Journal of the Air & Waste Management Association
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uawm20

Peroxyacetyl Nitrate in Atlanta, Georgia: Comparison and Analysis of Ambient Data for Suburban and Downtown Locations

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Published online: 27 Dec 2011.

TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **49**:177-184

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ABSTRACT

Peroxyacetyl nitrate (PAN) concentrations were measured at downtown and suburban locations in Atlanta, GA, in July and August 1992 as part of the SOS-SORP/ONA (Southern Oxidants Study–Southern Oxidants Research Program on Ozone Non-Attainment). PAN concentrations were generally higher at the downtown location than at the suburban location, but on days when the O_3 concentration exceeded 80 ppbv, PAN concentrations were similar at both locations. On days when O_3 did not exceed 80 ppbv, suburban PAN concentrations were much lower than downtown concentrations and resembled those reported for rural areas in the eastern United States. Regression analysis of PAN and O_3 on NO_x and total non-methane hydrocarbons (TNMHC) showed PAN to be most strongly dependent on morning NO_x concentrations, while O_3 was most dependent on morning TNMHC concentrations. NO_x, PAN, and meteorological data from the suburban site were used in a one-dimensional transport model to estimate the accumulation rate of PAN to be ~1.5×10^6 molecules cm^{-3} sec^{-1}. A simple kinetic model estimated peroxyacetyl radical concentrations to be ~0.5 pptv at the suburban location.

INTRODUCTION

As part of the Southern Oxidants Study–Southern Oxidants Research Program on Ozone Non-Attainment (SOS-SORP/ONA), an intensive field study was conducted in Atlanta, GA, during July and August 1992. As part of SOS-SORP/ONA, peroxyacetyl nitrate (PAN) was measured at two locations in the metropolitan Atlanta area.

IMPLICATIONS

Nitrogen compounds play a central role in atmospheric chemistry and are associated with today's major environmental issues, such as acidic deposition, global warming, and increase in photochemical oxidants in the troposphere. PAN has been known to be a strong eye irritant and phytotoxin. This paper shows that an urban area can inject significant levels of PAN into an advected air mass.

PAN is a photochemical oxidant formed by reaction of the peroxyacetyl radical (CH_3CO_3) with nitrogen dioxide (NO_2). PAN is an eye irritant,[1] a phytotoxin,[2] an important constituent of total reactive nitrogen, NO_y, (NO_y = NO + NO_2 + HONO + HNO_3 + N_2O_5 + PAN + NO_3^- + organic nitrates) in the lower troposphere,[3] a major constituent of NO_y in the middle troposphere,[4] and the dominant component of NO_y in Arctic air.[5] PAN decomposes rapidly at elevated temperatures (>25 °C), and when it does so in an NO_2^- deficient atmosphere, it will release NO_2 and peroxyacetyl radicals. Thus, PAN can be an important early morning source of free radicals, which quickly initiate photochemistry.[6]

In this article, we examine and compare PAN concentrations measured at a suburban location and a downtown location within metropolitan Atlanta, GA. These measurements provide a basis for a better understanding of the temporal and spatial distribution of PAN in a large urban area. PAN and NO_2 concentrations, together with appropriate kinetic data, are used to estimate ambient concentrations of the peroxyacetyl radical at the suburban site, and the results are compared to those from two rural sites in the eastern United States. Regression analysis of PAN, total non-methane hydrocarbon (TNMHC), oxides of nitrogen (NO_x), and ozone (O_3) concentrations at the suburban site will be used to estimate the relative dependence of the two photochemical oxidants, PAN and O_3, on their precursors. PAN concentrations from the suburban and urban sites, along with meteorological data from the suburban site, will be used in a one-dimensional Lagrangian model to estimate the accumulation rate of PAN in an air parcel as it travels between the two

sites. A better understanding of PAN concentrations, PAN precursor concentrations, and the accumulation rate of PAN in an urban environment are useful in the development of models used for oxidant control.

EXPERIMENTAL METHODS

PAN was measured at two sites in the metropolitan Atlanta area by two different air quality groups: North Carolina State University (NCSU) and DGA, Inc. The two sites were a suburban location (South Dekalb Community College, some 20 km southeast of city center) and a downtown location (Georgia Institute of Technology (GIT) campus). A site was assigned to each research group to measure PAN concentration; the NCSU research group carried out the suburban PAN measurement, and the DGA research group did the downtown measurement. A detailed map of the area showing the proximity of the two sites is shown in Figure 1.

The detection principle utilized for both PAN measurement sites was an electron capture (EC) gas chromatography (GC) of a cryogenically enriched sample of ambient air. The GC was equipped with a nickel column (60 cm long; 0.32 cm o.d.) 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). The carrier gas was 5% methane/95% argon and column flow rate was 70 cm^3 min^{-1}. An automated system was used to inject 5 cm^3 ambient air into the column every 15 min. Calibration of the PAN GC was carried out prior to and after the field sampling program. A bag of high-concentration (~15 ppm) PAN was synthesized by chlorine-atom-initiated irradiation of a mixture of acetaldehyde and nitrogen dioxide.[7] The concentration of the bag was then quantified by infrared spectrophotometry (Shimadzu IR6) with a 7.2-m-path-length multiple gas cell at 1,162 cm^{-1} wave number and known molar absorptivity.[1] Prepared PAN concentrations of 0.5, 1.2, and 5 ppbv were used for system calibration. After GC calibration, the high-concentration PAN in the bag was returned to the lab and reanalyzed by the IR spectrophotometer. No measurable loss or decomposition of PAN was observed over the typical 10-hr storage period.

Ambient levels of PAN were measured on GIT campus, about 3 km northwest of the Atlanta city center, by EC-GC using an SRI Model 8610 GC and Valco Model 140 BN EC detector. A Teflon-coated stainless steel column (70 cm long, 0.3 cm o.d.) packed with 10% Carbowax 400 on Chromosorp P was used. The column was washed with acid and treated with dimethyldichlorosilane.[8] The column and detector temperatures were 36 and 60 °C, respectively. The carrier gas was ultra high-purity nitrogen, and the column flow rate was 58 mL/min. Ambient air was continuously pumped through a 6.7-cm^3 stainless steel loop housed in the GC oven. The residence time in

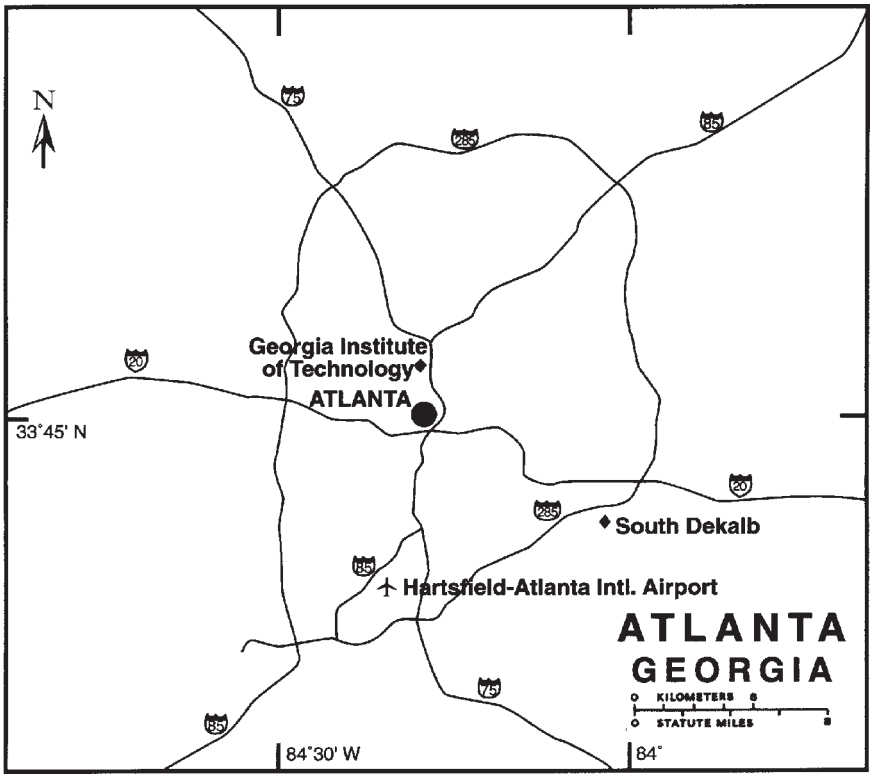

Figure 1. Map of Atlanta showing the location of the South Dekalb and Georgia Tech sites.

the sampling line was 185 sec. Ambient air was injected every 30 or 60 min with a timer-activated 10-port sampling valve.

To calibrate the EC-GC instrument, PAN was synthesized in the liquid phase in a two-step process involving oxidation of the commercially available anhydride (Aldrich, purity 97–99%) to the corresponding peroxy carboxylic acid, followed by acid-catalyzed nitration of the peroxy acid with nitric acid.[9] The PAN solution was stored in the dark at -5 °C. The ppb level of PAN in the gas phase was obtained by dilution with purified air of the output of diffusion vials containing aliquot of PAN in n-dedecane and maintained at 2 °C. Plots of PAN peak height versus PAN concentration used for calibration were constructed. The PAN concentrations were selected in the range of 0–12 ppb, the expected range of ambient PAN in the Atlanta area. The linear regression between PAN peak heights and PAN concentrations was conducted and revealed 14.9 ± 2.2 mm/ppbv of calibration factor.[8]

Ambient levels of O_3, NO, NO_x, carbon monoxide (CO), speciated volatile organic compounds (VOCs), and standard meteorological data were also measured at the two locations. The speciated VOCs were measured by GC (HP 5890 Series II) equipped with preconcentrator (ENTECH 2000) using a 16-port canister autosampler. Other trace gases were measured and collected by the Georgia Environmental Protection Department and the Georgia Institute of Technology. NO and NO_y were measured by a chemiluminescent method using a TECO 42 system; ambient ozone was measured by a UV photometric method using TECO 49 system. CO and SO_2 were also measured by TECO commercial instruments. Those measurements were checked for zero/span once a day and calibrated periodically according to the SOS (Southern Oxidants Study) QA/QC protocol.[10]

A comparison between the two data sets, as measured by the two different instruments used by the two research groups during the same time period, was carried out as part of the quality assurance (QA) component of SOS-SORP/ONA. The two analyzers were collocated on the GIT campus and sampled ambient PAN on July 24–25, 1992, through identical lengths of Teflon line. The two instruments had been independently calibrated using different techniques as described earlier in this section. The results of this comparison are shown in Figure 2. A least square linear regression of the data showed the following results: $NCSU_{PAN} = (1.33 \pm 0.04)\ DGA_{PAN} - (0.04 \pm 0.03)$ ppbv; $R^2 = 0.947$ and n = 54. Thus, the two instruments were within 16.5 ± 0.02% of the mean of the two sets of measurements. This agreement was deemed satisfactory. For comparison, the combined overall uncertainty of our measurements (i.e., propagation of errors inherent to calibration and measurement protocols) is estimated to be 15–20% for the range of PAN concentrations observed in ambient Atlanta air (i.e., < 3 ppb).[8,11,12]

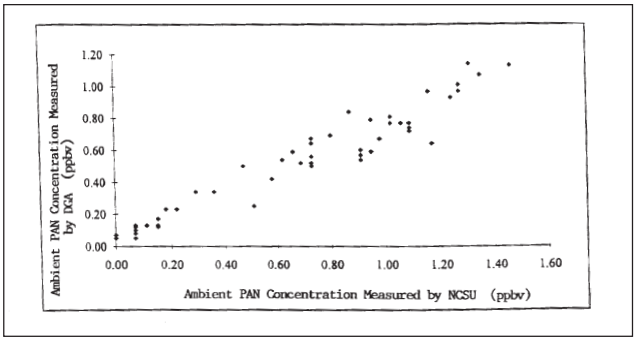

Figure 2. Intercomparison of ambient PAN by the NCSU and DGA analyzers, July 24–25, 1992.

RESULTS AND DISCUSSION

PAN Concentrations

Composite diurnal profiles for the suburban and downtown sites are shown in Figure 3. These profiles were obtained by averaging the PAN concentration for each specific hour of the day over the entire measurement period, August 1992. PAN exhibited strong diurnal variations at both locations, with pre-dawn or morning minima (often near the limit of detection of 50 pptv) and with late afternoon maxima typically occurring between 1600 and 1800 EDT.

Daily PAN maxima coincided with those of ozone, as was expected due to the common photochemical origin of both compounds. Late afternoon PAN maxima were observed in the Atlanta area during the experimental period. Constructing the composite diurnal profiles for Atlanta during this study and for data obtained in 1991 at southern California locations,[12,13] we may see a distinctive feature of summertime air quality in the Atlanta area:

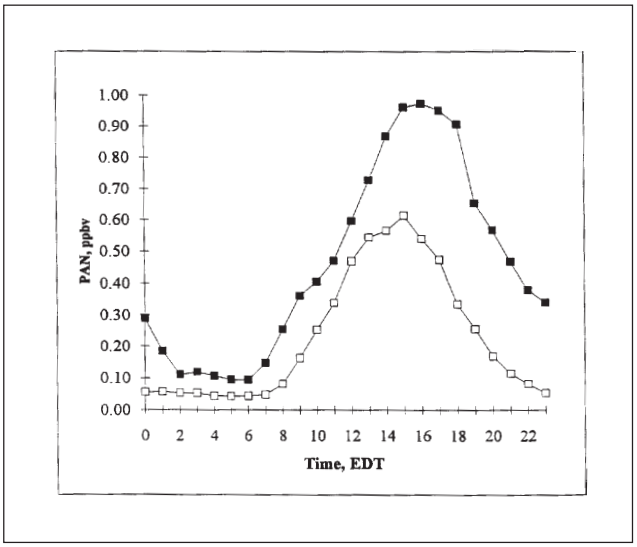

Figure 3. Composite diurnal profile of PAN at the suburban (open squares) and downtown (dark squares) locations, August 1992.

PAN maxima in downtown Los Angeles typically occurs around noon during the summer and not in the late afternoon as it does in the Atlanta area. Williams et al.[8] hypothesized this shift in PAN maxima observed for inland locations such as Atlanta to eastward transport of polluted air in the mid-afternoon leading to the PAN maxima. Again this comparison may be relevant to summertime air quality in Atlanta, where the late afternoon PAN maxima may reflect stagnation conditions, under which nitric oxide is only slowly converted to NO_2.[8] PAN concentrations downtown ranged from 0.05 to 2.9 ppbv; the average concentration was 0.43 ± 0.47 ppbv (n = 817, one standard deviation). Average daytime concentration (from 0900 to 2000 EDT) was 0.71 ± 0.53 ppbv. Daily maxima exceeding 2 ppbv were observed on eight days. Maximum PAN concentration at the suburban location was 3.1 ppbv; the average concentration was 0.23 ± 0.20 ppbv. Average daytime concentration (from 0900 to 2000 EDT) was 0.39 ± 0.16 ppbv. Daily PAN maxima exceeded 2 ppbv on two days and exceeded 1 ppbv on seven days.

PAN Concentrations on High and Low Ozone Days

The SOS-SORP/ONA Atlanta Intensive predicted days during the study that were expected to develop "high ozone" conditions (i.e., > 80 ppbv) in order to employ a wider spatial and temporal network of ozone precursor measurements on these "event days." Examination of the PAN concentrations showed that PAN maxima were similar for the two locations on "event days," while on "non-event days" the PAN maxima were considerably lower at the suburban location than downtown. To investigate the differences in PAN concentrations under the two conditions, the data were segregated into "high ozone" (maximum concentration > 80 ppbv) and "low ozone" days (maximum concentration < 80 ppbv). Composite diurnal profiles for the two locations under the high and low ozone conditions are shown in Figures 4a and 4b, respectively.

As expected, both locations showed an increase in PAN maximum on the high ozone days. The increase in PAN maximum was much higher at the suburban site than at the downtown site. The larger increase in PAN concentrations at the suburban location on high ozone days may be attributed to the greater variability in the abundance of PAN precursors at this site. About 30% occurrence of wind direction from the southwest sector was observed on high ozone days. Atlanta's Hartsfield International Airport and the surrounding area of greater industrial activity is ~3 km from the suburban site in this direction and likely contributes to higher PAN precursor concentrations when the wind is out of the southwest. There are, of course, other possible meteorological variables, as well as emissions from the Atlanta area, which can affect the PAN precursor concentrations (e.g., temperature and auto emissions). On these high ozone days, however, the variability of air temperatures was not significant. However, it is not clear yet whether PAN production is a regional or local phenomenon, since only surface wind data are measured at the site. To further understand this phenomenon, a detailed analysis is needed using upper air synoptic wind data during this period in the Atlanta area.

Figure 5 compares the composite diurnal PAN profile at the suburban site to that of a rural site in the central Piedmont area of North Carolina. Detailed measurements in the Piedmont site have been addressed elsewhere.[14] The daily maximum PAN concentrations were quite similar, suggesting that when the predominant wind is from rural areas, PAN profiles at the suburban site are indicative

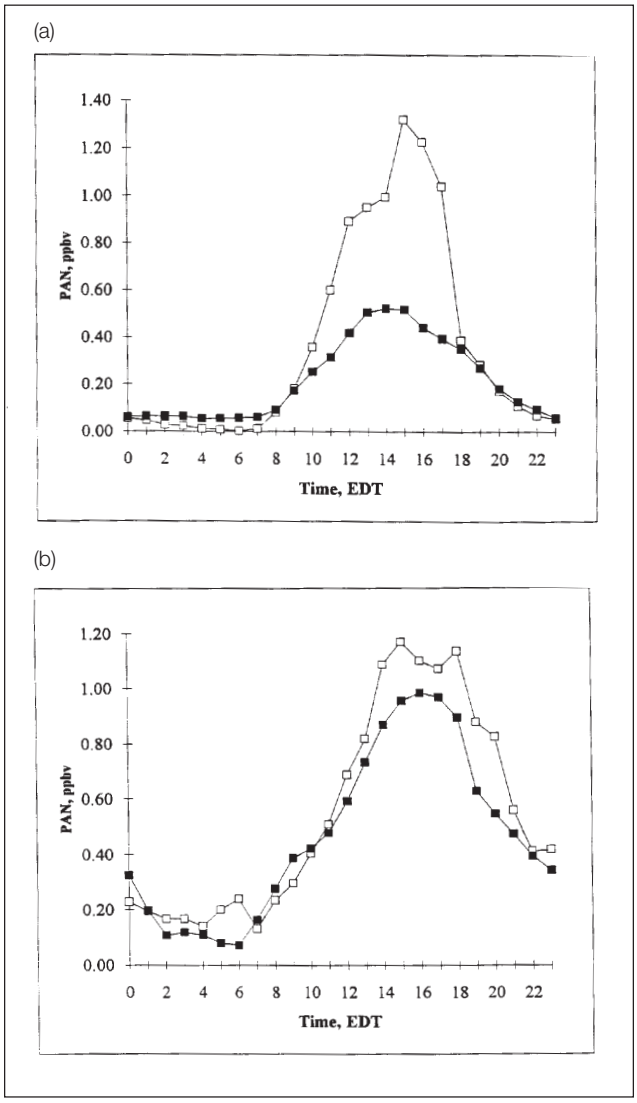

Figure 4. (a) Composite diurnal profile of PAN at the suburban Atlanta location on high ozone (open squares) and low ozone (dark squares) days. (b) Composite diurnal profile of PAN at the downtown Atlanta location on high ozone (open squares) and low ozone (dark squares) days.

of a regional PAN background. In this case, the local precursors are likely to make only modest contributions, at least at the suburban site. In order to support this hypothesis, more detailed analysis with surface and upper synoptic wind systems would be required.

Prevailing wind direction is less important for the downtown location, however, because its position near the center of the city provides relatively high precursor concentrations from all directions due to the density of precursor sources surrounding the downtown area. Figure 6 shows the average PAN daily maxima for the two wind sectors, southwest and east/southeast, for both locations. At the suburban location, the average maximum was 0.46 ppbv for southeast wind directions, and 1.05 ppbv for southwest wind directions (i.e., a 130% increase). For the downtown site, however, the increase in PAN maxima from the southeast to southwest sectors was from 1.25 to 1.58 ppbv, a modest 26% increase. This seems to suggest that precursors transported to the downtown area may only modestly affect PAN formation in this area because there were relatively fewer precursor sources in the southwest sector of the downtown areas. Other evidence that precursors are less abundant at the suburban location includes the lack of higher molecular weight peroxyacetyl nitrates ($RC(O)OONO_2$) at the suburban location. Both PPN ($R = C_2H_5$) and MPAN ($R = CH_2 = C(CH_3)$-) were detected at the downtown location by both instruments during the intercomparison, and throughout the study period by the downtown instrument, but neither were detected at the suburban location.[8]

Relative Importance of TNMHC and NO_x to PAN and O_3 Production at the Suburban Site

Linear regressions between the daily PAN maximum, the 8:00–9:00 a.m. TNMHC concentration,[15] the NO_x morning maximum, and the daily O_3 maximum were performed to assess the relative importance of VOC and NO_x concentrations to PAN and O_3 daily maxima at the suburban site. Performing this regression analysis without collecting data at the same time may contaminate the analysis results for a direct cause-effect relationship. However, there frequently occurred regional synoptic conditions favoring air mass stagnation (the surface wind speed is generally < 3 m/sec) during the experimental period, and most of the data used for the analysis were acquired during the stagnant weather conditions. The results of individual and multiple linear regressions of PAN and O_3 against TNMHC and NO_x are presented in Table 1. All regressions yielded R^2 values that explained significant portions of the variability in the PAN and O_3 daily maxima. All regressions were found to be significant at the 99% confidence level.

PAN was found to be positively correlated to ozone at the suburban location, as expected, due to the similar photochemical origins of the two species. Both PAN and O_3 were then regressed on TNMHC, NO_x, and both variables together. The correlations of PAN and O_3, when regressed on TNMHC and NO_x, resulted in different relationships between the two photochemical oxidants and their precursors. R^2 values for a linear regression can be interpreted as the percent of variability of the dependent variable that can be explained by the variability observed in the independent variable it is regressed on. For example, the regression of PAN on TNMHC indicates that 40% of the variability in PAN daily maxima can be explained by the variability in the morning TNMHC levels at the suburban site. NO_x concentrations in the morning, however, explain 60% of the variability in the PAN maxima. The multiple linear

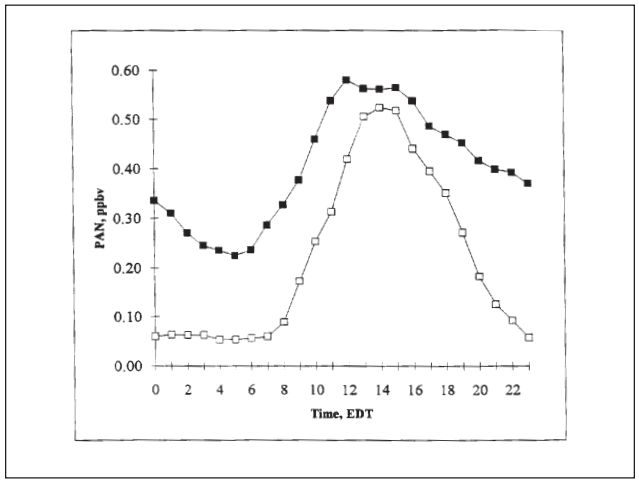

Figure 5. Diurnal profile of PAN at a rural North Carolina site (dark squares) and at the suburban Atlanta site (open squares) on low ozone days.

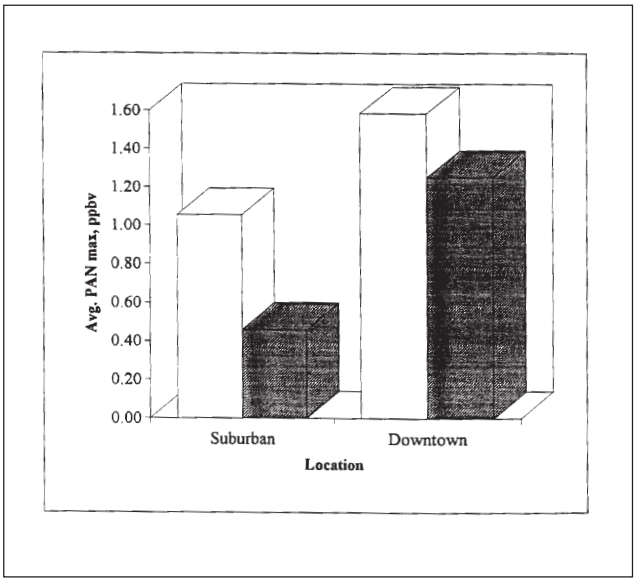

Figure 6. Comparison of average daily PAN maxima for southwesterly winds (open columns) and for southeasterly winds (dark columns) for both the suburban and downtown locations.

Table 1. Regression equations.

Regression Equation	R^2*
PAN = 0.42 ± 0.52 (TNMHC) + 10.17 ± 2.91 (NO_x) -0.48	0.61
PAN = 1.73 ± 0.43 (TNMHC) + 195	0.40
PAN = 11.88 ± 1.99 (NO_x) + 28.46	0.60
O_3 = 0.07 ± 0.017 (TNMHC) + 0.21 ± 0.09 (NO_x) + 26.54	0.77
O_3 = 0.49 ± 0.08 (NO_x) + 31.40	0.59
O_3 = 0.097 ± 0.011 (TNMHC) + 30.5	0.72

*Significant at the 99% confidence limit; n = 25 for all regressions; units: PAN, pptv; O_3, ppbv; TNMHC, ppmC.

regression of PAN against both TNMHC and NO_x increases the explained variability to 61%. This suggests that the availability of NO_x at the suburban location influences the day's PAN maxima more than the TNMHC concentrations do.

Ozone, on the other hand, is more dependent on the morning TNMHC concentrations than on NO_x availability. TNMHCs account for 72% of the variability in the daily O_3 maxima, while adding NO_x to the regression only increases the explained variability to 77%.

Lagrangian Accumulation Rate of PAN

On seven days during the period studied, the suburban site was upwind of the downtown site, with winds from the southeast over the Atlanta area, as indicated by average surface wind direction data (the opposite situation, in which the downtown site was upwind of the suburban site, did not occur during the period studied). For these days, a simple one-dimensional model for the rate of change of PAN concentration in Lagrangian concept, may be written as follows:

$$\frac{DPAN}{Dt} = \frac{\delta PAN}{\delta_t} + \bar{u}\,\frac{\delta PAN}{\delta_x} + \overline{w}\,\frac{\delta PAN}{\delta_x} + \text{sources} + \text{sinks} \quad (1)$$

where $\frac{D}{Dt}$ indicates the total rate of change and $\frac{\delta}{\delta t}$ indicates the local rate of change with time. This simplified equation elucidates the role of wind advection in the rate of change of PAN.

DPAN/Dt can be calculated from eq 1 under the following assumptions, which are valid under these stagnant meteorological conditions:

- the rate of change of PAN concentration at a fixed position, $\delta PAN/\delta t$, may be estimated from the slope of the diurnal profile of PAN at that location;
- the average horizontal velocity, $\bar{u}$, at the suburban site is indicative of the average wind speed and direction between the two sites;
- a straight line trajectory exists between the two sites so that δx is the distance between the two sites;
- crosswind concentration gradients are much smaller than those along the prevailing wind direction and are, therefore, neglected;
- vertical concentration gradients may be significant, but vertical advection is small because $\overline{w} \cong 0$; and
- due to the complexity of characterizing the sources and sinks of PAN between the two sites, these two terms are neglected in the calculations.

Figure 7 shows the change in DPAN/Dt with time for the days on which the suburban site was upwind of the downtown site. The rate of change of PAN concentration in a parcel traveling between the two sites was always positive on these days and increased with time during the photochemically active daytime hours. The rate of increase of PAN with time in Figure 7 was about 1.5×10^6 molecules cm^{-3} sec^{-1}. The rate of increase reached its maximum late in the afternoon, corresponding with the time of the maximum PAN concentration of the day. The rate then dropped to near zero, as recorded in the morning after 2000 EDT. The sudden reduction is attributed to the lack of strong solar radiation late in the day, thus limiting photochemical activity. Additionally, evening rush hour traffic released high quantities of NO into the atmosphere, which, along with the elevated temperatures (above 25 °C) common from urban heat island effect in Atlanta, which were observed at the site, make the continued formation of PAN unlikely.

Estimated Peroxyacetyl Radical Concentrations at the Suburban Site

Computer kinetic modeling of PAN chemistry in an urban environment would be aided by estimates of peroxyacetyl radical concentrations. The measured PAN and NO_2 concentrations, together with the relevant

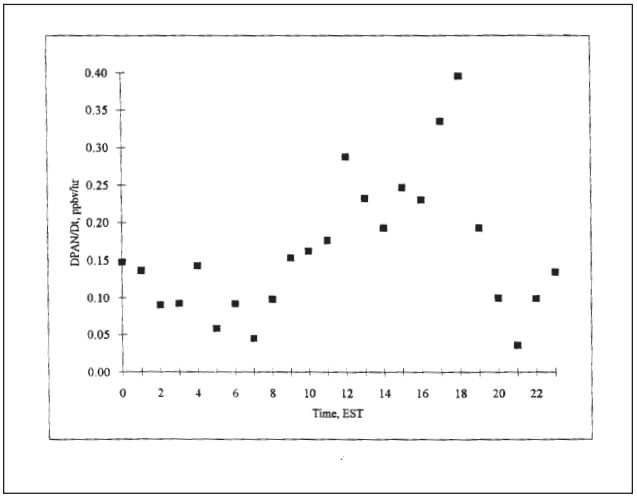

Figure 7. DPAN/Dt as a function of time calculated from eq 5 for the seven days when the suburban location was upwind of the downtown location.

reaction rate constants, allows the calculation of radical concentrations necessary to account for the observed concentrations of these species. PAN is thermally unstable. Therefore, thermal dissociation of PAN releases peroxyacetyl radicals into the ambient air. Again, peroxyacetyl radicals react with NO_2 and produce PAN. This formation of PAN in the atmosphere is an important loss process of peroxyacetyl radicals. There are, of course, loss processes for the peroxyacetyl radicals other than reaction with NO_2 to form PAN, most notably the reaction between peroxyacetyl radicals and the reaction with NO. A more accurate estimate of peroxyacetyl radical levels might come from a steady state treatment taking into account these other loss reactions. In that case, the peroxyacetyl radical levels would depend on the ratio of NO/NO_2.[16,17] In this paper, a preliminary estimation of PAN in urban polluted atmosphere was performed, assuming equilibrium between PAN formation and its thermal dissociation. We calculate peroxyacetyl radical concentration:

$$[CH_3CO_3] = \frac{k_2[PAN]}{k_1[NO_2]} \quad (2)$$

which is derived from the formation of PAN from peroxyacetyl radical and NO_2:

$$\frac{d[PAN]}{dt} = k_1[CH_3CO_3][NO_2] \quad (3)$$

and the thermal dissociation of PAN into peroxyacetyl radical and NO_2:

$$-\frac{d[PAN]}{dt} = k_2[PAN] \quad (4)$$

Peroxyacetyl radical may also be calculated using the estimated rate of change of PAN concentration at equilibrium between PAN formation and dissociation:

$$\frac{DPAN}{Dt} = k_1[CH_3CO_3][NO_2] - k_2[PAN] \quad (5)$$

Peroxyacetyl radical concentrations calculated using eq 2 averaged ~0.30 pptv with a maximum of 1.69 pptv; using eq 5, they averaged ~0.60 pptv with a maximum of 2.17 pptv. The difference in the peroxyacetyl radical concentrations calculated by the two different methods lies in the addition of the DPAN/Dt term to the calculation. The higher the value for DPAN/Dt, the larger the calculated peroxyacetyl radical concentration will be. The unknown distribution of sources and sinks of PAN between the two locations complicates this analysis. The values from the two calculations, however, are roughly similar and may represent the upper and lower bounds of peroxyacetyl radical concentrations at this suburban location. Peroxyacetyl radical concentrations were calculated as above for a rural site in North Carolina.[18,19] NO_2 concentrations were obtained from the experimental measurements at a rural site in the Central Piedmont area of North Carolina.[14] Ambient NO_2 was measured with the LMA-3 Luminol bared NO_2 analyzer (Scintrex, Ltd.). The detection limit of the instrument was 5 pptv calculated as the noise equivalent of a clean air sample. The radical concentration estimates suggest that peroxyacetyl radical concentrations may be similar in rural and suburban environments in the southeast United States Also, at the rural site in Pennsylvania, estimated peroxyacetyl radical concentrations have been reported[20] and ranged from 3.5 to 19.0 pptv on four photochemically active days. At the rural North Carolina site, peroxyacetyl radical concentrations ranged from 0 to 13.0 pptv during June and July 1992. The peroxyacetyl radical concentrations calculated for the suburban Atlanta site were on the same order as, and at the low end of, the range of values reported for the two rural sites. These similar characteristics of peroxyacetyl radicals in rural and suburban environments in the southeast United States seem to corroborate the results of the multiple regression analysis (Table 1), which show that PAN concentrations are more dependent on NO_x availability than on TNMHC concentrations. It is also now recognized that rural southeast United States is NO_x limited.[21]

CONCLUSIONS

PAN concentrations were generally higher at the downtown location than at the suburban location and were fairly consistent throughout the study. However, on days when the O_3 concentration exceeded 80 ppbv, observed PAN maxima at the suburban site were similar to those of the downtown site. On days when O_3 did not exceed 80 ppbv, PAN concentrations were much lower than downtown concentrations and resembled those reported for another rural area in the eastern United States. The most important factors for this phenomena are thought to be wind direction and speed; however, sources and sinks of precursors relating with atmospheric chemistry are also important factors in temporal and spatial distributions of PAN in urban environments. The position of the suburban site near the edge of the metropolitan area subjected it to different upwind precursor source areas, depending on wind direction. When the suburban site was downwind of more rural areas (i.e., days when ozone < 80 ppbv occurred frequently), the PAN diurnal profiles resembled those reported for another rural site in the eastern United States. When areas of more significant anthropogenic sources were upwind of the suburban site, however, the suburban PAN diurnal profiles and daily maxima were similar to those observed regularly at the downtown location. This seems to suggest that these differing precursor availabilities, according to wind direction, strongly influenced the PAN concentrations at the site.

Both PAN and O_3 daily maxima were regressed against the morning NO_x and TNMHC maxima and were found

to be strongly correlated to each of these variables and to each other. Multiple regression of PAN against NO_x and TNMHC morning maxima explained 61% of the variability of daily PAN maxima, while multiple regression of O_3 against NO_x and TNMHC morning maxima explained 77% of the variability in the daily O_3 maxima.

PAN data and meteorological data from the suburban site were used in a one-dimensional transport model to estimate the Lagrangian accumulation rate of PAN following an air parcel between the suburban site and the downtown site on days when the suburban site was upwind of the downtown site. The concentration data were also used in a simple kinetic model to estimate peroxyacetyl radical concentrations. These radical concentrations were then compared to those from two rural sites in the eastern United States. For the low ozone days, both PAN concentrations and peroxyacetyl radical concentrations were similar to concentrations reported for several rural sites in the eastern United States. The similarity of radical concentrations and PAN concentrations suggests that the low ozone day PAN concentrations from the suburban Atlanta location and the average PAN concentrations reported from rural eastern United States. sites may be indicative of a regional background PAN profile. The high ozone day PAN concentrations at the suburban location and the regularly higher PAN concentrations at the downtown location are thought to be indicative of urban spikes of higher PAN concentrations within the regional PAN background.

ACKNOWLEDGMENTS

This research has been funded by the U.S. Environmental Protection Agency through a cooperative agreement (S 9153) with the University Corporation for Atmospheric Research as a part of the Southern Oxidants Study–Southeast Oxidant Program on Ozone Non-Attainment (SOS-SORP/ONA). We thank Dr. W. Lonneman (EPA) for making available the PAN analyzer and providing advice regarding PAN measurements, E.L. Williams, II, and E. Grosjean (DGA, Inc.) for their support and cooperation during the field study, M. Rodgers, J. Wilburn, students and staff of the Georgia Institute of Technology, Z. Li and M. Das for their help in the field, and M. DeFeo and B. Batts for the preparation of the draft and final versions of the manuscript.

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