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Relationships between peroxyacetyl nitrate, O_3, and NO_y at the rural Southern Oxidants Study site in central Piedmont, North Carolina, site SONIA

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Abstract. Ambient peroxyacetyl nitrate (PAN) concentrations were measured during June and early July 1992 at site SONIA (Southeast Oxidants and Nitrogen Intensive Analysis), a rural site in the central Piedmont region of North Carolina, as part of the Southern Oxidants Study. PAN measurements were made as part of an effort to provide a comprehensive chemical climatology and to investigate the total nitrogen budget at this site. Gas chromatograph-electron capture detector (GC-ECD) was used to measure PAN every 15 min with a detection limit of 50 parts per trillion by volume. During the measurement period, maximum ambient levels of PAN reached 1.2 parts per billion by volume and averaged 0.41 ± 0.24 ppbv (n=1972) with an average daily maximum of 0.60 ppbv. The average daytime (0900-2100 EST) concentration was 0.52 ± 0.24 ppbv (n=986) while the average nighttime (2100-0900) concentration was 0.29 ± 0.07 ppbv (n=986). The O_3/PAN ratio was found to be 138 ± 98 (n=984) and the PAN/NOy ratio was 0.12 ± 0.11 (n=454). Hourly average PAN and O_3 concentrations showed a strong correlation with R=0.57 (n=984). Moreover, the composite hourly averages of PAN and O_3 for the entire measurement period showed an even stronger correlation of R=0.95. The strong correlation between O_3 and PAN suggest that mesoscale photochemical production plays a major role in PAN chemistry at site SONIA. An analysis of 10 m meteorological data suggests some correlation between regional meteorological conditions and between both the daily PAN maxima and the magnitude of the O_3/PAN ratio.

Introduction

The role of photochemically active nitrogen compounds in rural and regional tropospheric air pollution has come under increasing scrutiny [*Fahey et al.*, 1986; *Buhr et al.*, 1990; *Ridley et al.*, 1990; *Atlas et al.*, 1992; *Hübler et al.*, 1992]. Peroxyacetyl nitrate (PAN) is an important component of the odd-nitrogen compounds, NOy, which includes NOx, HNO3, NO3-, PAN, organic nitrates, and N2O5 [*Logan*, 1983; *Singh et al.*, 1985; *Bottenheim et al.*, 1986; *Fahey et al.*, 1986]. During June and early July 1992, total NOy several odd-nitrogen compounds, including PAN, were monitored continuously at site Southeast Oxidants and Nitrogen Intensive Analysis (SONIA), near Candor, North Carolina in the central Piedmont region of North Carolina. This intensive experiment was part of the Southern Oxidants Study (SOS), funded by the U.S. Environmental Protection Agency (EPA) to further the understanding of the photochemical oxidants in the southeast United States.

PAN has long been known to be a strong eye irritant and a phytotoxin [*Stephens et al.*, 1961; *Taylor*, 1969; *Mudd*, 1975]. The phytotoxicity of PAN may not be important at concentrations below 15 ppbv [*Temple and Taylor*, 1983], however, and PAN is not generally found in concentrations approaching this level even in urban areas with the exception of the Los Angeles basin where concentrations as high as 30 ppbv have recently been reported [*Williams and Grosjean*, 1990]. PAN is known to be an important constituent of NO_y in most tropospheric measurements and has been shown to be a major constituent of NO_y in the cool middle troposphere [*Ridley*, 1990] and is the dominant component of NO_y in the Arctic [*Bottenheim et al.*, 1986; *Bottenheim*, 1989]. PAN decomposes rapidly at elevated temperatures and in the presence of a favorable NO/NO_2 ratio will regenerate atmospheric NO_2 and release free radicals into the atmosphere. In contrast at low temperatures, PAN is very stable and is susceptible to medium- and long-range transport. The relationship of PAN stability to temperature has led to the hypothesis that PAN serves as a significant reservoir specie for reactive nitrogen compounds [*Crutzen*, 1979; *Singh and Hanst*, 1981; *Singh and Salas*, 1983] capable of long- range transport [*Nielson*, 1981; *Hov*, 1984; *Brice et al.*, 1984]. As a result, PAN can be an important source of reactive nitrogen and free radicals when it is transported from aloft to warm sites at the surface.

PAN measurements are available from a number of urban and rural sites in the United States, Canada, and Europe. Urban PAN concentrations are reported as high as 30 ppbv in the Los Angeles basin but range from 0.5 to 2.0 ppbv on average with average maxima ranging from 1 to 5 ppbv in most other urban areas. PAN concentrations at rural sites range from sub-ppbv to 2.5 ppbv maxima with average concentrations ranging from

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0.1 to 0.5 ppbv. PAN concentrations for the Southeast United States have been made in Atlanta, Georgia [*Westberg and Lamb*, 1985; *Williams et al.*, 1993; *B.E. Hartsell et al.*, manuscript in preparation, 1994], in Alabama as part of the Rural Oxidants in the Southern Environment (ROSE) experiment [*Cantrell et al.*, 1992], Giles County, Tennessee [*Meagher et al.*, 1991], and Whitetop Mountain, Virginia and Brasstop Bald, Georgia [*Parrish et al.*, 1993]. No reports of concentrations in the rural North Carolina Piedmont have been reported previously.

In this paper, PAN measurements at site SONIA will be presented to demonstrate typical diurnal PAN profiles and the relationship of PAN to other photochemical pollutants. Concurrent measurements of NO_y and O_3 are compared to PAN concentrations under differing conditions of air mass age and stagnation.

Experimental Setup

From June 6, 1992, to July 7, 1992, an intensive experimental program was conducted in which PAN, O_3, NO_y, NO, NO_2, CO, SO_2, H_2O_2, carbonyls, HNO_3, aerosol nitrate, speciated volatile organic compounds (VOCs), and meteorological data were all monitored simultaneously at the Southern Oxidants Study site SONIA in Candor, North Carolina (Figure 1). Two collocated monitoring stations, site SONIA and the adjacent National Dry Deposition Network (NDDN) site, contained the measurement instrumentation. Site location is classified as rural under the NDDN site classification scheme. Requirements include no large point sources of SO_2 or NO_x within 20-40 km, no major industrial complex within 10-20 km, no city of population >50,000 within 60 km, and a number of other requirements not listed here. The sampling site is in an open field (area ~ 1200 m^2) situated on a ridge with at least 100 m of fetch in all directions to the surrounding mixed deciduous and coniferous forest. The site is located on the eastern border of the Uwharrie National Forest and is in the central portion of the Piedmont region of North Carolina (35.26°N, 79.84°W, 197 m mean sea level (msl) elevation). Several areas of anthropogenic pollution are within a 120-km radius of the sampling site, including the urban areas of Raleigh-Durham, Greensboro, Winston-Salem, and Charlotte and the junction between two busy interstate highways, I-40 and I-85. All of these sources are expected to impact site SONIA, particularly under regional synoptic conditions leading to air mass stagnation and the resulting buildup of PAN precursor compounds across the region.

Measurements of the gas phase compounds were made at a height of 10 m by drawing air through a 7.5-cm ID glass sampling tower with a 30,000 lpm flow rate blower to minimize sample residence time to at most ~0.25 s. A 16-port glass manifold at the base of the tower allowed sampling access. PAN was measured with a 60 cm x 3.2 mm OD nickel column packed with 10% Carbowax 600 on 60/80 mesh Gas Chrom Z and equipped with an Ni^{63} electron capture detector (ECD) (Valco, model 140-BN, Austin, Texas). Retention time for the PAN peak was 2 min and 40 s or 45% of the retention time of the water vapor peak. The carrier gas was 5% methane/95% argon and column flowrate was 70 $cm^3 min^{-1}$. An automated system was used to inject 5 cm^3 ambient air onto the column every 15 min giving four data points per hour.

Calibration of the PAN GC was carried out prior to and after the field sampling program. A bag of high (~ 15 ppmv) concentration PAN was synthesized by chlorine atom initiated irradiation of a mixture of acetaldehyde and nitrogen dioxide [*Gay et al.*, 1976]. The concentration of the bag was then quantified by infrared spectrophotometry (Shimadzu IR6) with a 7.2 m pathlength multiple pass cell at 1162 cm^{-1} wave number and known molar absorptivity [*Stephens*, 1969]. Other determinations of PAN molar absorptivities have been performed since Stephens' original work [*Bruchkman and Willner*, 1983; *Tsalkani and Toupance*, 1989]. All reported molar absorptivities at the 1162 cm^{-1} wave number have agreed within 10% of Stephens' values. Stephens' value of 13.9 was

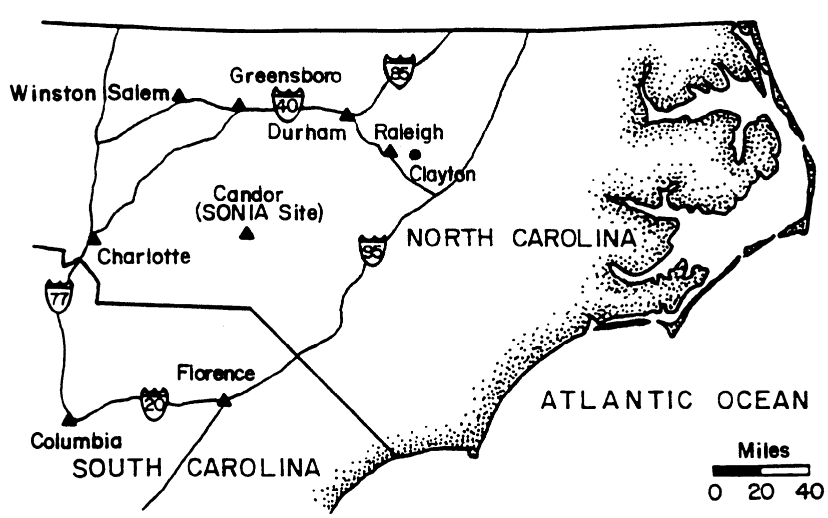

Figure 1. Map of sampling site SONIA (Southeast Oxidants and Nitrogen Intensive Analysis) near Candor, North Carolina.

used to maintain consistency with our previously published data. The standard preparation and quantification was performed at the EPA Environmental Research Laboratory in Research Triangle Park (RTP), North Carolina. The calibrated PAN sample bag was then transported to site SONIA where a multipoint calibration was performed on the PAN analyzer by syringe injection of aliquots of the high-concentration PAN mixture into bags containing metered volumes of zero grade air. Prepared PAN concentrations of 0.5, 1, 2, and 5 ppbv were used for system calibration. After GC calibration the high-concentration PAN bag was returned to the EPA lab in RTP and reanalyzed by the IR spectrophotometer. No measurable loss or decomposition of PAN was observed over the typical 10 hour storage period. The presampling study calibration yielded a response factor of 26.71 ± 0.91 ppbv mm^{-1} and the postsampling study calibration factor was 24.79 ± 1.57 ppbv mm^{-1}. An average response factor of 25.75 ppbv mm^{-1} was used for all the data.

Ambient NO and NO_y were measured with the commercially available TECO 42S (Thermo Environmental Instruments Incorporated) NO chemiluminescence analyzer similar in design to previously reported NO-NO_y analyzers [*Delany et al.*, 1982; *Dickerson et al.*, 1984; *Fehsenfeld et al.*, 1987]. The TECO 42S achieves high sensitivity by utilizing a cooled reaction chamber to reduce dark current, a prereaction chamber in which NO is titrated by O_3 before reaching the reaction chamber providing a dynamic measure of any artifact which is subtracted from both the NO and the NO_y channels, and a heated (325° C) molybdenum (Mo) converter to convert the reactive nitrogen compounds, NO_y, to NO. For this field study, a second, external Mo converter also heated to 325° C was mounted at the top of the 10 m sampling tower to maximize converter efficiency of all NO_y compounds. The inlet line to the external converter was cut as short as possible to minimize the loss of HNO_3 on the inlet. However, the possibility of some HNO_3 loss remains and should be noted. The output of this converter was then sent through the second converter inside the instrument. The TECO 42S was calibrated on a weekly basis first using a National Institute of Standards and Technology (NIST) traceable NO in N_2 standard to calibrate the response of the instrument and then tested for converter efficiency by calibrating through both Mo converters with a NIST traceable NO_2 in N_2 standard. Conversion efficiency of NO_2 was calculated to be >98% for the entire field study. Raw data were corrected using the NO calibration results and the NO_y raw data was also corrected for converter efficiency.

Ambient NO_2 was measured directly with the LMA-3 Luminol-based NO_2 analyzer (Scintrex, Limited). This instrument has been previously tested in field studies and has known interferences with both O_3 and PAN and also suffers from non-linearities at sub-ppb concentrations [*Fehsenfeld et al.*, 1990]. The Luminol II solution, developed to minimize problems with repeatability, storage lifetime, and linearity, was used in the field intensive to improve the quality of the NO_2 measurement. The interferences for PAN and O_3 have been reported as 25% and 1%, respectively [*Fehsenfeld et al.*, 1990]. The NO_2 data were not corrected for PAN interference but were corrected for O_3 interference through the use of an O_3 scrubber permanently mounted in the sample line which has been found to remove >95% of O_3 at 40 ppbv O_3 and only 5% NO_2 [*Fehsenfeld et al.*, 1990]. The LMA-3 received a weekly multipoint calibration using the output of a NO_2 permeation device and was checked daily for zero and span. All calibration curves yielded high r^2 but did show a nonzero intercept. Any nonlinearities in the sub-ppbv range were not corrected and are expected to result in a slight underestimation of the NO_2 concentrations in the sub-ppbv range.

Results and Discussion

During the measurement period, maximum ambient levels of PAN reached 1.2 ppbv and averaged 0.41 ± 0.24 ppbv (n=1972) with an average daily maximum of 0.60 ppbv. These results agree well with PAN concentrations from other rural sites in the Southeast United States [*Meagher et al.*, 1991; *Cantrell et al.*, 1992; *Parrish et al.*, 1993]. Figure 2 shows the composite diurnal profile of PAN at site SONIA for the entire measurement period. The black squares indicate the average hourly concentration while the bars denote ± one standard deviation. PAN minimum concentration occurs at 0500 EST at site SONIA followed by a steady increase to about 1200 EST. Morning minima and midday maxima are similar to those reported for other rural and urban sites in the Southeast United States [*Westburg and Lamb*, 1985; *Meagher et al.*, 1991; *Cantrell et al.*, 1992, *Parrish et al.*, 1993; *Williams et al.*, 1993]. PAN concentration remains relatively constant throughout the early afternoon hours and then declines steadily into the evening hours.

The early morning rise in PAN concentrations is generally attributed to downward mixing of undepleted air from above the nocturnal boundary layer (NBL) following the morning breakup of the NBL. The continued increase in PAN concentrations into the early afternoon is thought to be evidence of the photochemical production of PAN from either locally generated or transported precursor compounds. PAN concentrations gradually decrease in the evening as PAN production is overtaken by loss processes such as thermal dissociation and dry deposition under the subsiding boundary layer.

Ten-meter wind direction, wind speed, and total solar radiation measured at the site were used to segregate the data into two cases. Case 1 involved low wind speeds, predominantly northerly and southerly wind directions, and total solar radiation (TSR) >60% of the maximum attainable TSR during the daytime hours. Case 2 involved higher wind speeds, predominantly easterly wind directions, and lower TSR during the daytime hours. Case 1 was representative of conditions where high pressure dominated the weather pattern resulting in greater air mass stagnation, higher temperatures, and greater potential for photochemical production in the region. NO_x and NO_y concentrations were found to be generally higher in this case and oxidant accumulation more prevalent. Case 2 was representative of better ventilated, cooler, and cloudier conditions less conducive to photochemistry. NO_y and oxidant concentrations were lower under these conditions. Figures 3a-3f show the composite diurnal profiles of O_3, PAN, and NO_2 which were generated by segregating the data as described above. As shown in Figures 3b and 3e, both the magnitude and the time of the PAN peak are considerably different between the two cases. Both the rate of PAN accumulation and the daily PAN maxima are greater in case 1 than in case 2.

The formation of PAN is limited by the availability of its precursors, namely, NO_2 and hydrocarbons that can form the

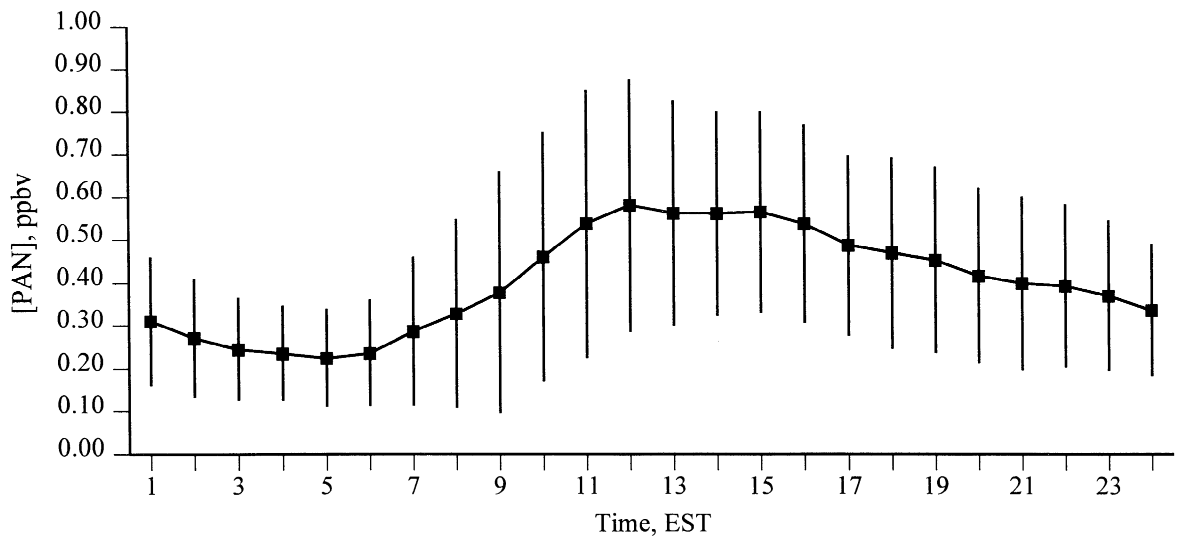

Figure 2. Composite diurnal profile of peroxyacetyl nitrate (PAN) for the entire measurement period. Vertical bars denote ± one standard deviation.

peroxyacetyl radical. Figures 3c and 3f illustrate NO_2 diurnal profiles under the two cases. The average magnitude of the daily NO_2 maximum, occurring at 0600 EST, was 220 % higher (2.4 versus 0.7 ppbv) in case 1 than in case 2. The relationship between the magnitude of NO_2 and the PAN in Figures 3c and 3f between the two cases suggests that accumulation of nitrogen precursors under conditions of higher stagnation may be fueling the mesoscale photochemical production of PAN in the NO_x-limited rural atmosphere.

Contribution of PAN to NO_y

Figure 4 shows the average percent contribution of PAN to total NO_y for each hour of the day. The contribution of PAN to NO_y was found to be similar to that measured at other rural sites [*Meagher et al.*, 1991; *Parrish et al.*, 1993]. PAN accounted for ~ 13% of the total NO_y measured on average during the entire measurement period. The diurnal profile of PAN contribution to NO_y was very similar to the diurnal profile observed for PAN. An ~8% contribution occurs during the 0400-0600 period steadily increasing to a maximum of ~21% during the midafternoon hours. The contribution then steadily declines overnight as PAN concentration decreases. Afternoon maximum PAN/NO_y ratios are expected since PAN production occurs with concurrent loss of NO_x (NO + NO_2). The slightly decreasing but largely flat profile of PAN/NO_y during the photochemically active afternoon hours could suggest that production and removal processes are in relative balance with removal proceeding only slightly faster than formation [*Buhr et al.*, 1990]. Early morning injections of NO_2, which significantly elevate total NO_y levels, are responsible for the lower PAN/NO_y observed during the early morning period.

Relationship Between Peroxyacetyl Nitrate (PAN) and O_3

PAN and O_3 were found to exhibit similar diurnal characteristics in case 1 but showed some differences when conditions were less favorable for photochemistry at site SONIA. Figures 3a through 3f show the composite diurnal profile of both compounds for the two conditions. In both data sets, O_3 exhibits a fairly typical diurnal profile with accumulation beginning around 0900 EST and peaking around 1800 EST. The magnitude and rate of accumulation of O_3 are smaller in case 2 but still show the same general pattern.

There is a marked difference, however, in the behavior of PAN in the two cases. In case 2 the onset of PAN accumulation is delayed until 0800 EST and the rate of accumulation is quite slow. The small magnitude and slow rate of PAN accumulation are the result of poor climate for photochemical activity just as with O_3. It appears, however, that the significantly lower concentration of NO_2 under case 2 has a more limiting effect on PAN formation than on O_3 accumulation.

In case 1, PAN and O_3 accumulation begins about the same time, ~0700, and continues to afternoon maxima. The similar morning increase is likely the result of the breakup of the NBL. The PAN accumulation rate, however, appears to be faster and reaches a maximum about 1-2 hours earlier than O_3. These differences are likely the result of differences in the pathways of photochemical formation of the two compounds. Under the less stagnant conditions, PAN and O_3 profiles are less distinct than under higher stagnation. Neither morning increases due to the breakup of the NBL nor afternoon maxima are as clearly observed due to the combined effect of lower precursor levels and limited photochemical activity.

Relative sensitivities of the O_3 and PAN measurement systems must also be taken into consideration when comparing the two compounds. An early morning production of only a few parts per billion by volume of O_3 would be difficult to detect over the existing ~30 ppbv background concentration. In the case of PAN however, an increase of only 50 pptv is more discernible against the background PAN concentration of ~250 pptv. Therefore the apparent difference in the time of the onset of O_3 and PAN accumulation may simply be a result of the difference in the sensitivity of the two instruments.

Another way to characterize the relationship between PAN and O_3 is through the O_3/PAN ratio. The O_3/PAN ratio for urban environments has been reported as 14 but is subject to

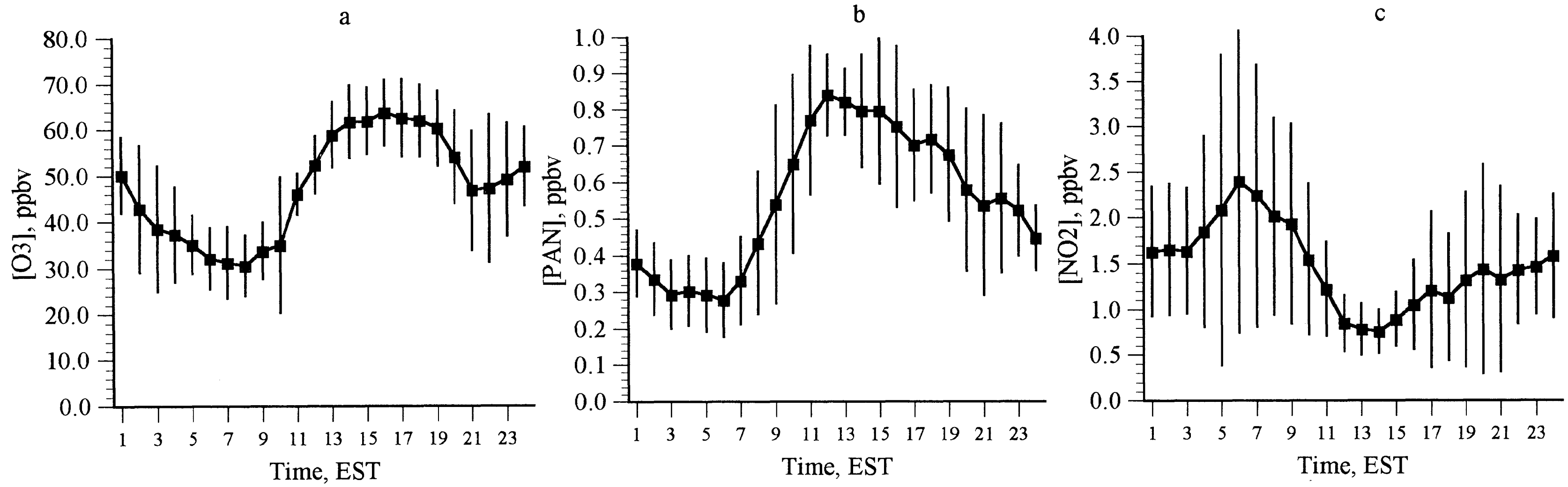

Figure 3. (a-c) Diurnal profiles of O_3, PAN, and NO_2 for case 1. Vertical bars denote ± one standard deviation.

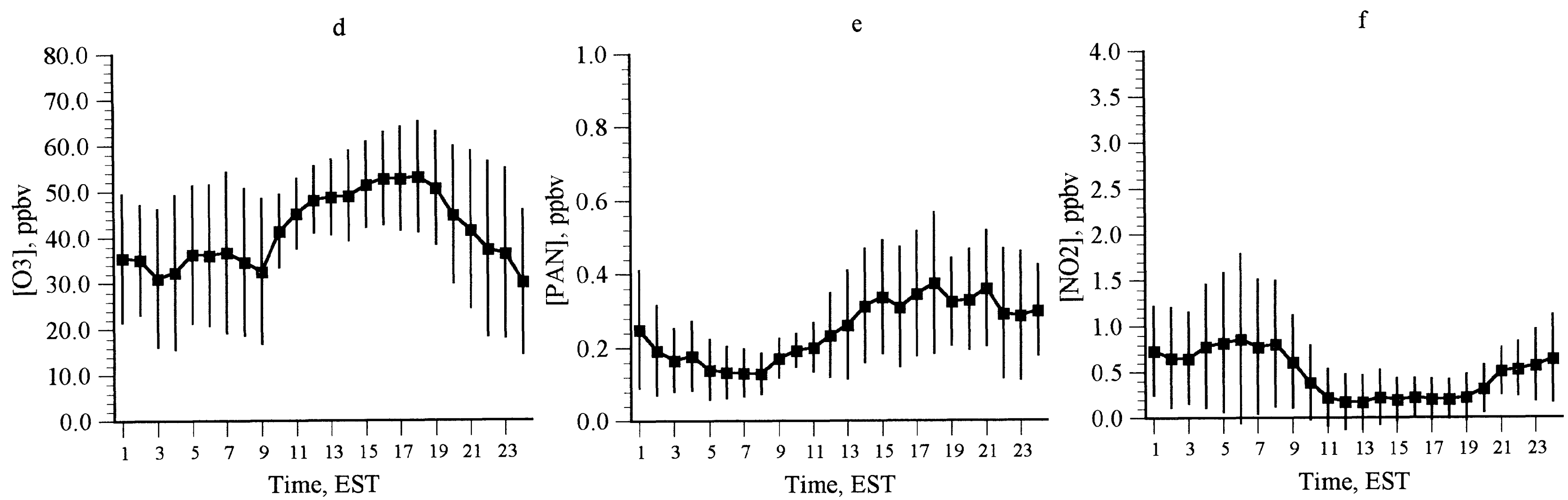

Figure 3. (d-f) Diurnal profiles of O_3, PAN, and NO_2 for case 2. Vertical bars denote ± one standard deviation.

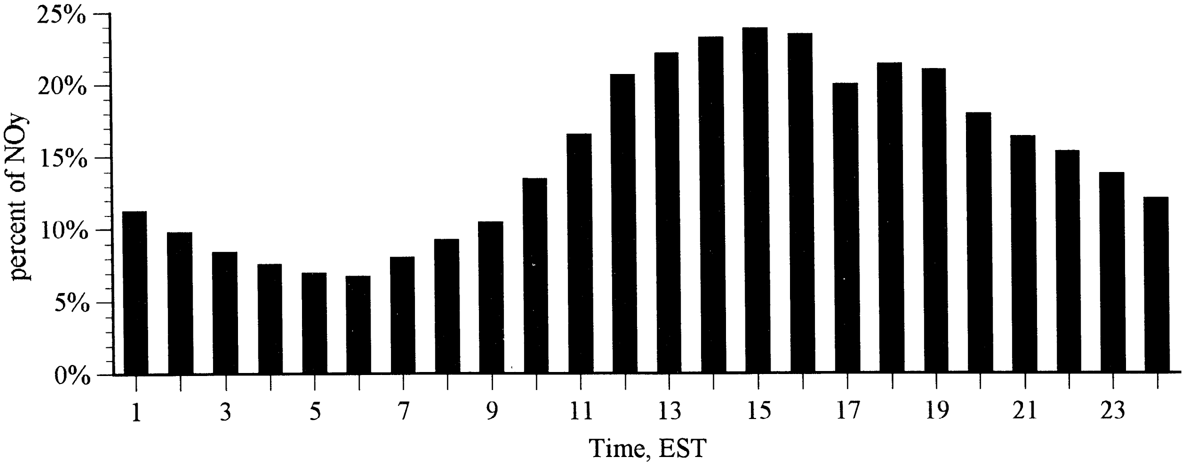

Figure 4. Average percent contribution of PAN to NO_y for the entire measurement period for each hour of the day.

significant variability [*Lonneman*, 1976; *Altshuller*, 1983]. Rural environments typically have higher ratios of 100 or more [*Altshuller*, 1983; *Shepson et al., 1992; Roberts et al.*, 1992]. Marine and remote environments and the free troposphere can have ratios of 200 or more [*Singh et al.*, 1990; *Hübler et al.*, 1992; *Parrish et al.*, 1992]. Variation in the O_3/PAN ratio can occur as the result of differing rates of production of the two compounds which are influenced by the availability of the necessary precursors. The ratio can also be influenced by the loss rates of the two compounds in ambient air.

Figure 5 exhibits the diurnal variation in the O_3/PAN ratio. The diurnal profile of the O_3/PAN ratio reaches a strong maximum at 0500 EST and declines steeply to a daytime minimum at 1200 EST. The ratio then steadily climbs in late evening and overnight to the next morning's maximum. The mechanism responsible for this diurnal profile may be explained by the difference in the rates of formation and/or transport, and deposition of the two compounds. A simple calculation of the change in compound concentration per unit time normalized by the average concentration of that compound during that time can be used to estimate the formation and destruction rates of each compound. The steep decline in the O_3/PAN ratio from its early morning maximum is likely the combined result of a relatively larger injection of PAN than O_3 from aloft during the breakup of the NBL and the apparently faster accumulation of PAN than O_3 in the morning due perhaps to more favorable temperature conditions for PAN

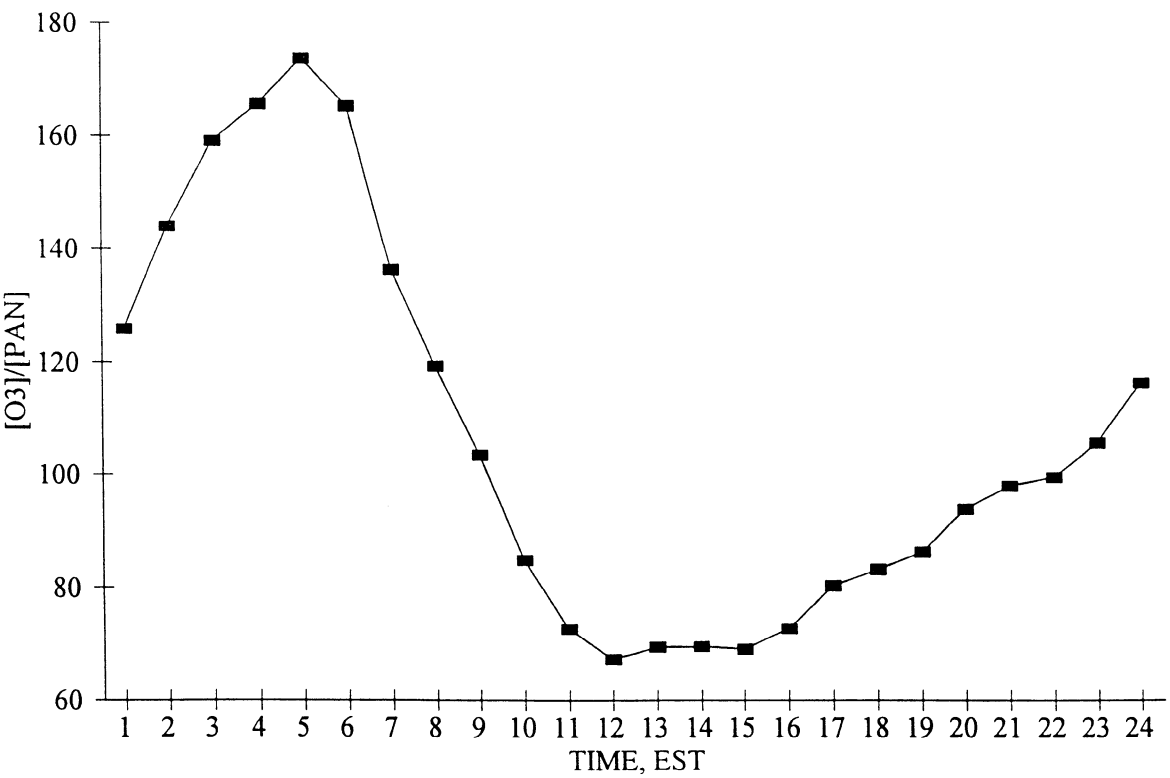

Figure 5. Diurnal variation of the O_3/PAN ratio.

formation. During the morning, PAN had a normalized formation rate of 0.105 $hour^{-1}$, while the formation rate of O_3 was only 0.075 $hour^{-1}$. Under these conditions one would expect the O_3/PAN ratio to drop as the day progressed. Conversely, at night the normalized destruction rate of PAN was 0.85 $hour^{-1}$ while that of O_3 was only 0.051 $hour^{-1}$ leading to an increasing O_3/PAN ratio.

The larger nighttime destruction rate of PAN over O_3 is somewhat surprising. Both compounds are expected to be stable during this period. Since NO_2 dominates NO overnight there is minimal net thermal decomposition of PAN because thermally released peroxyacetyl radical is more likely to recombine with NO_2 to reform PAN than react with NO. Low nighttime NO also means there is no significant titration of O_3 under these conditions. If one assumes that observed PAN and O_3 destruction rates of 0.085 $hour^{-1}$ and 0.051 $hour^{-1}$ respectively are related to deposition processes then an estimated ratio of $V_d(PAN)/V_d(O_3)$ of 1.67 is determined. Faster PAN deposition than O_3 deposition was also reported by *Shepson et al.* [1992] and it may be the faster deposition rate of PAN that leads to the increasing O_3/PAN ratio during the night.

Figure 6 shows a plot of daily average O_3/PAN ratio versus date of sampling. On the high O_3/PAN days of June 13-17 and June 29-30, conditions were less favorable for photochemical production than on the low O_3/PAN days of June 20-27. Again, the accumulation of precursor compounds under more stagnant conditions along with clear air conditions appears to lead to a higher potential for both ozone and PAN accumulation.

The quantity $(NO_y-NO_x)/NO_y$ has been used as a gauge of chemical aging of an air mass with a value of zero indicating a fresh air mass completely made up of NO_x and a value of one indicating an aged air mass where all NO_x has been converted to other odd-nitrogen compounds [*Aneja et al.*, 1994]. Figure 7 illustrates the change in the O_3/PAN ratio with air mass age at site SONIA. From the figure it is evident that both "aged" and relatively "fresh" air mass conditions occur at site SONIA. During the "aged" air mass condition the O_3/PAN ratio exceeds 200, while $(NO_y-NO_x)/NO_y$ is above 0.90. This condition generally occurs under case 2. Such an air mass can be referred to as "spent" or NO_x limited with little capability of producing either O_3 or PAN. Under case 1, however, the O_3/PAN ratios are generally about 60 with the value of $(NO_y-NO_x)/NO_y$ ranging from 0.20 to 0.60 and the air mass still has O_3 and PAN formation potential.

Regressions of O_3 and PAN were fitted to the data set for several different scenarios. The regression equation for the entire data set during the daylight hours of 0800-1800 EST is $[O_3]$ = 14.49 [PAN] + 43.59, R=0.76. This result is remarkably similar to that found by *Roberts et al.* [1992] who reported a regression equation of $[O_3]$ = 15.2 [PAN] + 42.7 for mostly rural sites in eastern North America. At a typical O_3 maximum of 55 ppbv this regression translates into an O_3/PAN ratio of ~70. On days with more stagnant conditions the regression equation is $[O_3]$ = 39.01 [PAN] + 17.39, R=0.89 which translates to an O_3/PAN ratio of 50 for a typical O_3 concentration of 75 ppbv whereas the regression equation for less favorable photochemical days is $[O_3]$ = 27.31 [PAN] + 31.44, R=0.61 which translates to an O_3/PAN ratio of 90 for a typical O_3 concentration of 45 ppbv. It appears then that O_3/PAN ratios at site SONIA are similar to urban and suburban air masses when regional stagnation increases the available precursor concentrations and creates more favorable conditions for photochemical formation of oxidants. The O3/PAN ratio is more indicative of rural/remote air masses when the site is better ventilated with lower NO_x precursor concentrations and is experiencing less favorable photochemical conditions.

Summary and Conclusions

PAN for the entire measurement period averaged 0.41 ppbv and reached a maximum value of 1.2 ppbv. The average daily maximum concentration was 0.60 ppbv and the average daytime concentration was 0.52 ppbv. Both the magnitude of concentrations and the diurnal profile of PAN at site SONIA agreed well with those reported for other sites in the eastern United States. Examination of the diurnal pollutant profiles measured at the SONIA site suggests that increased PAN concentrations occur during periods of regional air mass stagnation due to increased PAN precursor concentrations and more favorable atmospheric conditions of photochemical formation.

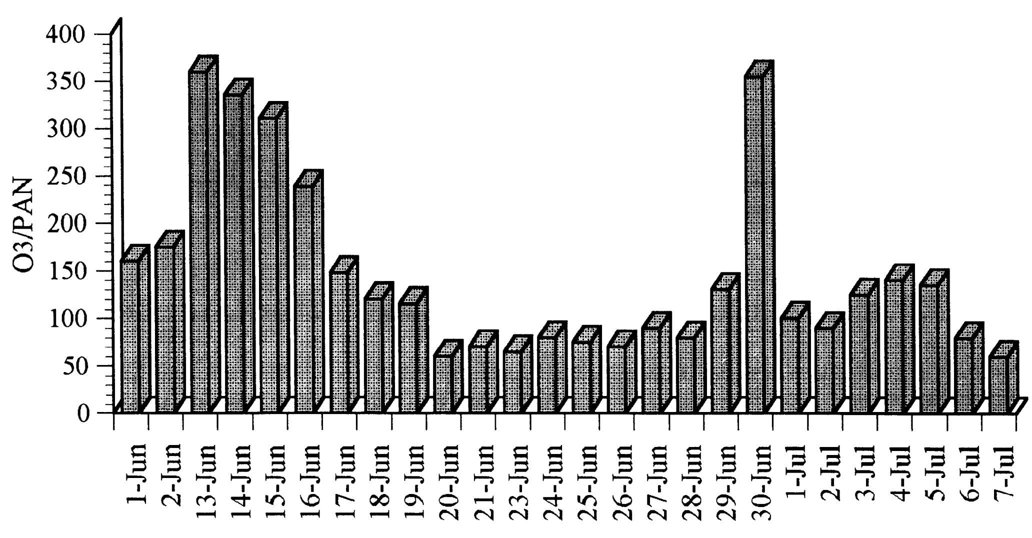

Figure 6. Average O3/PAN ratio for selected days during 1992.

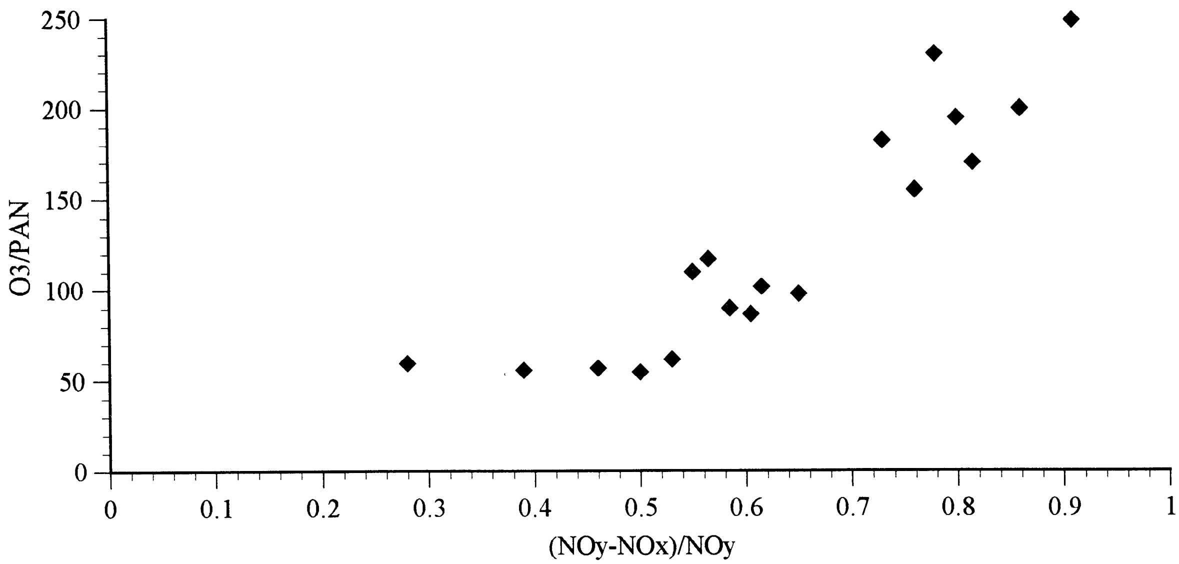

Figure 7. O_3/PAN ratio versus chemical air mass age. Each point represents the average of 20 data points sorted in ascending order of $(NO_y-NO_x)/NO_y$.

The overall contribution of PAN to total odd-nitrogen compounds, NO_y, was found to be 12 ± 11%. The contribution of PAN t NO_y showed a strong diurnal variation with a maximum contribution of ~20% occurring during the peak photochemical hours in the early afternoon. These results were similar to those reported for other rural U.S. sites.

The relationship between O_3 and PAN was similar to that observed in other studies. Under conditions of regional stagnation with the accompanying regional buildup of PAN precursors the O_3/PAN ratio approached values more typical of urban environments. Under less favorable photochemical conditions the O_3/PAN ratio rose to values typical of remote and marine environments. The change in the O_3/PAN ratio was interpreted to be the result of PAN and O_3 formation and loss mechanisms. Regression analysis of O_3 and PAN showed strong positive correlation indicating that both oxidants were formed by the photooxidation process. Likewise, the diurnal profiles of the two compounds supported mesoscale photochemical production of oxidant compounds, perhaps from a mixture of regional biogenic and transported anthropogenic precursors. The regression of O_3 and PAN also agrees well with those published in other studies.

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