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, $RC(O)OONO_2$), products of the photooxidation of VOCs in the presence of nitrogen oxides ($NO_x \equiv NO + NO_2$), 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 (NO_y) in rural and forested areas, including the Eastern United States depending on how aged the air sampled at the site is (e.g. Trainer et al., 1993, Nouaime et al., 1998). The fraction depends on air mass history and conditions, since wet deposition of nitric acid, the other major component, will affect total NO_y levels. PANs are ubiquitous reservoir species for NO_x and radicals in the atmosphere that affect the lifetime of NO_x and enhance tropospheric O_3 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 (Roberts, 2007). Scission of the thermally weak bond to NO_2 regenerates the PA radical (R1). Permanent loss of PANs occurs when the PA radical is lost (R2). With sufficient NO_x, this occurs via reduction by NO, and gas-phase PAN thermal lifetime, assuming steady-state for PA, depends on the ratio NO/NO_2 as equation (1). Peroxy radicals compete with NO for reaction with PA at low NO_x.

$PAN \rightleftharpoons PA + NO_2$, (R1, R-1)

$PA + NO \longrightarrow$ Products, (R2)

$$-\frac{d[PAN]}{dt}=k_1[PAN]\left(1-\frac{1}{1+\left(\frac{k_2[NO]}{k_{-1}[NO_2]}\right)}\right) \quad (1)$$

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 2 ppmv 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 ($\equiv OH + HO_2 + RO_2$) 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 reactions are HO_x+HO_x. At higher NO concentrations, O_3 production rate slows as OH is consumed by NO_x-removing chain termination reactions (HO+NO_2 and RO_2 + NO → $RONO_2$) that 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. PAN at sites with lower NO_x levels seem to be more sensitive to NO_x concentrations, as is seen for most of the rural sites in this region. 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 2.

$$[PAN] = A + B_1[MPAN] + B_2[PPN] \qquad (2)$$

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 (2) 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). The individual t-test, which is based on the Student's t statistic, is used to investigate the statistical significance of the individual B_1 and B_2. In a MLR statistical analysis, the magnitude of the standardized partial regression coefficients, β_i, which is calculated as a product of partial regression coefficient and the ratio between the standard deviation of the respective independent variable (MPAN or PPN) and the standard deviation of the dependent variable (PAN), is frequently used to compare the relative contribution of independent variables. The results of MLR statistical analysis are summarized in Tables S1 and S2.

Tatsuoka (1971) showed that R^2 from the MLR is equal to the sum of the product of the β_i and the zero-order (simple bivariate) correlation, r_i, which are obtained as results of MLR (see Table S2). That is, $R^2 = \Sigma\, \beta_i r_i$. Therefore, we used the fraction of R^2 based on the strength of relationship in each [MPAN] and [PPN] to [PAN] to describe the relative importance of BHC and AHC. Each partial R^2 is obtained as shown in equations 3 and 4.

$$R^2_{BHC} = \beta_1 * r_{MPANvs.PAN} \qquad (3)$$

$$R^2_{AHC} = \beta_2 * r_{PPNvs.PAN} \qquad (4)$$

This approach allows us to directly treat the R^2 in the MLR to assess the relative importance of BHC and AHC, including the strength of correlation with PAN.

Results from SOAS were compared with similar PAN data collected from Dickson, TN in 1999, another rural southeastern site, which show that the MLR model and regression coefficients for both MPAN and PPN at both sites were statistically significant to predict PAN (see Tables S1 and S2). During SOAS 2013, 60% of the variance in the measurements was explained by the MLR model (R^2=0.601). At the Dickson site in 1999, 77% of the variance was explained by the MLR model (R^2=0.766). The R^2 of MLR in the SOAS 2013 data was lower than that in Dickson 1999, which might result from the lower absolute PANs levels during SOAS 2013. In particular, SOAS MPAN and PPN data included a large number of below detection limit measurements, while Dickson 1999 data did not. The means of PAN, MPAN, and PPN in Dickson 1999 were three times higher than the mean for SOAS 2013, while NO_x levels were five times higher (see Table 1). In Figure 4, the relative importance of BHC and AHC was standardized to compare SOAS 2013 and Dickson 1999. Based on the PAN precursors represented by the variance explained by the

MLR, standardized relative percentiles (R^2_{BHC}/R^2 and R^2_{AHC}/R^2) estimate that 66% of PAN at SOAS 2013 came from biogenic precursors. In comparison, biogenic influence (mostly isoprene) from Dickson accounted for only 25% of PAN. Although both sampling locations were located in rural areas, the results using MLR indicate that the HC precursors were different.

3.3.2 Comparison of contribution of isoprene oxidation with computational modeling

We used two computational approaches to assess the contribution of isoprene oxidation to PAN formation by 1) orthogonal distance regression (ODR) between field measurements of MPAN and PAN and 2) simulation of the production of peroxyacetyl (PA) radicals, precursors of PAN, using an ambient 0-D photochemical model.

In ODR, the fraction of PAN production from isoprene oxidation can be expressed as $(d[PAN]_{isoprene}/dt)/(d[PAN]_{all}/dt)$. Assuming that MPAN is solely derived from isoprene oxidation, the relative yield of $(d[MPAN]/dt)/(d[PAN]_{isoprene}/dt)$ was obtained from an isoprene oxidation chamber experiment as 0.15±0.03 RSD. The reaction was initiated with 1.37 ppm isoprene, 268 ppb NO, and 206 ppb NO_2 under 5% RH in a 5.5 m^3 Teflon cylindrical bag. The OH radical was produced by photolysis of HONO. The fraction of PAN production from isoprene oxidation to total PAN formation in the field was rearranged as the following equation.

$$\frac{d[PAN]_{isoprene}/dt}{d[PAN]_{all}/dt} = 6.7 \times \frac{d[MPAN]/dt}{d[PAN]_{all}/dt} \qquad (5)$$

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

In the 0-D photochemical model simulation, the relative contribution to peroxyacetyl (PA) radicals from VOCs present at the field site is based on the Master Chemical Mechanism (MCM) v3.3. The ambient model included not only isoprene and its oxidation products (including $CH_3C(O)CHO$) but also acetone, acetaldehyde, and some mono-terpenes as precursors. The detail of the parameters for MCM set are described in Groff (2015).

These two methods were compared with the relative importance of BHC, $\beta_1 * r_{MPAN vs. PAN}$, from the MLR 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 Jul 12th 13:00 – 18:00) of data from SOAS 2013 were selected to run the 0-D model because the production ratio using ODR can only be used when PAN, MPAN and NO_x concentrations were appropriately high. The time ranges were chosen so that the boundary layer height would be stable and any dilution effect would be minimal. Results of the comparison are plotted in Figure 5. Although the relative importance of

BHC in the MLR model was less than 40% on June 3rd, it was statistically dominant on the other three days accounting for more than 68%. (Note: PPN on June 3rd did not have a significant level to predict PAN in MLR analysis, $p = 0.600$.) By comparison, the estimated contribution of isoprene oxidation using ODR on June 3rd had the steepest slope, however, the range of the 95% confidence interval (C.I.) on this day was large. On the other three days, the relative contributions of isoprene oxidation using ODR were estimated at 23 – 49%, lower than the results derived from the other two methods. This might be due to the differences between the chamber experiment and ambient conditions. Specifically, the ratio of secondary to primary oxidation products varies between chamber and ambient conditions, with likely relatively greater primary products under chamber conditions. Since PAN is formed via the oxidation of secondary products of isoprene, the $[\mathrm{MPAN}]/[\mathrm{PAN}]_{\mathrm{isoprene}}$ ratio would be higher in the chamber experiment than in ambient environment. This ratio is expected to derive results that are biased low, when used to estimate the ambient isoprene-derived PAN concentration. In addition, photolysis rates also are significantly different between the chamber and the field conditions. The results of the 0-D model suggest that isoprene oxidation significantly contributed to PAN formation with a mean range of 55–73% over all selected days. Hence, both methods, the MLR and the 0-D model, indicate that isoprene oxidation was the main source when high levels of PAN were observed during SOAS 2013.

4. Discussion

4.1 Comparison among MACR, IN, and MPAN

MACR is a first generation product of isoprene photooxidation mechanisms, and MPAN is derived from MACR oxidation (Bertman and Roberts, 1991; Kjaergaard et al., 2012). With enough NO_x, the OH adduct of isoprene that is the precursor to MACR in these mechanisms is also a precursor of gas-phase isomers of isoprene hydroxynitrates (IN) (Shepson, 2007; Grossenbacher et al., 2001, 2004; Barker et al., 2003; Paulot et al., 2009; Lockwood et al., 2010). Xiong et al. (2015) reported IN at SOAS, which affords the opportunity to study this aspect of NO_x sensitivity of isoprene oxidation. In this work, the daytime (10 am – 4 pm) relationships among MPAN, MACR and IN at SOAS was investigated using the Pearson's correlation statistical test. Missing data was treated as pairwise deletion (not listwise deletion). The correlation coefficient between the first generation products of isoprene, MACR and IN was 0.528 ($p < 0.001$) and indicated a statistically significant positive correlation, as would be expected. According to the known chemical pathways, a strong relationship is expected between MACR and MPAN, while a weak relationship is expected between IN and MPAN given that IN is a primary product, while MPAN is secondary. The results show, however, that daytime data over the whole campaign did not show a statistically significant correlation between MACR and MPAN ($r = 0.148$, $p = 0.104$). In contrast, IN has a statistically significant positive correlation with MPAN ($r = 0.499$, $p < 0.001$). Likely this relationship is a result of the NO_x dependence of both organic nitrate products. Because MACR can be produced in the absence of NO_x (Paulot et al., 2009b; Liu et al., 2013; Mao et al., 2013), MPAN is more dependent on NO_x than on MACR at this site, and isoprene nitrates constitute a larger fraction of gas-phase organic nitrates from BVOC than MPAN does, consistent with Romer et al. (2016). Figure 6 shows that the IN/MPAN ratio varies over a large range when NO_x <1ppb, corresponding to the range of high $P(HO_x)$ described by Thornthon et al., (2002). At higher NO_x levels, the ratio remains fairly constant around 2.5-3. This figure is suggestive of different chemical regimes operating under different NO_x conditions, reminiscent of the behavior of differential alkane loss when dominated either by OH or halogen chemistry in Jobson et al., (1994). The higher loss rate for MPAN expected with higher levels of HO_x may drive the IN/MPAN ratio at lower NO_x levels.

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 show 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).

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

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

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

The data was recalculated based on time and day. References: [*4]Frost et al. (1998);[*5]Buhr et al. (1995);[*6]Cantrell et al. (1992);[*7]Robert et al. (1998);[*8]Baumann et al. (2000);[*9]Starn et al. (1998);[*10]Nouaime et al. (1998);[*11]Barket et al. (2004);[*12]Roberts et al. (2002); and [*13]Thornton et al. (2002)

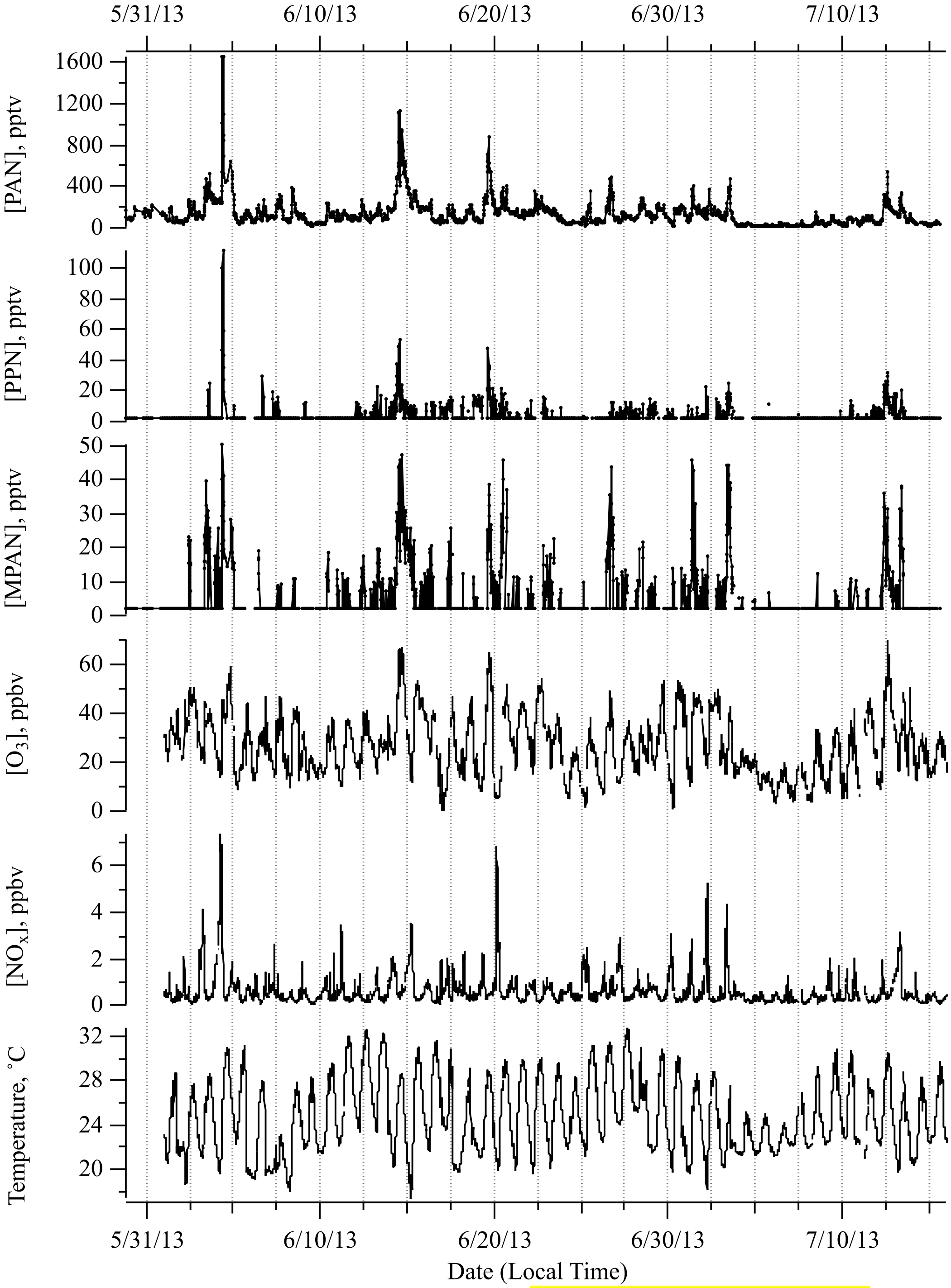


Figure 1. Time series of PAN, PPN, MPAN , O_3 and NO_x, and temperature during SOAS 2013 campaign. Data that were below detection limit (BDL) are included at half of the detection limit.

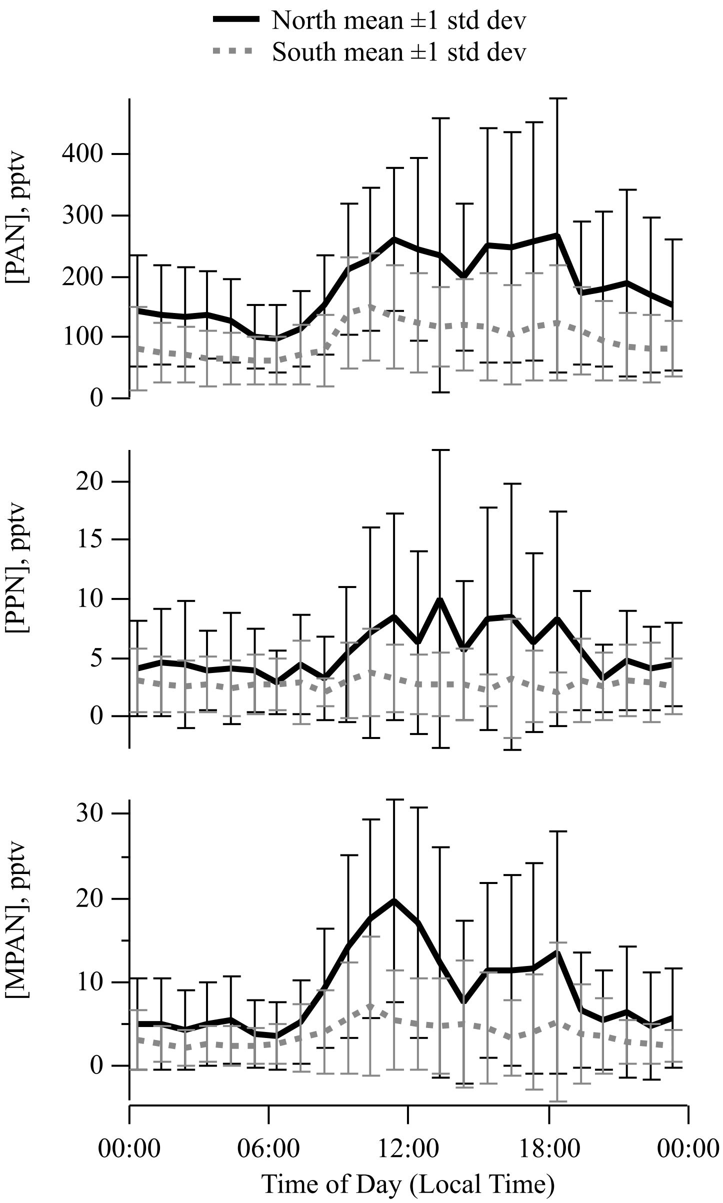


Figure 2. Diurnal behavior of PAN, PPN, and MPAN during SOAS 2013 with wind from South and North.

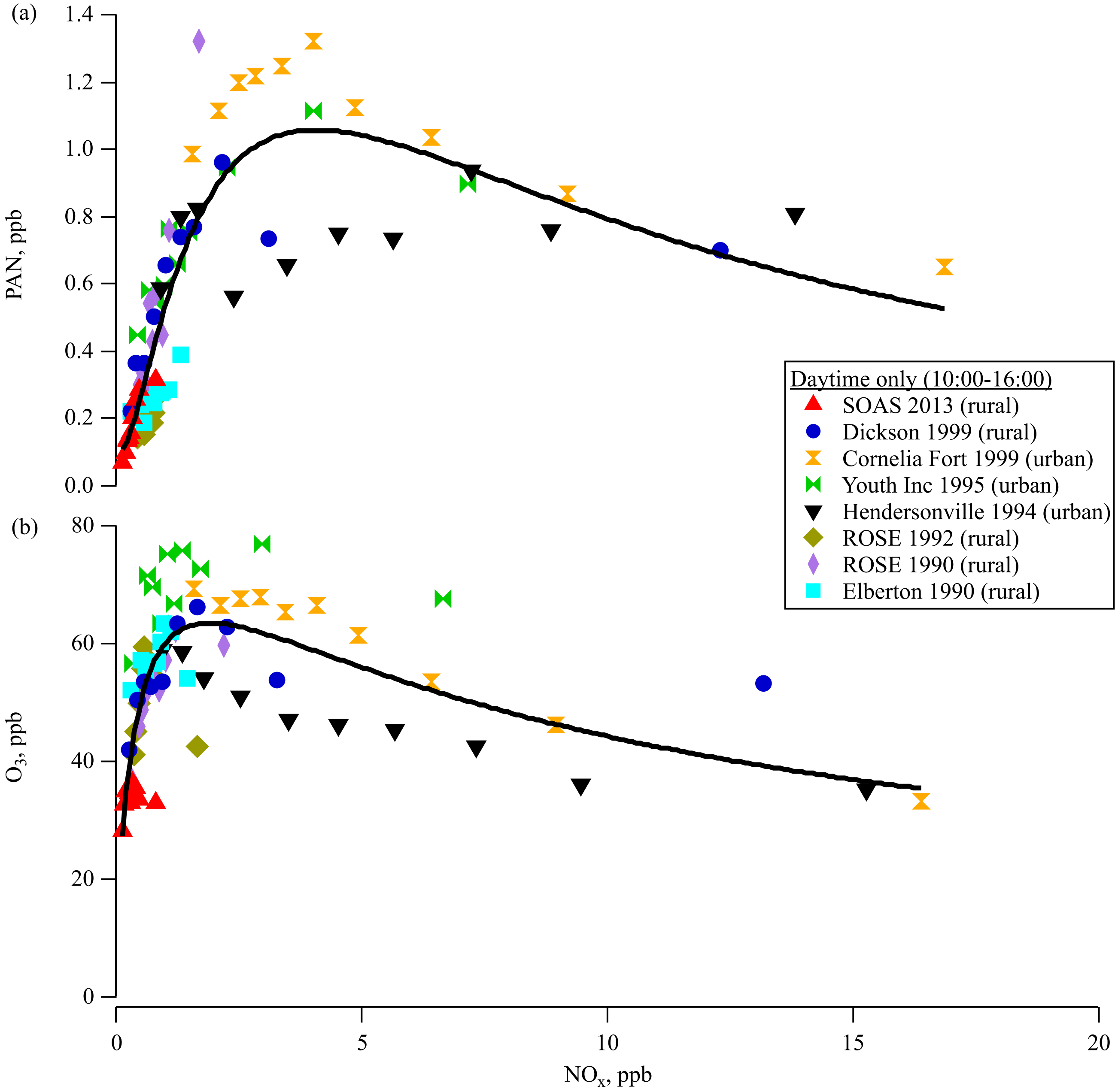


Figure 3. Surface (a) PAN and (b) ozone concentrations for each ground site in the Southeastern U.S. over the last 23 years for 10 am – 4 pm as a function of the Concentration of NO_x in deciles. The solid line indicates a fit line for all measurements.

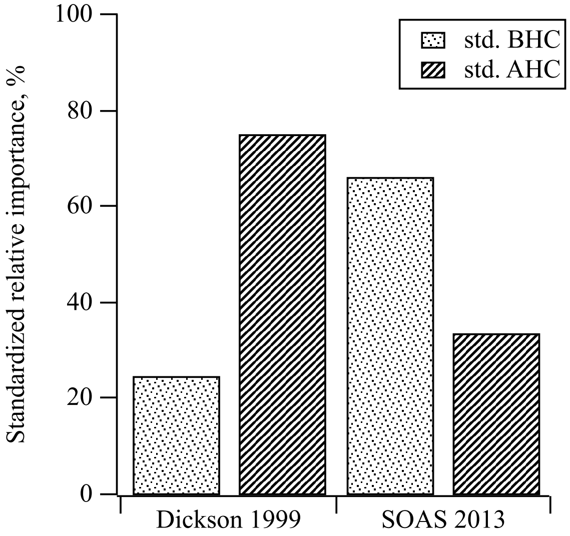
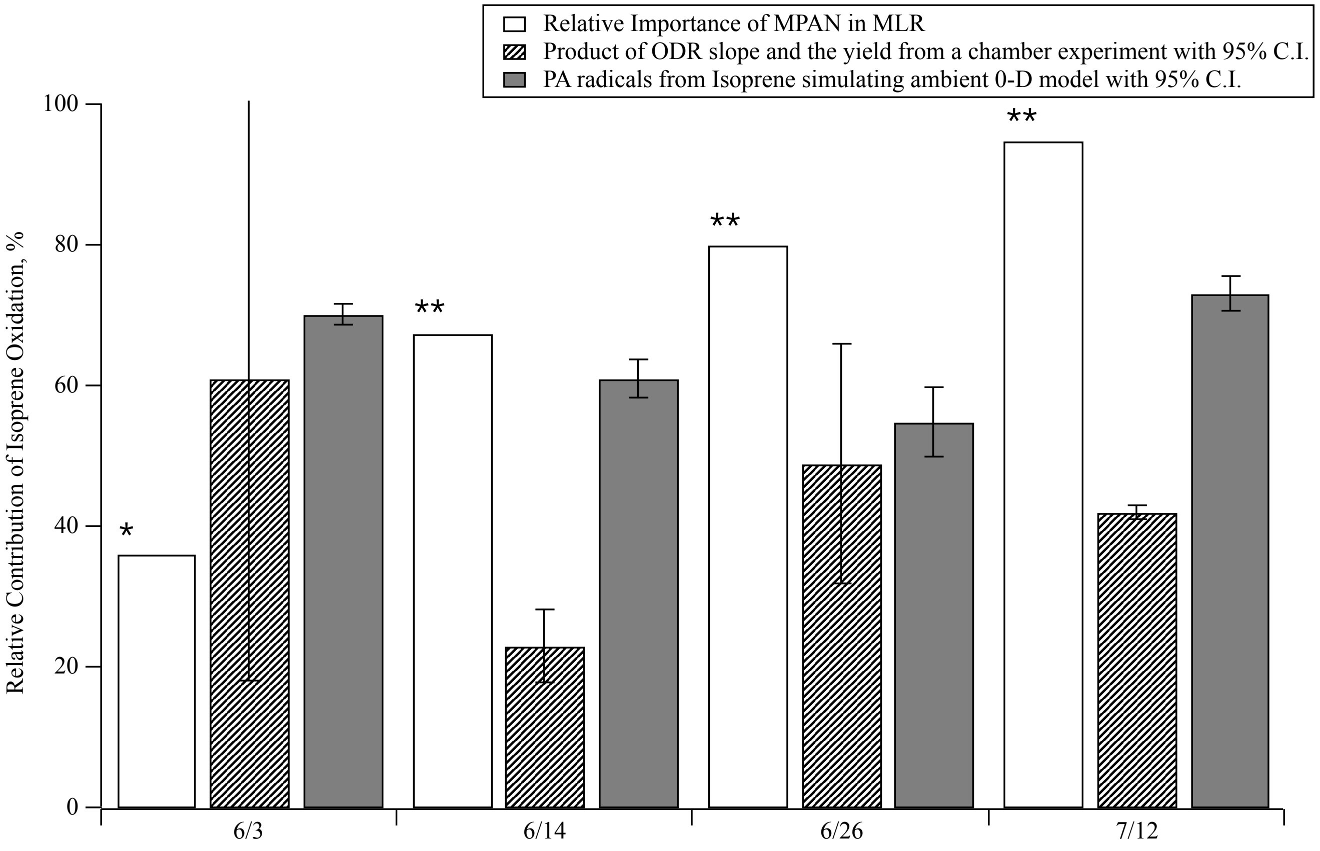


Figure 4. Comparison of standardized relative contribution to PAN formation from biogenic and anthropogenic hydrocarbons during the daytime in Dickson, TN in 1999 and SOAS, in Centreville, AL in 2013. The std. BHC and std. AHC mean that standardized relative importance of biogenic hydrocarbon and anthropogenic hydrocarbon respectively.



**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.

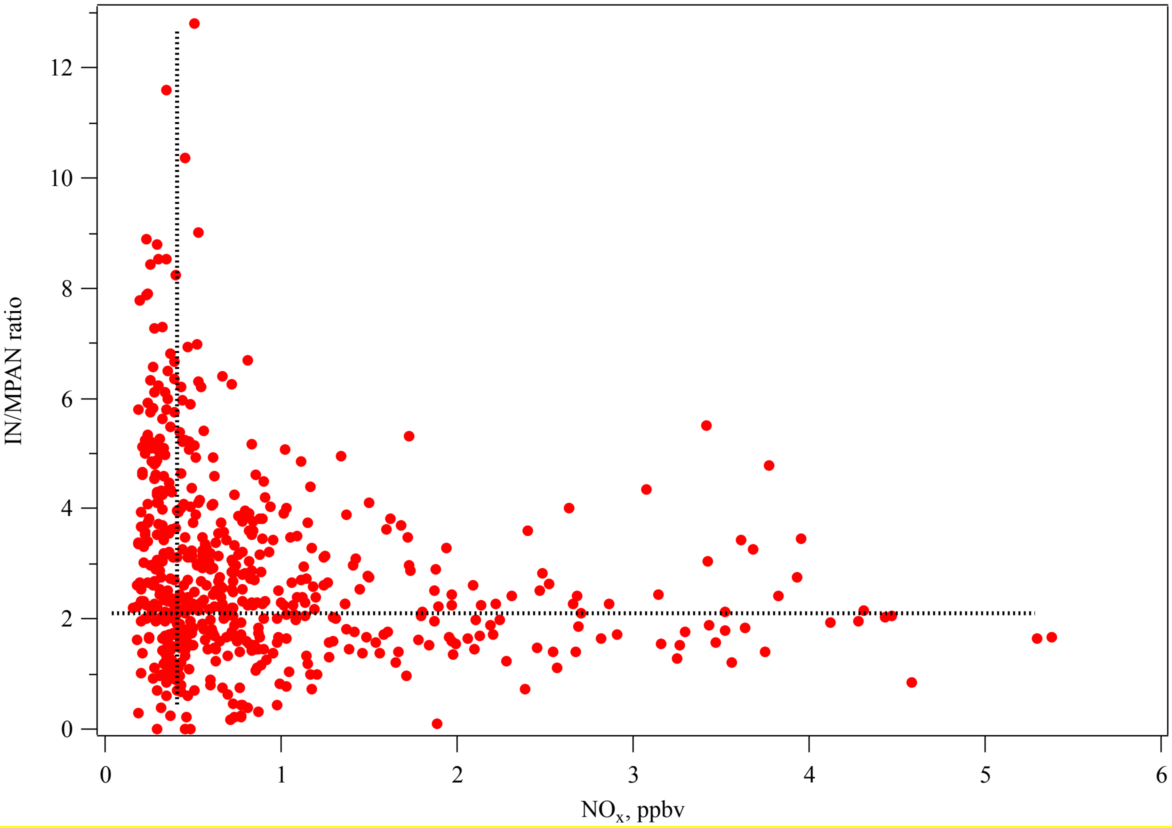


Figure 6. The relationship of daytime IN/MPAN ratio with NO_x concentration (10 am – 4pm). (The dashed vertical and horizontal lines are used for reference only.)

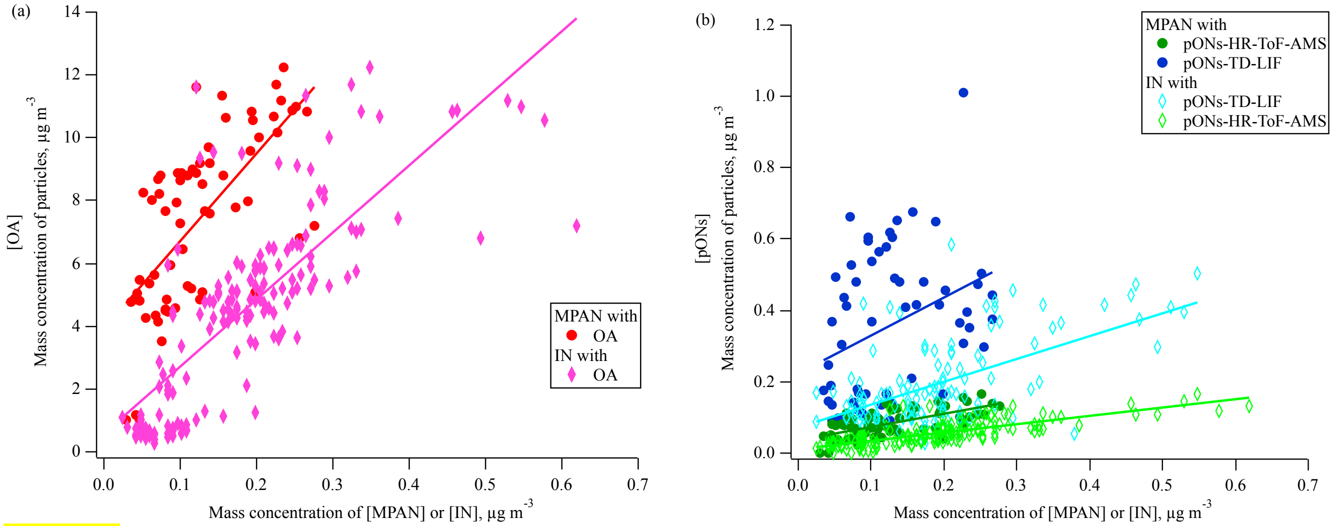


Figure 7. The relationship between mass of MPAN or IN in the gas phase and in organic aerosol during the daytime June 29 – July 15 (the time period when data on pONs-TD-LIF was available). (a) OA is organic aerosol (without organic nitrate) and (b) pONs is particle-phase organic nitrates. MPAN has a 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.