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PAN, PPN and MPAN Measurements and the Quantitative Relationship of PAN and MPAN in Biogenic Hydrocarbon Conditions

by

Chen Wangchun

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
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To
the love of Qi
and
Lizhen Chen, Ruxiang Fan

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Chen Wangchun

PAN, PPN and MPAN Measurements and the Quantitative Relationship of PAN and MPAN in Biogenic Hydrocarbon Conditions

Chen Wangchun, M.A.

Western Michigan University, 2001

Simultaneous measurements of PAN, PPN and MPAN were made during the SOS 1999 Nashville campaign at Dickson site. The PANs data at this site were rich and complex. PAN and MPAN showed obvious diurnal change but PPN did not during this period. PAN and ozone have a clear positive relationship. Due to the special location of the site, winds from different directions bring anthropogenic hydrocarbons (AHCs) or biogenic hydrocarbons (BHCs) to the site. The data showed that the influence of AHCs and BHCs on PANs compounds varied on different days. Average values of PAN/PPN and PAN/MPAN from MLR may be interpretable regionally to use to calculate the contribution of AHC and BHC on the formation of ozone. But care must be taken to consider the contribution on individual days because of the variance in the ratio of PAN/PPN in AHC condition. The ratio of PAN/MPAN in BHC condition is more complicated. The ratio may be influenced by NO_x and OH• level. No characteristic ratio is applicable in different complicated BHC conditions.

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CHAPTER I

INTRODUCTION

Problem of “Photochemical Smog”

Background

Air pollution is a serious environmental problem. Among air pollutants, there is a group called “photochemical smog” that is very important and greatly influences our global environment. Photochemical smog refers to particular mixtures of reactants and products that exist in the ambient air when hydrocarbons and oxides of nitrogen ($NO_x=NO_2+NO$) react in the presence of sunlight (Seinfeld, 1986). Photochemical smog first occurred with industrial development and increased dramatically with the appearance of the automobile. From these sources, many kinds of hydrocarbons (HCs), carbon monoxide (CO), sulfur dioxide (SO_2) and NO_x are emitted to the atmosphere. Among them, HCs and NO_x are primarily responsible for photochemical smog (Seinfeld, 1986).

Nitric oxide is emitted by both natural and anthropogenic sources. The burning of fuels at high temperatures is the primary anthropogenic source of NO, chiefly from power plants and cars in urban areas (Ryerson et al., 1998). Nitrogen dioxide (NO_2) is emitted along with NO and is also formed by the oxidation of NO in the atmosphere (Seinfeld, 1986). These reactions are as followed:

$$N_2 + O_2 \xrightarrow{\Delta} 2NO \qquad (1)$$

$$NO + O_2 \longrightarrow NO_2 \qquad (2)$$

NO_x is the catalyst for fomation of photochemical smog. The main source of hydrocarbons (HCs) is mainly from fuel combustion and industrial solvents (Finlayson-Pitts and Pitts, 2000). NO_x and HCs are very active in the atmosphere. In general, their lifetimes are relatively short (Frost et al., 1998). They can react rapidly to form secondary pollutants, such as ozone (O_3) and organic nitrates. Ozone is the most important secondary pollutant in ambient air (Seinfeld, 1986). Typical ground-level concentrations are around 20-200 parts per billion by volume (ppbv).

Formation of Ozone

In air free of HCs, ozone is produced photochemically from NO_x. The ozone production reactions is are followed:

$$NO_2 + hv \xrightarrow{k_1} NO + O\cdot \qquad (3)$$

$$O\cdot + O_2 \xrightarrow{k_2} O_3 \qquad (4)$$

$$NO + O_3 \xrightarrow{k_3} NO_2 + O_2 \qquad (5)$$

These three equations represent a rapid photochemical cycle. From them we can derive an expression for the concentration of ozone, $[O_3]=K[NO_2]/[NO]$, where K is equal to k1/k3 (Seinfeld, 1992). But in more polluted air (with HCs), additional ozone can be produced from reactions of hydrocarbons (HCs).

$$RH + OH\bullet \longrightarrow R\bullet + H_2O \qquad (6)$$

$$R\bullet + O_2 \longrightarrow RO_2\bullet \qquad (7)$$

$$RO_2\bullet + NO \longrightarrow RO\bullet + NO_2 \qquad (8)$$

Due to these reactions, the ratio of $[NO_2]/[NO]$ will be prone to increase, so the concentration of ozone will increase also (Ryerson et al., 1998).

The Influence of Ozone on the Environment

The atmospheric regions are separated into five major layers by temperature and pressure variations with altitude. The two layers closest to the earth are called the troposphere (~10-15 km altitude) and the stratosphere (~45-50 km altitude). Ozone exists in both layers. Stratospheric ozone is necessary for life on earth because it can prevent UV radiation from harming humans, animals and plants (Finlayson-Pitts and Pitts, 2000). But tropospheric ozone is a greenhouse gas (Finlayson-Pitts and Pitts, 2000). It can absorb infrared radiation, then convert this energy to heat by collisional deactivation. At last it emits infrared radiation back to the earth, but this occurs at low temperatures and high altitudes. That means the energy input to the troposphere is larger than the energy output from the troposphere. As a result, the total energy in the troposphere is increased, causing the global climate to become warmer. Also high concentrations of tropospheric ozone are detrimental to animal health and also can reduce the yield of crops and forests (Roberts et al., 1998). Several recent studies have shown that the level of global tropospheric ozone have been increasing over the course of the last 100 years (Marenco et al., 1994). So the increase of tropospheric ozone has become a global environmental problem.

In order to address the increase of tropospheric ozone, control strategies should focus on reducing the source of ozone, either NO_x or hydrocarbons. Tropospheric HCs are a mixture of anthropogenic (AHCs), and biogenic (BHCs). AHCs and BHCs in the air vary dramatically from place to place. That means in one place, AHC are the main source of ozone, but in another place, they may not be a main source. So it is important to know the contribution of AHC and BHC to the formation of ozone. Historically, ozone pollution was thought to mainly occur in urban areas (Kasibhatla et al., 1998). However, recently, the influence of BHCs on the formation of ozone has attracted more and more attention (Roberts et al., 1998). In some places, like the southeastern United States, large amounts of BHCs are released from vegetation in the area. In this region concentrations of ozone get very high in the summer. The reasonable explanation for this is that BHCs can accelerate the formation of ozone just like AHCs do. The ozone control strategies that try to reduce the AHCs will become inefficient in this area (Trainer,et al., 1987). In the recent years, BHCs have received significant attention due to their role in the formation of ozone. The main BHC is isoprene which consitutes about 80% of the hydrocarbons emitted from deciduous trees (Grosjean, et al., 1993). The isoprene reaction mechanism is complicated.

The Southern Oxidants Study

In order to expand our understanding of the formation, accumulation, fate and effects of ozone and other oxidants in the southeastern U.S., a scientific organization called The Southern Oxidants Study (SOS) was created. It consists of a group of researchers from universities, industries and governments from all over the country. The main focus of SOS is the reduction of ozone concentration. At present, we know that HCs and NO_x are the precursors of ozone. But what we do not know is which control strategy is more efficient at either reducing the NO_x emission or reducing the HCs emission in a special region. We need to know the importance of influence BHCs have on the formation of ozone. The answers to these questions will add the federal government in developing effective control strategies for the reduction of ozone (SOS policy).

PANs Chemistry

The Formation of PANs

In the course of the chemistry between HCs andf NO_x, a variety of secondary organic products are formed. Peroxyacyl nitrates (PANs) are secondary products of photochemical reactions that incorporate the nitrogen from NO_x into a relatively stable organic compound. The formation of PANs are shown below:

$$RH + OH\bullet \longrightarrow R\bullet + H_2O \tag{9}$$

$$R\bullet + O_2 \longrightarrow RO_2\bullet \tag{10}$$

$$RO_2\bullet + NO \longrightarrow RO\bullet + NO_2 \tag{11}$$

$$RO\bullet + O_2 \longrightarrow RC(O)H + HO_2\bullet \tag{12}$$

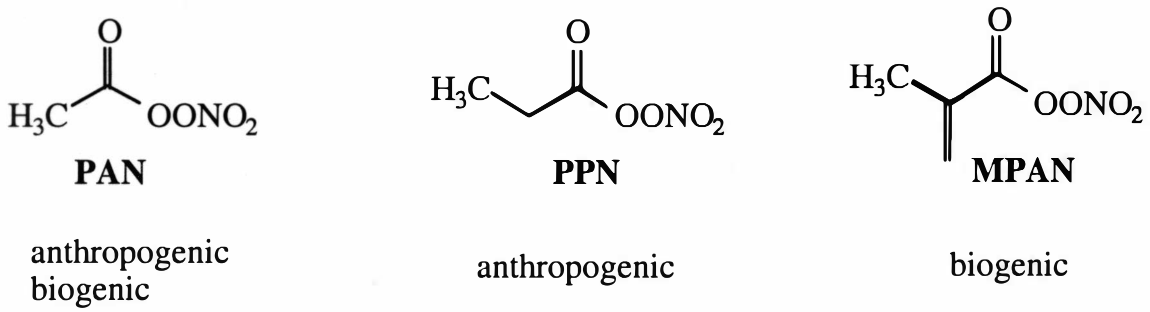
$$RC(O)H + OH\bullet \longrightarrow RC(O)\bullet + H_2O \tag{13}$$

$$RC(O)\bullet + O_2 \longrightarrow RC(O)OO\bullet \tag{14}$$

$$RC(O)OO\bullet + NO \longrightarrow RC(O)O\bullet + NO_2 \tag{15}$$

$$RC(O)OO\bullet + NO_2 \rightleftharpoons PANs \tag{16}$$

The most abundant and simplest of the PANs is peroxyacetyl nitrate (PAN). It was discovered in the 1950s by Stephens (Stephens et al.,1956). Since that time, it has attracted more and more attention among atmospheric scientists. Other important PANs include peroxypropionyl nitrate (PPN) and peroxymethacryloyl nitrate (MPAN). Other PANs, due to their low concentrations in the ambient air, were not considered in this study. The figures below show the chemical structures of PAN, PPN and MPAN and their type of precursor sources.



PAN

anthropogenic
biogenic

PPN

anthropogenic

MPAN

biogenic

Figure 1. The Chemical Structures of PAN, PPN and MPAN.

The Importance of PANs

Because PANs are secondary photochemical products of hydrocarbons and NO_x, they can be used as indicators of photochemical activity in ambient air (Roberts et al., 1998). They constitute a large percentage of the total atmospheric nitrogen budget. PANs have a relatively long lifetime at normal ambient temperatures, but they decompose readily at elevated temperatures. Transport of these compounds to areas downwind followed by thermal dissociation, their main loss process, provides a means by which radicals and NO_x can be delivered to regions that might not otherwise have such sources. Therefore, as a reservoir of NO_2, PANs play a crucial role in the formation and distribution of tropospheric ozone (Altshuller, 1993). PAN is important because of its relationship with ozone since they have similar formation pathways. When we try to probe the formation, accumulation and transportation of ozone, PAN should be considered. Experiments have shown that PAN and ozone often arrive at their highest concentrations at the same time (Altshuller, 1993). Finally, PANs are important in the ambient air also because they are phytotoxicants and eye irritants. Also they have possible mutagenic effects (Grosjean, et al, 1996; Shepson, et al, 1986).

The Precursors of PANs

The precursors of PAN can be either AHCs or BHCs. AHCs include alkanes, alkenes and aldehydes (for example, ethane, propene, 2-butene, etc.). These AHCs can react with OH• to form acetaldehyde, which is a direct precursor of PAN. The most important BHC in the ambient air is isoprene. Isoprene can react with OH• in the presence of NO_x and PAN is one of several products. AHCs such as propane, 1-butene, n-pentane, 2-pentene, n-hexane are the main precursors of PPN. After a series of photochemical oxidation reactions, proponal can be formed which is the direct precursor of PPN. Recently scientists have discovered that there exists some BHC precursors of PPN, like cis-Hexen-1-ol. (Grosjean et al., 1993; George, 1997) But these biogenic sources of PPN are not significant compared to the concentration of PPN in the air due to their relatively small amounts (Robert, et al., 1998).

MPAN's precursors are mainly from biogenic sources. Isoprene is the most important BHCs that contributes to the formation of MPAN. In the southeastern part of the U.S., scientists have found that the BHCs, chiefly isoprene, dominate the daytime photochemical reactions in rural areas (Williams et al., 1997). As the photochemical product of isoprene (see Figure 2), MPAN is an important indicator of biogenic photochemical activity and therefore can supply the direct evidence of the formation of ozone from biogenic sources. MPAN's direct precursor, methacrolein

(MACR) can be found in the vehicular exhaust emissions, but the amount is insignificant (Shepson et al., 1992). In summary, as shown in Figure 1, PAN's precursors are both AHCs and BHCs, PPN's precursors are mainly from AHCs and MPAN's precursors are mainly from BHCs.

To date there is no good approach to calculate or estimate the contribution of AHC and BHC to the formation of ozone. Due to the relationship between ozone and PANs, PANs have been used as an indicator of photochemical activity. So the question of how to get the contribution of AHC and BHC to the formation of ozone, although we can not solve it directly, but we can calculate the contribution of AHC and BHC to the formation of PAN. In AHC dominated condition, both PAN and PPN can be produced. They have positive relationship which can be expressed as PAN= bPPN+ c. In BHC dominated condition, both PAN and MPAN can be formed. They have positive relationship which can be expressed as PAN=aMPAN+c. Since in real ambient air, both AHC and BHC exist, the two chemical processes may assumed to be independent to each other. Overall PAN can be described as a linear combination of MPAN and PPN which is PAN=aMPAN+bPPN+c. This approach is called multivariate linear regression analysis (MLR). The original idea of using the equation is given by Williams [Williams, et al., 1997, Roberts, et al., 1998]. Investigation of the ratio of PAN/MPAN in BHC dominated conditions provides an opportunity to understand the isoprene photochemical reaction mechanism.

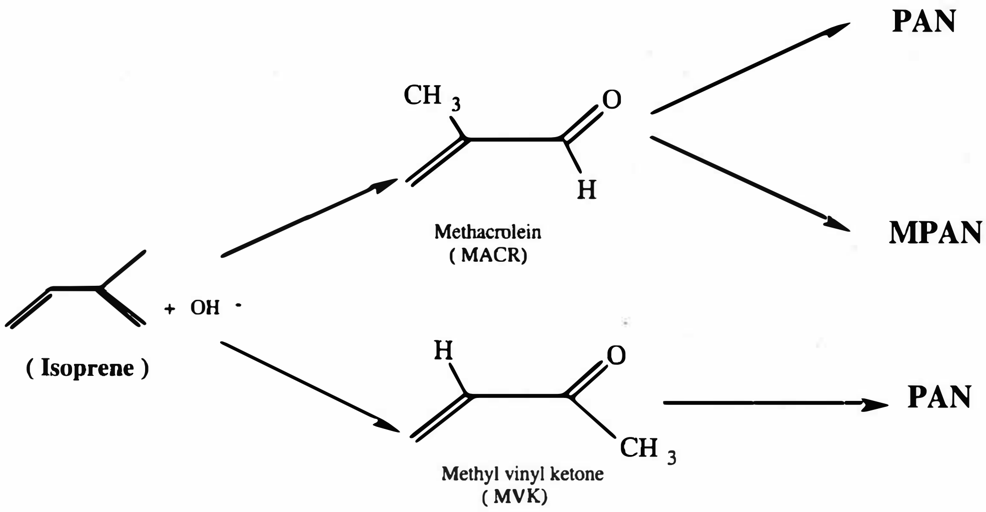


Figure 2. Simplified Isoprene Reaction Product Distribution.

My research objectives focus on two things. First, to try to use our ambient air measurement data to justify the MLR equation that is used to calculate to relative contribution of AHC and BHC to the formation of PAN and ozone. Second, to try to acquire the quantitative relationship between PAN and MPAN under BHC/NO_x photochemistry.

CHAPTER II

EXPERIMENTAL

Field Measurement Experiment

In the summer of 1999, SOS organized its third comprehensive field study in Nashville/Middle Tennessee. Our group from Western Michigan University (WMU) took part in this field campaign and were responsible for the measurement of peroxyacyl nitrates (PANs) and alkyl nitrates.

Measurement Site

The measurement site is located in Dickson, 30 miles west of downtown Nashville (see Figure 3). It was surrounded by dense grass and trees. This is a typical rural environment. There are three power plants around the Dickson area, among them, Cumberland power plant is the largest one, and it is the main source of NO_x in this area. The Urban center of Nashville is the main sources of AHC. The dense deciduous trees can emit BHC, mainly isoprene. There are also three interstate highways that pass through downtown Nashville which are the sources of NO_x and AHC.

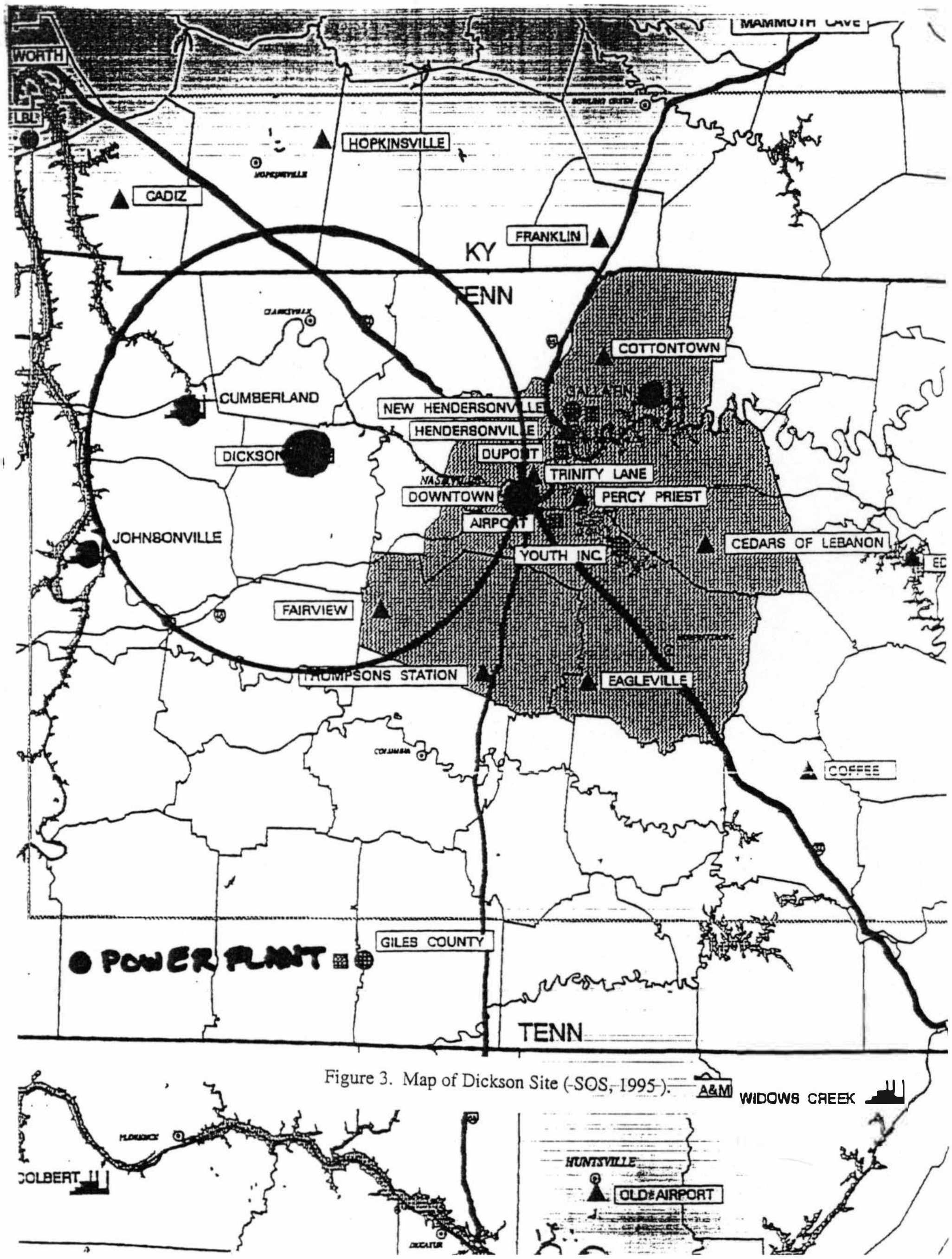


Figure 3. Map of Dickson Site (SOS, 1995).

Measurement Instrument of Peroxyacyl Nitrates (PANs)

The PANs and alkyl nitrates instruments were set up in a small trailer. Figure 4 shows the PANs measurement system. Air samples were drawn continuously from the inlet on the tower through 15m Teflon tubing. The sample inlet was positioned about 10m above the ground. The residence time of samples in the inlet was about 19 seconds. The PANs measurement system is showed on Figure 4.

PANs were measured using a GC with a Shimadzu Mini-2 electron capture detector (ECD). The GC column (J&W Scientific, DB-210, ID equal to 0.53mm), was wrapped around an aluminum block which was cooled using thermoelectrics and set at 15°C to minimize the thermal decomposition of PANs (Nouaime et al., 1997). Helium gas was used as the carrier and N_2 was used as the make-up gas with flow rates of 15 cm^3/min and 5 cm^3/min, respectively. An ambient air sample of 3 cm^3 was injected automatically every 20 minutes by a timer-activated Hamilton Teflon six-port rotary valve. The sample loop was made of 1/8 inch PFA Teflon. A pump was used to pump ambient air from the sample inlet through the whole measurement system at a rate of nearly 1.0-1.5 L/min. The sample loop flow rate was 50 mL/min. All flow rates were controlled by mass flow controllers (MFCs). The ECD temperature was kept constant at 55°C. The detection limit for PAN, PPN and MPAN are 6pptv, 5pptv and 7pptv respectively.

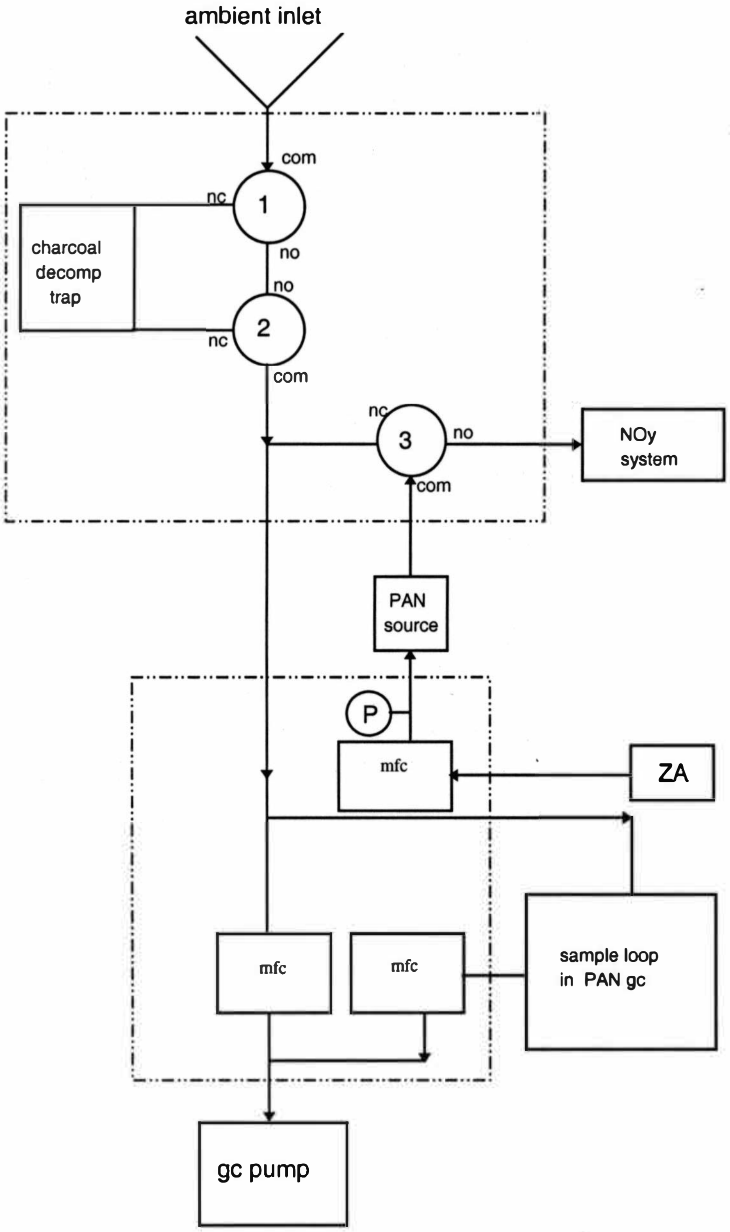


Figure 4. PANs Measurement System.

Calibration of PAN, PPN and MPAN was done prior to and during the measurement period. The PAN, PPN and MPAN standards were synthesized in the laboratory in dodecane solution. PAN is synthesized by reaction of peroxyacetic acid with nitric acid (Gafney et al., 1984). PPN and MPAN are synthesized by two steps: first the oxidation of appropriate anhydrides to the peroxycarboxylic acid, then followed by nitration of peroxycarboxylic acid by nitric acid to get PPN and MPAN. The synthesis of MPAN is more complicated since it contains a double bond, so it is easy to form a polymer during the reaction. Also it can contain PAN. The synthesis of MPAN has been described in detail previously (Bertman, 1991, Nouaime, 1997). The vials that hold standards were kept in dry ice to prevent standards from decomposing. During the calibration process, standards were put into a diffusion cell to give a continuous and stable gaseous flow of standards. Zero air was to introduce the standard into the GC-ECD measurement system. The PANs in the ambient air were removed by the adsorption on charcoal. Therefore the GC signal represents only the concentration of the standard sample. The standard sample flow will mix with the main inlet flow. By changing the flow rate of the main inlet, the standard concentration can be changed. Different GC signal strength (peak area) is observed with the change of concentration of standard.

The absolute mixing ratio was quantified using a chemiluminescence NO_x analyzer (Thermo Environmental Instruments, Inc.). Peroxyacyl nitrates can be heat decomposed to NO_2 at 325°C, then converted to NO on a molybdenum catalyst. The concentrations of PANs standards can be determined from the corresponding NO concentrations which can be calculated by comparing the relative signal strength to those from NO standard. A typical chromatogram of PAN-PPN-MPAN air sample is showed on Figure 5. There is a large, broad peak whose retention time is from 11th to 15th minute. It could be some sort of ozone reaction products on the column. In some clean days when ozone level is low, the peak is gone.

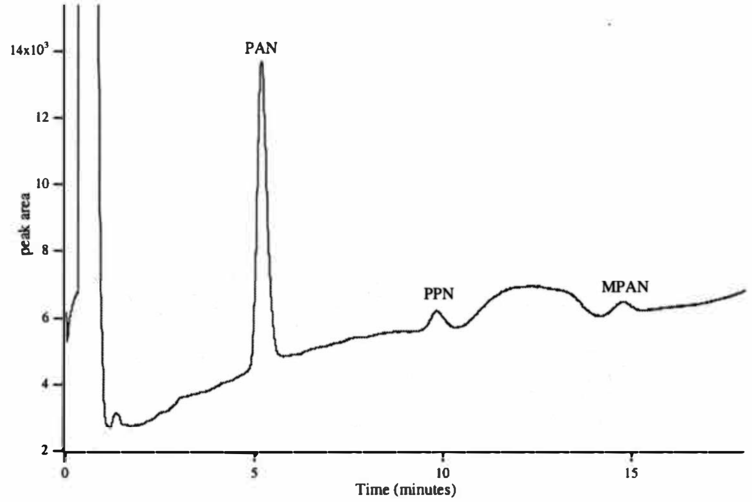


Figure 5. GC-ECD Chromatogram of a Typical PAN-PPN-MPAN Air Sample.

Data Analysis

Peak area integration for all ambient air chromatograms was done by hand using a custom program written in IGOR Pro software. The mixing ratios of PPN and MPAN were usually relatively small, so their peaks needed to be checked carefully by finding the precise position of the baseline. Mixing ratios were determined from a standard calibration. CDT (Central Daylight Time) was chosen for our time standard.

Experimental uncertainty is a combination of instrument precision and quantification error. Relative concentrations of the three compounds are proportional to their GC peak areas. Concentrations are determined by multiplying a quantification calibration factor by the area of each peak. The calibration error is calculated using propagation of errors from mass flow controllers, tank concentrations and baseline noise involved in quantification using the NOx Box. The error normally is about 2%. The error is equivalent for the three compounds, and the three compounds have similar calibration factor (similar sensitivity) for a given day. The conclusion is supported by the calibration we did in both lab and Dickson site. So their calibration factors are still statistically very close. Since the calibration factors for each of the three compounds measured on a given day are not statistically distinguishable, the uncertainty of a daily correlation of one compound with another is mainly due to the precision of integration. A typical calculation of precision is given in Appendix A. The results show that PAN had about 2% precision, PPN had 5% precision and MPAN had 7% precision.

As a result of the difficulty generating and delivering pure samples of authentic materials for calibration, the reproducibility of the calibration factor has relatively large error. This causes the large uncertainties of the concentrations of compounds when the data of the whole period were put together. There is no appropriate way to estimate the uncertainty of the whole period since we do not have enough calibration data.

Isoprene, MVK, MACR, propanal data were obtained from Purdue University and ozone, and the meteorological data were obtained from TVA.

WMU Chamber Experiment

In order to increase the understanding of the relationship between the formation of ozone, PAN, MPAN and isoprene, in summer of 1999, a chamber was constructed to simulate the photochemical reactions in biogenic conditions.

The original goal of creating a smog chamber was to identify an unknown that is produced from the reaction of isoprene and NO_x. Since from the chamber results we can know the ratio of PAN/MPAN, it provides an excellent opportunity to investigate the ratio of PAN/MPAN in an ideal biogenic-control (isoprene dominate) environment.

For a detailed description of the design and construction of smog chamber, see reference (Costales, 2000). A brief summary is followed. The chamber consisted of two parts: an outer chamber and an inner chamber. The outer chamber was used to house the 1000L inner chamber. It was big enough to leave room for repair and maintenance. Material used for constructing outer chamber was standard steel sheeting that was coated with a black Rustoleum® paint to prevent rust. The surface inside the outer chamber was covered with aluminum foil used to form reflective surfaces and isolated it from the outside light sources. Three banks of 4 ft fluorescent blacklight bulbs (two each bank) were mounted to the inside of outer chamber to supply the light sources needed. The inner chamber body was created with a 0.003-in. thick PTFE Teflon film. Teflon film was chosen because it is inert, minimizing the possibility of reaction between the surface of the inner chamber and the contents of the chamber. A frame made of steel was used to support the Teflon film since it is not rigid. A fan was mounted inside the chamber to mix the contents completely.

Purdue Chamber Experiment

Dr. Shepson's research group in Purdue University and our research group did another chamber experiment together. Similar chamber was used, but the chamber's volume is 6000 L instead of 1000 L. The experiment data were also analyzed in this study.

CHAPTER III

RESULTS AND DISCUSSIONS

General Measurement Results

Measurement Data Summary

Comparison Between Two Measurement Results

The Dickson study in 1999 followed a similar study at another site near Nashville in 1995 (Nouaime et al., 1997). PAN, PPN and MPAN were measured by the same method in both studies. Table 1 summarizes the measurement data from Dickson with the data acquired from the field campaign at Youth Inc. (Roberts et al., 1998; Nouaime et al., 1997). Statistically, there is no significant difference between the two data sets taken as a whole. But it can be seen that the mixing ratios of PAN, PPN, MPAN and Ozone are a little smaller in 1999 than they were in 1995. Naturally it is tempting to attribute the difference to the location of the measurement sites. However, the data for PAN, PPN and MPAN in Table 1 represent the average value of more than 1800 data points. These averages cannot reflect the value and change trend in individual days, which is important indeed. So the data summary here in two sets is not appropriate to give a direct comparison since it can cover up important information.

Table 1

Comparison of PAN, PPN, MPAN and Ozone Between 1995 and 1999 Nashville Campaigns on Different Sites

		Dickson, 1999 (June 15-July 14) (upwind)	Youth Inc. 1995 (June 29-July 26) (downwind)
PAN (pptv) *1894 points*	Maximum	1710	2140
	Minimum	46	35
	Median	307	400
	Mean	431	480
PPN (pptv) *1891 points*	Maximum	210	320
	Minimum	2.5	5
	Median	15.9	40
	Mean	32.9	50
MPAN (pptv) *1882 points*	Maximum	157.8	150
	Minimum	3.5	4
	Median	12.6	23
	Mean	20	30
Ozone(ppbv) *6301 points*	Maximum	98.9	136
	Minimum	6.1	<2
	Median	39.0	48
	Mean	43.3	49

Wind Direction Distribution at Dickson Site

A wind rose for 1999 is shown in Figure 6. A wind rose describes the local wind direction frequency around Dickson during the measurement period. Since the photochemical production of PAN, PPN and MPAN can only happen in the daytime, only daytime wind directions were considered. The length of black line in the figure tells the frequency of wind from a particular direction. Figure 6 shows that air came to the Dickson site are primarily from the south (>40%). The site was located northwest of downtown Nashville (>25 miles away from the urban center). The polluted air from the urban center can bring significant levels of anthropogenic VOCs and NO_x to the site, causing enhanced production of PAN, PPN and ozone. The statistical data in the table only shows the average mixing ratios of different compounds during the whole measurement period, much detail is lost regarding PAN, PPN, MPAN and ozone on individual days. It is necessary to make a more detailed analysis of the measurement data in order to draw conclusions.

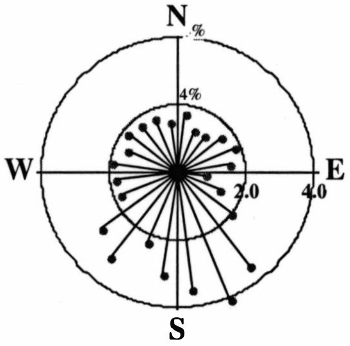


Figure 6. Wind Rose of Daytime (10:00-18:00) Ground-Based Measurements at Dickson.

The Mixing Ratios of PAN, PPN and MPAN

Figure 7 is a summary of the data recorded for the entire measurement period at Dickson in 1999. It shows that on most of the days the mixing ratio of PAN and MPAN experience a significant change over the course of individual days. PAN, PPN and MPAN are all formed photochemically and have similar chemistry. So at night, these compounds are produced slowly and they are lost rapidly to dry deposition. Their nighttime mixing ratios should be relatively low compared with the mixing ratios of them in daytime. At Dickson, the compounds typically achieve their maximum values at noon and drop down to their minimum value at night. However, PPN does not show the same pattern. Especially after June 25, the level of PPN does not change much over the course of a day. On some days, PPN is below detection limit. But before June, 25, the mixing ratio of PPN does show diurnal change, but the trend is not as obvious compared with PAN and MPAN due to its high mixing ratio even in the night.

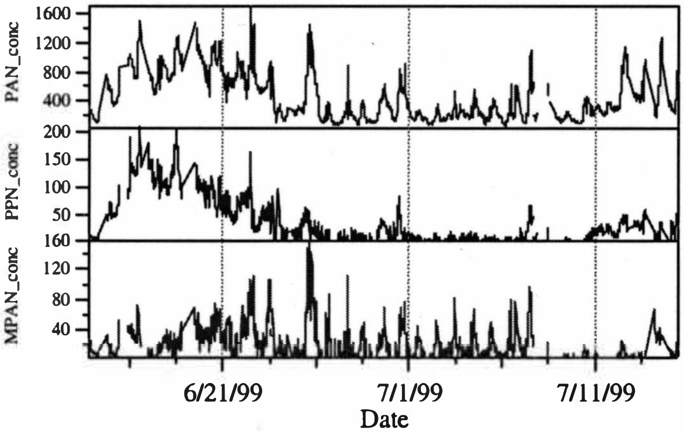


Figure 7. The Mixing Ratios of PAN, PPN and MPAN Versus Time During the Whole 5-Week Measurement Period.

Diurnal Change of PAN, PPN and MPAN

In order to see the diurnal change of PAN, PPN and MPAN more clearly, three average diurnal plots are shown in Figure 8-10. On these Figures, ‘Mean’ and ‘Median’ represent the mean and median value of the measurement data value in a special time. ‘Max’ is the maximum value of data in a special time. ‘67th ’and ‘90th percentile’ show the ranges that 67% and 90% data are located. From the change of mean value of the three compounds during a day, PAN, MPAN have a noticeable diurnal variation, but PPN seems unchanged. If the PPN data is separated into two sets, one is before June 25, the other is after June 25 (Figure 11-12). It can be seen that PPN does, in fact, have a diurnal trend before June 25. During that time period, PAN and PPN are produced actively from photochemical reactions. After June 25, both PAN and PPN mixing ratios are low, especially PPN. Again averaging over the whole periods caused loss of information. The dramatic difference in the behavior of PPN at different periods might be explained by the difference of the amount of precursors (VOCs) at different time.

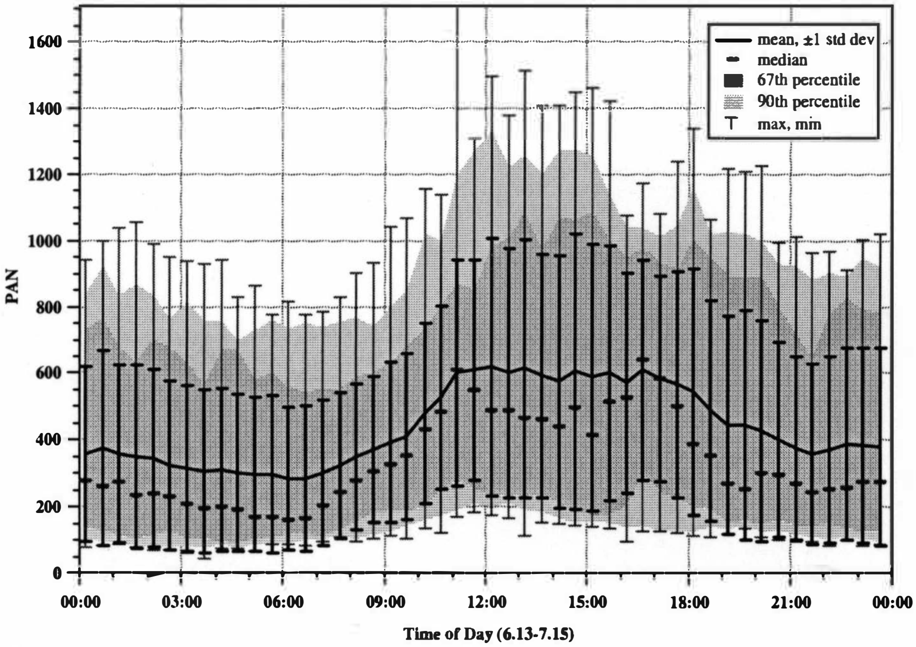


Figure 8. Diurnal Plots of PAN at Dickson from June 13 to July 15.

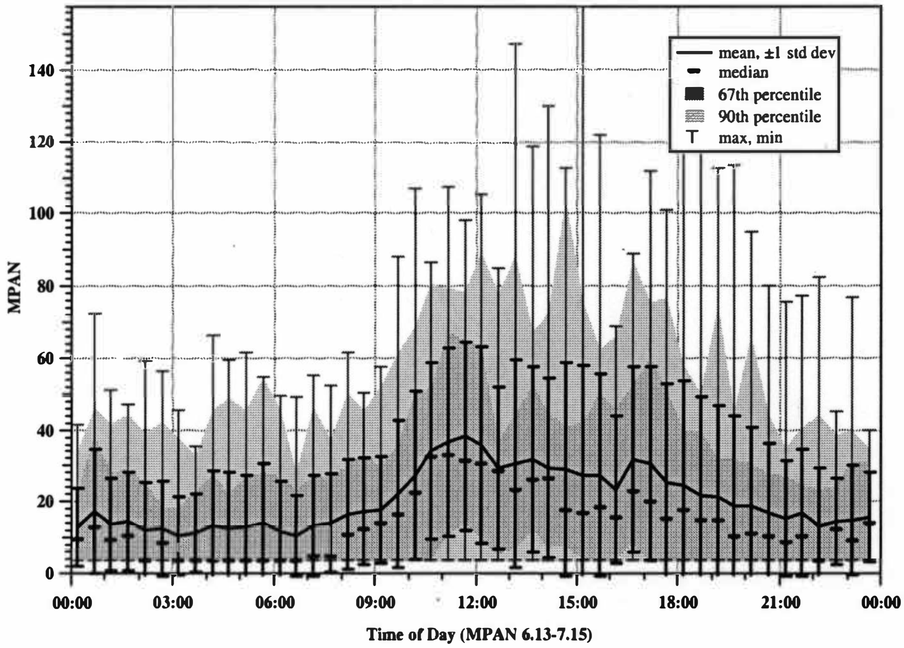


Figure 9. Diurnal Plots of MPAN at Dickson from June 13 to July 15.

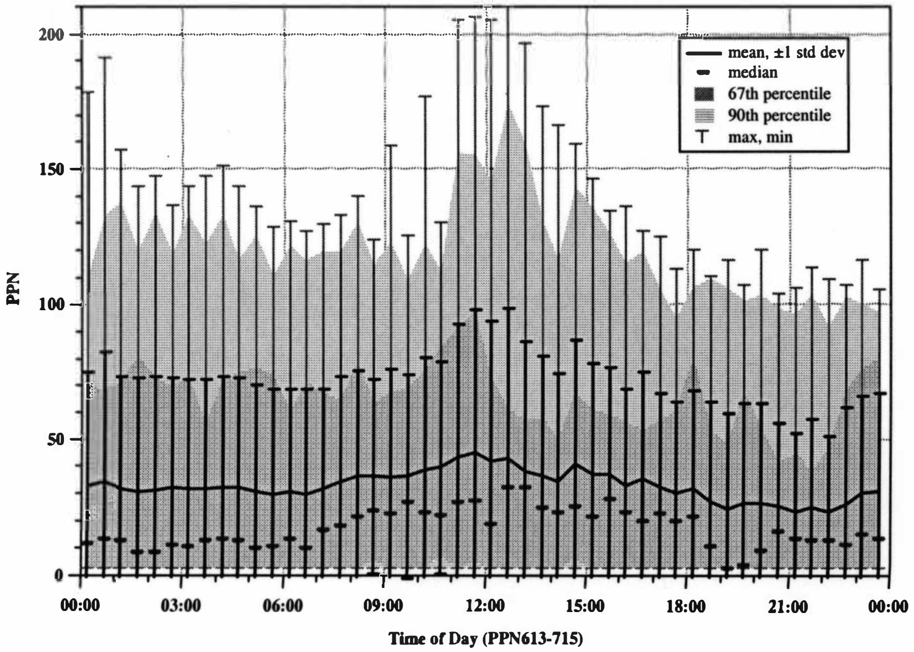


Figure 10. Diurnal Plots of PPN at Dickson from June 13 to July 15.

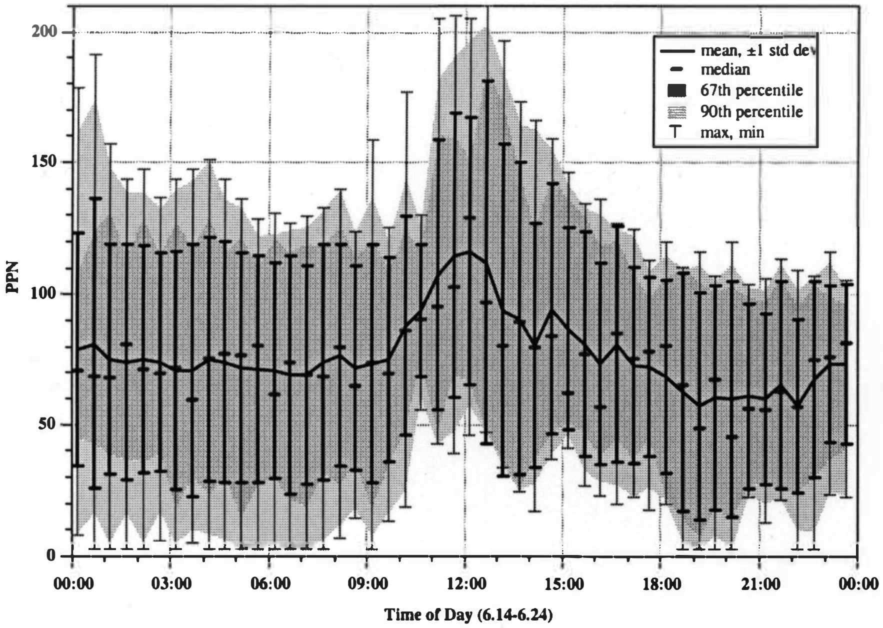


Figure 11. the Diurnal Plot of PPN from June 14 to June 24.

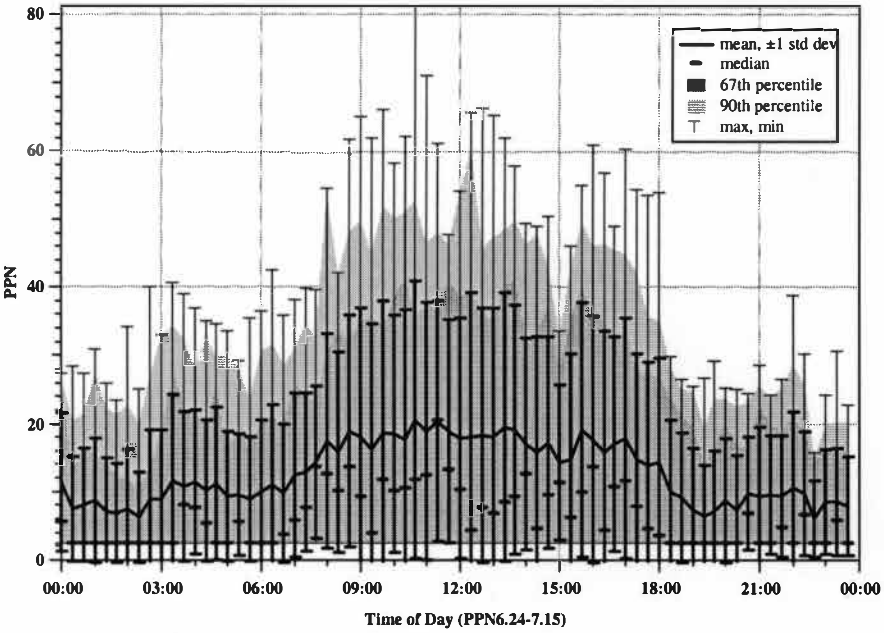


Figure 12. the Diurnal Plot of PPN From June 24 to July 15.

The Relationship Between Ozone and PAN.

Both ozone and PAN are secondary products of photochemical reactions involving NO_x and HCs. Figure 13 shows a positive relationship between ozone and PAN in the Dickson data. A linear regression analysis indicates they have good linear relationship (r^2=0.69). That means when PAN mixing ratio is large, large ozone ratio can be expected, so PAN can act as an indicator of ozone at this site.

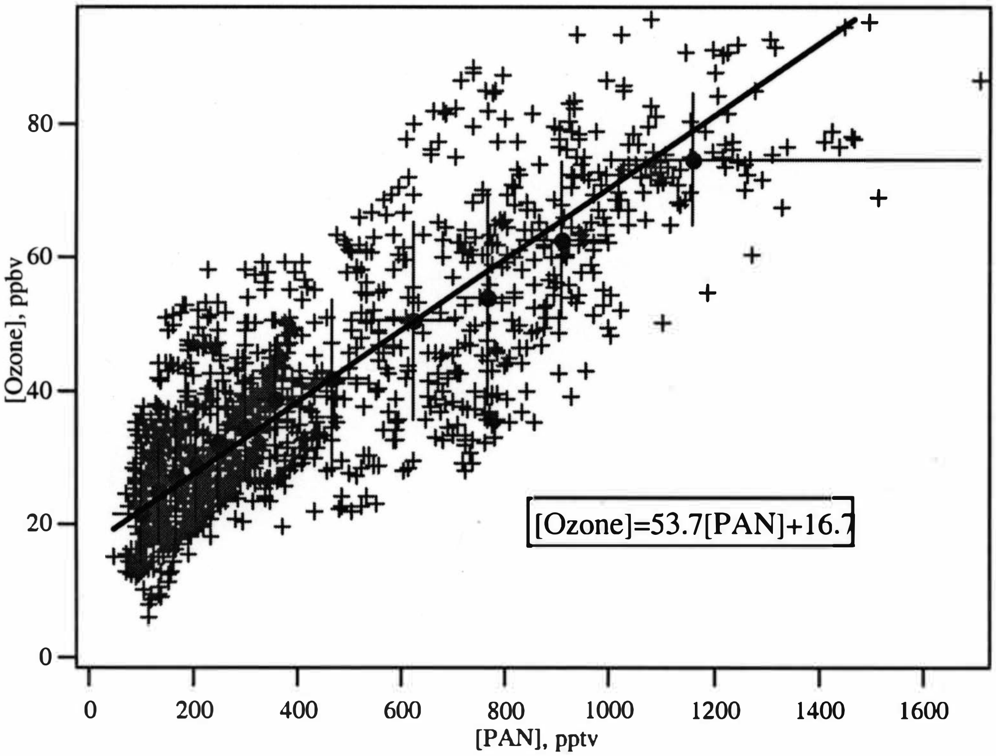


Figure 13. Ozone Versus PAN at Dickson (Ozone Data is Provided by TVA).

In Figure 13 it can be seen that the data points are scattered around the linear regression line. This suggests that the linear relationship between ozone and PAN need consider a range for the slope. That is, the slope is slightly different under different conditions. The formation of PAN and ozone are related to NO_2/NO and they share similar precursors, VOC and NO_x. But their loss processes are quite different. PAN is mainly removed by thermal decomposition. Ozone is mainly removed by photolysis and dry deposition processes. So their lifetimes are not on the same scale. Ozone typically has a much longer lifetime than PAN does in the boundary layer. That is the reason that cause the data of ozone versus PAN are scattered around the regression line.

The average slope between ozone and PAN can be used for comparison with other measurements. The slope of ozone versus PAN for Dickson shown in Figure 13 is 53.7. The average ratio of ozone/PAN was analyzed using the measurement data from 4 sites in eastern part of United States. The overall slope of ozone/PAN is 41.7. (Roberts et al., 1995). P. B. Shepson measured PAN and ozone in Ontario, where he selected three sites that represent urban, suburban and rural environment. And he compared the slope of ozone/PAN and got 24.3 (urban), 37.8 (suburban) and 70.6 (rural) respectively (Shepson et al., 1992). K. A. Kourtidis did similar measurement of PAN and ozone in Germany, the slope of ozone/PAN is between 37-51 (Kourtidis et al., 1993). By comparing the ratio of ozone-PAN at Dickson site with the slope of ozone-PAN from other measurements, it is reasonable to correlate the ozone and PAN with linear relationship.

The Mixing Ratio of PPN and MPAN Versus Wind Direction.

As mentioned in the introduction, PPN is mainly formed from AHC and MPAN is mainly formed from BHC. The Dickson measurement site supplied an ideal place to investigate the relationship between compounds and wind direction. From the local wind rose plot, we can see that air came to the site primarily from the south, but occasionally from the east. This is corroborated by back trajectory analysis. Since the main AHC sources are located to the east of the site, if the wind is from east, it will bring more AHCs, the precursors of PPN, to the site. On the other hand, when the wind is from southwest and south, the air will be relatively clean. It will contain less or even no precursors of PPN and more MPAN can be formed in this case.

From Figure 14, When the wind is from other directions except from the east, higher MPAN is seen. From Figure 15, it shows that when the wind is from east, higher concentration of PPN can be seen. So PPN and MPAN can act as the indicators of AHC chemistry and BHC chemistry respectively. The mixing ratios of PAN do not change as much according to wind direction. The mixing ratio of NO_x is highest when wind is from west and northwest, it suggests the strong influence of the Cumberland power plant, the main source of NO_x in the area.

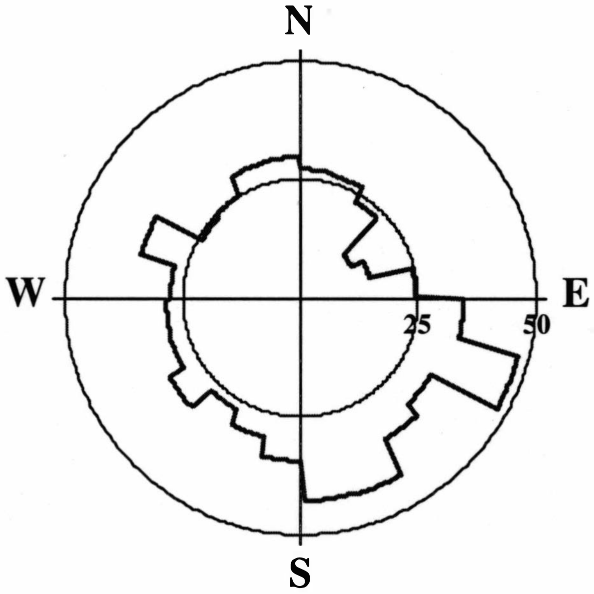


Figure 14. MPAN Versus Wind Direction (Daytime 10:00-18:00).

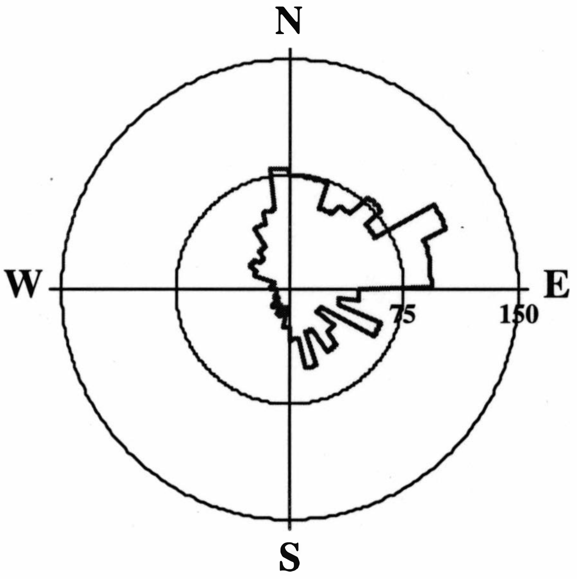


Figure 15. PPN Versus Wind Direction (Daytime 10:00-18:00).

Special Days, 6.18 and 6.25

It is safe to say that the wind direction influences the mixing ratios of PPN and MPAN if wind can bring different HCs from different direction. In some individual days, the wind direction is very constant and stable. Since different wind can bring different chemicals (AHC or BHC) to the site, it means in some days, AHC chemistry will dominate if the wind is from east, on the other hand, when the wind is from other directions except from east, the chemistry is mainly dominated by BHC. Two special days were chosen to support the almost complete separation of chemical regimes experienced at this site. On June 18 (Figure 16), the chemistry is dominated by AHC because the wind is from east (see Figure 17). Under AHC conditions, the PAN and PPN have a linear relationship since both PAN and PPN are from AHC, MPAN level is relatively low on that day due to the lack of precursors. On the other day-June 25 (Figure 18), the chemistry was dominated by BHC because the wind is

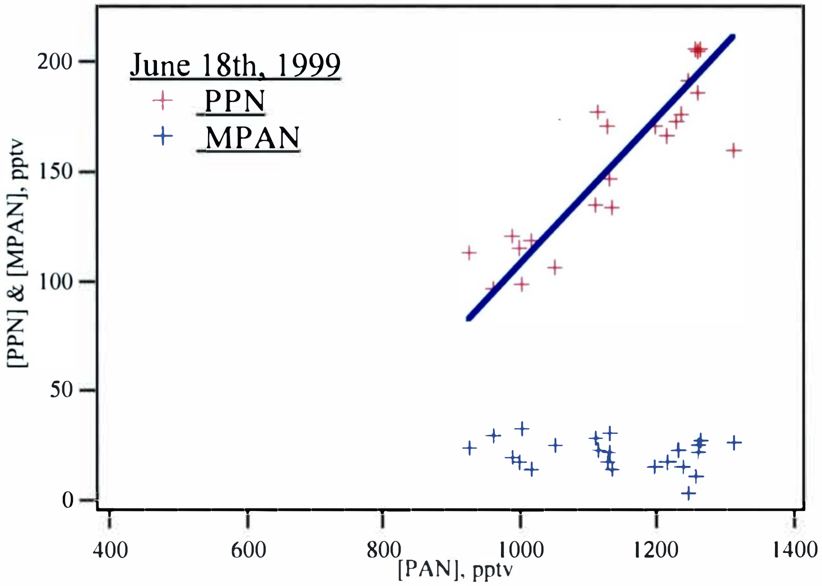


Figure 16. PPN and MPAN versus PAN on June18 (Wind Was From East).

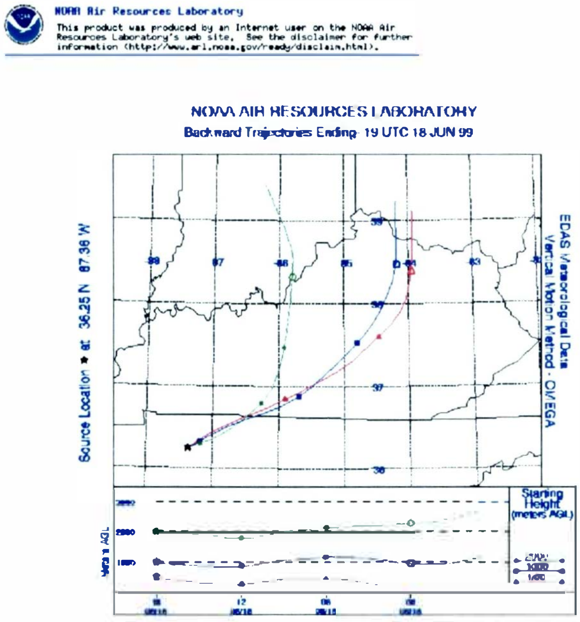

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Figure 17. The Back Trajectory of Wind on June 18, 1999.

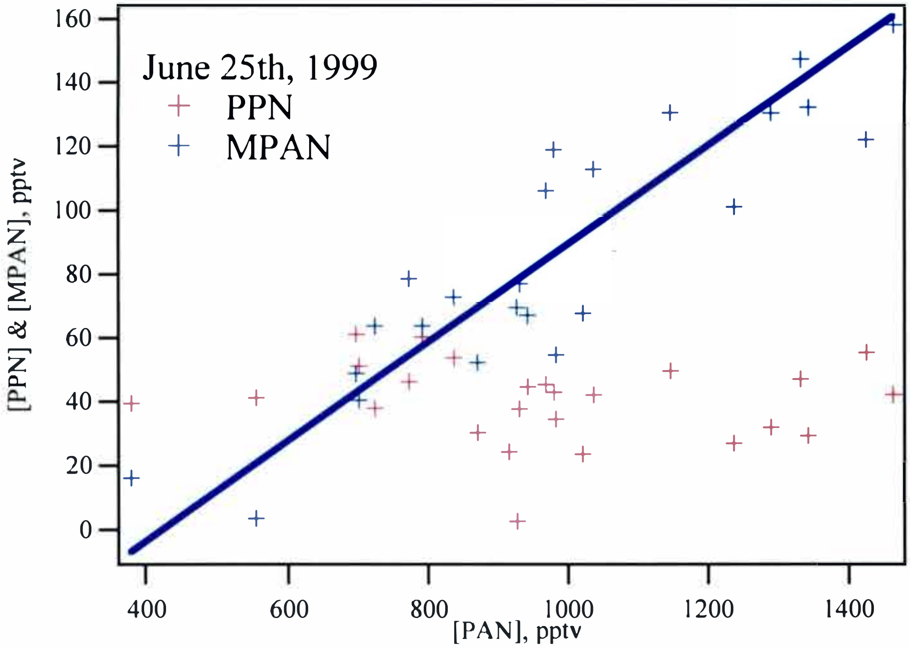


Figure 18. PPN and MPAN Versus PAN on June 25 (Wind is From Southwest).

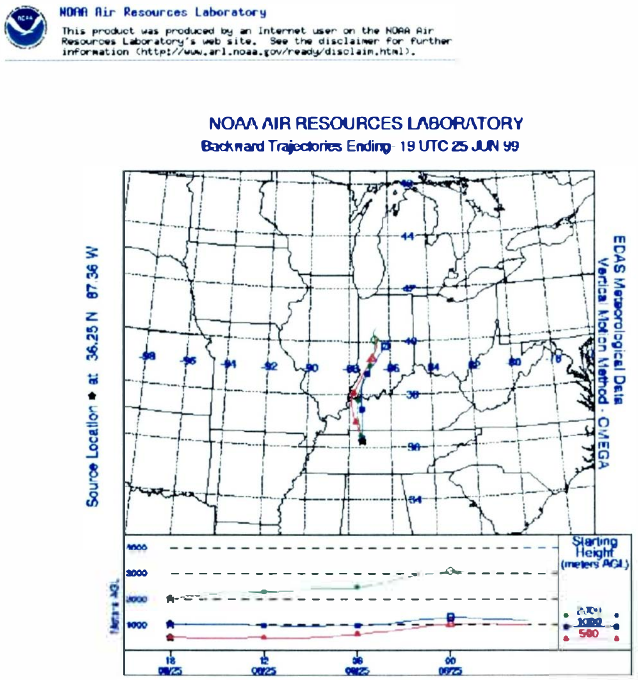


Figure 19. The Back Trajectory of Wind on June 25, 1999.

from northwest (Figure 19). PAN and MPAN are in good linear relationship since both of them can be produced from BHC. PPN is very low this day because no AHC precursors available.

The measurement data support that the AHC and BHC chemistry regimes can be separated completely at this site. Evidence of separation of two chemistry regimes can also be seen using two individual days from Youth Inc. (Nouaime et al., 1997). One is on July 19,1995, they observed the strong linear relationship between PAN and PPN, but the relationship between PAN and MPAN is very weak. Another day is on July 17, 1995. They found PAN and MPAN have correlative behavior than PAN and PPN did. But on that day, the trend was not very obvious. It seems that both PPN and MPAN correlate to PAN in some degree. That means that trying to get pure BHC chemistry is not very successfully in the real ambient air. But in Dickson site, from the Figure 16 and Figure 18, the pure AHC chemistry and BHC chemistry both can be acquired on individual days.

Since PPN is from BHC and MPAN is from AHC, on individual days, if the wind direction is relatively stable, eastern wind direction (AHC) always correspond to good linear relationship between PAN and PPN, very low mixing ratios of MPAN. On the other hand, the western wind direction (BHC) always correspond to good linear relationship between PAN and MPAN, low mixing ratios of PPN. When the dominated chemistry was filtered on individual days using the wind direction, the ratio of PAN/PPN in AHC condition and PAN/MPAN in BHC condition can be acquired. The ratios can reflect the ratio of PAN/PPN or PAN/MPAN for the relatively ideal state of AHC chemistry and BHC chemistry.

PAN can be formed both from AHC and BHC sources, so PAN can work as an indicator of total VOC photochemistry. PPN and MPAN can be used as indicators of photochemistry in AHC and BHC dominated conditions respectively. In pure AHC dominated chemistry, when only PAN and PPN can be formed, their relationship can be expressed as PAN=bPPN+c. On the other hand, in pure BHC chemistry dominated condition, only PAN and MPAN can be formed, their relationship can be expressed as PAN=aMPAN+c. Single linear regressions of PAN on PPN and MPAN using the entire daytime data set from Dickson (Figures 20 and 21) show that there is a relatively weak but positive relationship with the PPN/PAN relationship being much stronger. The PAN, PPN and MPAN data applied in the equations do not include the data that are under detection limit. Ideally, if the chemical regime were either pure AHC or pure BHC a much stronger relationship would be seen. Clearly the entire data set reflects some combination of AHC and BHC chemistry. Information about the relative contributions of the two chemical regimes could be obtained by separating the influence of each from the data.

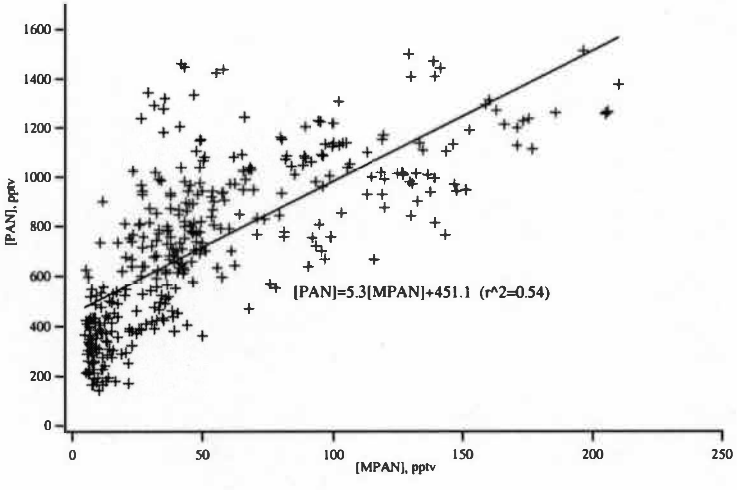


Figure 20. PAN vs. PPN for Daytime Data During the Whole Measurement Period.

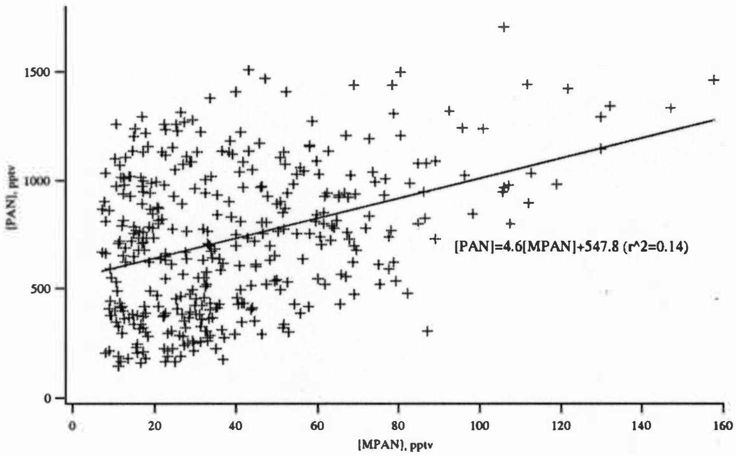


Figure 21. PAN vs. MPAN for Daytime Data During the Whole Measurement Period.

To Investigate the Equation of PAN=aMPAN+bPPN+c by Virtue of Their Sources

A multivariate analysis approach, first presented by Williams and Roberts considers PAN concentration to be equal to a linear combination of PPN and MPAN concentrations by solving the equation PAN=aMPAN+bPPN+c (Williams et al., 1997; Roberts et al., 1998). The coefficients 'a' and 'b' ideally represent a characteristic ratio of compounds that results from chemistry of a particular precursor mixture. This analysis method will be called MLR later. The MLR equation is based on two assumptions: one is that PPN and MPAN have different sources. Another assumption is that all three compounds are mainly lost at an equivalent rate of thermal decomposition (Williams et al., 1997; Bertman et al., 1991). The multivariate linear regression (MLR) analysis method applied to the data obtained at Dickson using PAN, PPN and MPAN daytime data (from 10 AM to 4 PM) gives the following equation:

$$\text{PAN}=4.9(\text{MPAN})+5.4(\text{PPN})+252.6 \quad (r^2=0.71) \tag{17}$$

The PAN, PPN and MPAN data applied in the equation do not include the data that are under detection limit. Using this expression, PAN values can be calculated at each point using the actual PPN and MPAN values. In Figure 22 the measured data are compared to the calculated data. This plot shows that when the PAN is expressed as a function of the sum of the contribution of AHC and BHC, the stronger correlation fit is obtained. The black dash line represents the linear regression fit of PAN from measurement versus PAN from MLR calculation.

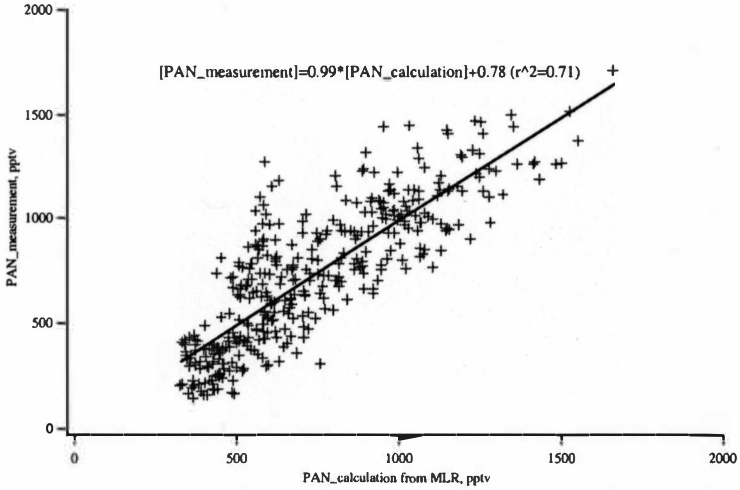


Figure 22. PAN Measured at Dickson vs. PAN Calculated Using MLR.

In order to demonstrate that the PAN from MLR and the PAN from measurement have a statistically significant linear correlation, the residual plot is shown in Figure 23. This figure shows that the residuals of PAN are distributed randomly.

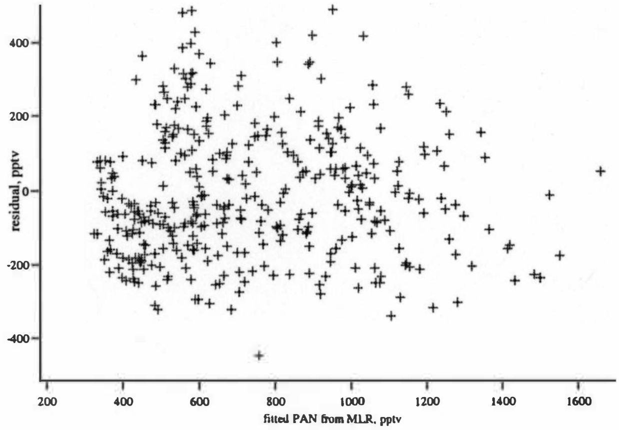


Figure 23. Residual Versus Fitted Value From MLR Analysis.

Comparison Between the Two MLR Equations

The next discussion will focus on which equation is more reasonable, PAN=aMPAN + bPPN + c or PAN= aMPAN + bPPN. The result is the first equation is better. The question is what does the 'c' represent? In fact, the concentration of PAN consists of two parts, one part is the photochemical reaction products of HCs and NO_x, the other is transportation from other places. Because PAN has a long lifetime in the air when the temperature is low, as it is in this case, troposphere chemistry and transport are both important, The influence of transport on the concentration of PAN can not be ignored. So in the equation of PAN=aMPAN+bPPN+c, 'c' accounts for the PAN from transportation, in other words, background PAN. 'aMPAN+bPPN' means the PAN from the photochemical reactions (Roberts, 1999).

Test of Coefficients Obtained from MLR

The goal of previous investigations was to use the values of a (MPAN/PAN) and b (PPN/PAN) to express the relative contribution of AHC and BHC to the formation of PAN and ozone (Williams et al., 1997; Roberts et al., 1998). Only if both coefficients of MPAN/PAN and PPN/PAN are correct will the right contribution of AHC and BHC chemistry to the formation of PAN can be obtained using b (PPN/PAN) and a (MPAN/PAN). Scatter about the 1:1 line in Figure 22 shows that these coefficients do not always describe the relative contribution with complete accuracy. The coefficients from MLR were obtained from all the daytime data during the whole measurement period. That means they are average values. On individual days, the PAN-PPN-MPAN relationship could be quite different. So when the average coefficients are applied to all data that consists of individual days, these data points are scattered.

In real ambient air conditions, if there is biogenic influence, both AHC and BHC exist, so PAN, PPN and MPAN all can be formed. The formation of MPAN and PPN do not interfere with each other. Based on the assumption that there is a consistent product yield from reactions of the two classes of precursors, the best fit for each ratio should be that which represents the pure ratio. With the data from Dickson, we have the unique opportunity to test this idea by identifying days that appear to be mostly or completely dominated by one or the other precursor class. In this way we can determine the limit of the usefulness of the MLR analysis performed on an entire data set. In other words, we can test how robust the coefficients obtained from MLR are using our ambient data.

The method of selection of AHC dominated days and BHC dominated days is as follows. The AHC chemistry dominated days are chosen from those individual days in which PAN and PPN have good linear relationship but PAN and MPAN do not. Also the wind is constantly from east. The BHC chemistry dominated days are defined for those days in which PAN and MPAN have good linear relationship but PAN and PPN do not. The wind is constantly from all the directions except east. The so called mixing days are defined as those days which PAN-PPN and PAN-MPAN both have positive relationship, but the correlations are not as good as it did in AHC dominated days or BHC dominated days. In this case, the wind is not constant and is from different directions on one day. The value of r^2 is applied here to represent the goodness of a linear relationship. The criteria are summarized in Table 2. Due to the complexity of ambient air data and the uncertainty of the measurements, the r^2 we got normally are rarely greater than 0.8. This is good enough to reflect the relationship between PAN-PPN and PAN-MPAN. In some BHC days, the r^2 of PAN-PPN fit is larger. But in those days, most of PPN data are below detection limit. So those days are treated as BHC days although r^2 are larger.

Table 2

Selection Criteria for Designating Days as Being Dominated by Either AHC or BHC Condition

	r^2 of PPN	r^2 of MPAN
AHC condition	>0.76	<0.24
BHC condition	<0.25	>0.54

Coefficients 'a', 'b', 'c' obtained from MLR and the variance of PAN between measurement value and MLR fit value is showed in Table 3. Similarly, Coefficients 'a', 'b', 'c' obtained from single linear regression and the variance of PAN between measurement value and single linear fit value are showed in Table 4 and Table 5.

Table 3. PAN, PPN and MPAN Daily MLR Results for the Dickson Data
(Daytime Data only 10:00-18:00 CDT)

		Multivariate linear regression PAN=aMPAN+bPPN+c			
		a	b	c	σ
Whole time period (June 16-July 13)		4.9±0.4	5.4±0.2	252.6±20.3	184.1
Mixing days	June 17	12.3±4.1	4.9±1.2	64.1±144.0	105.9
	June 22	6.6±1.6	2.7±1.1	445.9±92.3.0	158.2
	June 23	3.8±1.3	3.4±1.8	331.6±96.5	107.8
AHC days	June 16	1.0±2.6	7.2±1.4	-16.9±275.0	104.4
	June 18	1.0±1.8	2.9±0.4	671.8±77.3	54.4
	June 19	1.0±1.8	6.8±1.4	413.9±135.0	78.4
	June 20	-1.3±0.7	3.9±0.5	813.0±58.9	43.4
	July 13	1.5±4.5	14.6±0.9	92.9±38.3	56.8
BHC days (low NOX)	July 1	3.3±0.7	2.8±2.0	117.4±16.0	31.8
	July 2	4.8±0.7	0.2±2.2	100.9±15.1	36.9
	July 3	3.6±0.7	10.9±5.8	119.8±20.4	54.5
	July 4	4.2±0.6	7.2±2.2	171.3±19.4	42.9
	July 5	4.1±1.0	6.1±2.9	208.3±22.9	44.2
BHC Days (high NOX)	June 25	6.1±0.6	-3.2±1.9	587.7±95.7	115.7
	June 27	7.0±0.4	-7.5±2.5	176.3±19.6	54.9
	July 6	6.2±0.5	-5.0±6.3	110.3±20.4	48.6

Table 4. PAN and MPAN Daily Linear Regression Results for the Dickson Data
(Daytime Data only 10:00-18:00 CDT)

		Single linear Regression PAN=aMPAN+c			
		a	c	σ	R^2
Whole time period (June 16-July 13)		4.6±0.6	547.8±28.5	310.3	0.14
Mixing days	June 17	16.5±5.2	605.6±79.1	142.9	0.31
	June 22	9.1±1.4	424.0±101.0	178.3	0.65
	June 23	4.9±1.2	410.1±87.2	121.1	0.53
AHC days	June 16	-1.7±5.3	1238.8±254.0	240.0	0.01
	June 18	-4.1±3.4	1225.9±75.7	113.4	0.06
	June 19	5.2±2.7	995.0±116.0	141.3	0.24
	June 20	-3.1±1.4	1203.5±72.8	89.1	0.17
	July 13	12.6±16.3	567.1±94.7	211.6	0.25
BHC days (low NOX)	July 1	3.6±0.6	125.2±15.2	33.2	0.57
	July 2	4.8±0.5	101.3±14.4	36.9	0.78
	July 3	4.5±0.5	131.3±20.6	58.7	0.92
	July 4	4.9±0.7	199.5±21.0	52.7	0.56
	July 5	4.8±1.0	231.1±21.9	48.7	0.54
BHC Days (high NOX)	June 25	6.1±0.6	458.6±58.8	123.2	0.81
	June 27	6.5±0.5	139.1±17.8	65.4	0.88
	July 6	5.9±0.4	102.7±17.8	49.3	0.90

Table 5. PAN and PPN Daily Linear Regression Results for the Dickson Data
(Daytime Data only 10:00-18:00 CDT)

		Single linear regression PAN=bPPN+c			
		b	c	σ	R^2
Whole time period (June 16-July 13)		5.3±0.3	451.1±17.7	226.6	0.54
Mixing days	June 17	5.8±1.3	129.9±166.0	126.7	0.46
	June 22	5.6±1.1	735.3±73.6	207.8	0.52
	June 23	5.9±2.0	431.3±108.0	138.5	0.39
AHC days	June 16	7.1±1.3	48.7±208.0	105.9	0.81
	June 18	2.9±0.3	702.0±51.7	54.8	0.78
	June 19	7.1±1.2	413.8±131.0	79.6	0.76
	June 20	4.1±0.5	727.1±37.3	46.6	0.77
	July 13	14.7±0.8	99.1±32.7	56.9	0.91
BHC days (low NOX)	July 1	5.9±2.7	171.2±16.6	46.1	0.16
	July 2	9.0±3.1	160.9±22.1	66.9	0.25
	July 3	31.5±5.7	153.3±27.5	79.3	0.51
	July 4	12.7±3.4	244.2±27.4	74.8	0.36
	July 5	9.9±3.5	266.9±23.9	59.3	0.25
BHC Days (high NOX)	June 25	-3.1±4.5	1097.5±192.0	279.7	0.02
	June 27	4.9±7.9	266.1±63.4	190.3	0.02
	July 6	41.3±13.7	185.6±52.7	134.9	0.25

Table 4 shows results from the PAN-MPAN regression fit and Table 5 shows results from the PAN-PPN regression fit. Among the three tables, the first column always shows individual days in three different conditions that are AHC dominated days, BHC dominated days and mixing days. From some literatures, there is an idea that the NOx level may influence the ratio of PAN/MPAN in BHC conditions (pippin, 2000). The discussion on this will be given later. Here in order to test the assumption, in these tables, BHC dominated days are divided into two separated cases according to NO_x levels. Average NO_x levels above 3 ppbv are defined as high NO_x level. Average NO_x levels below 1 ppbv are defined as low NO_x level. The variances of coefficients of these fits have been considered in these tables due to the nature of ambient data.

From the table 3, the coefficient of PAN/MPAN and PAN/PPN (including one standard deviation) from MLR analysis is 4.9±0.4 and 5.4±0.2 respectively. It is surprising to see the variance of coefficients is so small because the measurement data is scattered in a large scale (Figure 22). From Figure 20 and Figure 21, it is clear that the PAN data versus PPN or MPAN is in a more scattered range. Still the coefficient of PAN/MAPN and PAN/PPN from single linear regression is 4.6±0.6 and 5.3±0.3 respectively (table 4 and table 5). In order to make sure the variance of coefficients is correct, the group data of PAN and PPN during the whole measurement period is applied here to check. Using linear regression analysis on PAN and PPN, the coefficient standard deviation of PAN/PPN is 0.3 (Table 5). Table 6 gives a summary on how to get the standard deviation from statistical calculation. The result is same as 0.3, it shows the calculation of standard deviation from computer software is correct.

Table 6. Calculation of Standard Deviation of the Ratio of PAN/PPN From the Correlation of PAN Versus PPN According to Statistical Equation

Σ (pan - pan_cal)^2	MSE	Σ (ppn – ppn_avg)^2	STD(β)
19351879	51331	812504	0.3

Another method is applied here to check the 95% confidence interval of the correlation of PAN versus PPN. According to definition of 95% confidence interval, two lines are drawn in Figure 24 to express the range of 95% measurement data should located in around the fitted line. The width from one of the two lines to the fitted line reflects the difference between fitted Y value and actual Y value at any given individual X. The value of the width (called W later) can be calculated using the equation below:

$$W= [t_{(0.025,\, n-2)}]^{*}\sqrt{MSE} \qquad (18)$$

The ‘t’ data can be obtained from statistical table, it can be treated equal to 2 when the data set is large, ‘MSE’ (Mean Square Error) is acquired from table 6 since they are from the same data set. The ‘W’ from calculation is 450.0. From the Figure it is very clear the width is closely equal to 450.0, the calculated value from equation 18.

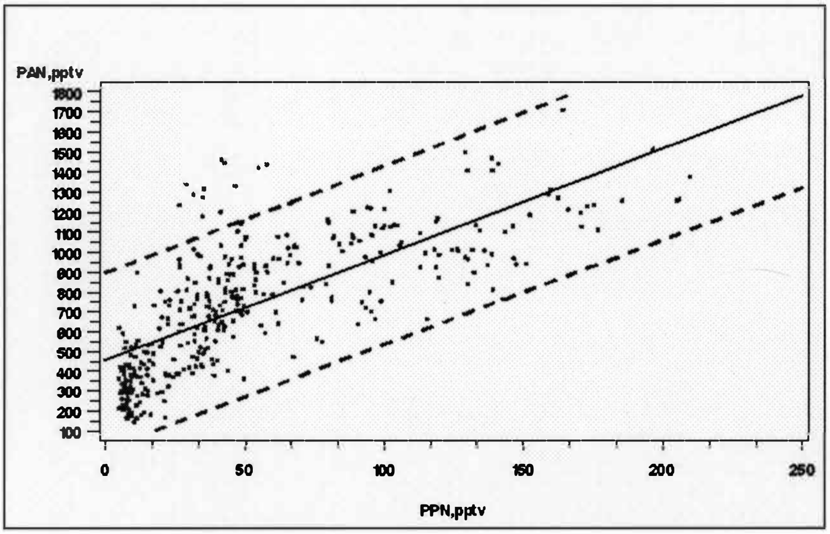


Figure 24. The Correlation of PAN Versus PPN for the Whole Period With 95% Confidence Limit Line.

From the calculation above, it shows that the variance of coefficient is really small. From statistics analysis, both standard deviation calculation and the 95% confidence interval, the small variance of coefficient does make sense. But on the other hand, the difference between PAN measurement data and fitted PAN data is very large even in such small coefficient variance. That means the coefficient obtained from whole period is not appropriate to use on individual days. Especially when we consider the experiment error for the whole period. Our experiment error for the whole period may be very large due to variation of the calibration factor error. The error is difficult to estimate because of insufficient calibration data. Therefore, the actual variances of coefficients are large and unpredictable. So the coefficients are not accurate. On individual days, the relative measurement error is not great and comparable to the variance from regression analysis. The error of coefficient for PAN/MPAN and PAN/PPN is 0.073 and 0.054 respectively (Appendix A). On individual days, the variance of coefficient obtained from regression analysis and the variance of coefficient from experiment error is compared. The larger one is used for the final variance of the coefficient.

As mentioned before, the coefficients of PAN/PPN and PAN/MPAN obtained from MLR for the whole period may not be accurate due to relatively large experiment error. The coefficients of ‘b’ from AHC individual days are given a comparison in appendix B. The coefficients of ‘a’ from BHC individual days are given a comparison in appendix C. The coefficient of ‘a’ is given a comparison when BHC days are divided into high NO_x level and low NO_x level in appendix D. On individual AHC days, it has been shown clearly that four out of five coefficients are significantly different. On individual BHC days, it is more complicated. After looking at the coefficient closely, the conclusion is that the coefficient of PAN/MPAN in high

NO_x condition group or low NO_x condition group do not show any statistical difference. But when compare the coefficients from the two different groups, the comparison shows that seven out of fifteen comparisons show statistically difference.

From the comparison, it shows that it is not enough to acquire the coefficients for the whole period to calculate the relative contribution of AHC and BHC to the formation of PAN on individual days. More work need focus on the results of individual days to check the variation of ratio since the contribution of AHC and BHC to PAN can be quite different on different days. So when we set up an ozone control strategy, it is preferable to check data from individual days to obtain the AHC and BHC contribution to the ozone rather than finding the average contribution of AHC and BHC by MLR method using whole period data. The question is why can the ratio be so different on different days under AHC condition or BHC condition?

Under AHC dominated conditions, the ratio of PAN/PPN could vary due to variations of the relative amount of AHC precursors for PAN and PPN on individual days. Since in BHC chemistry, PAN and MPAN have the same precursor (isoprene), the ratio of PAN/MPAN might be predicted to be constant. From the comparison above, it does show that the ratio is statistically same when NOx level is relatively close on individual BHC days. But from the comparison of appendix D, it appears that the ratio is higher in higher NO_x level. The trend is not very obvious from our data. 7 out of 15 comparisons show statistically difference, but not all of them. An Explanation for the variation of the ratio of PAN/MPAN due to NO_x level in BHC dominated condition is necessary to quantify the amount of ozone produced from BHC.

As mentioned above, isoprene reacts with OH• to produce MVK and MACR. The detailed reaction pathway is showed below in Figure 25 (Carter et al., 1996).

Isoprene reacts with OH• by addition to produce four radicals based to the location that OH• is added. Then the four radicals react with oxygen followed by reaction with NO to get four ß-hydroxyalkoxy radicals. After that the four radicals decompose to get MVK and MACR respectively. The reactions of MVK and MACR are very complicated. Ultimately, PAN and MPAN can be produced. The detailed reaction pathway is given below (Figure 26 and 27). MVK reacts with OH• by addition. The resulting carbon radical reacts with oxygen and NO finally decomposing to form methylglyoxal (MGLY) and PAN. MGLY can react with OH• or photolyze to produce PAN also. So from MVK, PAN is the final product. The reaction between MACR and OH• is done by two ways: OH• addition reaction and H abstraction reaction. From H abstraction, followed by reaction with oxygen and NO_2, MPAN is produced. From OH• addition reaction, the reaction is similar as the reaction of MVK-OH• reaction. The product is MGLY. Then MGLY reacted with OH• or photolysis to produce PAN.

Overall, from the production pathway of PAN and MPAN, PAN can be treated as three steps of NO_x dependence reaction product whereas MPAN is the two steps of NO_x dependence reaction product of NO_x. That means PAN's formation maybe is more sensitive to NO_x than MPAN does. Therefore, when NO_x increases, the ratio of PAN/MPAN increases.

Recent work shows that the MPAN + OH reaction rate constant is larger than previously measured. The findings show that MPAN reacts faster with OH than PAN does (Orlando et al., 2001). So MPAN can be lost more quickly from OH• reaction. As we know, PAN and MPAN's main loss pathway is thermal decomposition and the decomposition rate are similar (Bertman et al., 1991). From this, PAN and MPAN have close lifetime. But right now we know that if there is a lot of OH• around, the reaction of PAN and MPAN with OH• will become significant. In this case, MPAN's lifetime will be shorter than PAN's lifetime. So the ratio of PAN/MPAN will increase when OH• level increases. Therefore it is necessary to consider the influence of NO_x and OH• levels when investigating the ratio of PAN/MPAN in BHC dominated condition.

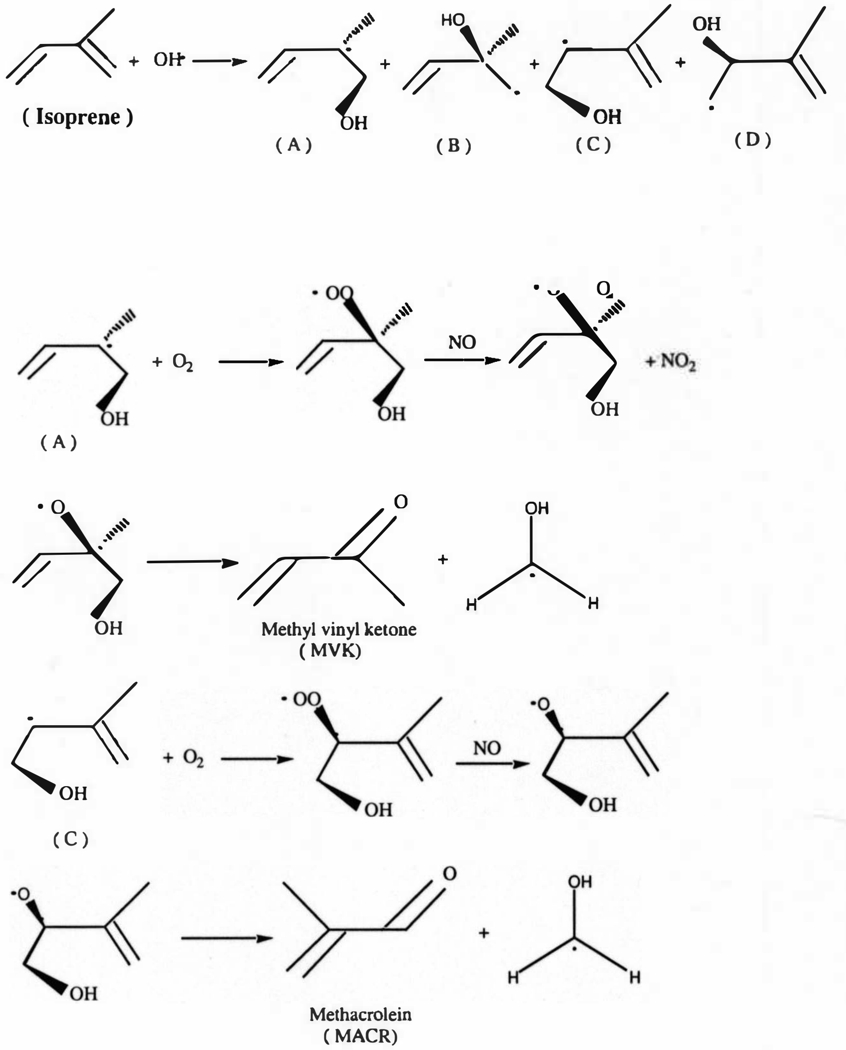


Figure 25. Isoprene Reaction Pathway to Form MVK and MACR.

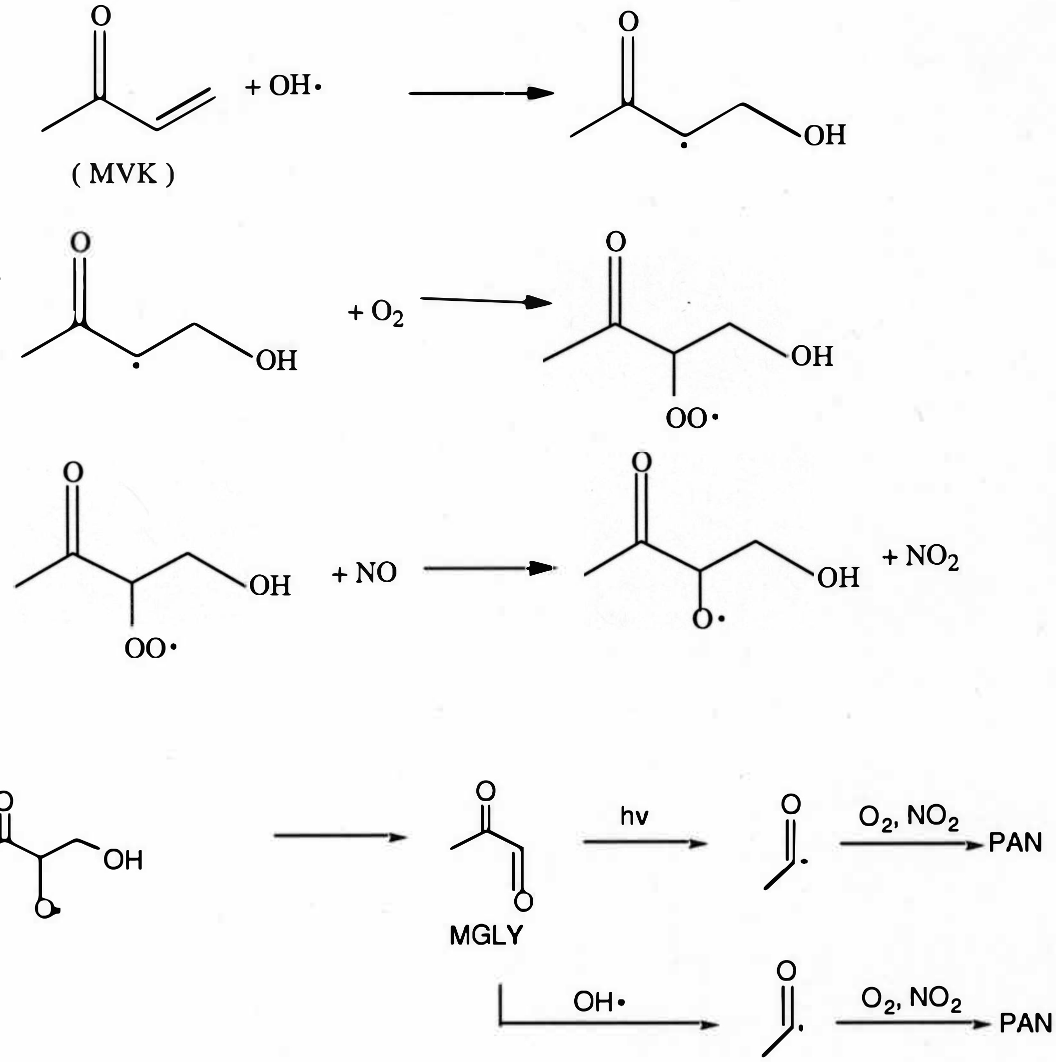


Figure 26. MVK Reaction Pathway.

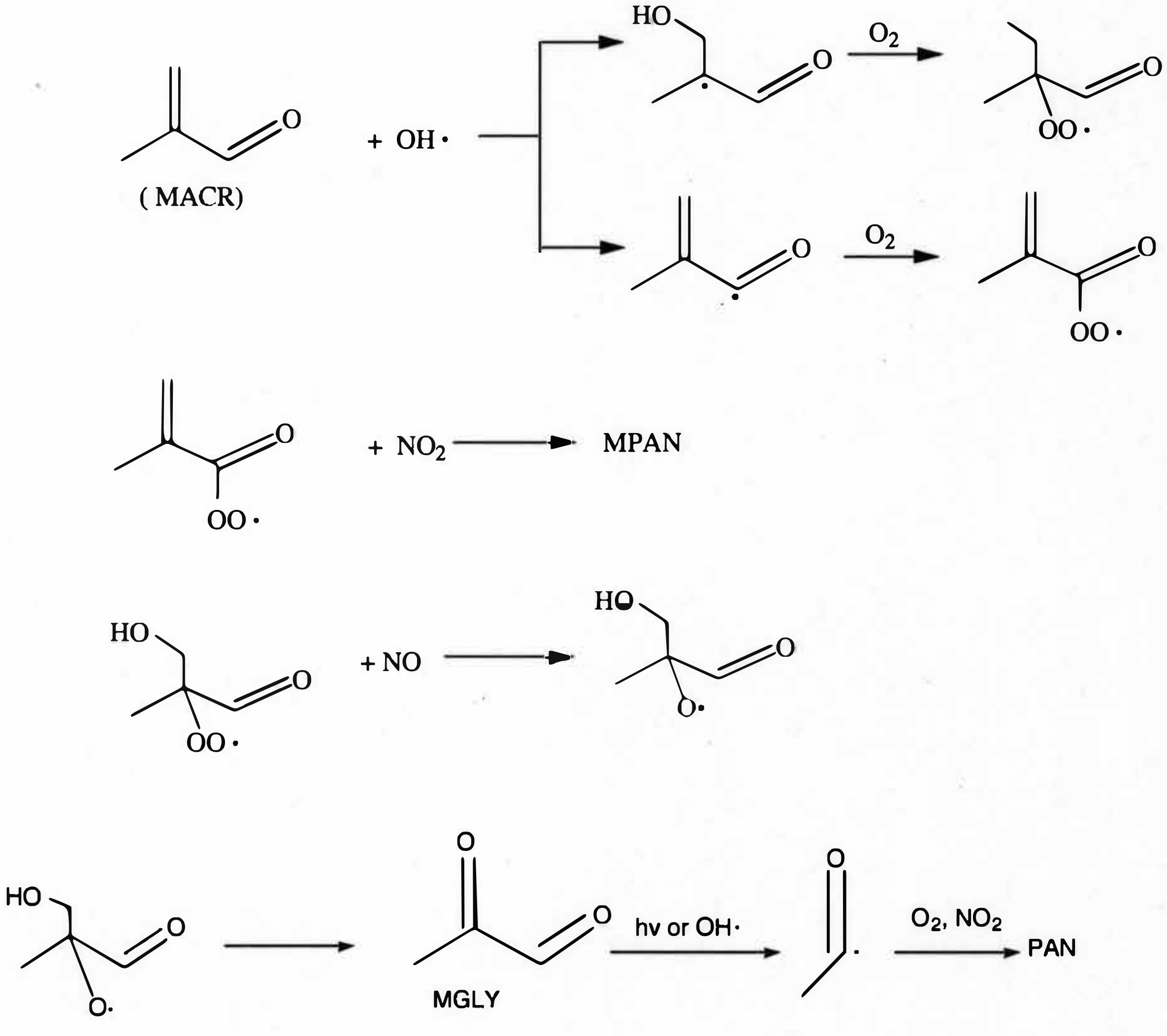


Figure 27. MACR Reaction Pathway.

From the discussions above, it can be seen that the coefficients from the MLR equation are not appropriate to be used on individual days. Because on individual days the coefficient of ‘a’ and ‘b’ varied under AHC conditions and BHC conditions. On BHC days, the ratio of PAN/MPAN increases when NO_x level increases, the trend is not very obvious from my data set. But from the isoprene reaction mechanism, it is reasonable. It points out again how important it is to look at individual day data.

Looking at the average ratio to decide the contribution of AHC and BHC to the formation of PAN and ozone is dangerous and can cause incorrect evaluation and an inappropriate control strategy.

Comparison of the MLR and Linear Regression on Individual Days

If looking at the table 3-5 in different way, a comparison can be made by examining the results of MLR and single linear regression analysis on individual days.

Mixing Days

In mixing days, both AHC and BHC exist. Therefore both PPN and MPAN have positive linear relationship with PAN, so MLR can describe the formation of PAN by the combination of PPN and MPAN quite well, just like it did for the whole measurement period. An example like this is showed here-June 23. In this day, from single linear regression analysis, the two results are as followed:

$$PAN=4.9MPAN+410.1 \quad (r^2=0.53) \qquad (19)$$

$$PAN=5.9PPN+431.3 \quad (r^2=0.39) \qquad (20)$$

From both equations we can see that PAN vs. MPAN and PAN vs. PPN have positive linear relationship. It is expected that the MLR equation give a stronger correlation fit for PAN and it does:

$$PAN=3.8MPAN + 3.4PPN +331.6 \quad (r^2=0.62) \qquad (21)$$

So the conclusion is that MLR works better on mixing days when both AHC and BHC have unignoreable influence to the formation of PAN.

AHC Days or BHC Days

On BHC dominated chemistry, in the ideal state, the multivariate analysis of PAN=aMPAN+bPPN+c and the single linear analysis of PAN=aMPAN+c should keep consistent in the ratio of 'a'. At the same time, the ratios of 'b' for PPN in multivariate analysis should be zero since on pure BHC chemistry dominated condition. It should not have any PPN because no contribution of AHC to the PAN. On AHC dominated chemistry, same results should be expected.

PAN/MPAN in AHC and PAN/PPN in BHC.

From table 3, it can be seen that the 'a' of MPAN under AHC condition varied dramatically. So did the 'b' of PPN under BHC chemistry dominated conditions. The main reason was that on individual day, the coefficient of 'a' under AHC condition and 'b' under BHC condition have very small arguments and have too few data to do the multivariate analysis for one day. So statistically, the ratios varied dramatically. They are not equal or close to zero as expected.

PAN/MPAN in BHC and PAN/PPN in AHC.

From table 2, the 'a' of MPAN in BHC control condition or 'b' in AHC control condition from MLR are very close to the 'a' and 'b' from single linear regression.

The results are not surprising. . Because under AHC condition, the aMPAN can be very small and under BHC condition, the bPPN can be very small. They can be treated them as zero. In relative pure BHC or AHC condition, PAN=aMPAN+c or PAN=bPPN+c can be treated as a simplification of the MLR of

PAN=aMPAN+bPPN+c. So the ‘a’ in BHC and the ‘b’ in AHC are close in both regression analysis.

r^2 in MLR and Single Linear Regression.

On individual days of BHC dominated conditions or AHC dominated conditions, from these examples above, it shows that the r^2 is always better from MLR than from a single linear regression. How can this be explained? In fact, it is easy to explain it from the mathematics theory. In MLR, since both PPN and MPAN were considered, there are two coefficients to balance with the PAN, so always the better linear regression was acquired from the MLR.

The Total Trend of PAN-PPN and PAN-MPAN

During the data analysis, an obvious trend has been noticed: During the time of June 15 to July 5 (Figure 28 and 29). At the beginning the PAN and PPN have good linear correlation, the mixing ratio of PPN is relatively large. Then the mixing ratio of PPN decreased, during the process, the linear relationship of PAN and PPN also become weaker and weaker. At the same time, the mixing ratio of MPAN keeps increasing and the linear relationship of PAN and MPAN become better and better. The process keeps going like this. The increase of MPAN make up the decrease of PPN, and the linear relationship of PAN and MPAN become very good, but the linear relationship of PAN and PPN become very poor at last. These trends can be demonstrated more clearly by examining Figure 30, which shows the change of r^2 during the period. It can be seen clearly that the r^2 of PAN-PPN decrease and at the same time, the r^2 of PAN-MPAN increase.

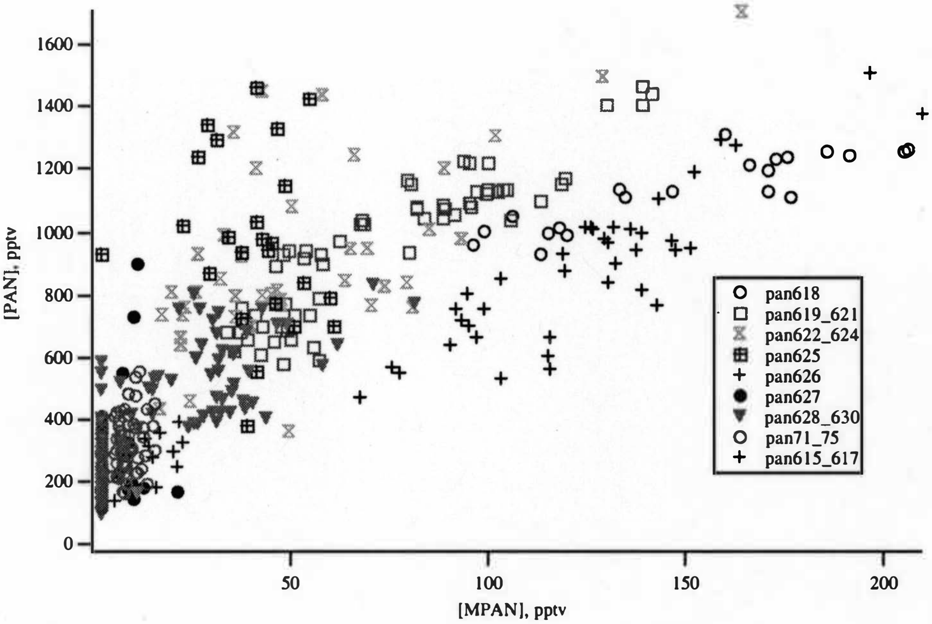


Figure 28.PAN-PPN Trend During the Whole Measurement Period.

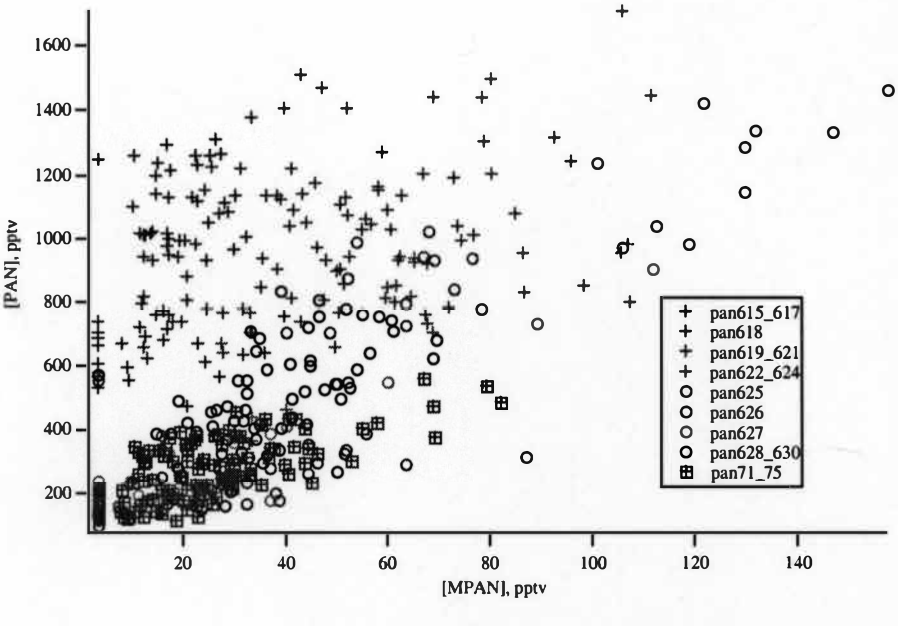


Figure 29. PAN-MPAN Trend During the Whole Measurement Period.

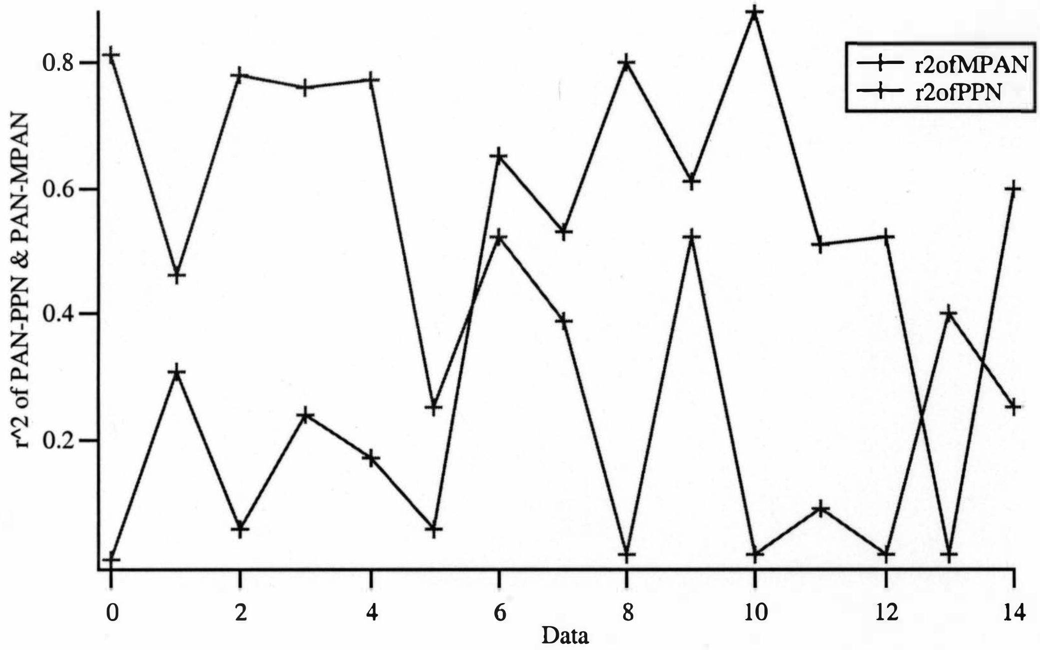


Figure 30. The r^2 Change of PPN and MPAN From June16 to July 5.

A Summary About Part 2

PAN=aMPAN+bPPN+c is reasonable to use for acquire the average contribution of AHC and BHC to the formation of PAN for the whole measurement period. But the ratio of 'a' and 'b' varied on individual days, that means the contribution of AHC and BHC are quite different under different conditions. So it is important to check the results of individual days to find the correct contribution of AHC and BHC.

On individual days, a comparison of the ratio of 'a' and 'b' using MLR and single linear regression shows that the 'a' in AHC and 'b' in BHC varied between the two analysis. But on the other hand, the 'a' in BHC and 'b' in AHC are relatively close between the two analyses. In any cases, the MLR equation always get the best r^2 according to the mathematics principles. But according to statistical analysis, the goodness of r^2 does not represent the goodness of MLR on individual AHC days and BHC days. In fact, on those days, the coefficients obtained from PAN-PPN or PAN-MPAN single linera regression are more reasonable to use.

Investigate the Quantitative Relationship Between PAN and MPAN in BHC Dominated Environment

The Importance of the Topic

In recent years, the influence of isoprene to the formation of ozone has attracted a lot of attention (Pippin, 2000; Costales, 1999). Isoprene can reacted with OH•, oxygen and NO_x to produce MVK and MACR. MACR can produce both PAN and MPAN while MVK can produce PAN (see table 7). The oxidation reaction mechanism of isoprene is complicated so till now it remained uncertain (Grosjean et al., 1993). Investigation of the ratio of PAN/MPAN and comparison of the ratio under different BHC conditions can help to decide how robust this ratio is and which factor influence the value of the ratio, therefore increase the understanding on the isoprene mechanism.

Table 7

The Main Reaction Pathway of Isoprene

Isoprene → MVK+ MACR
MVK → PAN
MACR → MPAN and PAN

Below some recent results on investigating the ratio of PAN/MPAN are discussed. The first data set is from our Dickson measurement data, the second and the third experiment are from our chamber and Purdue's Chamber experiments, the fourth data set is from UM box model. All these experiments had the same objective: try to figure out the ratio of PAN/MPAN under BHC condition. At last, a theoretical calculation on the ratio is given.

Investigate the Ratio of PAN/MPAN in BHC Conditions

Dickson Data

At Dickson site, as previously shown, the pure BHC (isoprene) dominated chemistry can be acquired in some individual days. (see table 3). From these data, it shows that the ratio of PAN/MPAN is NO_x-sensitive. In relative low NO_x level (NO_x<1ppb), the ratio ranges from 4.0 to 5.3. In relative high NO_x level (NO_x >3ppb), the ratio ranges from 5.5 to 6.5.

Smog Chamber

WMU Chamber.

Chamber experiments were also done to investigate the ratio of PAN/MPAN. The chamber experiments really supplied a completely ideal BHC environment to investigate the quantitative relationship between PAN and MPAN.

From the chamber experiments, two sets of data were obtained successfully. Figure 32 shows the results of the chamber experiment on July 27, 1999. Another chamber experiment was done on August 2, 1999. The two experiments show very similar results.

From Figure 31, the up-slope data shows both PAN and MPAN concentrations are increasing. The down-slope data shows from MPAN concentration start to decrease.

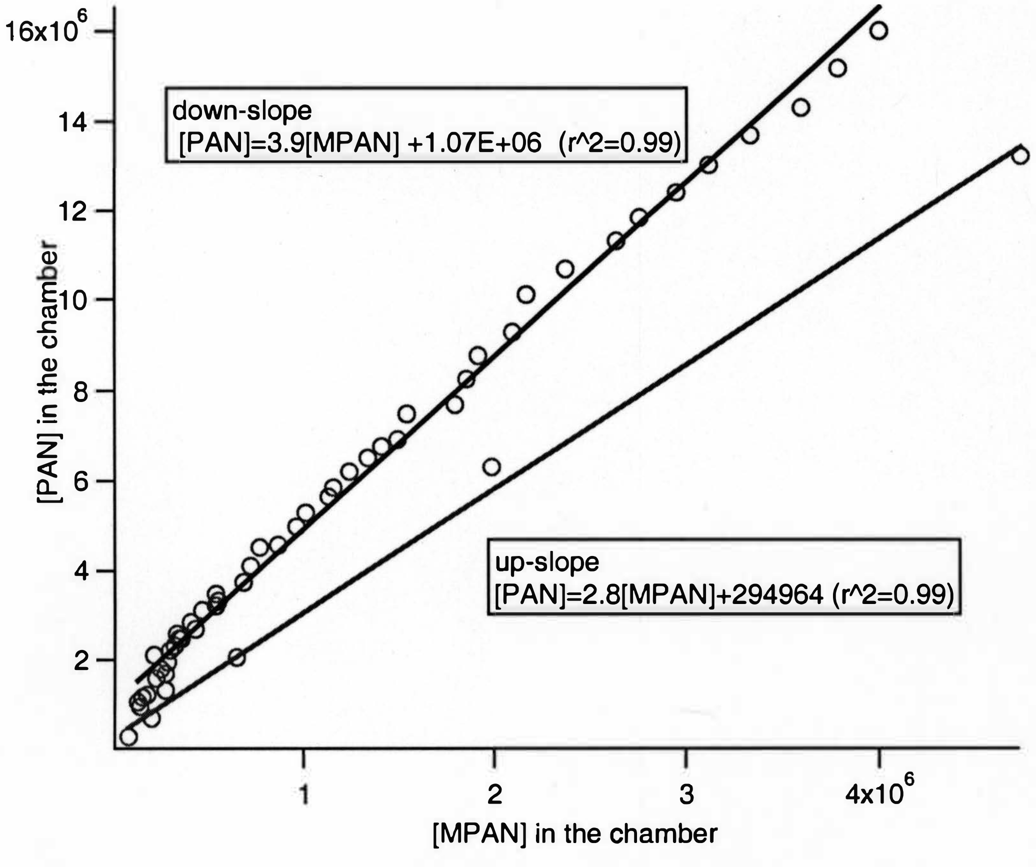


Figure 31. PAN vs. MPAN in WMU Chamber Experiment (July 27, 1999).

a. By looking at the intercept, it is found that intercept is so small compared with the value of PAN that it can be ignored. It demonstrates that in the chamber experiment that there are no additional sources of PAN, all the PAN are produced from isoprene photochemical reaction.

b. The data analysis results show that the linear relationship between PAN and MPAN have two slopes, PAN=3.9MPAN (down slope), PAN=2.8MPAN (up slope). It is important to decide which slope can represent the ratio of PAN/MPAN. In fact, the total slope ‘a’ is very close to the down-slope because there are much more data in down-slope process, the mixing ratio of PAN and MPAN keep decreasing for a long time, so down-slope can represent the stable biogenic condition. On the other hand, the up-slope really reflected the ratio under the BHC photochemical reaction.

c. From the difference of the up-slope and down-slope, it can be seen that the loss rate of MPAN is faster than that of PAN. It can be demonstrated by looking at the two lines of Figure 31. At the up-slope line, PAN=2.8MPAN, at the down-slope line PAN=3.9MPAN. In fact, the data of PAN and MAN acted like this: PAN keep increasing, but MPAN begin to drop down. So two lines are formed and the slope of down-slope line is greater than that of up-slope line. From Figure 8-9 in part 1 that shows the diurnal change of PAN and MPAN, it was found that MPAN has the largest peak earlier than PAN’s largest peak (about 1 hour). From the point, Ambient air data and chamber experiment data show the same trend. The reason of MPAN loss faster might because MPAN have larger reaction rate constant with OH• than PAN does.

Purdue Chamber.

Another chamber experiment was done in Purdue University. The final result for the ratio of PAN/MPAN is as followed (2 data sets):

1. PAN=6.78MPAN –0.036 (up-slope) (22)
2. PAN=5.7MPAN+213805 (up-slope) (23)

The Figure 32 shows the chamber experiment data in Purdue.

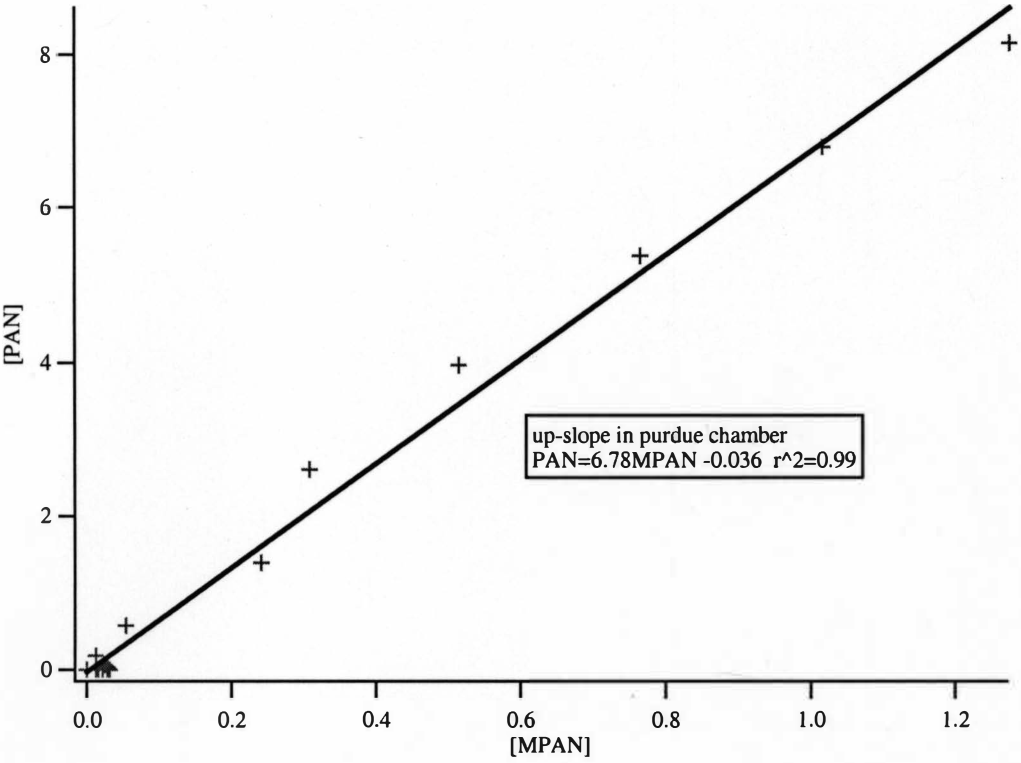


Figure 32. PAN vs. MPAN in Purdue Chamber Experiment.

Comparison Between the Two Chamber Experiments.

The slope of purdue chamber was much greater than that of the WMU chamber. From the plot of WMU smog chamber and Purdue chamber, we can see that during the process of PAN and MPAN increasing, in WMU chamber, the PAN and MPAN increase at almost the same rate. While in Purdue chamber, the PAN increase faster than MPAN did. This could be the reason which caused the slope of PAN vs. MPAN in Purdue chamber to be greater than those of WMU chamber.

We know that the NO_x level can influence the ratio of PAN/MPAN in isoprene reaction in ambient air. It also happened in the chamber experiment. In the Purdue chamber, the NO_x level was about 1ppb. This value is very close to the average NO_x level in real ambient air. Unfortunately there are no NO_x data for the WMU chamber experiment. So it is uncertain about difference of the two chamber experiments.

Comparison the PAN/MPAN Between the Ambient Air and Chamber Experiment

From the ambient air data, the ratio of PAN/MPAN is about 4.0-5.3 (low NO_x level), from WMU chamber, the ratio is about 2.8-3.4. No doubt, the ratio of PAN/MPAN acquired from realistic BHC chemistry conditions is greater than that of obtained from its ideal BHC chemistry experiments. Why?

In ambient air measurement, a relative ideal BHC environment is only an assumed one, it still has AHCs in the air, that means PAN still can be formed from AHCs while MPAN can not. Therefore the ratio is greater in ambient air data. Another explanation is that after PAN and MPAN are formed in the ambient air, they still can react with ozone and OH•. MPAN, because it contains an unsaturated double bone, it is more active than PAN. Like we already know, the OH• reaction rate of MPAN is faster than that of PAN. This is in agreement with the MPAN mixing ratio that start to drop down earlier than PAN in both chamber and ambient experiment. This also caused the PAN/MPAN ratio to be greater in the ambient air than in the ideal BHC environment.

UM Model Box

The air model box in UM is used to probe the relationship between PAN and MPAN. They create some computer modal box according to the reaction mechanisms, by input the amount of NO_x and isoprene and the rate constants of chemicals, try to simulate the real atmospheric reactions and got the quantitative relationship between PAN and MPAN (Pippin, 2000)

Model	NO_x=4ppb, PAN/MPAN=4-5
	NO_x=1ppb, PAN/MPAN=2-3
	NO_x=0.3ppb, PAN/MPAN=1-2

From the model calculation, it shows that in isoprene chemistry, the ratio of PAN/MPAN is NO_x-sensitive.

Theoretical Calculation

The possible mechanism and kinetics reactions should be well understood for explaining the relationship of PAN and MPAN in isoprene chemistry (Pippin, 2000). The main reaction is given on the Figure 2. PAN and MPAN can also react with ozone, OH•, but these reactions are slow and not as important as the others (Grosjean, et al. 1993). Since isoprene chemistry has already been studied by other people from different steps recently (Paulson et al., 1992; Carter et al., 1996; Pippin, 2000; Grosjean et al., 1993), It is very necessary to give a theoretical calculation utilizing other people's results.

From the reaction of isoprene going to MVK and MACR, many people already do some work to investigate the ratio of MVK/MACR. Their main results are listed in table 8.

Table 8

The Ratio of MVK/MACR in BHC Condition

MVK/MACR=1.4 when isoprene reacted with OH• in daytime (Stam, et al. 1998)

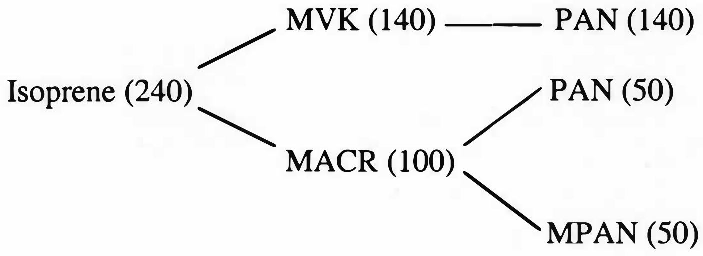
MVK/MACR=1.3-1.4 (Paulson, 1992)

MVK/MACR=1.22-1.24 (Purdue ambient air measurement, data is used here)

MVK/MACR=1.4 (Wenfang Lei et al., 2000), they get the ratio according to the molecular orbital theory and unimolecular rate theory calculations.

The ratio of MVK/MACR=1.4 will be used in this work as many people used previously. From MVK, only PAN can be formed. From MACR, both PAN and MPAN can be produced. The oxidation reaction of MACR proceeds by 50% OH addition and 50% H abstraction. From OH addition, PAN is produced. From H abstraction, MPAN is produced. So in general, in the reaction of MACR with OH, the production of PAN and MPAN can be treated having equal faction(Pippin, 2000)

From these results above, the plot below gives a clear summary:



So the PAN/MPAN=190/50=3.8 (theory)

The ratio from mechanism analysis above lies between our chamber and ambient results.

The first chamber experiment which focuses on isoprene chemistry mechanism was done by Gresjean in California (Grosjean et al., 1993). The ratio of PAN/MPAN is 1.5.

Here a summary is presented, the results of investigating the ratio of PAN/MPAN in BHC chemistry condition is listed to the table 9 below.

The isoprene chemistry has received more and more attention due to its role in ozone formation in rural area. Probing the mechanism of isoprene chemistry is still a challenge, Investigation of the ratio of PAN/MPAN supply a useful method to increase the understanding on the isoprene chemistry mechanism and therefore to the formation of ozone in BHC condition. Under different BHC conditions, the ratio varied with the NO_x level, the relative amount of OH radical and ozone. In the ambient air, the ratio also can be influenced by complicated weather condition. More work need to be done on the quantification of the ratio, from the model (theory) to small chamber, then to the ‘large chamber’ (ambient air).

Table 9

PAN/MPAN Ratio Under Different BHC Control Condition

Method	Experiments	PAN/MPAN
Ambient	1999 SOS/Dickson	4.0-5.6 (low NO_x)
	1999 SOS/Dickson	5.5-6.8 (high NO_x)
Smog Chamber	OH initiated isoprene-NO_x reaction; WMU chamber	3.4-3.9 (down slope) 2.8 (up slope)
Smog Chamber	OH initiated isoprene-NO_x reaction; Purdue chamber	5.7-6.8 (up slope)
Kinetic model	Fully specialized box model	3.0-5.0
Calculation	Product yield	3.8
Grosjean Chamber		1.5

CHAPTER IV

CONCLUSIONS

Simultaneous Measurements of PAN, PPN and MPAN were made during the SOS 1999 Nashville champaign at Dickson site. The PANs data at this site was rich and complicated. PAN and MPAN have obvious diurnal change but PPN does not always during the period. PPN do have diurnal change in some periods. PAN and ozone have a clear positive relationship. Due to the special location of the site, wind from different direction brings AHC or BHC source to the site. It shows that the influence of AHC and BHC to PANs compounds varied on individual days. Average values of PAN/PPN and PAN/MPAN from MLR may be interpretable regionally to calculate the contribution of AHC and BHC to the formation of ozone. But care must be taken to consider the contribution on individual days because the ratio of PAN/PPN in AHC condition varied on individual days. The ratio of PAN/MPAN in BHC condition is more complicated. The ratio may be influence by NO_x and OH• level. So no characteristic ratio is applicable under different complicated BHC condition. The investigation of PAN/MPAN is helpful in understanding the isoprene reaction mechanism.

Appendix A

Calculation of Measurement Error of PAN, PPN, MPAN, PAN/PPN and PAN/MPAN on Individual Days

PAN, PPN and MPAN measurement error on individual days				
PAN (integration area precision at different concentration in calibration)				error
78824	38869	27380	21742	
77119	39596	26645	21003	
78915	39320	27972	21551	
77531	40049	27879	21231	
908.2	494.7	607.7	328.9	
78097.3	39458.5	27469	21381.8	
0.01	0.01	0.02	0.015	0.02
PPN (integration area precision at different concentration in calibration)				error
42427	20021	14795	11005	
42351	21124	15631	10508	
43036	20543	14150	10589	
41132	21789	13927	11725	
797.6	760.8	764.6	556.5	
42236.5	20869.3	14625.8	10956.7	
0.02	0.04	0.05	0.05	0.05
MPAN(integration area precision at different concentration in calibration)				error
9081	4295	3291	1956	
8680	4925	3374	2020	
8702	4383	3058	2135	
225.4	341.2	163.8	90.7	
8821	4534.3	3241	2037	
0.025	0.07	0.05	0.04	0.07

the coefficient variance from measurement error

a=PAN/MPAN	SQRT(0.07^2+0.02^2)=0.073
b=PAN/MPAN	SQRT(0.05^2+0.02^2)=0.054

a	0.073
b	0.054

Appendix B

Comparison of PAN/PPN on AHC Days

b1	sd(b1)	b2	sd(b2)	diff	std	z*	$z_{0.05}$	conclusion
7.1	1.3	2.9	0.3	4.2	1.33	3.15	1.96	S, 5%
7.1	1.3	7.1	1.2	0	1.77	0.00	1.96	NS, 5%
7.1	1.3	4.1	0.5	3	1.39	2.15	1.96	S, 5%
7.1	1.3	14.7	0.8	-7.6	1.53	4.98	1.96	S, 5%
2.9	0.3	7.1	1.2	-4.2	1.24	3.40	1.96	S, 5%
2.9	0.3	4.1	0.5	-1.2	0.58	2.06	1.96	S, 5%
2.9	0.3	14.7	0.8	-11.8	0.85	13.81	1.96	S, 5%
7.1	1.2	4.1	0.5	3	1.30	2.31	1.96	S, 5%
7.1	1.2	14.7	0.8	-7.6	1.44	5.27	1.96	S, 5%
4.1	0.5	14.7	0.8	-10.6	0.94	11.24	1.96	S, 5%

note:
1. The table shows the comparison of two coefficients obtained by regression analysis.
2. b1 and b2 are the regression coefficients.
3. sd(b1) and sd(b2) are the standard deviation of b1 and b2.
4. Both b1 and b2 follow normal distribution, these two distributions are independent. So the difference (diff) of b1 and b2 also follow normal distribution with mean equal to difference between mean of b1 and mean of b2. the standard deviation (std) is SQRT(sd(b1)^2+sd(b2)^2).
5. z*=diff/std
6. $Z_{0.05}$ is 5% upper level standard normal value, if z* is larger than $Z_{0.05}$, it means the two coefficients are statistical different. Otherwise, they are not statistical different.
7. S, 5% means statistical different at 5% significant level.
8. NS, 5% means not statistical different at 5% significant level.

Citation: Neter, et al., 1996

Appendix C

Comparison of PAN/MPAN on BHC Days

b1	sd(b1)	b2	sd(b2)	diff	std	z*	z 0.05	conclusion
3.6	0.6	4.8	0.5	-1.2	0.78	1.54	1.96	NS, 5%
3.6	0.6	4.5	0.5	-0.9	0.78	1.15	1.96	NS, 5%
3.6	0.6	4.9	0.7	-1.3	0.92	1.41	1.96	NS, 5%
3.6	0.6	4.8	1	-1.2	1.17	1.03	1.96	NS, 5%
3.6	0.6	6.1	0.6	-2.5	0.85	2.95	1.96	S, 5%
3.6	0.6	6.5	0.5	-2.9	0.78	3.71	1.96	S, 5%
3.6	0.6	5.9	0.4	-2.3	0.72	3.19	1.96	S, 5%
4.8	0.5	4.5	0.5	0.3	0.71	0.42	1.96	NS, 5%
4.8	0.5	4.9	0.7	-0.1	0.86	0.12	1.96	NS, 5%
4.8	0.5	4.8	1	0	1.12	0.00	1.96	NS, 5%
4.8	0.5	6.1	0.6	-1.3	0.78	1.66	1.96	NS, 5%
4.8	0.5	6.5	0.5	-1.7	0.71	2.40	1.96	S, 5%
4.8	0.5	5.9	0.4	-1.1	0.64	1.72	1.96	NS, 5%
4.5	0.5	4.9	0.7	-0.4	0.86	0.46	1.96	NS, 5%
4.5	0.5	4.8	1	-0.3	1.12	0.27	1.96	NS, 5%
4.5	0.5	6.1	0.6	-1.6	0.78	2.05	1.96	S, 5%
4.5	0.5	6.5	0.5	-2	0.71	2.83	1.96	S, 5%
4.5	0.5	5.9	0.4	-1.4	0.64	2.19	1.96	S, 5%
4.9	0.7	4.8	1	0.1	1.22	0.08	1.96	NS, 5%
4.9	0.7	6.1	0.6	-1.2	0.92	1.30	1.96	NS, 5%
4.9	0.7	6.5	0.5	-1.6	0.86	1.86	1.96	NS, 5%
4.9	0.7	5.9	0.4	-1	0.81	1.24	1.96	NS, 5%
4.8	1	6.1	0.6	-1.3	1.17	1.11	1.96	NS, 5%
4.8	1	6.5	0.5	-1.7	1.12	1.52	1.96	NS, 5%
4.8	1	5.9	0.4	-1.1	1.08	1.02	1.96	NS, 5%
6.1	0.6	6.5	0.5	-0.4	0.78	0.51	1.96	NS, 5%
6.1	0.6	5.9	0.4	0.2	0.72	0.28	1.96	NS, 5%
6.5	0.5	5.9	0.4	0.6	0.64	0.94	1.96	NS, 5%

With the explaination of this table, refer to Appendix B.

Appendix D

Comparison of PAN/MPAN Between High NO_x and Low NO_x

b1± sd(b1)	b2± sd(b2)	diff=b1-b2	std	z*	z 0.05	conclusion
3.6±0.6	6.1±0.6	-2.5	0.85	2.95	1.96	S, 5%
4.8±0.5	6.1±0.6	-1.3	0.78	1.66	1.96	NS, 5%
4.5±0.5	6.1±0.6	-1.6	0.78	2.05	1.96	S, 5%
4.9±0.7	6.1±0.6	-1.2	0.92	1.30	1.96	NS, 5%
4.8±1.0	6.1±0.6	-1.3	1.17	1.11	1.96	NS, 5%
3.6±0.6	6.5±0.5	-2.9	0.78	3.71	1.96	S, 5%
4.8±0.5	6.5±0.5	-1.7	0.71	2.40	1.96	S, 5%
4.5±0.5	6.5±0.5	-2	0.71	2.83	1.96	S, 5%
4.9±0.7	6.5±0.5	-1.6	0.86	1.86	1.96	NS, 5%
4.8±1.0	6.5±0.5	-1.7	1.12	1.52	1.96	NS, 5%
3.6±0.6	5.9±0.4	-2.3	0.72	3.19	1.96	S, 5%
4.8±0.5	5.9±0.4	-1.1	0.64	1.72	1.96	NS, 5%
4.5±0.5	5.9±0.4	-1.4	0.64	2.19	1.96	S, 5%
4.9±0.7	5.9±0.4	-1	0.81	1.24	1.96	NS, 5%
4.8±1.0	5.9±0.4	-1.1	1.08	1.02	1.96	NS, 5%

Note:

1. the table shows the comparison of two coefficients obtained by regression analysis.
2. b1 and b2 are the regression coefficients.
3. sd(b1) and sd(b2) are the standard deviation of b1 and b2.
4. Both b1 and b2 follow normal distribution, these two distributions are independent. So the difference (diff) of b1 and b2 also follow normal distribution with mean equal to difference between mean of b1 and mean of b2. the standard deviation (std) is SQRT(sd(b1)^2+sd(b2)^2).
5. z*=diff/std
6. $Z_{0.05}$ is 5% upper level standard normal value, if z* is larger than $Z_{0.05}$, it means the two coefficients are statistical different. Otherwise, they are not statistical different.
7. S, 5% means statistical different at 5% significant level.
8. NS, 5% means not statistical different at 5% significant level.

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BIBLIOGRAPH

Altshuller, A.P., PANs in the Atmosphere, Air & Waste, 43, 1221, (1993).

Bertman, S.B., and J. M. Roberts, A PAN ANALOG FROM ISOPRENE PHOTOOXIDATION, Geophys. Res. Lett., 18(8), 1461-1464, (1991).

Bertman, S. B., Personal communication, (2001).

Bertman, S. B., Presentation on the American Chemical Society, (2001).

Carter W. P. L., and R. Atkinson, Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x, International Journal of Chemical Kinetics, 28, 497-530, 1996.

Chameides, W. L., E. B. Cowling, The State of the Southern Oxidants Study (SOS): Policy-Relevant Findings In Ozone Pollution Research, 1988-1994, (1995).

Costales C. C., Design and Construction of an Atmospheric Chamber for Qualitative Study of an Unknown Compound Generated by the Photochemical Reaction between Isoprene and NO_x, a B.A. paper, (2000).

Finlayson-Pitts, B. J., and Pitts, J.N., Chemistry of the Upper and Lower Atmosphere, (2000).

Gafney J. S., R., & Senum, G. I., An Improved Procedure For High Purity Gaseous Peroxyacetyl Nitrate Production: use of Heavy Lipid Solvents, Atoms. Environ., 15, 215-218, (1984).

Grosjean Danlel, Edwin L. Williams II, and Eric Grosjean, A Biogenic Precursor of Peroxypropionyl Nitrate: Atmospheric Oxidation of cis-3-Hexen-1-ol, Environ. Sci. Technol. 27, 979-981, (1993).

Grosjean Danlel, Edwin L. Williams II, and Eric Grosjean, Atmospheric Chemistry of Isoprene and of Its Carbonyl Products, Environ. Sci. Technol. 27, 830-840, (1993).

Grosjean Eric, Daniel Grosjean, Matthew P. Fraser, and Glen R. Cass, Air Quality Model Evaluation Data for Organics. 3. Peroxyacetyl Nitrate and Peroxypropionyl Nitrate in Los Angeles Air, Environ. Sci. Technol. 30, 2704-2714, (1996).

Kasibhatla P., W. L. Chameides, R. D. Saylor, and D. Olerud, Relationships between regional ozone pollution and emissions of nitrogen oxides in the eastern United States, J. Geophys. Res., 103D, 22,663-22,669, (1998).

Kleindienst, T. E., RECENT DEVELOPMENTS IN THE CHEMISTRY AND BIOLOGY OF PEROXYACETYL NITRATE, Res. Chem. Intermed., 20, 335-384 (1994).

Kourtidis K. A., P. Fabian, C. Zerefos and B.Rappengluck, Peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and PAN/ozone ratio measurements at three sites in Germany, Tellus, 45B, 442-457, (1993).

Lei Wenfang, Renyi Zhang, W.Sean McGivern, Agnes Derecskei-kovacs, and Simon W. North, Theoretical study of isomeric branching in the isoprene-OH reaction: implications to final product yields in isoprene oxidation, Chemical Physical Letters, 326, 109-114, (2000).

Marenco A., Gouget H., and Nedelec P., Evidence of a long-term increase in troposphere ozone from PIC DU MIDI data series-consequences-positive radiative forcing, J. Geophys. Res., 99D, 16,617-16,632, (1994).

Neter John, Micheal H. Kutner, Christopher J. Nachtsheim and William Wassermen, Applied Linear Statistical Models, 4/e, (1996).

Nouaime, G., S. B. Bertman, C. Seaver, D. Elyea, H. Huang, P. B. Shepson, T. K. Starn, D. D. Riemer, R. G. Zika, and K. Olszyna, Sequential oxidation products from tropospheric isoprene chemistry: MACR and MPAN at a No$_x$-rich forest environment in the southeastern United States, J. Geophys. Res., 103D, 22,463-22,471, (1998).

Nouaime, G., PAN, PPN and MPAN Measurements and the Systematic Relationship Between MPAN and MACR at a Semi-Rural Site in Tennessee, a M.A. Thesis, (1997).

Orlando J. J., G. S. Tyndall, S. B. Bertman, W. Chen, J. B. Burkholder, Rate Coefficient for the Reaction of OH with $CH_2{=}C(CH_3)C(O)OONO_2$ (MPAN), Atmospheric Environment, Manuscript Submitted for Publication.

Paulson, S. E. and J. H. Seinfeld, Development and evaluation of a photooxidation mechanism for isoprene, Journal of Geophysical Research, 97, 20703-20715, 1992.

Pippin M. R., A MODEL-BASED EVALUATION OF SECONDARY REACTION PRODUCTS FROM BIOGENIC HYDROCARBONS, Ph.D. dissertation, 2000.

Roberts, J.M., Jonathan Williams, Karsten Baumann, Martin P. Buhr, Paul D. Goldan, John Holloway, Gerhard Hubler, William C. Kuster, Stuart A.Mckeen, Thomas B. Ryerson, Michael Trainer, Eric J. Williams, Fredrick C. Fehsenfeld, Steven B. Bertman, George Nouaime, Graig Seaver, Gil Grodzinsky, Michael Rodgers, Valerie L. Young, Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville Intensives of the Southern Oxidants Study: Implications for regional ozone production from biogenic hydrocarbons, J. Geophys. Res., 103D, 22,473-22,490, (1998).

Roberts, J. M., R. L.Tanner, L.Newman, V. C. Bowersox, J. W. Bottenheim, K. G. Anlauf, K. A. Brice, D. D. Parrish, F. C. Fehsenfeld, M. P. Buhr, J. F. Meagher, E. M. Bailey, Relationships between PAN and ozone at sites in eastern North America, J. Geophys. Res., 100D, 22,821-22,830, (1995).

Ryerson T. B., M. P. Buhr, G. J. Frost, P. D. Goldan, J. S. Hollowway, G. Hubler, B. T. Jobson, W. C. Kuster, S. A. Mckeen, D. D. Parrish, J. M. Roberts, D. T. Sueper, M. Trainer, J. Williams, and F. C. Fehsenfeld, Emissions lifetimes and ozone formation in power plant plumes, J.Geophys. Res., 103D, 22,569-22,583, (1998).

Seinfeld, J. H., Atmospheric Chemistry and Physics of Air Pollutiion, (1986).

Shepson, P. B., D. R. Hastie, K. W.So, H. I. Schiff and P. Wong, Relationships between PAN, PPN and O3 at urban and rural sites in Ontario, Atmospheric Environment, 26A, 1259-1270, (1992).

Shepson, P. B., T. E. Kleindienst, E. O. Edney, C. M. Nero, L. T. Cupitt, and L. D. Claxton, Acetaldehyde: the mutagenic activity of its photooxidation products, Environ. Sci. Technol, 20, 1008-1013(1986).

Starn T.K., P. B. Shepson, S. B. Bertman, D. D. Riemer, R. G.Zika, and K. Olszyna, Nighttime isoprene chemistry at an urban-impacted forest site, J. Geophys. Res., 103D, 22,437-22,447, (1998).

Starn T. K., P. B. Shepson, S. B. Bertman, J. S. White, B. G. Splawn, D. D.Riemer, R. G.Zika, and K. Olszyna, Observations of isoprene chemistry and its role in ozone production at a semirural site during the 1995 Southern Oxidants Study, J.Geophys. Res., 103D, 22,425-22,435, (1998).

Trainer, M., E. J.Williams, D. D.Parrish, M. P. Buhr, E. J. Allwine, H. H. Westberg, F. C. Fehsenfeld, and S. C. Liu, Models and observations of the impact of natural hydrocarbons on rural ozone, Nature, 329, 705-707, (1987).

Williams, J., J. M. Roberts, F. C. Fehsenfeld, S. B. Bertman, M. P. Buhr, P. D. Goldan, G. Hubler, W. C. Kuster, T. B. Ryerson, M. Trainer, and V. Young, Regional ozone from biogenic hydrocarbons deduced from airborne measurements of PAN, PPN, and MPAN, Geophys. Res. Lett., 24(9), 1099-1102, (1997).