic nitrates in the aerosol phase at low aerosol pH (Rindelaub et al., 2016; Jacobs et al., 2014; Guo et al., 2015) While organic nitrates such as the INs may partition to the aerosol phase, they are quickly converted to inorganic nitrate ion and other products by hydrolysis.

5. Conclusions

The level of PAN compounds measured at the ground site during SOAS 2013 is lower than measured in the Southeastern U.S. over the past two decades. We show here that PAN concentrations at SOAS were limited by NO_x availability. Russell et al. (2012) show that NO_x in the eastern US has been decreasing rapidly, due to effective emission control, and lower NO_x levels seem to result in lower ambient PAN concentrations. As this process continues, PAN may continue to be a smaller fraction of NO_y, as peroxy radicals such as $CH_3C(O)OO$ react with HO_2 and RO_2 rather than with NO_x. PAN appears to be most sensitive up to $[NO_x]$ approximately 3.5 ppb, above which PAN concentrations switch to a NO_x-saturated (or VOC-limited) regime. Overall, MPAN did not show a statistically significant correlation with MACR, but did show a statistically positive correlation with IN. These results indicate that both organic nitrate products were NO_x dependent (MPAN being more sensitive to NO_x than to MACR precursor) at SOAS.

We estimate that biogenic precursors, particularly isoprene, account for more than half of PANs and that gas-phase MPAN shows a correlation with OA growth consistent with laboratory and chamber studies, but less correlation with nitrogen-containing pONs during the daytime. This may suggest that the nitrogen of MPAN is removed during oxidation to other low vapor pressure products involved in particle growth, as suggested by the HMML (Kjaergaard et al., 2012) and MAE mechanisms (Worton et al., 2013).

6. Acknowledgments

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Table 1. Summary of selective Southern Oxidants Study (SOS) since 1990. Mean±standard deviation.

Year	1990	1990	1992	1994	1995	1999	1999	2013[*2]
	Elberton, GA	ROSE, AL	ROSE, AL	New Hendersonville, TN	Youth Inc., TN	Dickson, TN	Cornelia Fort Airpark, TN	Centreville, AL
	Ground	Ground	Ground	9m AGL[*1]	Ground	Ground	10m AGL	7.5m AGL
	June 24 - July 13	June 10 - July 20	June 19 - July 2	June 22 - July 19	June 29 - July 25	June 15 - July 14	June 14 - July 14	June 1 - July 15
PAN (ppt)								
Daytime	258±157	519±455	259±177	764±662	765±400	583±360	1078±519	169±129
All day	203±138	376±346	195±159	473±439	485±366	431±316	694±487	126±110
PPN (ppt)								
Daytime	n/a	25±24	n/a	92±106	72±47	39±45	141±83	5±7
All day		19±18		54±66	50±39	33±40	93±72	4±5
MPAN (ppt)								
Daytime	n/a	n/a	n/a	50±41	38±25	31±26	91±48	9±10
All day				37±32	30±21	20±21	64±45	5±7
PPN/PAN								
Daytime	n/a	0.068±0.134	n/a	0.118±0.039	0.092±0.028	0.054±0.041	0.127±0.036	0.033±0.032
All day		0.059±0.078		0.112±0.042	0.094±0.034	0.061±0.049	0.128±0.048	0.042±0.044
MPAN/PAN								
Daytime	n/a	n/a	n/a	0.073±0.034	0.055±0.031	0.061±0.045	0.105±0.070	0.049±0.035
All day				0.089±0.047	0.064±0.036	0.049±0.040	0.108±0.065	0.046±0.038
PANs[*3]/NO_y								
Daytime	0.125±0.053	0.255±0.128	0.060±0.028	0.171±0.132	0.140±0.047	0.136±0.046	0.132±0.062	0.155±0.081
All day	0.091±0.051	0.172±0.113	0.042±0.029	0.080±0.090	0.101±0.058	0.101±0.052	0.064±0.061	0.110±0.067
O3 (ppb)								
Daytime	56±10	52±14	63±6.2	51±21	70±23	54±19	60±23	34±11
All day	39±19	36±18	51±15	31±21	51±27	44±20	37±27	26±13
NOy (ppb)								
Daytime	2.1±0.6	2.2±1.1	3.1±0.9	7.3±4.5	7.2±4.9	5.4±5.6	10.2±5.3	1.1±0.4
All day	2.4±0.8	2.6±1.9	3.5±2.0	11.1±8.8	8.0±5.5	5.1±3.9	18.6±15.5	1.2±0.8
NOx (ppb)								
Daytime	0.8±0.3	0.87±0.71	0.67±0.29	5.2±4.4	2.0±2.3	2.6±5.5	5.35±4.6	0.34±0.22
All day	1.1±0.7	1.8±2.0	1.7±1.9	10.6±9.5	3.8±3.9	2.9±3.9	16.5±17.6	0.63±0.60
Isoprene (ppb)								
Daytime	6.2±3.2	5.4±2.4	2.9±1.2		1.3±0.8	2.0±1.2	0.5±0.3	5.2±1.9
All day	4.7±4.1	3.9±3.2	2.2±2.0		1.0±1.0	1.7±1.8	0.5±0.8	3.4±2.4
Temperature (°C)								
Daytime		30.9±2.6	31±3.3	28.4±2.7	29.2±2.7	25.9±2.8		27.5±2.5

	All day	27.8±4.3	28.6±4.5	25.3±3.3	25.7±3.9	23.1±3.8		24.7±3.2
		*4,*5,*6	*5	*7,*8	*9,*10	*11	*11,*12,*13	

1

2 [*1]AGL means above ground level. Daytime is 10 am – 4pm local time.

3 [*2]The data on June 4th was not included. PPN and MPAN include data of below detection limit, 1.8 and
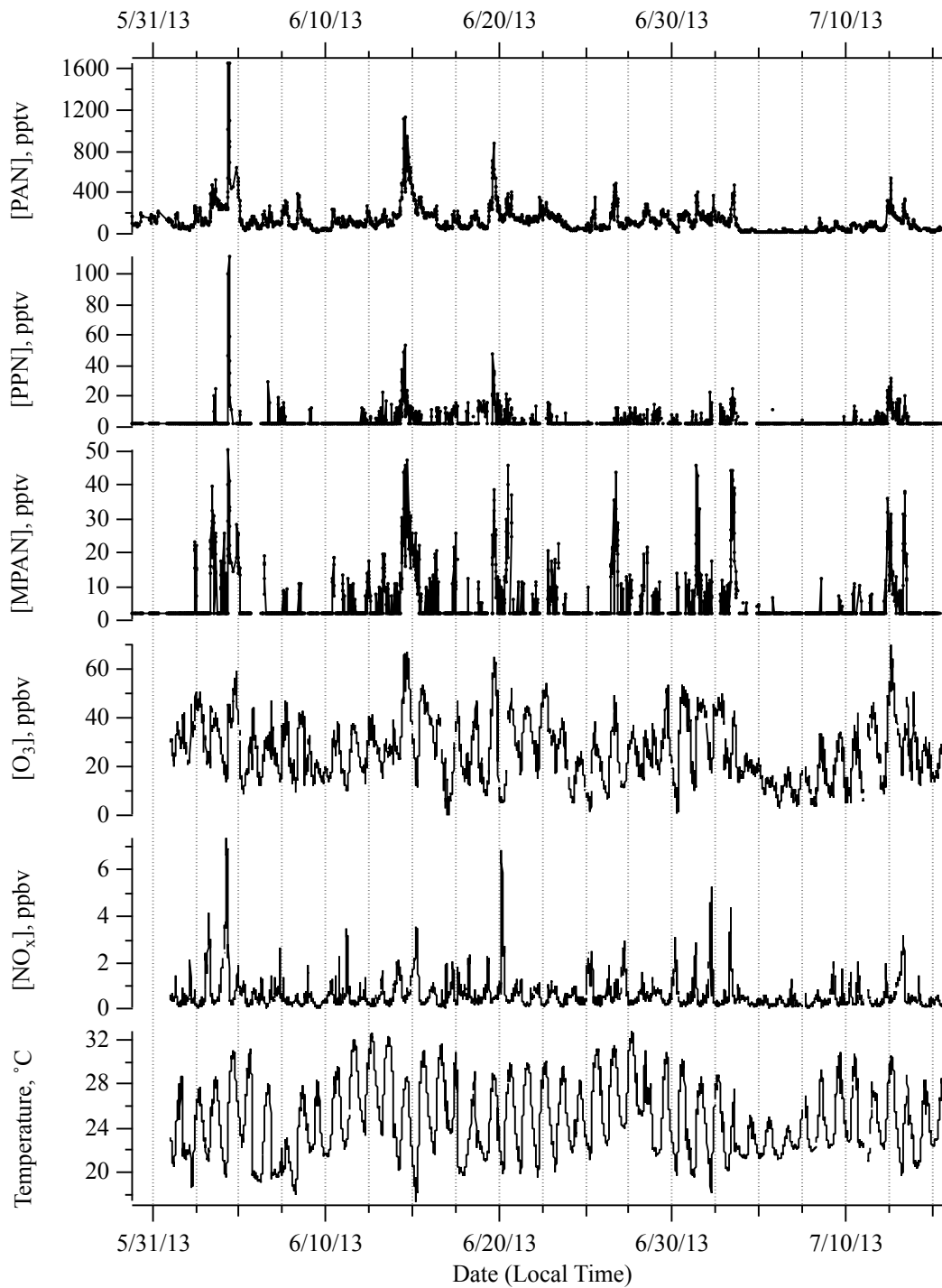
4 1.9 pptv respectively.

5 [*3] PANs were calculated as the sum of PAN, PPN, and MPAN.

6 The data was recalculated based on time and day. References: [*4]Frost et al. (1998);[*5]Buhr et al.

7 (1995);[*6]Cantrell et al. (1992);[*7]Robert et al. (1998);[*8]Baumann et al. (2000);[*9]Starn et al.

8 (1998);[*10]Nouaime et al. (1998);[*11]Barket et al. (2004);[*12]Roberts et al. (2002); and [*13]Thornton et al.

9 (2002)

10

1
2 Figure 1. Time series of PAN, PPN, MPAN , O₃ and NOₓ, and temperature during SOAS 2013
3 campaign. Data that were below detection limit (BDL) are included at half of the detection limit.
4
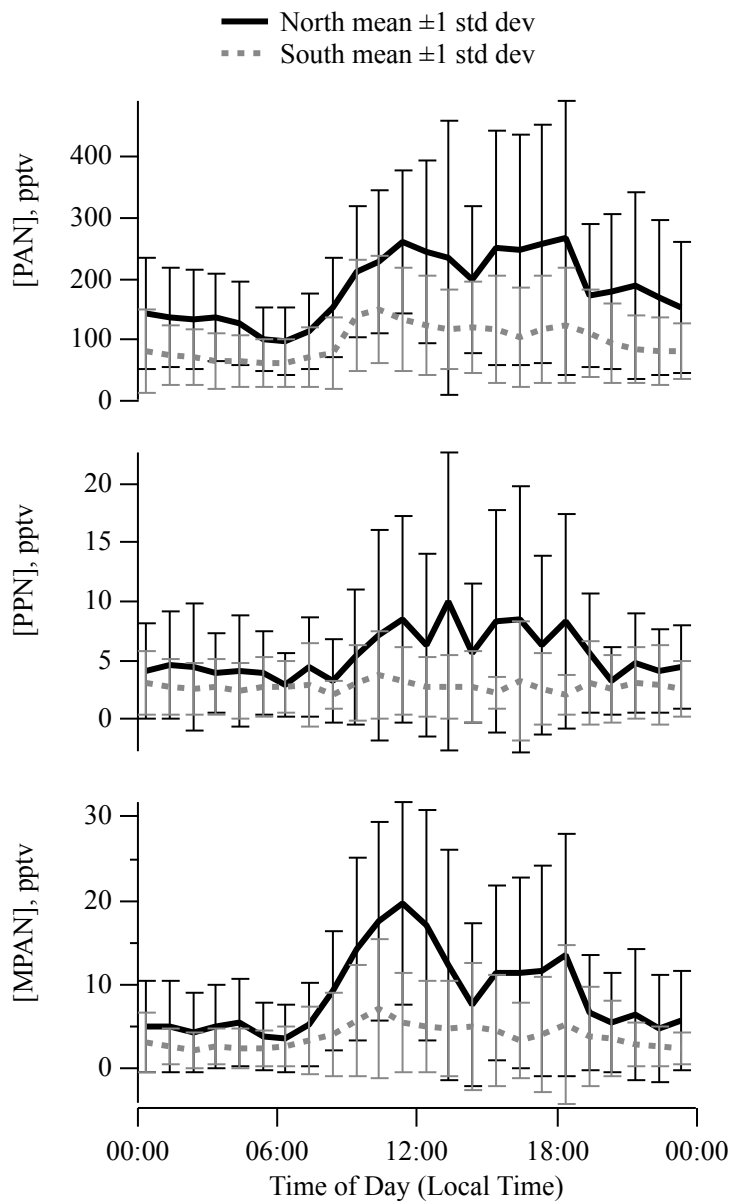
1
2 Figure 2. Diurnal behavior of PAN, PPN, and MPAN during SOAS 2013 with wind from South and
3 North.
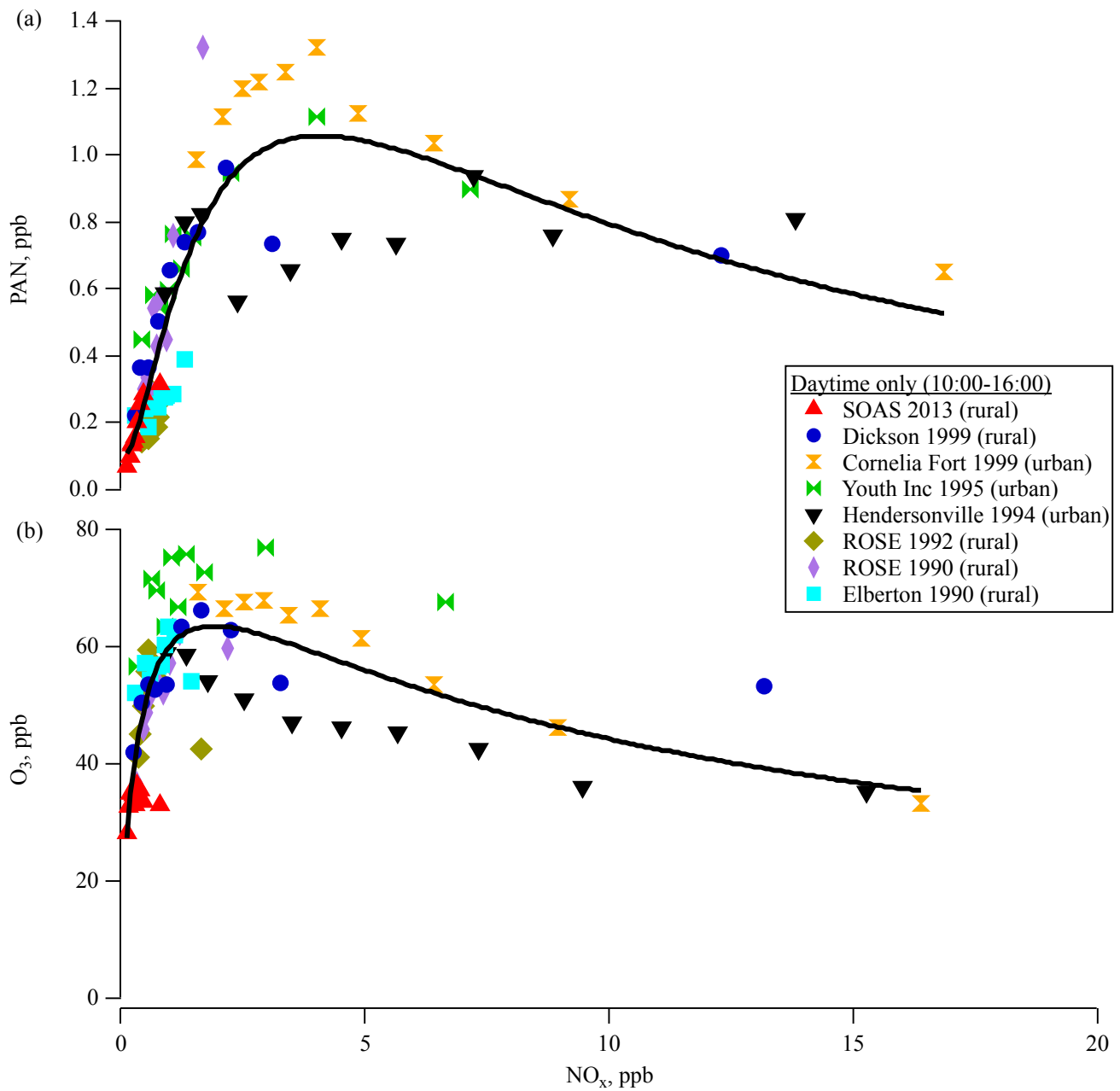
Figure 3. Surface (a) PAN and (b) ozone concentrations for each ground site in the Southeastern U.S. over the last 23 years for 10 am – 4 pm as a function of the Concentration of NO_x in deciles. The solid line indicates a fit line for all measurements.

1
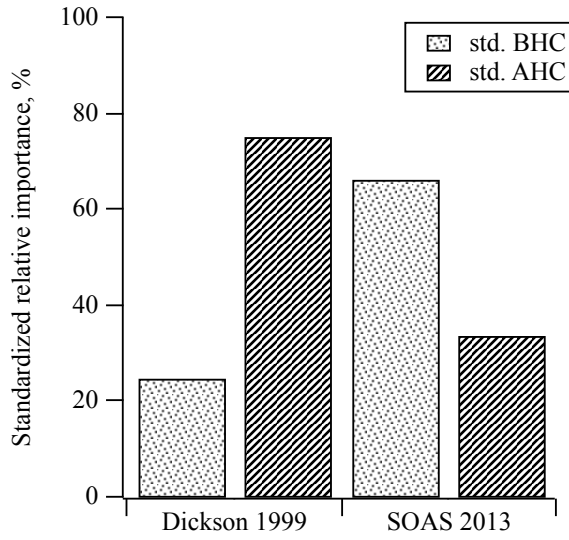
2
3 Figure 4. Comparison of standardized relative contribution to PAN formation from biogenic and
4 anthropogenic hydrocarbons during the daytime in Dickson, TN in 1999 and SOAS, in Centreville, AL
5 in 2013. The std. BHC and std. AHC mean that standardized relative importance of biogenic
6 hydrocarbon and anthropogenic hydrocarbon respectively.
7
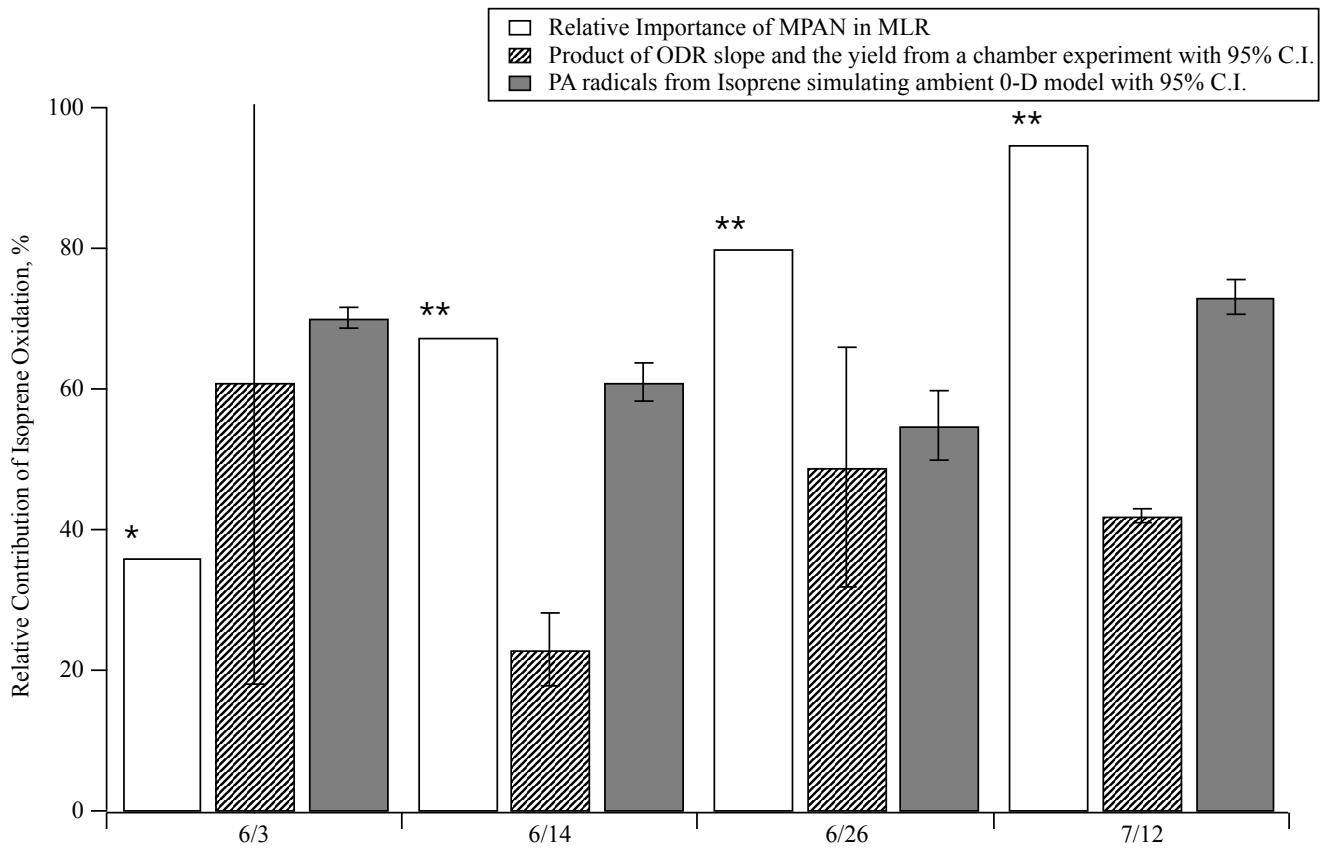
*P<0.05, **P<0.001*

Figure 5. Estimates of the relative contribution of isoprene oxidation to PANs formation during 4 specific days of SOAS 2013 using three different approaches: multiple regression analysis, ODR with chamber data, and simulation of PA radicals using a 0-D model. *P* indicates the calculated probability of the t-test; C.I. = confidence interval.
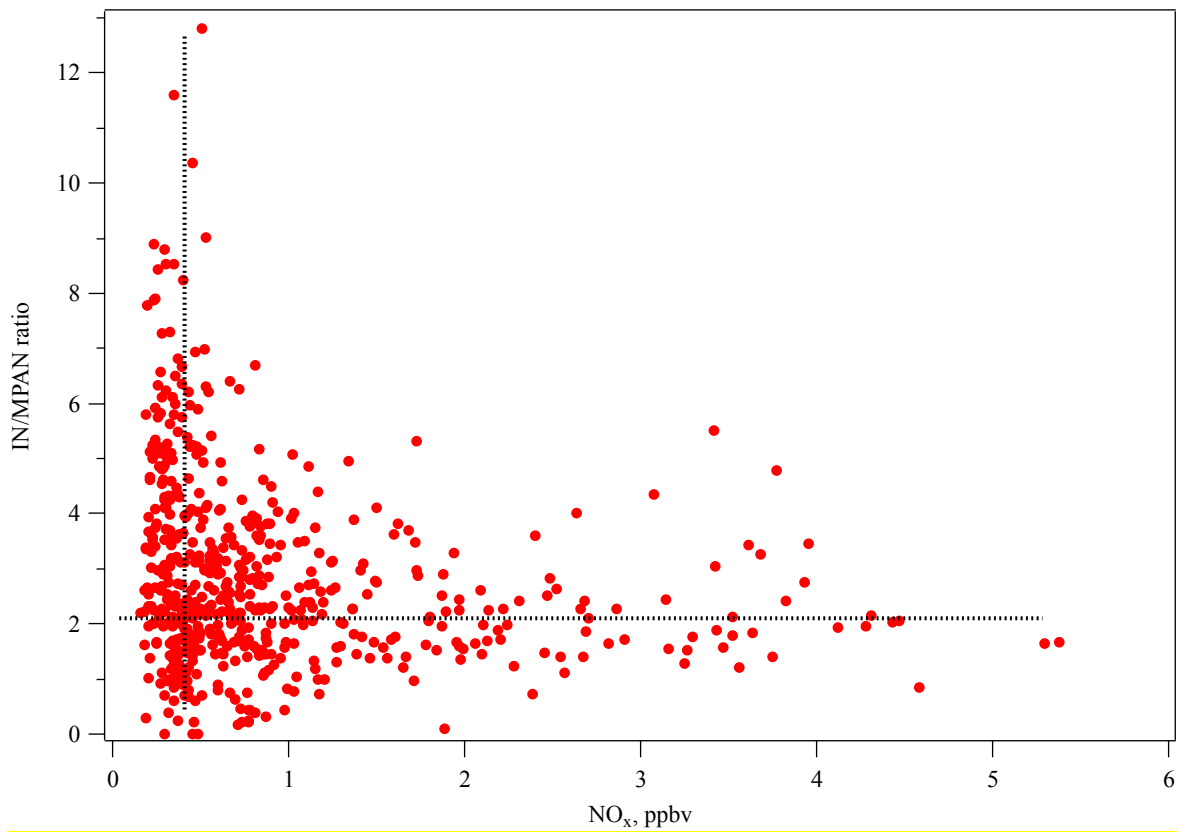
1
2 Figure 6. The relationship of daytime IN/MPAN ratio with NOx concentration (10 am – 4pm). (The
3 dashed vertical and horizontal lines are used for reference only.)
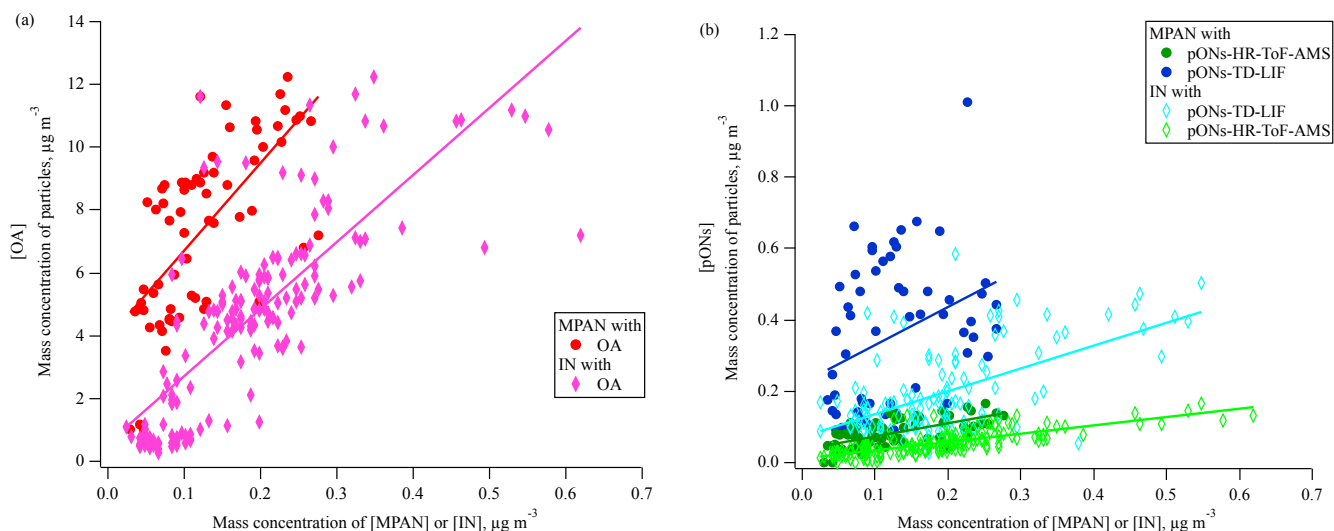
Figure 7. The relationship between mass of MPAN or IN in the gas phase and in organic aerosol during the daytime June 29 – July 15 (the time period when data on pONs-TD-LIF was available). (a) OA is organic aerosol (without organic nitrate) and (b) pONs is particle-phase organic nitrates. MPAN has a linear slope (R^2) of 27.8 (0.455) vs. OA, 0.4 (0.437) vs. pONs-HR-ToF-AMS, and 1.1 (0.120) vs. pONs-TD-LIF. IN has a linear slope (R^2) of 21.4 (0.606) vs. OA, 0.2 (0.603) vs. pONs-HR-ToF-AMS, and 0.6 (0.341) vs. pONs-TD-LIF.

Supplementary Information for

"Importance of Biogenic Volatile Organic Compounds to Peroxyacyl Nitrates
(PANs) Production in the Southeastern U.S. during SOAS 2013"

4	**S. Toma et al.**

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5

==Comparison of PANs measurements among WMU, ARA, and UC Berkeley==

During the SOAS 2013 campaign, two other research groups measured the sum of total PANs without identification of each species. ARA measured total PANs using thermal dissociation into NO_2 at 160 °C on top of ambient NO_2 located within 30 m of the WMU instrument and at the same height. The Berkeley group measured total PANs using thermal dissociation from the tower approximately 100 m north of the WMU instrument and approximately 25 m above the ground. Total PANs from all three groups showed statistically significant ($p < 0.01$) positive linear correlations with each other based on results from Spearman's rank correlation test (a nonparametric test was used due to non-normal distributions). The correlation coefficient, r_s of each pair ($PANs_{WMU}$ vs. $PANs_{ARA}$, $PANs_{WMU}$ vs. $PANs_{UC}$, and $PANs_{ARA}$ vs. $PANs_{UC}$) was 0.754, 0.926, and 0.714 respectively. However, a Friedman test resulted in statistically different medians of PANs from three groups. The relationships with $PANs_{WMU}$ are plotted in Figure S1. Overall, the measurement of $PANs_{UC}$ was 50% greater than $PANs_{WMU}$, while the measurement of $PANs_{ARA}$ was 30% less than $PANs_{WMU}$. The strong statistical correlation of all datasets allows the investigation of PANs behavior despite the systematic differences.

20
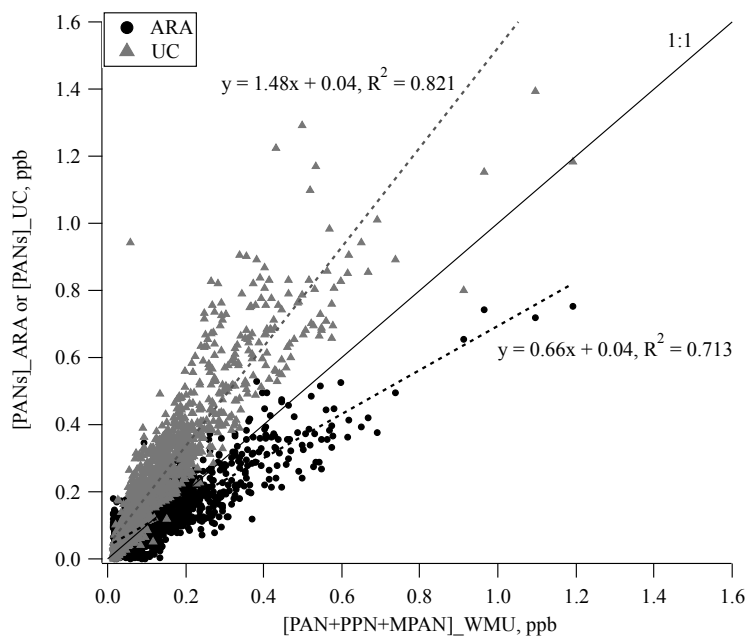
1
2 Figure S1. Relationship of total PANs with other research groups during SOAS 2013 campaign.
3 The means with standard deviation of PANs from ARA, UC, and WMU were 0.129 ± 0.092,
4 0.245 ± 0.194, and 0.138 ± 0.119 ppb respectively. The medians of PANs from ARA, UC, and WMU were
5 0.111, 0.204, and 0.103 ppb respectively.
6
7
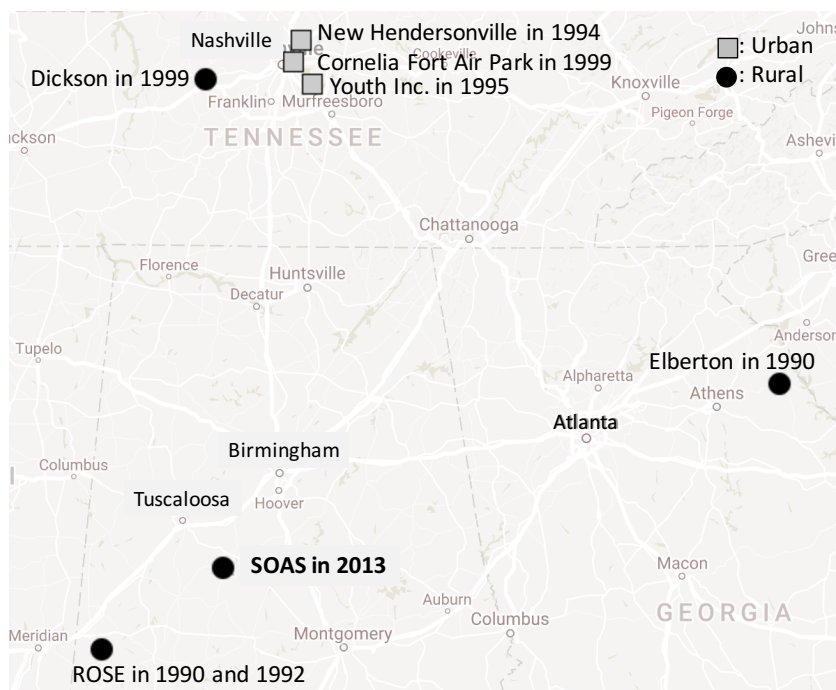
8
9
10 Figure S2. Various Locations of Other Measurements in the Southeastern U.S. since 1990. Sampling
11 term: Elberton (June 24th – July 13 in 1990), ROSE 1990 (June 10th – July 20th in 1990), ROSE 1992
12 (June 19th – July 2nd in 1992), Henderson (June 22nd – July 19th in 1994), Youth Inc. (June 29th – July
13 26th in 1995), Dickson (June 13th – July 15th in 1999), Cornelia Fort Ground Site (June 14th – July 14th in
14 1999), and SOAS 2013 (June 1st – July 15th in 2013). (*Data map: Google map, 2016).*
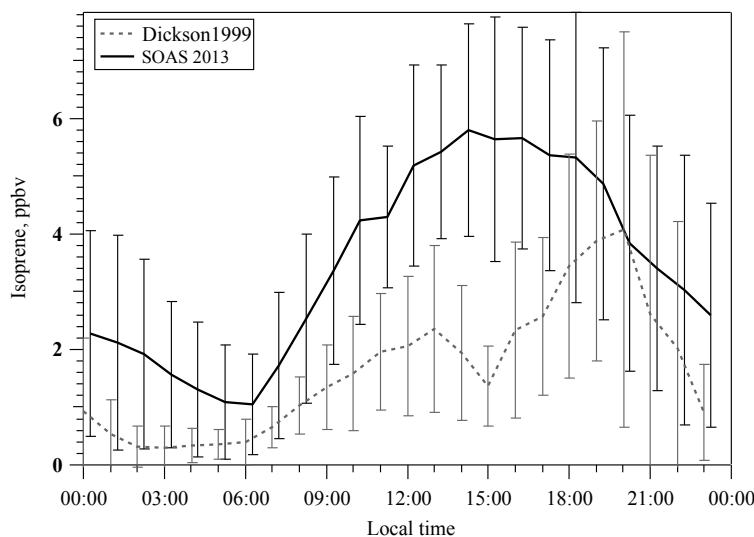
(a) PAN (b) PPN (c) MPAN (d) Isoprene, ppbv
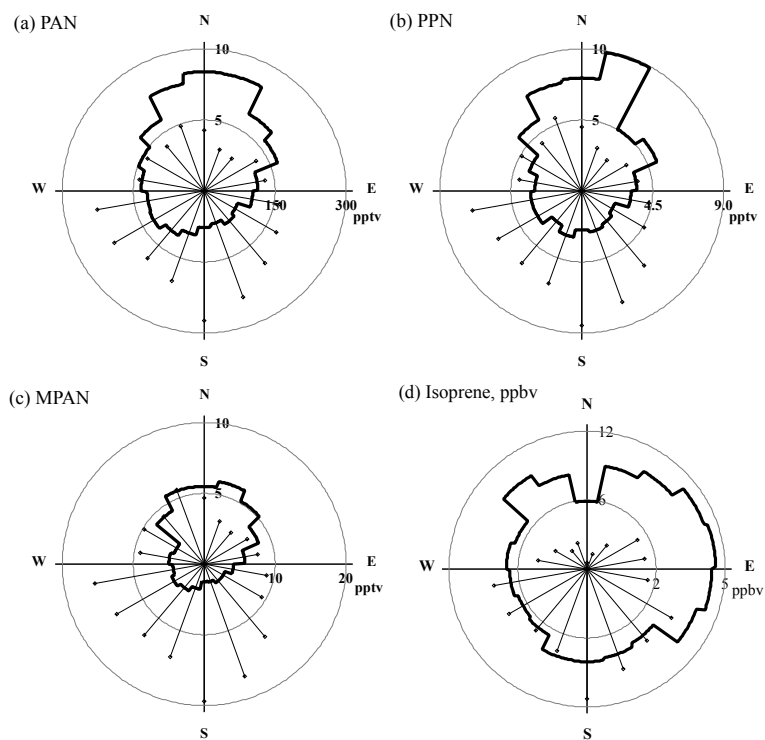
Figure S3. Polar plots of PANs and isoprene concentrations as a function of wind direction in SOAS 2013 (excluded June 4th). The bold trace line in each plot indicates the average concentration of each compound and the solid lines from the center are the frequency of wind direction.

1

2   (a)
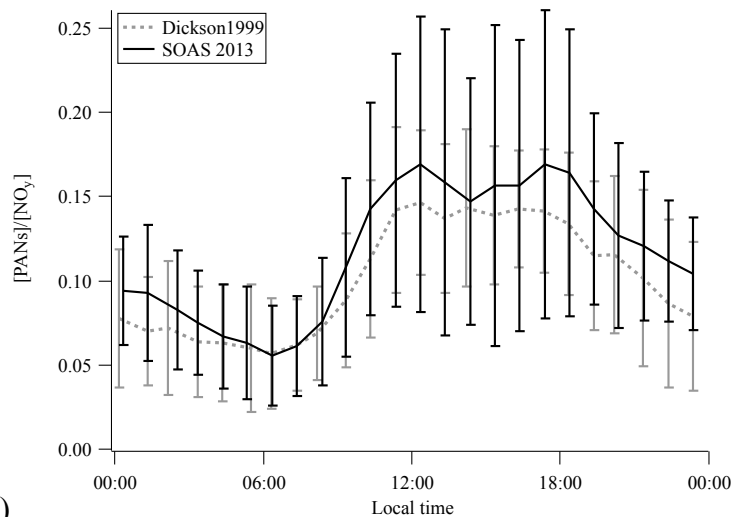
3   (b)
4
5 <mark>Figure S4. Hourly diurnal profiles of mean (a) PANs/NO$_y$ and (b) isoprene with one standard deviation</mark>
6 <mark>from the Dickson 1999 and SOAS 2013 campaigns.</mark>
7
8
9 **Methods and Results of MLR analysis for PANs**
10

$$[PAN] = A + B_1[MPAN] + B_2[PPN] \tag{1}$$

11
12   In a multiple linear regression (MLR) model as Equation (1), [PAN] is treated as a response
13 variable and [MPAN] and [PPN] are used as independent predictor variables. B_1 and B_2 are partial
14 regression coefficients on [MPAN] and [PPN]. The MLR statistical analysis conducted two steps of
15 statistical testing. First, the F-test in ANOVA and R^2 investigated how well the model Eq. (1) fits the
16 measurement data. However, F-test is impossible to directly find out which predictor variable is
17 significantly useful. Therefore, in the next step, the significant utility of each partial regression coefficient

4

1 was explored using the Student's *t*-test. The respective *t*-value was calculated from each partial regression

2 coefficient divided by the standard error. When results of the *t*-test indicate presence of statistical

3 significance for the partial regression coefficients, the magnitude of the standardized partial regression

4 coefficient, β_i, allows us to compare the relative contribution of each independent predictor variable within

5 the model.

6   As the notice to conduct MLR statistical analysis, high multicollinearity causes effects on the

7 results of the analysis (e.g. Mendenhall et al., 2009). Although the assumption of the MLR statistical

8 analysis on [PAN] takes a stance that each predictor variable is derived from different hydrocarbon

9 precursor independently, the values of "tolerance" or "variance inflation factor (VIF)" were helpful to

10 assess the impact of the multicollinearity. The tolerance is calculated as 1- $R^2_{MPAN-PPN}$, where $R^2_{MPAN-PPN}$

11 is the coefficient of determination between MPAN and PPN and VIF is 1/tolerance. Large VIF value

12 indicates strong multicollinearity of predictor variables. According to Stevens (2012), if the value of VIF

13 is greater than 10, it indicates effective multicollinearity.

14   The statistical analysis was conducted using SPSS statistics software (versions 16, IBM). Results

15 of *F*-test and R^2 on the MLR model for SOAS 2013 during the daytime are summarized in Table S1.

16 Similar PANs data collected from Dickson, TN during the SOS experiment in 1999 is used as a

17 comparable reference. The small *p*-value (*P* in Table S1) of *F*-test indicated that the overall fit of the

18 model Eq. (1) is statistically significant in both the SOAS 2013 and Dickson 1999, and at least one

19 independent predictor variable was significantly useful.

20

Table S1. Summary of the *F*-test and R^2.

Year	Number of data	*P* of *F*-test	*R*	R^2
Dickson, TN in 1999	486	<0.001	0.876	0.766
SOAS 2013	498	<0.001	0.775	0.601

21

22   A summary of coefficients of MPAN and PPN in both SOAS 2013 and Dickson 1999 is shown in

23 Table S2. Since all VIF values were less than 10, there was no impact of multicollinearity in the MLR

24 statistical analysis in both SOAS 2013 and Dickson 1999. The small *p*-value (*P* in Table S2) of the *t*-test

25 of both MPAN and PPN in SOAS 2013 and Dickson 1999 indicates both predictor variables were useful

26 to predict PAN. Therefore, respective partial regression coefficient values were available to estimate PAN

27 in SOAS 2013 and Dickson 1999.

28

Table S2. Summary of coefficients on each independent predictor variable in t- test.

	Dickson, TN in 1999		SOAS 2013	
	MPAN	PPN	MPAN	PPN
Partial regression coefficient	B_1 5.098	B_2 5.762	B_1 7.596	B_2 6.910
Std. error of coefficient	0.305	0.178	0.469	0.725
P of t-test	<0.001	<0.001	<0.001	<0.001
VIF	1.036	1.036	1.427	1.427
β_i	0.374	0.725	0.549	0.323
r_i	0.509	0.795	0.726	0.624
Partial $R^2 = \beta_i\, r_i$	0.190	0.576	0.399	0.202

Std. error of coefficient means standard error of partial regression coefficient. P is calculated probability. β_i is standardized partial regression coefficient. r_i is zero-order correlation. All dataset was during the daytime, 10 am – 4 pm.
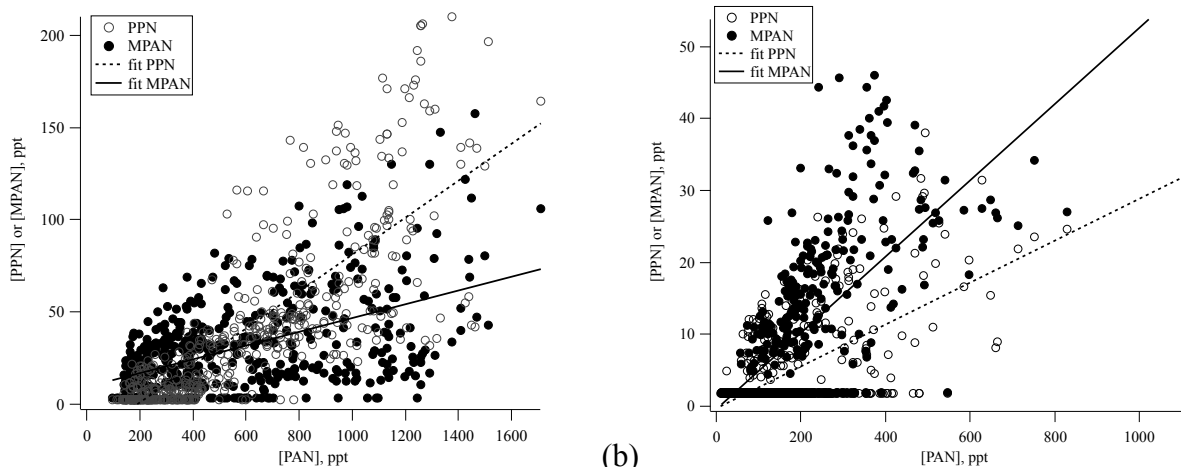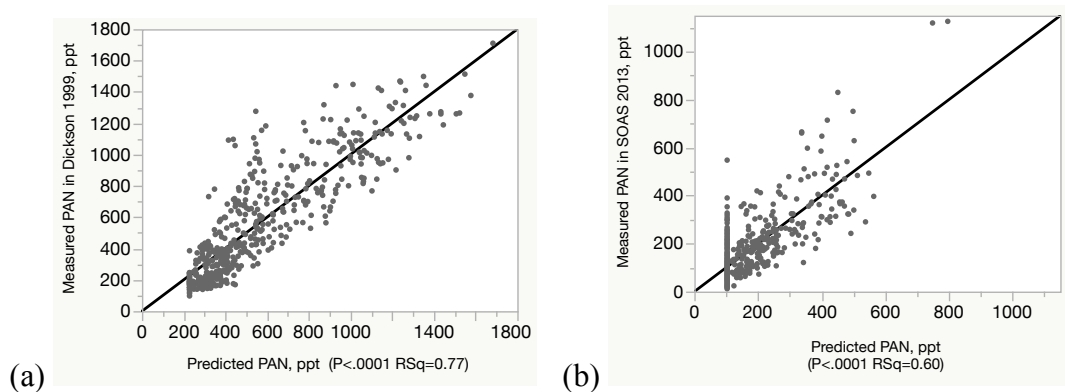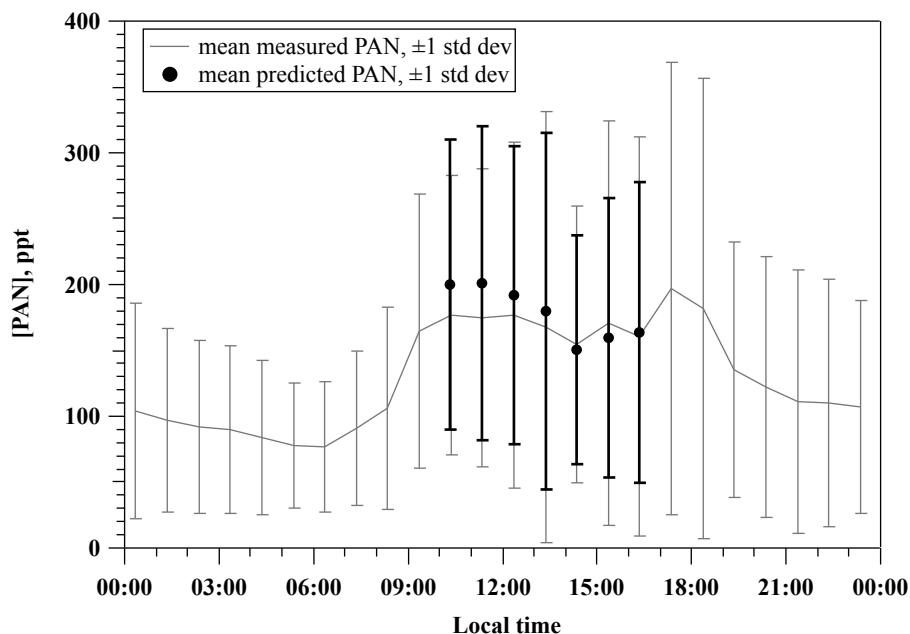

(a)   (b)

The below detection limit data were included at half of the detection limit. The solid line is the fit for MPAN to PAN and the dash line is the fit for PPN to PAN. The slopes with standard deviation were 0.037±0.003 (R^2=0.259) for MPAN to PAN and 0.100±0.003 (R^2=0.633) in Dickson 1999, and 0.053±0.002 (R^2=0.530) for MPAN to PAN and 0.029±0.002 (R^2=0.390) in SOAS 2013.

(a)   (b)

The below detection limit data for PPN and MPAN in SOAS 2013 were included at half of the detection limit in this experiment to avoid to lose the low concentration information. (JMP version 12.1.0, SAS Institute Inc.)

(Note: this measured PAN was not filtered by wind direction like Figure 2.) Predicted PAN was calculated based on measured PPN and MPAN during the daytime (10 am – 4pm).

7