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Relationships between PAN and ozone at sites in eastern North America

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Abstract. Measurements of ozone and PAN (peroxyacetic nitric anhydride) were made at four sites in eastern North America; Bondville, Illinois, Egbert, Ontario, Scotia, Pennsylvania, and Whitetop Mountain, Virginia., in July and August of 1988 as part of a study of regional oxidant photochemistry. The concentrations of PAN ranged from <0.010 to 9.2 parts-per-billion by volume (ppbv) and those of O_3 ranged from <2 to 139 ppbv. Diurnal concentration profiles showed PAN and O_3 to be removed within nocturnal boundary layers, especially if nitric oxide was present, and that O_3 was, for most sites, more rapidly removed than PAN. The only mountain top site at which PAN was measured showed distinctly different diurnal profiles in which O_3 was actually higher at night, suggesting that convective flow driven by surface cooling served to transport air down from higher in the mixed layer at night. The afternoon production of PAN and O_3 was also apparent and led to an overall linear correlation of O_3 and PAN between the hours of 1300 and 1800. The comparison of this result with other measurements, estimates of PAN formation rates, and model calculations indicates that the production of PAN relative to ozone is far greater (x3) than can be accounted for by acetaldehyde reactions with OH, there is a wide disparity in model descriptions of PAN production, and confirms the non-linear dependence of O_3 production on NO_X.

Introduction

The impacts of photochemically-generated pollutants on human health and plant life have long been of concern. Ozone (O_3) and peroxyacetic nitric anhydride (commonly called peroxyacetyl nitrate, PAN) are two of the more important compounds in this regard [*Folinsbee, et al.* 1988; *Heck et al.*, 1982; *Skarby and Sellden*, 1984; *Temple and Taylor*, 1983; *Woodman and Cowling*, 1987; *Kleindienst et al.*, 1990]. The interest in these two species has expanded since it is now recognized that O_3 is a greenhouse gas and plays a central role in tropospheric radical chemistry, and PAN is often the most abundant tropospheric odd nitrogen (NO_y) species on continental and global scales [*Singh et al.* 1985; *Bottenheim et al.* 1986; *Singh* 1987].

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The production of O_3 and PAN is driven by photochemical reactions involving the oxides of nitrogen, NO_x ($NO + NO_2$), and hydrocarbons (HCs), [*Leighton*, 1961; *Stephens*, 1969]. The absolute and relative efficiencies of production are dependent on factors such as concentrations of precursors and the ratio of HC/NO_x. An understanding of how these factors govern production is required before valid control strategies can be devised. Specifically, the dependencies of O_3 and PAN production on anthropogenic hydrocarbons (AHCs) and biogenic hydrocarbons (BHCs) must be better defined.

Numerous sets of O_3 and PAN measurements have shown these two species to be correlated, not only in air masses highly impacted by urban emissions but also in those more characteristic of the remote Northern hemisphere [*Roberts*, 1990]. The correlation in urban-impacted air masses results from the rapid photochemical co-production of these species and appears as afternoon maxima in concentrations [*Hanst et al.*, 1982; *Altshuller*, 1983; *Grosjean*, 1983; *Peake and Sandhu*, 1983; *Anlauf et al.*, 1985; *Singh et al.*, 1985; *Corkum et al.*, 1986; *Perros et al.*, 1988; *Tsani-Bazaca et al.*, 1988; *Ridley et al.*, 1990; *Wunderli and Gehrig*, 1991]. More remote air masses do not bear this signature [*Penkett and Brice*, 1986; *Bottenheim et al.*, 1987; *Brice et al.*, 1988] but show springtime maxima, resulting from conversion of precursors that were widely distributed over the winter months.

The measurements reported here were conducted in July and August of 1988 as part of a study of regional oxidant photochemistry. Measurements of O_3 were made at all sites, Bondville, Illinois, Brasstown Bald, Georgia, Egbert, Ontario, Scotia, Pennsylvania, Whiteface Mountain, New York, and Whitetop Mountain, Virginia, but PAN measurements are reported here for only four sites, Bondville, Egbert, Scotia, and Whitetop. This summer was characterized by high-pressure periods of unusual frequency and persistence. This resulted in temperatures that were much higher than

average. Several previous papers from this data set by *Parrish et al.* [1993] and *Trainer et al.* [1993] have dealt with the composition and behavior of total odd nitrogen (NO_y) at these sites, and the relationships of O_3 to NO_y and NO_x, respectively. The diurnal behavior of ozone and PAN will be examined in this paper and the relationships between PAN and O_3 will be explored for both afternoon periods of high photochemical activity and nighttime periods when deposition is evident.

Experimental Approach

The PAN measurements reported here were made with very similar techniques at all sites, using packed-column gas chromatographs with electron capture detection (GC/ECD). Variations of column type and instrument conditions were minor, as described below. The methods used for standardizing the instrument response to PAN varied from one group to the next; however, efforts were made to compare PAN standards to the standards used for the measurement of the other NO_y species. The frequency of PAN measurements varied from site to site, from every 15 min at Bondville and Whitetop to every 30 min at Egbert and Scotia. Ozone measurements were made using standard commercial instruments that employed UV photometry. Instruments from different manufacturers were used; however, the detection limits (2-4 parts-per-billion-by-volume (ppbv)) and precision (±10% at 40 ppbv) were similar throughout. Ozone measurements were made with a variety of frequencies, usually more frequent than one per minute, however, 5- or 15-min averages were compiled and reported, except in the case of Bondville, Illinois, where 1- hour averages were used. Details concerning the individual sites are given below.

Bondville, Illinois

The Bondville site is operated by the Illinois State Water Survey (ISWS) as a facility for conducting research on dry deposition. The site consists of a 108 x 230-m clearing surrounded by agricultural land on which corn, soy beans, and alfalfa were grown. The clearing has a limited access dirt road on its southern edge, over which 2-3 vehicles pass per day. A sparsely used county road is about 200-m east of the clearing. The BNL van was set up approximately 200-m south of the area used by ISWS and just south of the dirt road.

The PAN GC and calibration systems have been described in detail elsewhere [*Roberts et al.,* 1988;1990] and will be only briefly discussed below. A common inlet, consisting of 7.5-mm ID Teflon-PFA tubing held 6 m above the ground, was used for the $NO/NO_2/NO_y$, PAN, and O_3 instruments. The flow through this inlet was in excess of 6 L min^{-1} STP (0°C, 760 torr), 25 cm^3 min^{-1} STP of which was drawn through the inlet valve of the PAN GC via a 50-cm length of 1.5-mm ID Teflon-PFA tubing. The inlet of the GC (Shimadzu GC-mini-2) was an all-Teflon-TFE six-port valve (Hamilton) fitted with a 5 cm^3 sample loop consisting of polyethylene tubing. The column was made of Teflon-PFA tubing (60-cm-long, 1.5-mm ID) packed with 10% Carbowax 400 on Chromosorb W HP, and was operated at 33°C and a flow rate of 40 cm^3 min^{-1} STP. The ECD was of the constant current variable frequency type and was operated at 60°C. Under these conditions, PAN had a retention time of 3.8 min and water produced a large negative peak beginning at 9.5 min and lasting to about 15 min. Therefore sample turnaround times of 15 min could be achieved.

The calibration system was very similar to those described by *Fehsenfeld et al.* [1987] and *Buhr et al.* [1990] and consisted of a solution of PAN in n-tridecane ($C_{13}H_{28}$) contained within a capillary diffusion cell. The PAN was synthesized from peroxyacetic acid and nitric acid at ice-water temperatures via a modification of the procedure reported by *Gaffney et al.* [1984]. The diffusion cell consisted of a glass bulb of approximately 5 cm^3 to which a capillary tube (4.5-cm-long, 1-mm ID) was attached. The outlet of the tube was connected to a small volume through which 50 cm^3/min STP N_2 flowed. The cell was kept in an ice/water dewar which provided a constant, low temperature so that a stable PAN output was obtained. Laboratory tests of the output stability with time and the levels of impurities emitted showed this source to emit a constant (±5%) pure (>95% as NOy) concentration of PAN. The effluent from the PAN standard was diluted with up to 2 L min^{-1} STP of air to provide a range of mixing ratios. The fundamental calibration of this source was achieved by conversion to NO (>95% efficient) with determination by $NO-O_3$ chemiluminescence versus the National Institute of Standards and Technology (NIST) 5 parts-per-million-by-volume (ppmv) NO Standard Reference Material (SRM). In consideration of the above, the precision of repeated GC analyses, and the effects of humidity, an uncertainty of ±25% was estimated for mixing ratios of 1 ppbv. The detection limit of the system was 10 parts-per-trillion-by-volume (pptv) (S/N=2).

Egbert, Ontario

The measurements near Egbert were made at the Clean Air Facility (CAF) of the Centre for Atmospheric Research Experiments (CARE) of the Atmospheric Environment Service. The site is approximately 70 km north of Toronto, with major highways 8 km to the east and 6 km to the south. Local county roads carrying occasional, mostly daytime, traffic run closer to the site. The CAF itself is about 150 m removed form the main CARE facilities on top of a grassy hill. The surrounding land is used mainly for agriculture.

Details of the PAN GC and calibration have been described earlier. In short the PAN GC consists of a modified HP 5710 GC, outfitted with a PU 4500 electron capture detector [*Trivett et al.,* 1988]. The column was made of silanized Pyrex glass (6.5-mm OD, 75 cm long), filled with 5% Carbowax 400 on Chromosorb G AW DMCS. Column temperature was 40°C, and UHP N_2 at a flow rate of 60 cm^3 min^{-1} was used as a carrier gas. The detector was of the constant current/variable frequency type and was held at 60°C. Air was sampled at 30-min intervals from the roof of the building, about 5 m above the surface, through a Teflon intake filter, and 5-m length of 3.2-mm OD preconditioned stainless steel tubing. Calibration of the instrument was performed 3 times during the 6 weeks of the study, using the method described by *Brice et al.* [1988]. The GC used for the Egbert measurements was recently involved in an intercomparison with another GC, which was calibrated by an independent method. The ambient PAN concentrations measured by the two GCs agreed to within 15% [*Blanchard et al.,* 1990]. The Egbert data are estimated to have an absolute uncertainty of ±25%.

Scotia, Pennsylvania

The Scotia site is in westcentral Pennsylvania, about 7 km southwest of State College, in a clearing within a predominantly oak/hardwood forest. The site is surrounded by

a number of major industrial point sources at distances of 100 km or more, and the city of Pittsburgh is 180 km to the west. The prevailing winds are from the southwest, roughly in the direction of most of the point sources and the Pittsburgh area. The site is located near the bottom of a shallow (200 m) valley that is approximately 15 km wide. As a result the meteorology is characterized by strong nocturnal inversions occurring nearly every night during the summer.

The experimental details of the PAN measurements at Scotia were recently discussed by *Buhr et al.,* [1990] and are given only briefly here. Air was sampled from a height of 10 m above the ground through an inlet system consisting of 6.3-mm OD Teflon tubing. A three-way valve permitted a charcoal trap to be switched inline close to the top of the inlet line and standard gases were added just downstream of the trap. The instrument used was a custom-built GC [*Kuster et al.,* 1981] that could be sealed and flushed with clean nitrogen for ultra-high-purity operation. The column was made of stainless steel tubing (3.2-mm OD, 152 cm long) packed with 10% Carbowax 600 on Supelcoport. A flow rate of 30 cm^3 min^{-1} of N_2 and a temperature of 35°C were used. The detector was of the constant frequency/variable current type and was held at 45°C. The apparatus used for PAN calibration was similar to that described above for Bondville, and the fundamental means of calibration was by the NO_y method. The uncertainty in these PAN measurements was estimated to be ±30%.

Whitetop Mountain, Virginia

The Whitetop Mountain site is operated by the Tennessee Valley Authority as a high-elevation research station. It is located in the Mount Rogers National Recreation Area of the Jefferson National Forest in southwestern Virginia. The Whitetop research station is at the summit of Whitetop Mountain, Virginia and straddles the main ridge line of the Appalachian range. The site consists of a 3600-m^2 clearing. Several portable buildings and 20-m towers are located in the clearing. At the summit of Whitetop Mountain there extends a contiguous closed stand of red spruce approximately 400 ha in size. Spruce extends down to an elevation of about 1400 m aggrading into a red spruce-yellow birch cover type. An unpaved road (switchback) runs to the site. Several vehicles a day typically come to the site since it is located in a recreational area.

The sampling manifold for PAN and NO_2 consisted of a 5 cm I.D. Teflon tubing whose inlet was 3 m above the ground. The flow through this sampling manifold was in excess of 50 L min^{-1}. Samples for PAN analysis were withdrawn continuously through a 76-cm length of 1.5-mm ID Teflon-PFA tubing at a flow of 150 cm^3 min^{-1} into the inlet valve of the gas chromatograph. The inlet valve of the GC (Shimadzu GC-mini-2) was a Teflon six-port valve (Valco) fitted with a 2 cm^3 sample loop consisting of 1.5-mm ID Teflon-PFA tubing which was in the sample stream. Approximately every 15 min the valve was automatically activated to the inject position for 10 s to sweep out the sample from the sample loop. The column was made of Teflon tubing (60-cm-long, 1.5-mm ID) packed with 10% Carbowax 600 on Chromosorb Z 80/100 mesh. The carrier gas was UHP nitrogen at 60 cm^3 min^{-1}. The column was operated at 35°C and the electron capture detector was operated at 40°C.

The PAN GC response was checked daily using a bag dilution method. One microliter of a PAN stock solution was injected into a 100-L Tedlar bag filled with clean air containing about 20 ppbv NO_2. The PAN was synthesized using the procedure reported by *Gaffney et al.* [1984] and the stock solution concentration was determined by Fourier transform infrared spectroscopic analysis. The bag dilution method was used to calibrate the PAN GC at the start and end of the field study. A 30% uncertainty is estimated for the Whitetop PAN data. The limit of detection was estimated at 0.2 ppbv since peak detection became erratic for mixing ratios below 0.2 ppbv. Results that were below the detection limit were included as 0.1 ppbv in the analysis presented below.

Results

The time periods during which measurements were made were different for each site, however the last two weeks in August were common to all sites. For the purposes of this paper, all measurements made in July and August will be used, in order to best characterize the photochemistry. The measurements of PAN and O_3 are presented as averages versus time of day in Figure 1. The profiles were constructed by averaging all the measurements within each hourly period.

The profiles at Bondville, Illinois, show that PAN and O_3 both exhibit afternoon maxima. The PAN profile showed large variability due to the influence of the highest PAN concentrations which were observed the first few days of the period (August 16-18). The PAN averages at 0700-0900 LST (local standard time) were low because ambient measurements were not made during part of the initial period, due to instrument calibrations. Likewise, the peak PAN concentration between 1600 and 1700 is accentuated because of the initial high measurements. The averages for the remaining period, August 19-30, showed a profile that was smoother and very similar to that of O_3. The PAN profile

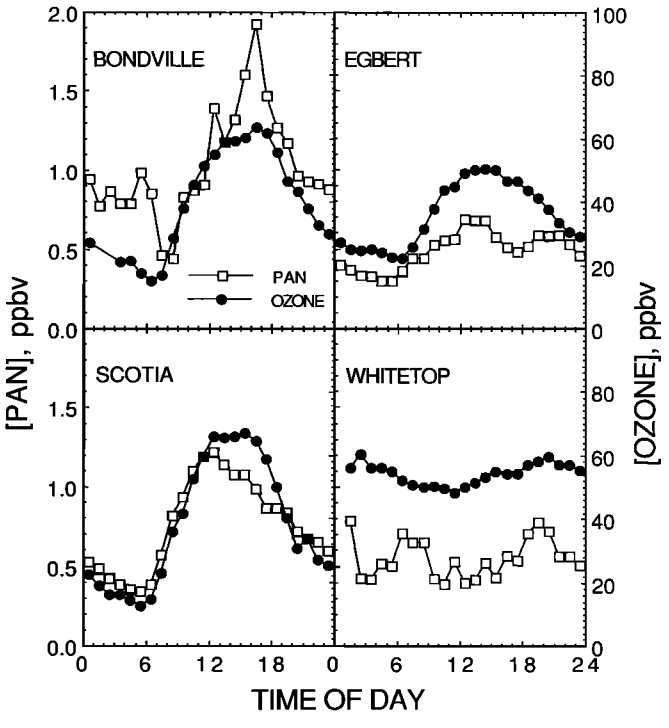

Figure 1. Average peroxyacetic nitric anhydride (PAN) and O_3 mixing ratios versus time of day (EST, except for Bondville which was CST) for measurements at Bondville, Illinois, Egbert, Ontario, Scotia, Pennsylvania, and Whitetop Mountain, Virginia.

showed a typical midafternoon maximum (in this case 1.9 ppbv) resulting from a combination of photochemical production and vertical mixing of the boundary layer. Such vertical mixing serves to transport air from the upper boundary layer that has not been depleted in materials due to deposition, or reaction with species that have a surface source. The profile of O_3 concentration shows a steady decrease through the nighttime due to the surface removal of ozone within the isolated nocturnal boundary layer. The rapid increase after sunrise 0700-0800 CST was due to the vertical mixing associated with the breakup of the inversion. The afternoon maximum in O_3 (64 ppbv) is likewise a combination of photochemical production and maximal vertical mixing. The morning-to-afternoon modulation in O_3 (about x4) is larger than that of PAN.

The PAN profile at Egbert showed only a slight afternoon maximum, and the average mixing ratio was at most 0.7 ppbv. PAN concentrations close to the average daytime maximum persisted into late evening. The O_3 profile was smother and more typical of the other flatland sites, exhibiting a midafternoon maximum and a steady decrease into the evening. The modulation in the O_3 profile was a factor of 2.5 day to night.

The PAN and O_3 profiles at Scotia tracked very closely and showed a high degree of day-night modulation (a factor of 6 in O_3). The PAN profile tracked that of O_3 very closely from midnight to noon, but fell off gradually from a noontime maximum (1.2 ppbv). The O_3 concentration had a broad maximum (67 ppbv) throughout the midafternoon and began to drop rather rapidly, before sunset. A steady decrease in O_3 is also seen through the nighttime to early morning hours. The Scotia site is in a shallow valley, which probably accounts for the low nighttime O_3 concentrations. For Scotia a downslope flow is created at night when the surface cools, so that air drains to the bottom of the valley. This drainage would be accompanied by more efficient O_3 destruction at the surface compared to a stagnant inversion.

The profiles at Whitetop Mountain were entirely different than those of the other sites. There was very little day-night difference in either PAN or O_3, with slightly higher values of O_3 at night. The PAN averages showed some variability, ranging from 0.4 to 0.78 ppbv, that did not appear to be systematic. The O_3 values were much less variable ranging from an average of 48 to 60 ppbv. The other mountain sites, Brasstown Bald and Whiteface Mountain, showed a similar lack of day-night modulation in O_3 concentration [*Parrish et al.*, 1993], because for these sites, the formation of a nocturnal boundary layer causes downslope flow, transporting air down from higher up in the mixed layer [*Broder et al.*, 1981]. This air was higher in O_3 because it has had less opportunity for dry depositional loss at the surface. This effect has been observed in other ozone measurements made in the eastern or southeastern United States [*Mueller*, 1994; *Aneja et al.*, 1991; *Aneja and Li.*, 1992]. PAN concentrations were as high or slightly higher at night compared to the day time because of the typical presence of layers of polluted air at or just above the top of the daytime boundary layer. These layers are fairly high in PAN because of lower temperatures and middle to high precursor concentrations.

The relationships between PAN and O_3 concentrations are a result of the photochemistry that produces them and the subsequent transport and removal processes. Figure 2 shows the correlations of PAN with O_3 for the individual sites. Ozone was chosen as the independent variable in these plots since its daytime mixing ratio is more broadly representative of regional photochemical oxidant production. The overall

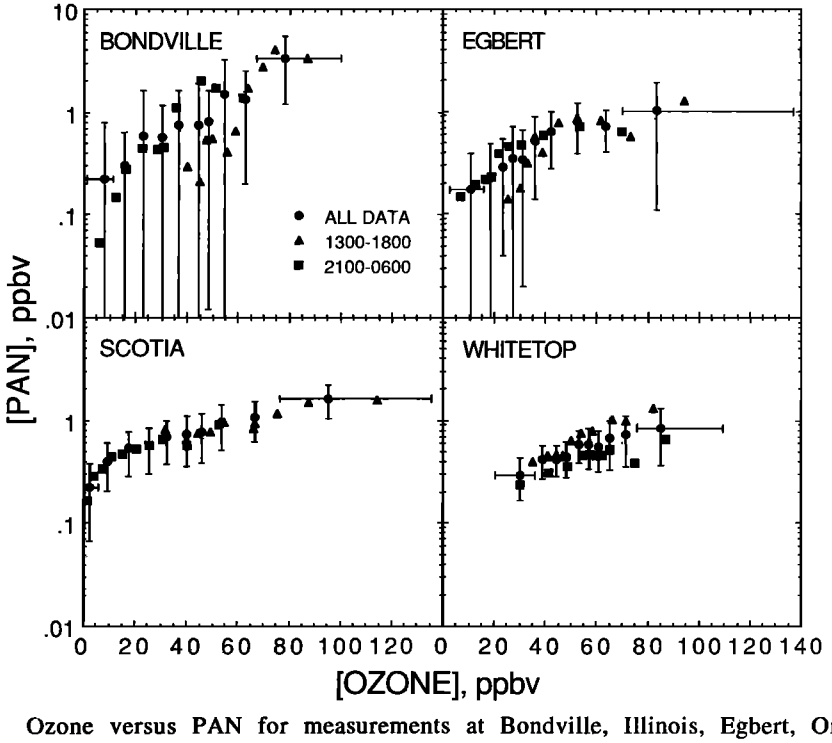

Figure 2. Ozone versus PAN for measurements at Bondville, Illinois, Egbert, Ontario, Scotia, Pennsylvania, and Whitetop Mountain, Virginia. Each point represents 103, 24 or 38 (Bondville), 135, 35 or 50 (Egbert), 159, 37 or 56 (Scotia), or 146, 35 or 47 (Whitetop) individual measurements for the whole data set, 1300-1800, and 2100-0600 respectively.

correlations plus those for the time periods 1300-1800 and 2100-0600 EST (CST at Bondville) are shown. The data sets were sorted by O_3 mixing ratio, divided up into 10 bins of equal number of points and the mean PAN was calculated for each bin. The vertical bars on the overall points are plus or minus one standard deviation about the mean, and the horizontal bars at the high and low points give the range of the highest and lowest bins and therefore define the range of the whole data set.

The O_3 and PAN concentrations at Bondville, Ill., were correlated in the overall data set and in each time period, although the correlations were not very smooth. The afternoon points exhibited higher O_3 concentrations than the nighttime points and the average difference in O_3 concentration afternoon-night was 15-20 ppbv O_3 for a given PAN concentration. The afternoon points showed an increase in PAN with O_3 overall; however, the PAN concentrations were relatively constant with increasing O_3 at the highest O_3 concentration. The lowest O_3 and PAN concentrations were observed at night and ranged all the way down to the detection limits of each measurement (0.01 ppbv PAN and 2 ppbv O_3).

The Egbert, Ontario, measurements showed the least correlation of PAN with O_3 of any of the sites. The afternoon points showed a trend in PAN with increasing O_3 and almost no increase in PAN with O_3 in the range 45 ppbv and above. The afternoon points, in general, exhibited higher O_3 mixing ratios than the nighttime points, with differences in O_3 of 20 ppbv at some PAN concentrations. The nighttime measurements showed the same trend as the daytime measurements with an increase in PAN with O_3 at the lowest concentrations and virtually constant average PAN levels at the highest O_3.

The Scotia, Pennsylvania, measurements showed relatively smooth correlations overall and in both time periods. The afternoon points had the highest PAN and O_3 concentrations, but the trend in the afternoon appears no different than at night in the midconcentration ranges. The nighttime observations were much lower in O_3 and PAN and showed on average a larger change in PAN relative to O_3.

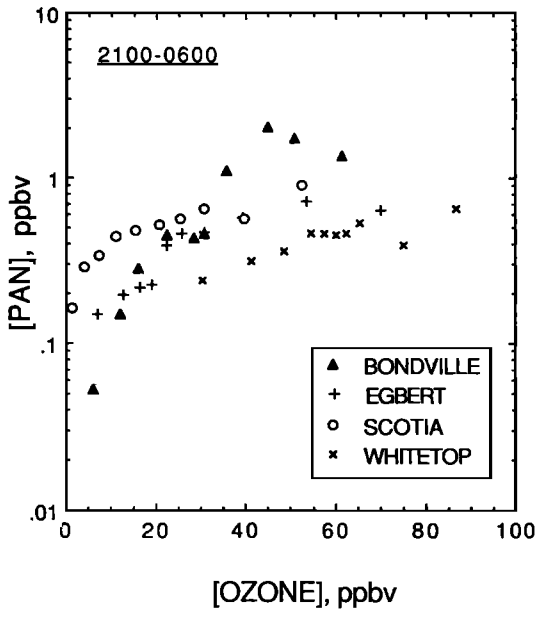

Figure 3. Summary of all the nighttime measurements.

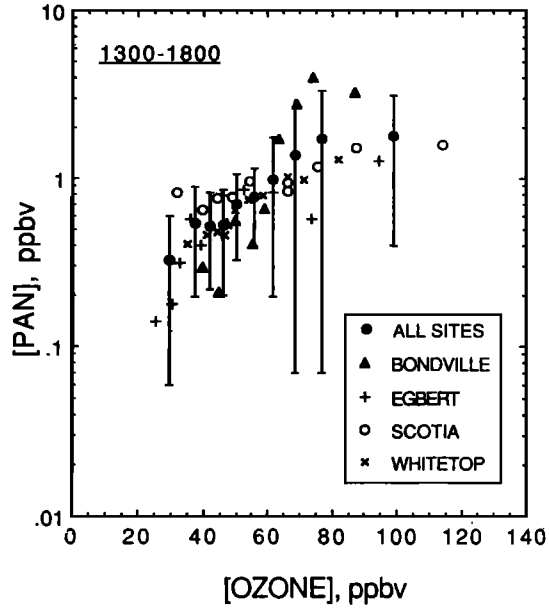

Figure 4. Summary of all the afternoon measurements (n=1301), plotted both from the individual sites and as a combined data set. The vertical bars represent one standard deviation about the mean and the horizontal bars show the range of the highest and lowest measurements.

The Whitetop Mountain, Virginia, measurements showed relatively tight correlations of O_3 with PAN. The key feature of these data is that there is very little overall diurnal variation, with both PAN and ozone levels slightly higher at night. Another feature of this site is that the ranges of O_3 and PAN concentrations were smaller than at any of the other sites.

The nighttime correlations are plotted together in Figure 3 wherein it is obvious that a wide range of conditions existed at the various sites. Scotia, PA., had the lowest O_3 overall and Whitetop Mountain, VA., the highest. Egbert and Bondville showed very similar trends in the O_3 range below 35 ppbv. The afternoon data are all plotted together in Figure 4. A tighter envelope of points were observed, and the data from Scotia and Bondville diverged at the highest concentrations of PAN and O_3. The points representing the combined data set were plotted in addition to those from individual sites, where the combined measurements (n=1301) were sorted by O_3 concentration and divided into 10 equal bins. The vertical bars are one standard deviation about the mean, and the horizontal bars show the range of the highest and lowest O_3 measurements.

Discussion

The behavior of PAN and O_3 in the troposphere is governed by their associated formation and removal processes and the rates thereof. Both species are products of NMHC/NO_x photochemistry. In the daytime, net O_3 production occurs through the following reactions:

$$\text{(R1)} \quad HO_2^{\cdot} + NO \rightarrow OH + NO_2$$

$$\text{(R2)} \quad RO_2^{\cdot} + NO \rightarrow RO^{\cdot} + NO_2$$

followed by

$$\text{(R3)} \quad NO_2 + h\nu \rightarrow NO + O$$

$$\text{(R4)} \quad O + O_2 + M \rightarrow O_3$$

PAN is produced as a result of the reaction of peroxyacetyl radicals with NO_2

$$\text{(R5)} \quad CH_3C(O)OO^{\cdot} + NO_2 \rightarrow CH_3C(O)OONO_2$$

peroxyacetyl radicals having been formed as products of organic photo-oxidation. Major PAN precursors include acetaldehyde, acetone, other ketones of the structure $CH_3C(O)R$, methyl glyoxal, and biacetyl. The formation of PAN can be thought of as a reversible sink for radicals and NO_x, because the formation of peroxyacetyl radicals is often initiated by reaction of a precursor with OH.

The removal of O_3 from the atmosphere can occur through various processes. The reactions

$$\text{(R6)} \quad O_3 + HO_2^{\cdot} \rightarrow OH + 2O_2$$

$$\text{(R7)} \quad O_3 + OH \rightarrow O_2 + HO_2^{\cdot}$$

which occur in the gas phase under low NO_x conditions and the reaction

$$\text{(R8)} \quad O_3 + O_2^{-} + H_2O \rightarrow 2O_2 + OH + OH^{-}$$

which is thought to be important in the aqueous phase [*Lelieveld and Crutzen,* 1990], are the major chemical sinks in the bulk atmosphere. The reaction

$$\text{(R9)} \quad O_3 + NO \rightarrow O_2 + NO_2$$

when followed by reactions (R3) and (R4) in the daytime is not a net sink for O_3, however reaction (R9) is a chemical sink for O_3 at night. The deposition of O_3 on surfaces is also recognized to be fast, for example v_d= 0.53 cm s^{-1} [*Colbeck and Harrison,* 1985], and is generally thought to be irreversible.

The removal of PAN in the bulk atmosphere occurs through thermal and photolytic decomposition and by reaction with OH. Thermal decomposition is by far the fastest process in the lower troposphere and proceeds primarily via bond homolysis

$$\text{(R-5)} \quad CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO^{\cdot} + NO_2$$

followed by reaction of peroxyacetyl with NO, $HO_2^{\cdot}$ or $RO_2^{\cdot}$

$$\text{(R10)} \quad CH_3C(O)OO^{\cdot} + NO \rightarrow CH_3C(O)O^{\cdot} + NO_2$$

$$\text{(R11a)} \quad CH_3C(O)OO^{\cdot} + HO_2^{\cdot} \rightarrow CH_3C(O)OOH + O_2$$

$$\text{(R11b)} \quad CH_3C(O)OO^{\cdot} + HO_2^{\cdot} \rightarrow CH_3C(O)OH + O_3$$

$$\text{(R12)} \quad CH_3C(O)OO^{\cdot} + RO_2^{\cdot} \rightarrow \text{products}$$

the acetoxy radical ($CH_3C(O)O^{\cdot}$) decomposes to $CH_3^{\cdot}$ and CO_2. Thus the rate and pathway of PAN decomposition depends on the concentrations of NO and NO_2. When [NO] is high, the rate of thermal decomposition is the rate of reaction(-5) multiplied by the factor $k_{10}NO/k_5NO_2$. The rate of deposition of PAN at surfaces appears to be moderate to slow [*Hill,* 1971; *Garland and Penkett,* 1976; *Schurath et al.,* 1984] owing in part to the fact that it is not very soluble, and does not decompose rapidly in aqueous solution [*Lee* 1984; *Holdren et al.,* 1984].

Although their production is intimately linked, it is difficult to derive a simple quantitative relationship between PAN and O_3 based on photochemical reactions. Some simplifying assumptions were used in a recent study by *Sillman et al.,* [1990], to derive the following equation;

$$[PAN] = (k_{13}\, k_5\, k_9 / k_{-5}\, k_{10}\, j_3)\, [OH][CH_3CHO][O_3] \qquad (1)$$

where the rate constants refer to the reactions described above and the following:

$$\text{(R13)} \quad CH_3CHO + OH \rightarrow CH_3C(O)^{\cdot} + H_2O$$

which was considered to be the sole source of peroxyacetyl radicals in this calculation. Note that acetyl radicals [$CH_3C(O)^{\cdot}$] react rapidly with O_2 to form peroxyacetyl radical. This expression was arrived at by combining the expression for PAN formation from acetaldehyde with that for the net thermal decomposition rate at high NO_x, with the substitution of the expression for the NO_x "photostationary state" that is traditionally derived from reactions (R3), (R4) and (R9). Several major limitations exist in this analysis. There are several other processes aside from (R13) that are also responsible for production of peroxyacetyl radical. It is widely recognized that the photostationary state is not in balance but rather reactions (R1) and (R2) also drive the conversion of NO to NO_2. The extent of this imbalance is such that there would often have to be twice or more times the equivalent ozone concentration present to account for the ratio of NO_2/NO, or in other words the ratio NO_2/NO is a factor of 2 or more higher than predicted by the photostationary state [*Carroll et al.,* 1987].

Figure 5 shows the correlation of O_3 and PAN for the whole data set, in which the relation [PAN] = -0.45 + 0.0242[O_3] is found to fit the data. The slope (0.0242) can be combined with assumptions about average conditions to see how the chemistry compares to that predicted by equation (1). Table 1 lists the average conditions to be used for this comparison. The rate constants were taken from *DeMore et al.,* [1992], and the parameters j_3, [OH], and T, are estimates of average conditions for summer days at 1500. The mixing ratio of acetaldehyde, 5.4 ppbv, was calculated from the above conditions and the slope of the ambient data, assuming an average deviation from the photostationary state of a factor of 2 in NO_2/NO. This value of [CH_3CHO] can be considered a summertime afternoon average, and is a factor of over 3 higher than the average acetaldehyde concentrations found at the Egbert and Scotia [*Shepson et al.,* 1990, 1991] sites, which ranged up to 1.6 ppbv for the afternoon hours. This observation is consistent with the idea that many other processes, other than reaction of CH_3CHO with OH, are likely producing peroxyacetyl radicals, apparently at a total rate several times faster. We note that several of the sites discussed here are forested and as such are influenced by local emissions of isoprene. Under these conditions it may be that methyl glyoxal ($CH_3C(O)CHO$) and methyl vinyl ketone ($CH_3C(O)CHCH_2$), isoprene photooxidation products, are major peroxyacetyl radical precursors. Moreover, it is clear that a number of other sources of peroxyacetyl radicals are possible from anthropogenic hydrocarbons.

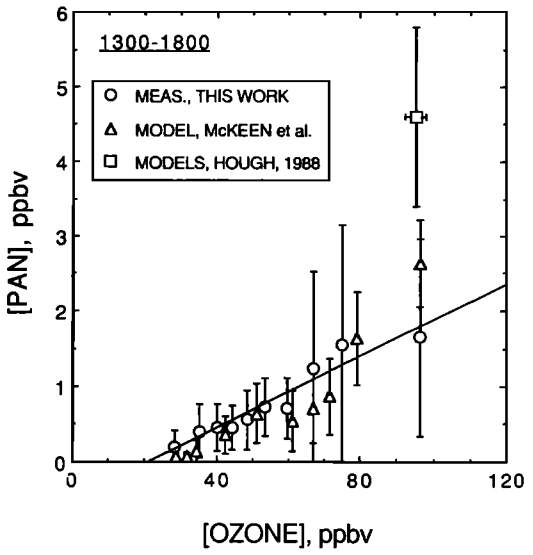

Figure 5. The combined data set for the hours 1300-1800, plotted on linear scales. The equation for the line fitting the data is [PAN] = -0.45 + 0.0242[O_3], and r^2 = 0.919 for the 10 cell points. The point from *Hough* [1988] represents the average result of nine of the most recent photochemical models used for regional oxidant modeling, and the horizontal and vertical bars denote one standard deviation about the mean. The triangles and error bars are averages and standard deviations from the model of *McKeen et al.* [1991], as described in the text.

The reaction of NO_3 with CH_3CHO. has been proposed as a nighttime source of PAN [*Cantrell et al.*, 1986] through the reaction

$$\text{(R14)}\ CH_3CHO + NO_3 \rightarrow HNO_3 + CH_3C(O)^{\cdot}$$

followed by reaction with O_2 and NO_2. The rate of formation of peroxyacetyl radicals from reaction (R14) is estimated from the rate constant (2.1 x10^{-15} cm^3 $molecules^{-1}s^{-1}$) and average NO_3 (50 pptv) [*Noxon et al.*, 1980; *Platt et al.*, 1980; 1984] and CH_3CHO (1.6 ppbv) concentrations to be less than 10% of the daytime formation rate given by equation (1) and the observed slope. Therefore it appears that reaction (R14) is only a very minor contributor to PAN formation under these conditions.

The comparison of model results with the measurements reported here is problematic, due to the difficulty in simulating transport, especially within the surface layer. One way to minimize problems with transport is to limit the comparison to the afternoon hours, in which the mixing of the boundary layer is the most rapid. Under these conditions, surface measurements come the closest to representing the average concentrations of the mixed layer. *Hough* [1988] reports the comparison of chemical models that have been used for the simulation of regional atmospheric chemistry, using the same initial conditions. The average and standard deviations of afternoon PAN and O_3 concentrations are plotted in Figure 5 for the nine most modern models examined. Also plotted are the results of a regional photochemical model developed by *McKeen et al.* [1991]. The points shown were calculated from the modeled concentrations on June 27, 1990, at 1500 for the lowest layer of the model. The model domain extended from roughly 30°N to 51°N latitude and 69°W to 102°W longitude. Often the models with the most complex transport simulations require that short-cuts be taken in simulating the chemistry. One common tactic, used by the majority of the nine models examined by *Hough* [1988], is to lump all of the PAN-type compounds together with PAN as one species. *Atherton and Penner* [1988] have shown that this can lead to the overprediction of PAN by as much as 25%. It can be seen from Figure 5 that the models overpredict PAN somewhat compared to the measurement results, and that there is a very large spread in PAN concentrations predicted. The results of the McKeen et al. model appear to be in reasonable agreement with the measurements at low to middle ozone concentrations, but the model trends to higher PAN at the highest ozone concentrations. The chemical mechanism of McKeen et al. was essentially that developed by *Lurman et al.* [1986], which is one recognized to slightly overestimate PAN. However, the McKeen et al. model uses a more sophisticated and realistic treatment of PAN and O_3 deposition than that of *Hough* [1988]. *Trainer et al.* [1991] modeled the reactive nitrogen chemistry at a rural site (Scotia, Pennsylvania, 1986) and found that isoprene photooxidation produces a significant amount of PAN, a result that supports the analysis derived above from equation (1). *Hough* [1988] has concluded, based, in part, on the agreement of these models on PAN concentrations, that many models do not simulate some product species (PANs, H_2O_2) better than a factor of 2.

Simultaneous measurements of PAN and O_3 have been reported for other sites, often close to urban areas. A summary of such measurements can be found in the work of *Altshuller* [1983], and there have been numerous reports since that time

Table 1. Rate Constants and Conditions Consistent With the O_3-PAN Correlation

Parameter	Value	Units	Reference
k_5	1.1 x10^{-11}	cm^3 $molecule^{-1}s^{-1}$	a
k_{-5}	3.7 x10^{-4}	s^{-1}	a
k_9	1.8 x10^{-14}	cm^3 $molecule^{-1}s^{-1}$	a
k_{10}	2.4 x 10^{-12}	cm^3 $molecule^{-1}s^{-1}$	a
k_{13}	1.4 x10^{-11}	cm^3 $molecule^{-1}s^{-1}$	a
j_3	7 x10^{-3}	s^{-1}	average at 15:00
[OH]	2 x10^6	molecule cm^{-3}	average at 15:00
T	298	°K	average summer day
[CH_3CHO]	1.6	ppbv	calculated from slope

a, DeMore et al. [1992]

[*Hanst et al.*, 1982; *Grosjean*, 1983; *Peake and Sandhu*, 1983; *Anlauf et al.*, 1985; *Singh et al.*, 1985; *Corkum et al.*, 1986; *Perros et al.*, 1988; *Tsani-Bazaca et al.*, 1988; *Ridley et al.*, 1990; *Wunderli and Gehrig*, 1991]. The correlation between PAN and O_3 has been explicitly examined in only a few of these data sets. Measurements at Niwot Ridge, [*Singh et al.*, 1985; *Ridley et al.*, 1990] and Boulder, Colorado [*Ridley et al.*, 1990], have shown PAN and O_3 to be correlated. The data reported by *Singh et al.* [1985] were only divided between Summer and Fall measurements, not between night and day, so that the resulting slope of the correlation is not comparable to that observed in this work. The measurements reported by *Ridley et al.* [1990] were divided into midmorning to afternoon periods 1000-1700. The slope of the PAN/O_3 correlation at Niwot Ridge, under high anthropogenic impact, was 0.048, and that for Boulder was 0.038. There are also reports of individual measurements of PAN and O_3 made under highly polluted conditions in the Los Angeles air basin [*Hanst et al.*, 1982; *Grosjean*, 1983]. These measurements are plotted in Figure 6 together with the averages and least squares fit of the data from this study. The PAN and O_3 concentrations found in highly polluted air lay above the correlation line from this work, in other words, the production of PAN was more efficient relative to that of ozone in more highly polluted urban air masses. This follows from the dependence of the efficiency of O_3 formation on the concentration of NO_x, which has been the subject of recent modeling studies [*Lin et al.*, 1988] and is discussed by *Trainer et al.*, [1993] in reference to the results from these measurements. These studies have examined O_3 production relative to NO_x conversion to products and found that O_3 production is relatively inefficient at high NO_x and non-methane hydrocarbons (NMHC) and becomes more efficient (for the same NMHC/NO_x) as the absolute concentration of NO_x decreases. Some of the reasons cited for this are that in highly polluted air the reaction of OH with NO_2 (and to some extent reactive hydrocarbons) and the reaction that forms PAN (R5), serve to remove radicals ($HO_2\cdot$, $RO_2\cdot$). This feature of the O_3- PAN chemistry is not reflected in the simple analysis represented by equation (1), nor the data set as a whole, however the PAN-O_3 correlations from some of the sites, Bondville in particular, show an increase in slope with increasing O_3. The correlations of O_3 with NO_y and NO_y-NO_x for these sites [*Trainer et al.*, 1993] clearly show this nonlinear dependence of O_3 production on NO_x.

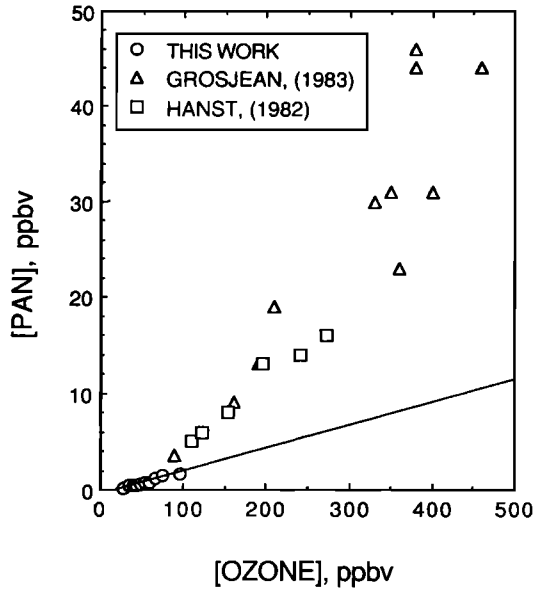

Figure 6. The measurements of PAN and O_3 reported by *Hanst et al.* [1982] and Grosjean [1983] in the Los Angeles basin and the points and correlation line resulting from the measurements reported here.

The gross features of the day/night variation in PAN and O_3 concentrations at theses sites can be explained in terms of the formation and breakup of the shallow nocturnal boundary layer. The degree to which PAN and O_3 were modulated day/night by this effect was dependent on the topography of each site. The two that show the largest contrast in this respect are the Scotia, Pennsylvania, site which is located in a shallow valley within a heavily forested area and the Whitetop Mountain, Virginia, site which is located on top of a 1680 m (5500 ft) high mountain. The degree to which PAN and O_3 differ in this day/night modulation is dependent on the relative rates of removal of these species within the nocturnal boundary layer. Two modes of removal occur for these species under these conditions, deposition at the surface and reaction with NO (following reaction (R-5) for PAN). Nitric oxide is not usually present at night because of reaction (R9), however at several sites, there were small amounts of NO present probably from soil emissions and occasionally substantial concentrations of NO present from power plant sources. Under stagnant conditions where little or no NO was present, deposition to the surface may be the dominant removal process for both O_3 and PAN. From the data presented here for these sites, it was apparent that O_3 was more rapidly deposited than PAN, in agreement with experimentally derived deposition velocities [*Hill*, 1971; *Garland and Penkett*, 1976]. Recent results at three sites in Canada, Dorset, and Egbert, Ontario, and Kejimkujik, Nova Scotia, [*Shepson et al.*, 1992], showed faster deposition of PAN relative to ozone during certain periods.

Conclusions

The measurements of PAN and O_3 at four sites in this study show the two species to be products of the photochemistry occurring throughout eastern North America. The diurnal profiles of both species indicate that daytime photochemical production and surface destruction are important features of their chemistry. Sites that have flat terrain or are in valleys exhibit distinct diurnal profiles in which surface deposition is obvious. Although quantitative determination of deposition velocities is not possible, the deposition of O_3 appears to be faster than that of PAN. Given the importance of surface deposition of PAN at these sites, more accurate measurements are needed of PAN deposition velocities on a variety of surfaces. The effect of surface cooling appeared to be intensified at the Scotia site, which is located in a shallow valley. Cooling of a sloped surface produces convective down slope flow, so that the air reaching the bottom of the slope has been transported within the surface layer. In accord with this the sole mountain top site at which both species were measured showed altogether different profiles. In this case, O_3 was higher at nighttime as a result of this convective downslope flow, which served to transport air from higher up in the mixed layer down to the site.

The coproduction of PAN and O_3 during the afternoon period was found to result in an overall linear relationship between

the two. A comparison of the slope obtained from the data with that predicted by a simple photochemical relationship indicated that many processes beside the reaction OH + CH_3CHO produced the peroxyacetyl radical. Other measurements of PAN and O_3 in moderately polluted air masses had slopes that implied more efficient production of O_3 relative to PAN and measurements in highly polluted air masses have indicated less efficient production of O_3. These observations underscore the generally held precepts that O_3 production is nonlinearly dependent on NMHC/NO_x and the absolute concentration of NO_x. Comparison of the results of these measurements with commonly used photochemical models showed that models consistently overpredict PAN concentrations. The results from this experimental period, which was unusually hot and stagnant, should be compared to future studies made under different conditions in different locations.

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