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**ALKYL NITRATES IN DICKSON DURING
THE SOS 1999 FIELD CAMPAIGN**

by

Mei Ma

**A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Arts
Department of Chemistry**

**Western Michigan University
Kalamazoo, Michigan
August 2001**

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2001

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When I started to write my acknowledgments, the first thing came into my mind is that I am lucky to have Dr. Steve Bertman as my advisor. I want to thank him for his good educating, instructing, encouraging, and, especially, patience and understanding. I appreciated that he not only provided me a chance to study science, but also brought a lot of fun to our lab. Many thanks also to my committee, Dr. Jay Means and Dr. John Chateaufneuf, for their guidance, suggestions and time.

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Without my parents' encouragement and support, I would not believe I could insist my study here. No word is better than 感谢你们, 亲爱的爸爸妈妈! Of course, great thanks also to my sister and brother for their love, their care-packages to me.

Mei Ma

ALKYL NITRATES IN DICKSON DURING THE SOS 1999 FIELD CAMPAIGN

Mei Ma, M. A.

Western Michigan University, 2001

Measurements of alkyl nitrates were performed during the Southern Oxidants Study (SOS) 1999 Summer Field Campaign in Dickson, TN from June 10 to July 15, 1999. The developed GC-ECD method was tested and used successfully. Nine alkyl nitrates were measured and six alkyl nitrates were quantified. The measured alkyl nitrates except methyl nitrate showed higher mixing ratios under northeasterly and southeasterly wind, which brought anthropogenic sources to the measurement site, and lower mixing ratios when wind came from northwest and southwest, which brought NO_x and clean air, respectively. The contribution of the measured alkyl nitrates to the total oxidized nitrogen species, NO_y ranged from 1.1% and 1.9%, indicating that alkyl nitrates account for a small part of NO_y in Dickson. The investigation of the ratios of alkyl nitrates from the same parent hydrocarbons showed that the ratio of isopropyl nitrate with n-propyl nitrate had different behaviors from that of 2-butyl nitrate with n-butyl nitrate ratio. The relationship of n-propyl nitrate with propionyl nitrate was also studied. A photochemical box model was developed to study the relationship of alkyl nitrates and NO_x. The test and comparison with a complex model indicated that the output of the model for alkyl nitrates was correct and efficient to study the chemistry of alkyl nitrates in troposphere. The results from the model for alkyl nitrates may imply that the sources of alkyl nitrates could vary with wind direction.

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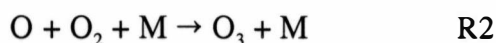
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CHAPTER I

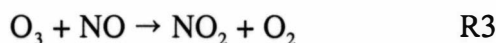
INTRODUCTION

Chemistry of Alkyl Nitrates

As we know well, ozone is very important to the earth because not only is it a greenhouse gas but it also plays a role in controlling the oxidizing capacity of the troposphere (Roberts et al., 1998). It is not directly emitted from any source but is photochemically produced in the troposphere from the oxides of nitrogen (NO_2 and NO). Its formation undergoes the following two reactions (Bertman et al., 1995):



Where M represents N_2 , O_2 or another third body which can stabilize the O_3 formation. Once formed, O_3 can react with NO to reproduce NO_2 :



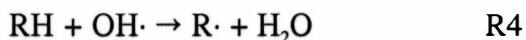
Reaction R2 is the only significant resource of O_3 in the atmosphere (Bertman et al., 1995), so the oxides of nitrogen, NO_x ($\text{NO} + \text{NO}_2$), play a unique role in tropospheric ozone chemistry. Increasing the ratio of NO_2/NO will cause the net increase of O_3 production, decreasing this ratio will have opposite effect. The change in NO_2/NO can occur due to the human activities, such as transportation, electric power generation, or industrial and domestic fuel combustion, which could emit considerable amount of NO into air, thus producing NO_2 by oxidation of NO . In addition, the photochemical products of NO_x , NO_y , were also found to have significant impact on NO and NO_2

levels, thus on O₃ formation (Roberts et al., 1998). Therefore a detailed investigation of the factors that affect the NO_x concentrations in atmosphere and the photochemical products of NO_x is required to study O₃ chemistry.

NO_y, which is defined as the sum of NO_x and all oxidized nitrogen species, consists of a number of different inorganic and organic forms (Roberts, 1990). NO, NO₂ and HNO₃ are inorganic components. The most abundant tropospheric organic species is PAN (peroxyacetyl nitrate) (Roberts, 1990). Early studies of O₃ chemistry mostly focused on PAN and its family species PPN (peroxypropionyl nitrate) (Lonneman, 1977; Grosjean, 1984; Singh and Salas, 1989). Alkyl nitrates are also one of the organic species included in NO_y. Since they have relatively low concentrations compared to other NO_y components, they were not brought into emphasis until the observations of NO_y “shortfall”, in which the sum of the concentrations of individual inorganic and organic species is less than the measured total NO_y (Buhr, 1990). These observations resulted in the suggestions that the missing part may be alkyl nitrates, and that they could also be potentially important to the O₃ formation. (Calvert and Madronich, 1987; Buhr et al., 1990; Roberts, 1990).

Alkyl nitrates contain an alkyl group covalently bonded to a nitrate group (-ONO₂), and are monofunctional compounds with saturated hydrocarbon chains (Roberts 1990; Bertman et al., 1995). They are formed in the troposphere mainly via the initial hydrocarbon-OH radical reactions followed by NO_x-alkyl peroxy radical reactions.

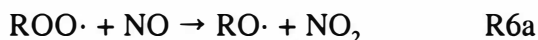
Anthropogenic alkanes (RH), which are assumed as the only parent source of alkyl nitrates (Atkinson et al, 1982), are initiated with OH radicals to give alkyl radicals R:



The resulting alkyl radicals then react quickly with O_2 to form organic peroxy radicals, $ROO\cdot$,



The organic peroxy radicals undergo reactions with NO by two paths. One is the oxidation of NO to NO_2 and the formation of alkoxy radicals,



and the other is the formation of alkyl nitrates,

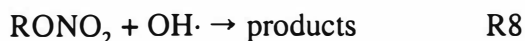
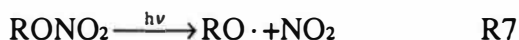


The hydrocarbon-OH radical reactions prefer the formation of secondary alkyl radicals over primary or tertiary radicals for a given carbon chain length (Atlas, 1991), thus the above mechanism favors the secondary alkyl nitrates. Studies have shown that the yield of alkyl nitrates from the oxidation of alkanes increases with increasing carbon chain length (Atkinson et al., 1982; Atlas et al., 1992; Flocke et al., 1998). The yield of alkyl nitrates is from < 0.014 for ethane to 0.33 for n-octane (Atlas et al., 1992).

Studies (Roberts, 1990; Bertman et al., 1995; Flocke et al., 1998) indicated that the branching ratio of the production of $RONO_2$ in reaction R6b to that of $RO\cdot$ in reaction R6a is very important. It impacts significantly not only the production of alkyl nitrates, but the tropospheric ozone production from organic compounds as well.

Alkyl nitrates undergo decomposition in a variety of ways. Roberts (1990) summarized that the destruction of the gas-phase organic nitrates are reactions with OH radicals, photolysis, and thermal decomposition. Multi-phased organic nitrates are removed by the uptake of cloud-water, aerosol or precipitation, and deposition on the

ground surface (Roberts, 1990). The importance of these processes is different to each compound type. For alkyl nitrates, the dominant decomposition processes are photolysis and reaction with OH radicals (Roberts and Fajer, 1989).



According to Bertman et al. (1995), the importance of these two decomposition pathways for alkyl nitrates is different under different conditions. Alkyl nitrates with long carbon chains can undergo destruction through both pathways. However, for alkyl nitrates $\leq \text{C}_5$, photolysis becomes to be predominant in their atmospheric removal. In general, primary alkyl nitrates favor reaction with OH radical, while secondary alkyl nitrates, mainly undergo decomposition by photolysis.

The lifetimes of alkyl nitrates in atmosphere are on the order of days. Short chain alkyl nitrates ($\text{C}_1\text{-C}_5$) have lifetimes ranging from weeks to several days. The lifetimes of long-chain alkyl nitrates decrease with increasing chain length. Alkyl nitrates are not very soluble in water, thus are not easily removed by wet deposition (Bertman et al., 1995; Roberts et al., 1989).

Due to the relative long life times of alkyl nitrates, Atlas (1988, 1992) and other researchers (Atherton, 1989) reported that alkyl nitrates can be transported from polluted, continental sites into clean, marine areas far from the source regions. They could act as a temporary reservoir of reactive nitrogen while transported long distances and release NO_x which could participate in photochemical reactions in remote areas (Bottenheim et al., 1993; Muthuramu et al., 1994) due to their decomposition under reaction R7. They have been also used as an index to study the anthropogenic influence on air mass history at remote sites (Bertman et al., 1995; Roberts, 1996). Because of

their formation from NO, alkyl nitrates could also be used as tracers to investigate the photochemical O₃ production from anthropogenic sources.

Overview of Measurement Methods

Since Atlas (1988) first identified a range of >C₃ alkyl nitrates in nonurban areas, more research has been performed on alkyl nitrates, and different sampling techniques and detection methods have been used for ambient measurements.

Sampling Methods

The methods that have been used to collect ambient samples include charcoal adsorption, cryogenic sampling and trapping on Tenax.

Charcoal adsorption tubes have often been used to collect ambient air samples for alkyl nitrates measurements (Atlas, 1988; Leitch, et al., 1994; O'Brien et al., 1995; Beine et al., 1996). After collecting the samples on the charcoal tubes, the alkyl nitrates were extracted with benzene or cyclohexanol (Atlas and Schauffler, 1991). After extraction, the charcoal tubes were cleaned and can be reused. Charcoal adsorption method usually worked for alkyl nitrates whose abundance is small in the atmosphere. This method is not capable of measuring methyl and ethyl nitrates which are the most abundant among alkyl nitrates.

A cryogenic sampling system was described in detail by Flocke et al. (1991) and Ridley et al. (1990). A piece of Teflon tubing used as a sample loop was connected to a six-port valve which can switch automatically. When sampling, the sample loop was immersed into liquid nitrogen to load ambient air. After loading, the sample loop was heated to allow the sample to enter into the GC column and be detected by electron capture detection (ECD). Significant advantages of the cryogenic system is that it can

perform the routine measurements automatically with a computer, and the sample volume is low, so it is applicable to field measurements. However the high detection limit of cryogenic system inhibits measurement of alkyl nitrates with low concentrations.

Tenax, which is a solid adsorbent, has been recently used to trap alkyl nitrates with C_3 to C_6 (Schneider et al., 1998; Ostling, 1999). Tenax was packed into a piece of stainless steel tube or silicosteel tube to make a sample trap. The amount of packed Tenax varied in different studies. Schneider et al. (1998), and Schneider and Ballschmiter (1999) packed 70-90mg to get 8 to 30L of ambient air; Ostling (1999) applied 3mg of Tenax to trap 100ml. After sampling, the Tenax traps were heated to desorb the alkyl nitrates and were then injected into capillary column and detected by ECD. Like cryogenic sampling system, this technique can also be used with a six-port electronic valve to make the sampling and injecting perform automatically. These advantages, including the low detection limit of the ECD, make it more appropriate in field measurements. However long trap times for large sample volumes sometimes lowered the efficiency of the measurements.

Separation and Detection

Alkyl nitrates are typically measured by gas chromatography (GC) with different detectors. ECD is usually used as a common detector, mass spectrometry (MS) is used to verify the results from the ECD, and chemiluminescent detection (CLD) is often used to quantify the alkyl nitrates. Buhr et al. (1990) measured alkyl nitrates by GC with ECD on a Carbomax 600 packed column, but they found that neither ethyl and 2-propyl nitrates, nor n-propyl and 2-butyl nitrates could be separated. Ostling (1999) used a DB-210 column and ECD to measure the C_1 - C_5 alkyl nitrates and found that

methyl, ethyl, 3-pentyl and n-pentyl nitrates co-eluted with unidentified compounds, and 2-butyl and isobutyl also co-eluted with each other.

The major problem of using ECD is the interference of halocarbons (Atlas et al., 1991; Atlas et al., 1992; Ostling, 1999), because ECD is more sensitive to halogenated hydrocarbons than to alkyl nitrates. In most cases, methyl and ethyl nitrates are very difficult to separate from halocarbons due to co-elution, thus causing difficulty in their quantification.

Research Objective

The air quality of a region is affected by not only local conditions, but also the chemical and transport history of the air, which is related to NO_x and NO_y. Alkyl nitrates play an important role in tropospheric chemistry, but their contribution is not yet understood well. To investigate further the relative importance and distribution of alkyl nitrates, measurements were made during the Southern Oxidants Study (SOS) 1999 Field Campaign in Nashville, TN. The research described here is a part of this event.

A main objective of this work is to improve on a previous method (Ostling, 1999) for alkyl nitrate measurement, which is applicable in a field study, to get high resolutions of alkyl nitrates separation and detection. In addition, the influence of air mass origin on alkyl nitrates levels will be investigated as well as the importance of alkyl nitrates to the total NO_y at a rural site in Dickson. The relationship of alkyl nitrates isomers and the relationship of alkyl nitrates with other organic nitrates will be also studied. Lastly, a photochemical box model will be developed for exploring the alkyl nitrates-O₃ chemistry.

CHAPTER II

EXPERIMENTAL

Measurement Site

Alkyl nitrates measurements were conducted at a rural site in Dickson, TN, 53 km northwest of the center of Nashville. This measurement site is located on a private farmland which contains a residence, and is surrounded by local vegetation. The site is influenced by the emissions of three nearby power plants. The Cumberland power plant, which gives off the largest amount of NO_x in North America, is located to the northwest of the site. The Johnsonville power plant is located to the southwest and the Gallatin power plant is to the northeast of the site. These two power plants are a further distance from the site and have lower NO_x emissions than the Cumberland power plant. Three highways pass by this site and converge in downtown Nashville. The map of measurement site is shown in Appendix A.

During the measurement, no other automobiles were allowed to pass through this site except the cars for that household in order to minimize the effect of local activities on the air samplings.

Analytical System

Alkyl Nitrates measurement was performed in Dickson from June 10 to July 15, 1999. Nine alkyl nitrates were measured: methyl (MN), ethyl (EN), isopropyl (IPN), n-propyl (NPN), 2-butyl (2BN), n-butyl (NBN), 3-pentyl (3PeN), 2-pentyl (2PeN) and n-pentyl (NPeN) nitrates.

Ambient air samples were drawn in by a pump from an inlet box mounted on a 10m tower in the field. The inlet box on the tower and instrument in the trailer were connected with Teflon tubing. Three three-port valves in the inlet box directed the flow of air (Figure 1). Valve 1 and valve 2 were used to scrub the ambient air to obtain a blank and for calibration runs. When these two valves were unpowered, the ambient air went through common (C) and normally open (NO) paths to the GC system. When they were powered, the ambient air was directed through a charcoal trap which was used to remove the organics from the ambient air to obtain a blank. Valve 3 was used for introducing a standard source of alkyl nitrates. When it was unpowered, standards went to a dump line. When doing calibrations, it was switched to powered mode, introducing the standards into the scrubbed ambient air to enter into the GC.

The air flow rates were set by using MKS mass flow controllers. The main inlet flow was approximately 1000 sccm and the sample flow was approximately 20 sccm. The air samples for alkyl nitrates were measured by a Varian 3500 GC with an ECD modified for automatic injection. A six-port Teflon rotary valve (Hamilton) was used to trap and inject the air samples (Figure 2). The measurement system is shown schematically in Figure 1.

There are two positions for the rotary valve. When sampling, the rotary valve was in the load mode so that the air samples were trapped for 5 minutes in a 22.86 cm length of silicosteel column packed with 31mg Tenax. After completion of the loading, the valve was switched to the inject mode, during which time, the trap was heated from room temperature ($\sim 20^{\circ}\text{C}$) to 175°C . The temperature was held constant at 175°C for 6 minutes to allow desorption of all air samples from Tenax, after which, the air samples were injected into the GC column (ID=0.32mm, length=30m, Restek Corp. DB1701)

Helium was used as the carrier gas at a flow rate of 3.0 ml/min. Nitrogen was

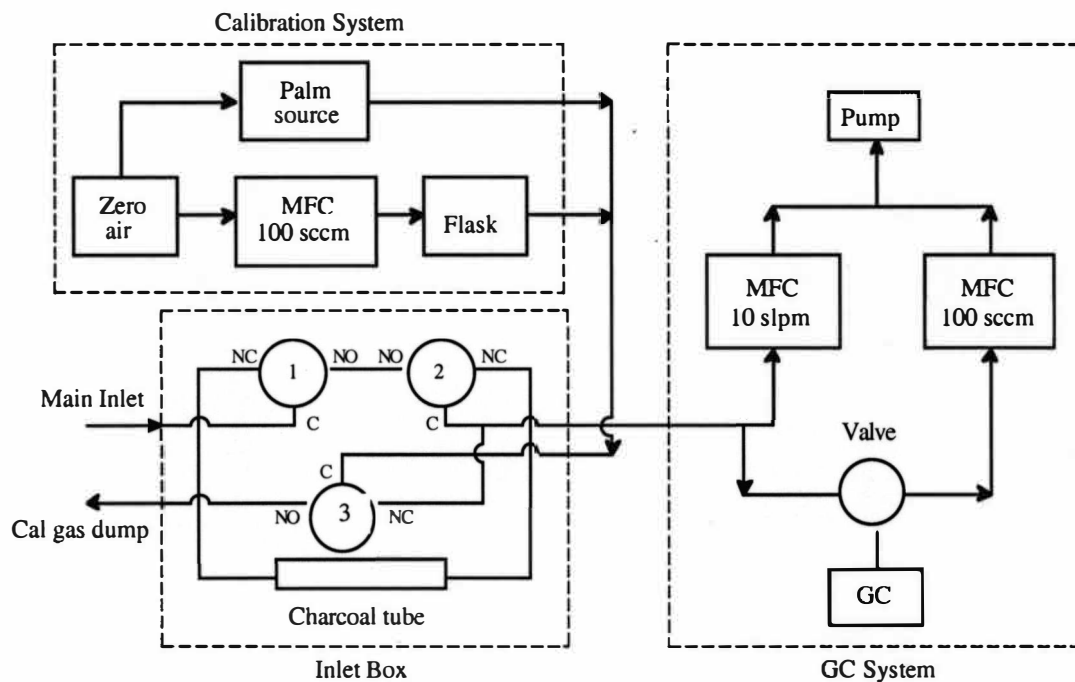


Figure 1. Scheme of Analytical System Used in Dickson.

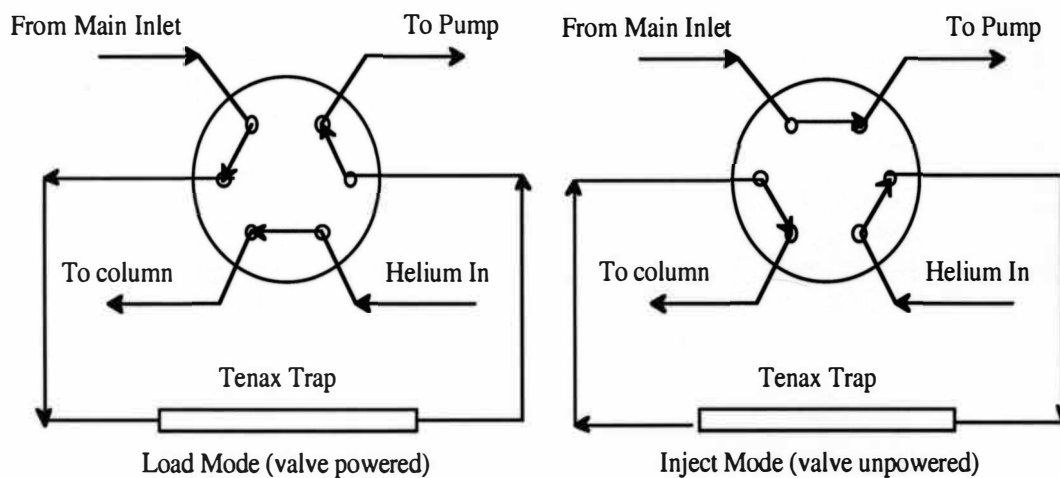


Figure 2. Diagram of 6-Port Valve Used in Dickson.

used as the makeup gas at a flow rate of 12 ml/min. In order to get optimal resolution of chromatograms, a temperature program for the GC column was adopted which is shown in Table 1. The detection limit under applied conditions is 0.07pptv. The above process was repeated for every air sample. Ambient air sampling was performed every 30 minutes. All these processes were operated automatically by the computer, so the sampling and measurement could be performed during the day and night.

Table 1
Temperature Program

| |
|--|
| Initial column temperature: 40°C |
| Final column temperature: 100°C |
| Initial temperature hold time: 10.00 min |
| Final temperature hold time: 1.00 min |
| Column rate in °C/min: 3.6 |
| Detector Temperature: 150°C |
| Method complete – end time: 27.66 min |

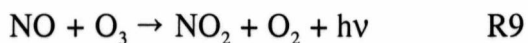
Calibration and Quantification

Separate calibrations for the measured alkyl nitrates were performed prior to and during the field measurement by using standards. Three methods were applied for the calibrations. A Pyrex flask or a diffusion cell was used qualitatively for the determination of the retention times of the alkyl nitrates. A permeation source or diffusion cell was used quantitatively to determine the response of the GC to the concentrations of the alkyl nitrates standards. Since 3-pentyl, 2-pentyl and n-pentyl

nitrates were very low during the measurement period, only six alkyl nitrates were calibrated quantitatively (methyl, ethyl, n-propyl, isopropyl, n-butyl and 2-butyl nitrates). The standard sources of methyl, isopropyl and n-propyl nitrates were supplied by permeation source while ethyl, 2-butyl and n-butyl nitrates standards were contained in diffusion cells when doing calibrations. To obtain the chromatographic peaks on scale, the trap time of the standards was adjusted. The calculated concentrations for standards was scaled to 5 minutes as air samples.

The concentrations of six alkyl nitrates standards were determined by a commercial NO_x chemiluminescence detection instrument (Thermal Environmental Instruments, model 42S). The principle of this calibration technique is as follows.

When the gas phase NO reacts with O₃, excited NO₂ will be produced. It then decays to the ground state, giving off a photon of light.



The light intensity is linearly proportional to the concentration of NO. When a standard alkyl nitrate sample is introduced into this calibration system, it will first undergo a conversion to NO in a molybdenum converter at 325°C. Calibration was performed using a standard NO source (Scott-Marrin, Inc.).

Multipoint calibrations were performed 11 times during the whole measurement period, and spot calibrations were done every few days throughout the whole field time to ensure the measurement quality. The sensitivity of Model 42S NO_x analyzer as a function of time and the calibration factors of alkyl nitrates vs time are shown in Appendix B. The precision of all quantified alkyl nitrates are less than 5%.

Syntheses of Alkyl Nitrates Standards

Except isopropyl nitrate, which was bought commercially from Aldrich, the remaining alkyl nitrates standards were synthesized in the lab. The syntheses of methyl and ethyl nitrates were from the reactions of methanol and ethanol with nitric acid, respectively (Blatt, 1943). The others were synthesized by the reactions of corresponding alkyl bromides and silver nitrate in acetonitrile (Ferris et al., 1953). All synthetics were purified by vacuum distillation.

CHAPTER III

RESULTS

Chromatography

With the developed GC method described in Chapter II, methyl, ethyl, isopropyl, n-propyl, 2-butyl, n-butyl, 3-pentyl, 2-pentyl and n-pentyl nitrates were measured and were quantified except for 3-pentyl, 2-pentyl and n-pentyl due to quite low mixing ratio showing in the ambient air. Figure 3 shows the chromatogram of the mixture of standard alkyl nitrates in dodecane in Dickson. A typical chromatogram of ambient air sample in Dickson is showed in Figure 4.

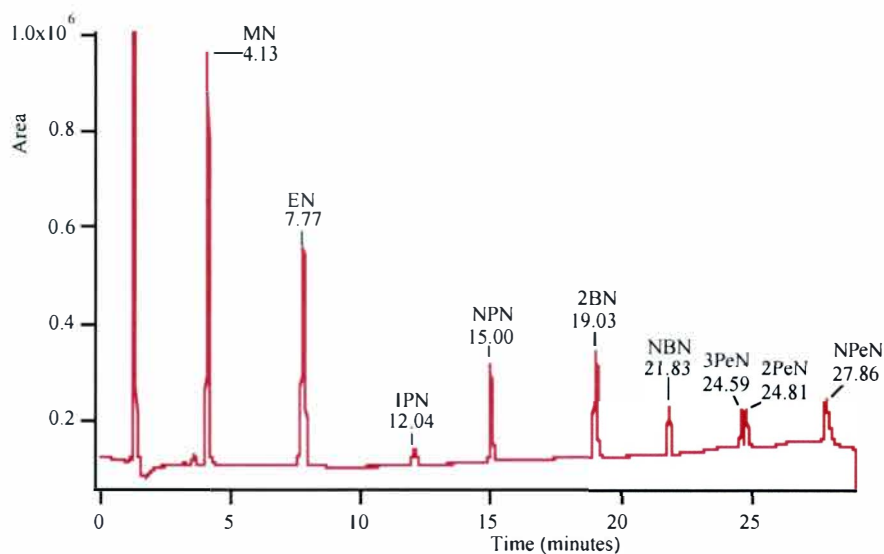


Figure 3. Chromatogram of the Standard Alkyl Nitrates Mixture in Dickson During the 1999 SOS Field Campaign.

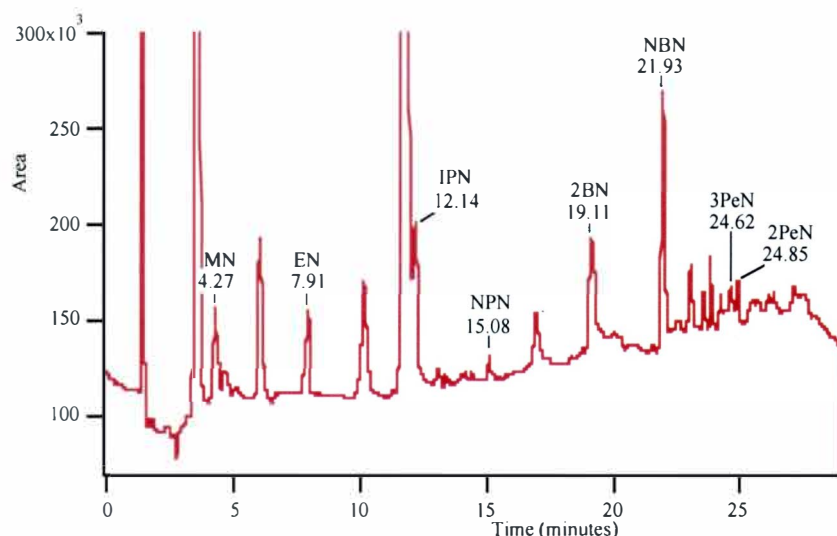


Figure 4. Chromatogram of Ambient Alkyl Nitrates in Dickson During the 1999 SOS Field Campaign.

Isopropyl nitrate co-eluted with an unidentified compound. The peaks of 3-pentyl and 2-pentyl nitrates were very small. n-pentyl nitrate was not resolved. The remaining alkyl nitrates did not co-elute with other compounds, indicating the developed GC method is applicable for most of the considered alkyl nitrates.

General Results

The variation in mixing ratios of the alkyl nitrates as a function of time are shown in Figure 5-10. The statistics of alkyl nitrates are listed in Table 2.

As can be seen from Figure 5, methyl nitrate showed two highest peaks, one was between June 22 and June 23, another was around June 26; the lowest mixing ratio period was seen from July 4 to July 6. The highest mixing ratio of ethyl nitrate was shown around June 21 (Figure 6), while from July 2 to July 7, it showed very low concentrations.

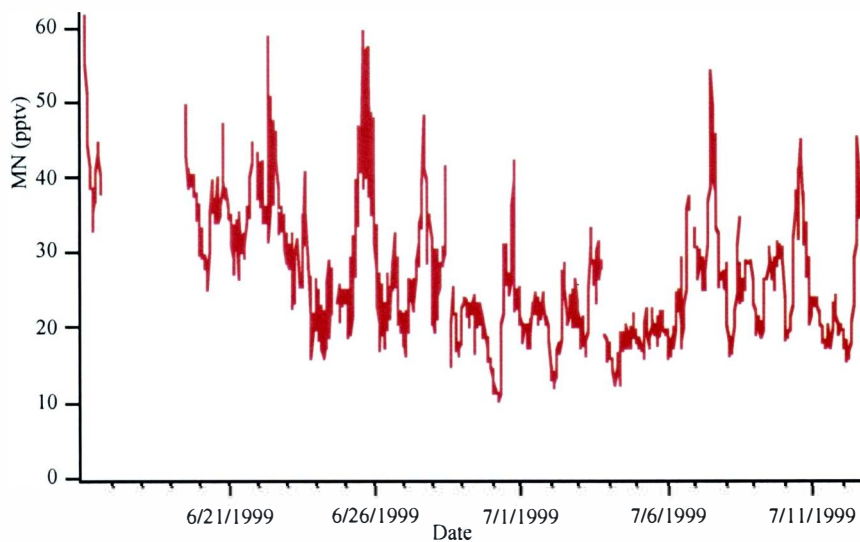


Figure 5. Time Series of Methyl Nitrate in Dickson During the 1999 SOS Field Campaign.

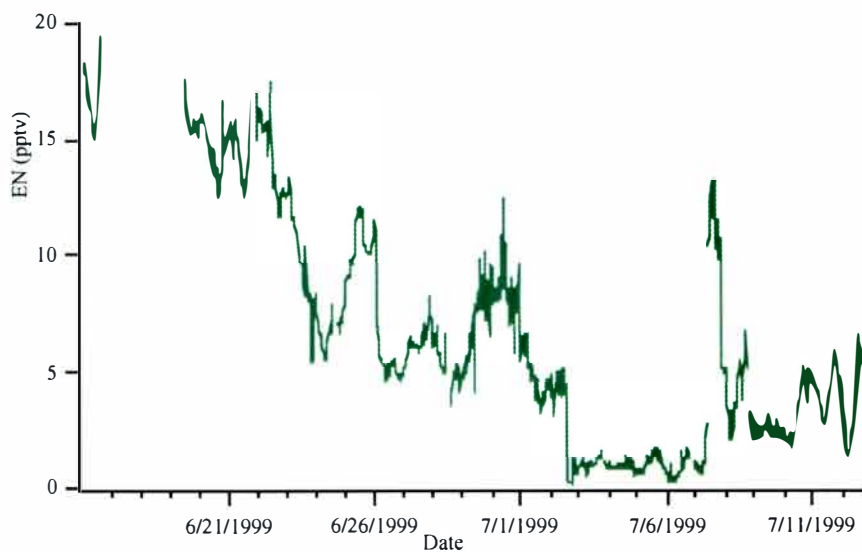


Figure 6. Time Series of Ethyl Nitrate in Dickson During the 1999 SOS Field Campaign.

Isopropyl nitrate showed very similar trend to ethyl nitrate. It also had the

highest peaks around June 21, and had low mixing ratios from July 2 to July 7 (Figure 7). Figure 8 showed that n-propyl nitrate had the highest peak between June 22 and 23,

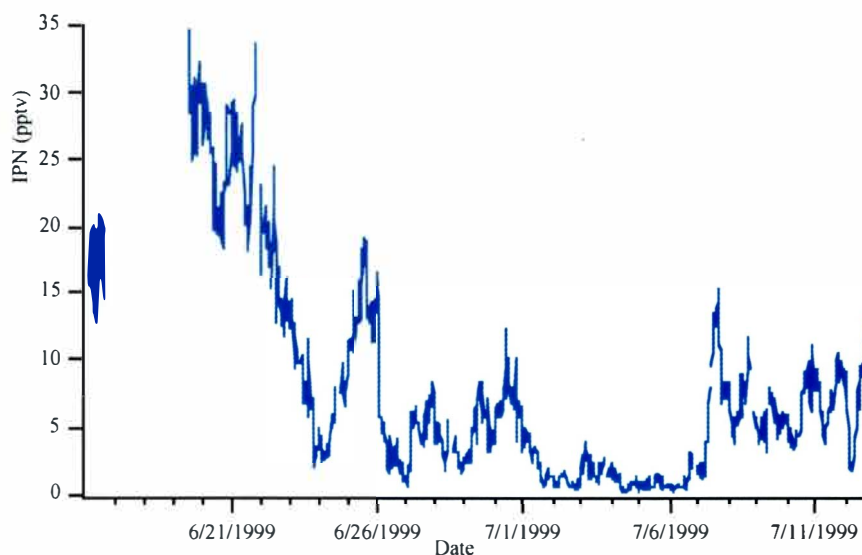


Figure 7. Time Series of Isopropyl Nitrate in Dickson During the 1999 SOS Field Campaign.

the lowest peak period was around July 5.

Figure 9 is the variation of mixing ratios of 2-butyl nitrate with time. Two higher peaks were seen from June 22 and June 25 respectively. The lowest mixing ratios were shown between July 4 and July 6. For n-butyl nitrate, the mixing ratios were higher before June 23, and reached the highest levels around June 23, after that, the mixing ratios decreased and kept low (Figure 10).

The average mixing ratios of the sum of C1-C4 alkyl nitrates over the whole measurement period was 56.83 pptv, with a range from 17.50 to 139.0 pptv (Table 2). Among these alkyl nitrate, methyl nitrate showed the most abundant, n-propyl nitrate was the least.

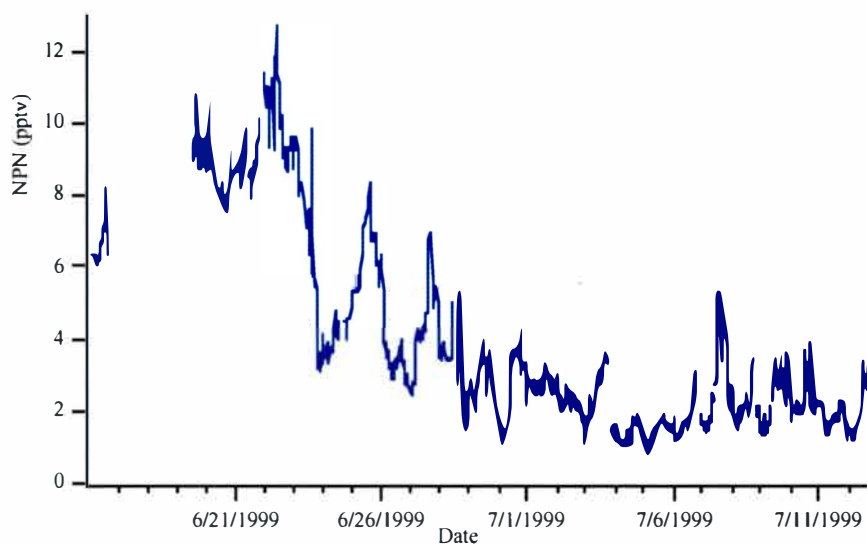


Figure 8. Time Series of n-Propyl Nitrate in Dickson During the 1999 SOS Field Campaign.

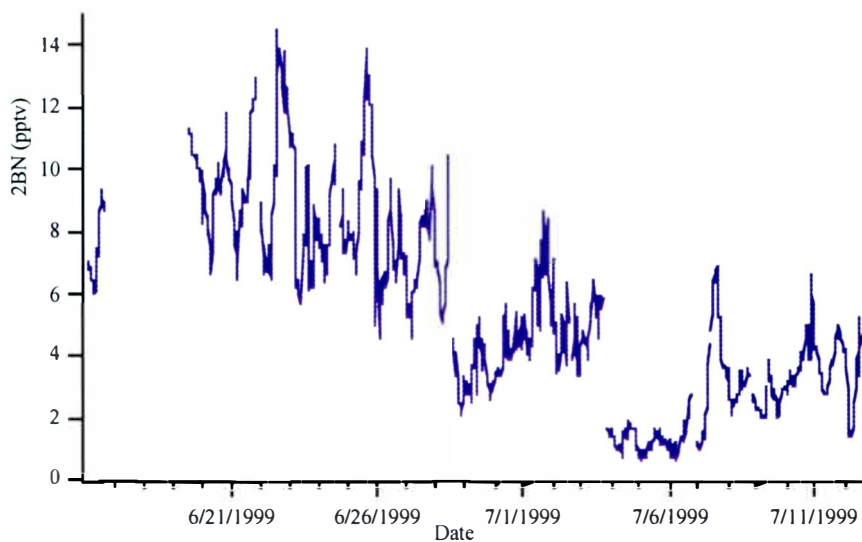


Figure 9. Time Series of 2-Butyl Nitrate in Dickson During the 1999 SOS Field Campaign.

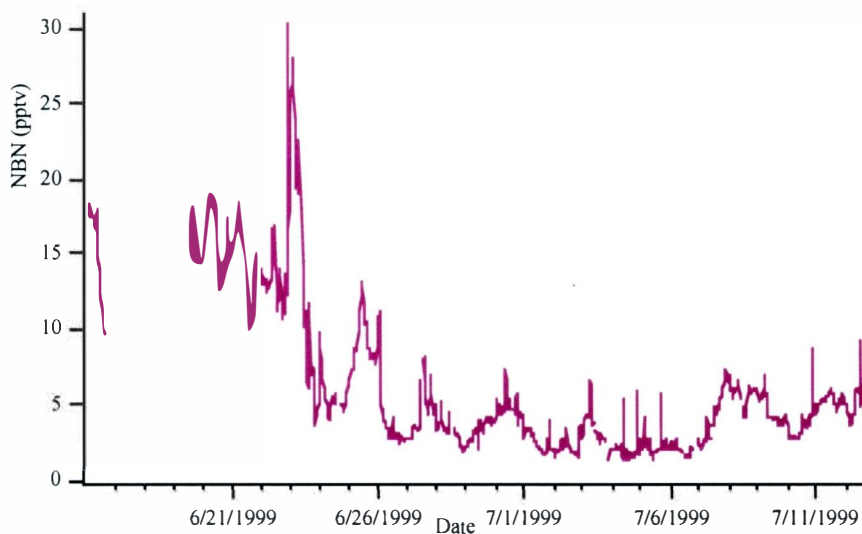


Figure 10. Time Series of n-Butyl Nitrate in Dickson During the 1999 SOS Field Campaign.

Table 2

Statistics of Alkyl Nitrates During 1999 SOS Field Campaign

| Compound | Number of Detectable Points | Average (pptv) | Minimum (pptv) | Maximum (pptv) |
|--------------------------|--------------------------------|-------------------|-------------------|-------------------|
| MN | 1094 | 26.68 | 10.43 | 61.62 |
| EN | 1091 | 8.36 | 1.91 | 19.40 |
| IPN | 1091 | 7.88 | 0.07 | 34.60 |
| NPN | 1090 | 3.96 | 0.79 | 12.72 |
| 2BN | 1087 | 5.46 | 0.62 | 14.54 |
| NBN | 1084 | 6.34 | 1.43 | 30.30 |
| ΣRONO_2^* | 1088 | 56.83 | 17.50 | 139.0 |
| NO_y^{**} | 6800 | 5.08 | 0.80 | 78.70 |

Table 2-Continued

| Compound | Number of Detectable Points | Average (pptv) | Minimum (pptv) | Maximum (pptv) |
|--------------------|--------------------------------|-------------------|-------------------|-------------------|
| NO ** | 1452 | 0.25 | bd | 6.14 |
| NO ₂ ** | 1232 | 1.37 | 0.07 | 16.43 |

*. The sum of MN, EN, IPN, NPN, 2BN and NBN. Same to the following.

**. Data from Tennessee Valley Association (TVA). Unit is ppbv.

bd. Below detection limit.

CHAPTER IV

DISCUSSION

Influence of Air Mass Origin on Alkyl Nitrates Levels

The atmosphere acts like a chemical reactor, in which volatile organic compounds (VOC) and other reduced gases are emitted from various biogenic and anthropogenic sources. These emissions are transported by winds and turbulence, chemically processed and converted to products. Since it is an open system in which energy and mass can be exchanged, and transport and chemistry can be coupled due to the similarity of chemical lifetimes and transport time scales (Kley, 1997), the atmospheric chemistry in a region is affected not only by local conditions but transport as well. For example, a city can be taken as a point source of air pollution, from this point, the polluted air can be spread into and mixed with the clean surrounding air due to advection and convection, meanwhile the polluted air is diluted as it spreads out. So mixing and dilution play significant roles in the regional chemistry. On the other hand, transport may import chemical species that originated far away into the local ambient air. Chemical reactions in troposphere also depends on temperature, solar flux, time spent in different regime, thus making chemistry more complex in ambient air than in isolated chambers. Therefore it is important to analyze the chemical and transport history in order to understand the local air mass composition and its aging.

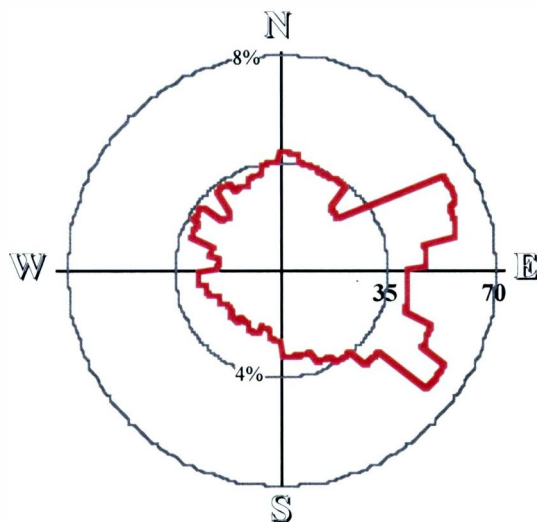
As described before, the Dickson site is surrounded by local vegetation, power plants and urban area. Transport of air masses from different directions could bring different emissions. In order to study the influence of air mass origin on alkyl nitrates levels, the alkyl nitrates data was filtered according to the wind direction (Figure 13 and

14). Wind direction was separated into quadrants in this study: ①. Northeast (NE). ②. Southeast (SE). ③. Northwest (NW). ④. Southwest (SW). Since Nashville is located in the east of Dickson, anthropogenic sources would be brought to the site when wind came from northeast and southeast. Wind from NW would bring NO_x from Cumberland power plant. Transport from the southwest would bring clean rural air. Since alkyl nitrates are assumed to form primarily from anthropogenic sources, higher mixing ratios could be seen with wind from the northeast and southeast. Lower mixing ratios of alkyl nitrates were seen with flow from southwest where there are little anthropogenic sources to the site.

Since all measured alkyl nitrates except for methyl nitrate showed similar behaviors under different wind directions, they are reported in one plot as the sum of their mixing ratios with wind directions (Figure 11). Methyl nitrate is shown in Figure 12. There was no significant change in the mixing ratio of methyl nitrate with wind direction. The other alkyl nitrates had higher mixing ratios under northeast and southeast flows, and lower mixing ratios when air came from the northwest and southwest.

Some studies (Flocke et al., 1998; Walega et al., 1992) also reported that the behaviors of methyl nitrate was different compared to other alkyl nitrates. Several possible reasons have been pointed out: a possible reaction of methanol with HNO₃ to produce methyl nitrate, the competition of the production rate of CH₃O₂ to methyl nitrate with the production rate of CH₃O radicals, which react with O₂ to form formaldehyde, the intramolecular decomposition of peroxyacyl nitrates to methyl nitrate (Flocke et al., 1998). Since no further evidence can verify these assumptions, more study should be done on methyl nitrate.

The distribution of alkyl nitrates under different wind direction is shown in



Note: The red curves indicate the mean mixing ratios of alkyl nitrates averaged over 20 degree intervals of wind. The numbers on circles indicate the mixing ratios. This note also applies to the following wind plots.

Figure 11. Sum of C₂-C₄ Alkyl Nitrates with Wind Direction.

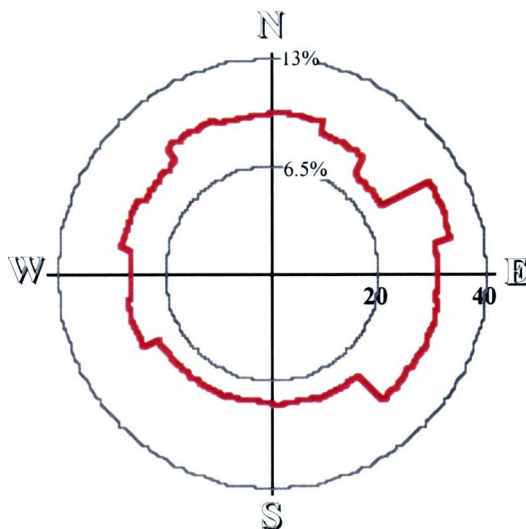


Figure 12. Methyl Nitrate with Wind Direction.

Table 3. Alkyl nitrates were seen the highest from northeast with average mixing ratios 68.12, while the lowest from northwest with 24.81 for the average mixing ratios.

Table 3
Statistics of Sum of Alkyl Nitrates Under Wind Direction

| Wind Direction | # of points | Average (pptv) | Maximum (pptv) | Minimum (pptv) |
|----------------|-------------|-------------------|-------------------|-------------------|
| Northeast | 123 | 68.12 | 131.0 | 29.40 |
| Northwest | 194 | 24.81 | 130.0 | 23.00 |
| Southeast | 306 | 59.48 | 139.0 | 18.60 |
| Southwest | 358 | 46.98 | 121.0 | 17.50 |

Contribution of Alkyl Nitrates to Total Oxidized Nitrogen

The initial interest to alkyl nitrates resulted from an attempt to account for the shortfall of total NO_y. Studies indicated that alkyl nitrates contribute different amounts to NO_y in different areas. The diurnal trend of $\sum \text{RONO}_2/\text{NO}_y$ (Figure 13) shows that the contribution of C₁-C₄ alkyl nitrates to NO_y ranged from 1.1% to 1.9%, indicating these C₁-C₄ alkyl nitrates were a small part of NO_y in Dickson. $\sum \text{RONO}_2/\text{NO}_y$ was higher in the afternoon and early evening than in the morning and midnight. The individual diurnal behaviors of $\sum \text{RONO}_2$ and NO_y are shown in Figures 14 and 15. As can be seen, $\sum \text{RONO}_2$ has a similar diurnal trend to that of $\sum \text{RONO}_2/\text{NO}_y$. However, the diurnal trend of NO_y shows differently from that of $\sum \text{RONO}_2/\text{NO}_y$, higher levels of NO_y was seen in the morning and lower levels around early evening.

The diurnal trends of $\sum \text{RONO}_2/\text{NO}_y$ under different wind directions were also explored (Figures 16, 17, 18, 19). It is interesting to see that $\sum \text{RONO}_2/\text{NO}_y$ did not

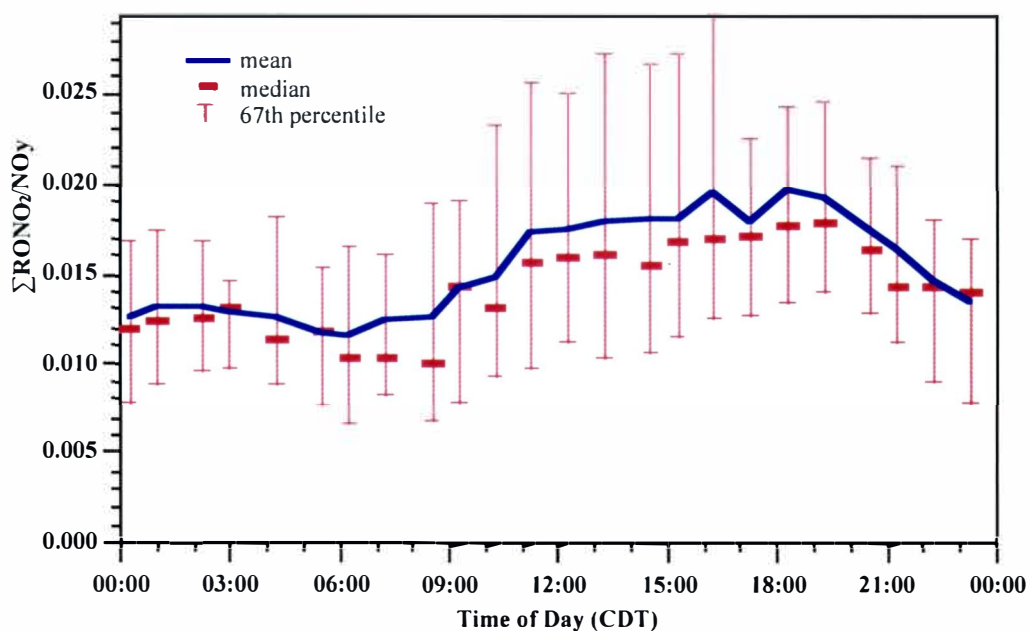


Figure 13. Diurnal Trend of $\Sigma \text{RONO}_2/\text{NO}_y$ in Dickson.

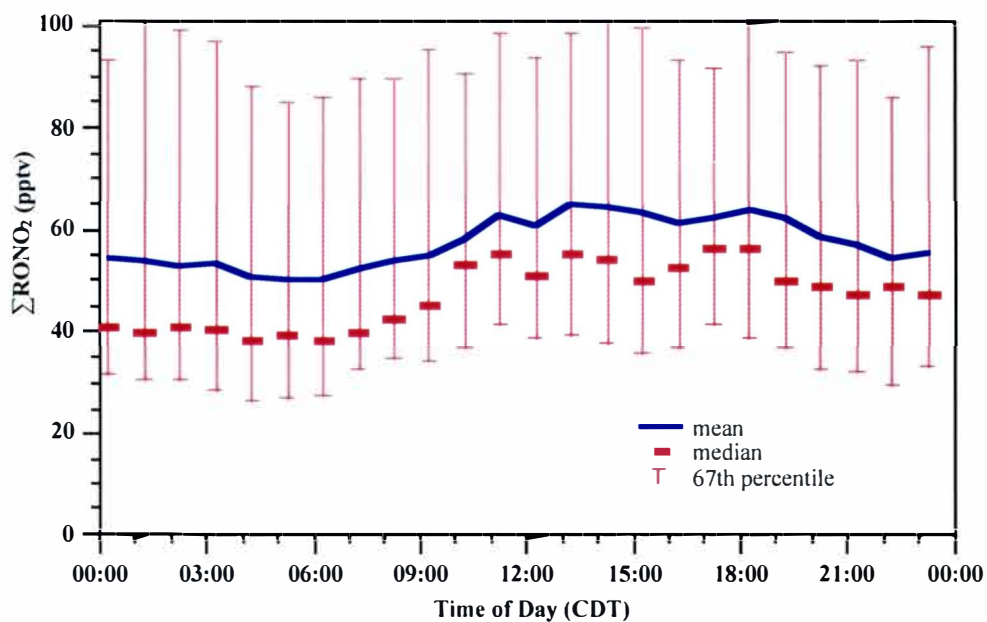


Figure 14. Diurnal Trend of the Sum of Alkyl Nitrates in Dickson.

show any diurnal trends under any of the four wind directions. However, the ratio of the sum of alkyl nitrates to NO_y under southwesterly wind was generally higher than that from other flow directions.

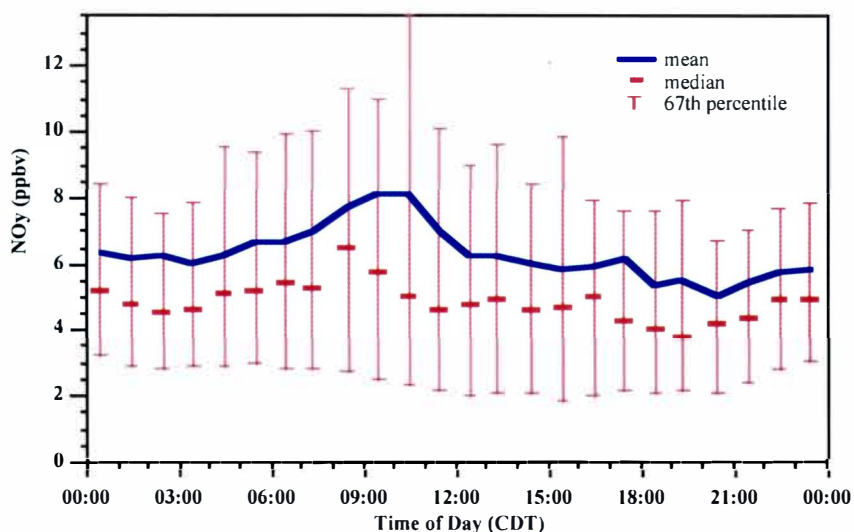


Figure 15. Diurnal Trend of NO_y in Dickson.

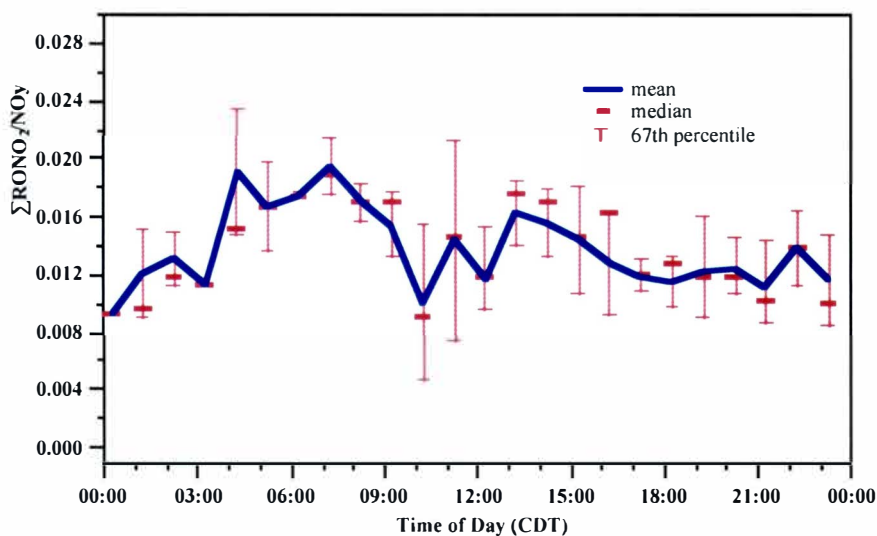


Figure 16. Diurnal Trend of $\Sigma\text{RONO}_2/\text{NO}_y$ Under Northeast Wind.

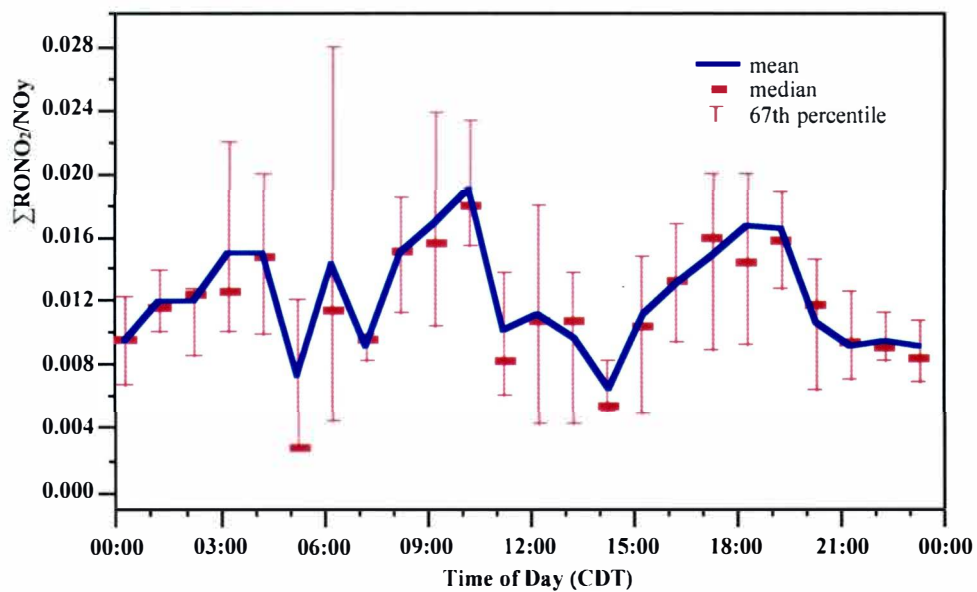


Figure 17. Diurnal Trend of $\Sigma\text{RONO}_2/\text{NO}_y$ Under Northwest Wind.

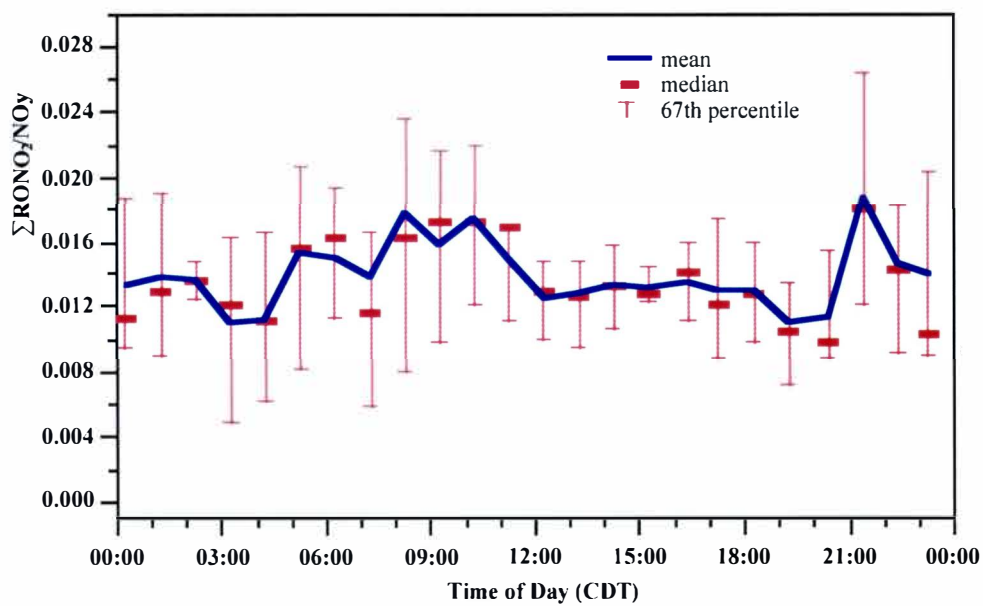


Figure 18. Diurnal Trend of $\Sigma\text{RONO}_2/\text{NO}_y$ Under Southeast Wind.

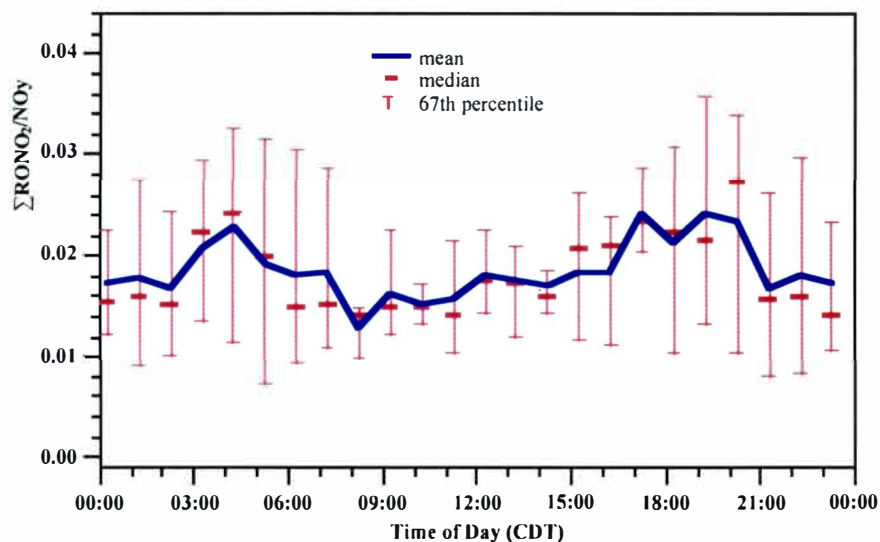


Figure 19. Diurnal Trend of $\Sigma\text{RONO}_2/\text{NO}_y$ Under Southwest Wind.

The contribution of alkyl nitrates to NO_y as a function of wind direction (Figure 20) also shows that the highest ratio was seen with southwest flows, which brought

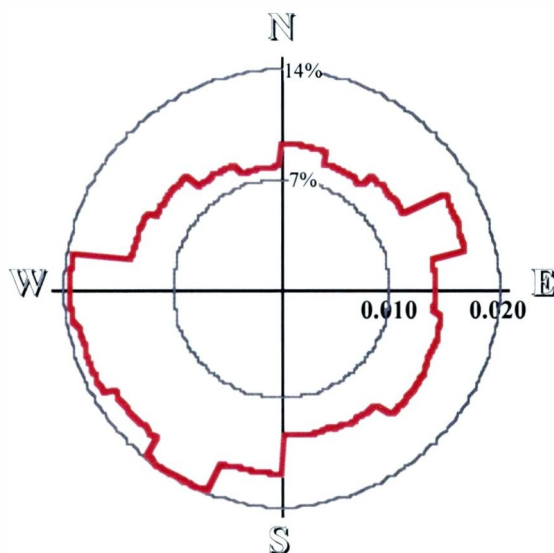


Figure 20. $\Sigma\text{RONO}_2/\text{NO}_y$ with Wind Direction.

clean air. Possible explanations for this phenomenon could be made as follows. When air flow came from southeast and northeast, NO_y species formed more than they lost, because air flow kept bringing anthropogenic emission. However, under southwesterly wind, some NO_y species which count for considerable amount to NO_y can be lost during transport without anthropogenic emission due to their short lifetimes, such as HNO₃ (Finlayson-Pitts and Pitts, 2000). Figure 21 verified the above assumption. NO_y showed higher level under wind from northeast and southeast than under southwest. Since alkyl nitrates have longer lifetimes, they did not lose too much compared to NO_y, thus resulting the high ratios of $\Sigma\text{RONO}_2/\text{NO}_y$ under southwesterly wind.

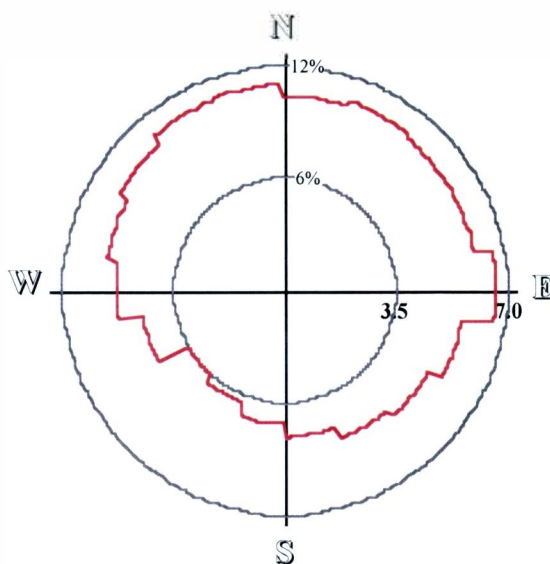


Figure 21. NO_y with Wind Direction.

Relationship Between Alkyl Nitrates Isomers

The relationship of two alkyl nitrates isomers which originate from the same parent hydrocarbon can be illustrated schematically in Figure 22 by taking butyl nitrates as an example.

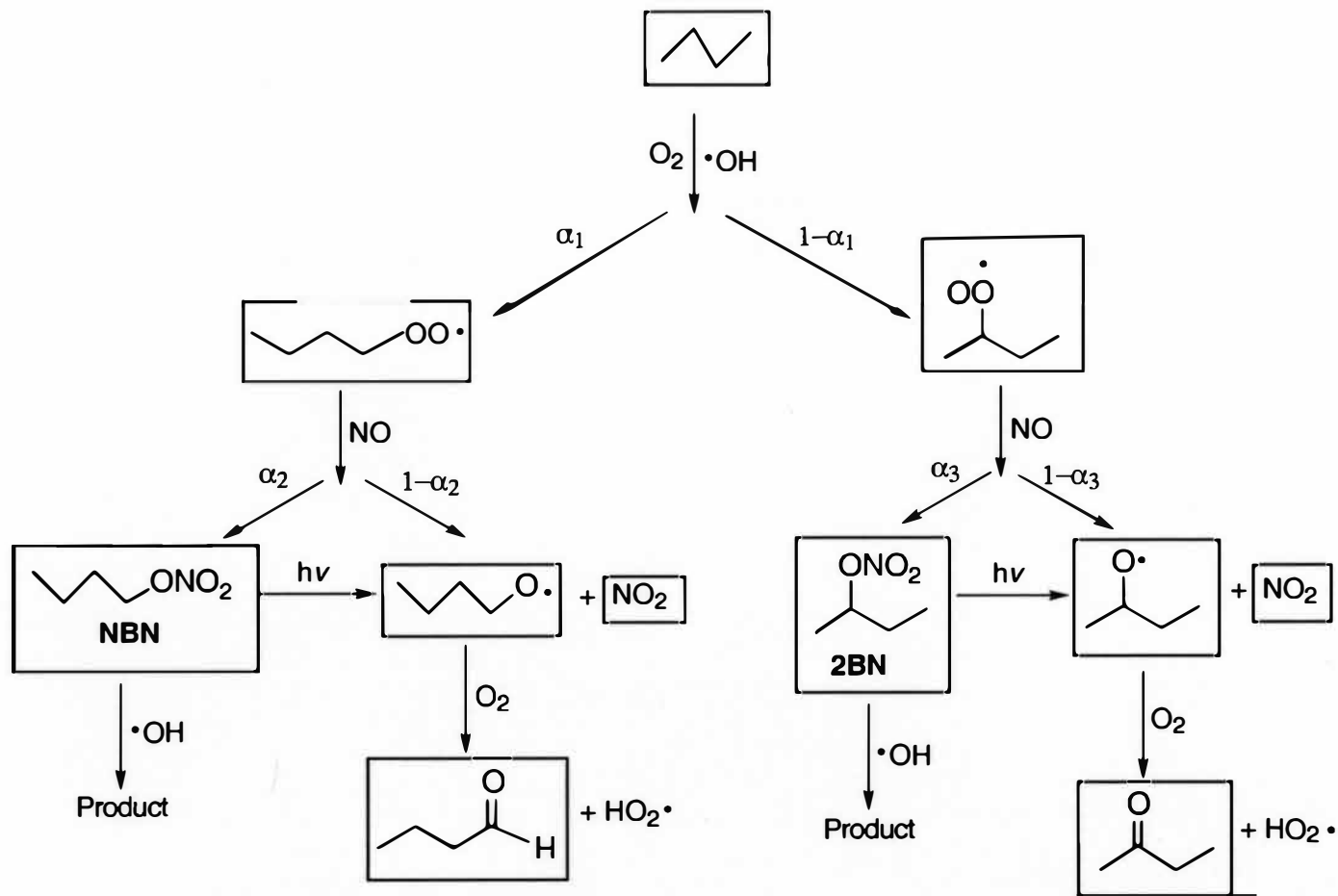


Figure 22. Formation of Butryl Nitrates in Troposphere.

The formation of the primary alkyl nitrate NBN and the secondary alkyl nitrate 2BN depend on the branching ratios: α_1 , α_2 , α_3 . Assuming the photochemical losses of alkyl nitrates are negligible compared to production, the ratio of the secondary to the primary alkyl nitrates are related according to:

$$\frac{[\text{RONO}_2]_s}{[\text{RONO}_2]_p} = \frac{(1 - \alpha_1)\alpha_3}{\alpha_1\alpha_2} \quad \text{R10}$$

where $[\text{RONO}_2]_s$ and $[\text{RONO}_2]_p$ are the primary and secondary alkyl nitrates respectively.

Since alkyl nitrates formation favors the secondary alkyl nitrates, and the primary alkyl nitrates have shorter atmospheric lifetimes than secondary nitrates, if assuming that the only sources of alkyl nitrates are their parent hydrocarbons and no loss or the same loss rate of alkyl nitrates isomers, the ratios of IPN/NPN and 2BN/NBN should increase with increasing the photochemical processing time. Under air flow from the southwest, which brought clean rural air, the ratios of IPN/NPN and 2BN/NBN should be higher than those under the other air flow. The measured ratios of IPN/NPN and 2BN/NBN in Dickson as a function of wind direction are shown in Figure 23 and 24. It is interesting to note that the higher ratio of IPN/NPN was seen under northeast flows, while 2BN/NBN has higher ratios in air from the southwest. The behaviors of IPN/NPN ratios observed at Dickson may indicate that the above assumption could not be applicable in Dickson, and other sources for the formation of IPN or NPN or both could be important, such as the cleavage of larger alkoxy radicals with longer carbon chain to form smaller alkoxy radicals (Finlayson-Pitts and Pitts, 2000). Since no measurements of such larger alkoxy radicals were performed during SOS, more studies should be explored in the future.

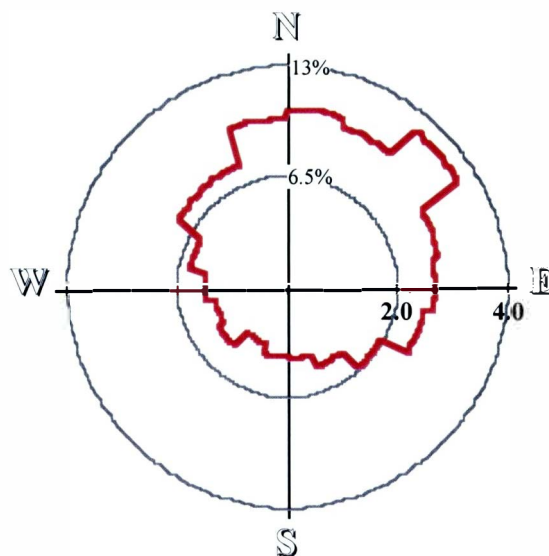


Figure 23. IPN/NPN Ratio with Wind Direction.

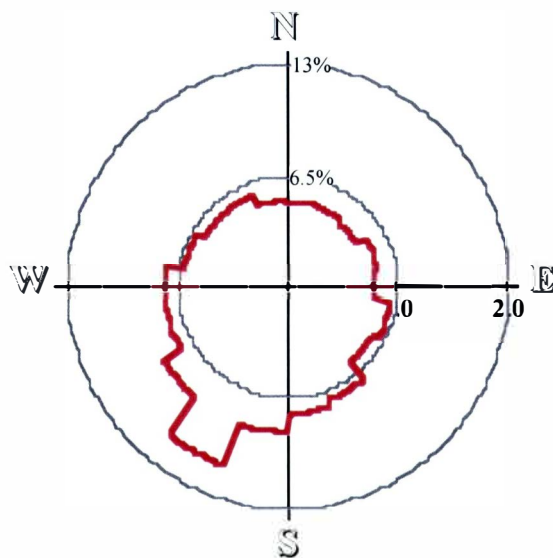


Figure 24. 2BN/NBN Ratio with Wind Direction.

Relationship Between NPN and PPN

When an air mass is transported to the measurement site, photochemical

reactions can occur. Flocke et al. (1998) indicated that the ratio of alkyl nitrate isomers can be used as an index to classify an air mass by the extent of photochemical processing, which is also referred as photochemical age. Since n-propyl nitrate (NPN) and peroxypropionic nitric anhydride (PPN) are formed from propane as shown in Figure 25, the ratio of NPN/PPN could also be used to learn something about

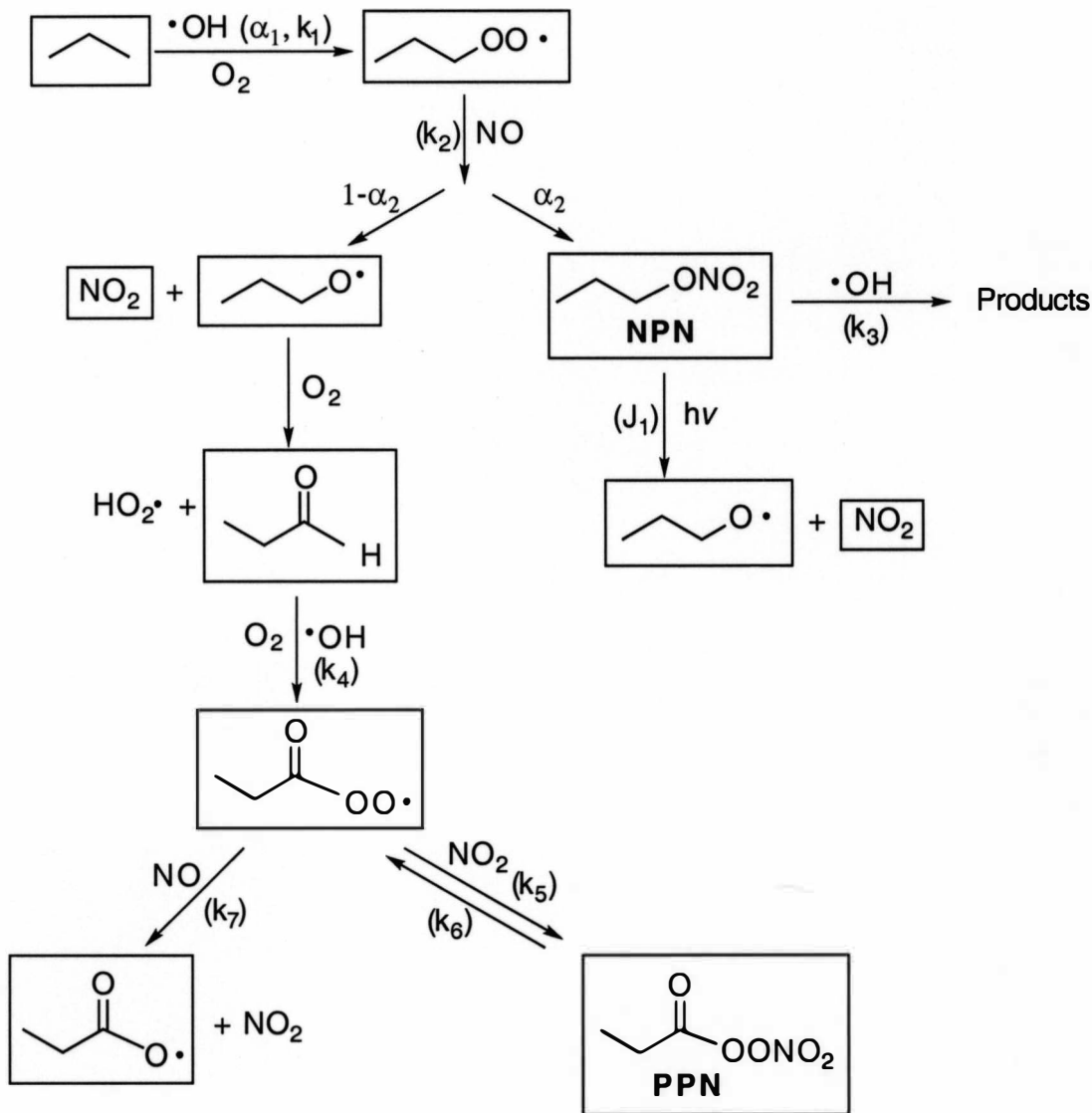


Figure 25. Formation of NPN and PPN in Troposphere.

photochemical age of air mass. Since the lifetime of PPN is shorter than that of NPN, the ratios of NPN/PPN in photochemically aged air should be higher than those in air under fresh emissions. Figure 26 shows the ratios of NPN/PPN as a function of wind directions. The ratio of NPN/PPN is at the highest in air flow from southwest, indicating air was photochemically aged. The lowest ratio levels are seen in air flow from the northeast, so air was relatively fresh. Further investigation is needed to verify the assumption that NPN/PPN ratios can be used as an index of air mass age.

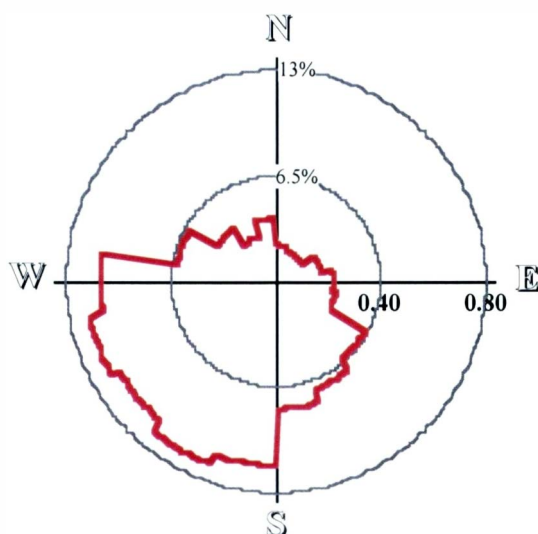


Figure 26. NPN/PPN with Wind Direction.

Photochemical Box Model Simulation

As indicated in the previous chapter, the measured ratios of alkyl nitrates isomers exhibit different behaviors under different air flows. The potential reason for that phenomenon is that wind could bring not only different organic precursors of alkyl nitrates but also different NO_x levels. The measured NO_x levels as a function of wind is shown in Figure 27. It can be seen that NO_x levels were much higher under northwest

air flow, because Cumberland power plant emitted a considerable amount of NO_x. In order to understand different behaviors of alkyl nitrates isomers with various NO_x

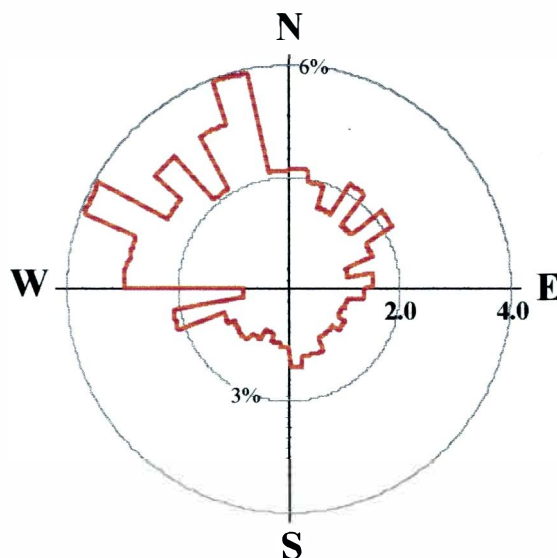


Figure 27. NO_x Under Wind Direction.

levels, and further, to assess the formation of alkyl nitrates isomers or the relationship of alkyl nitrates with organic nitrates, a powerful tool is to build a kinetic photochemical box model (PBM) (Jin and Demerjian, 1993) which simulates the chemistry properly and effectively.

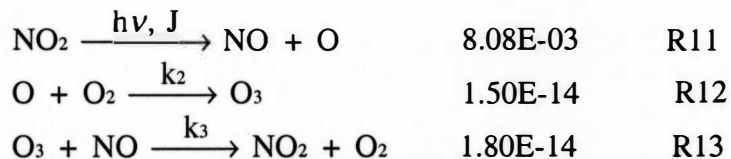
In photochemical box models, the chemical reactions are gas-phase and simulated using kinetic mechanism that may include diurnal variation of photolytic rate constants (Schere and Demerjian, 1978). Temperature, relative humidity and some other meteorological factors can also be incorporated into model. Dilution can occur and emission can be injected during the simulation (Schere and Demerjian, 1978). In PBM, hydrocarbons and NO_x are converted to O₃ and other secondary pollutants such as PAN, PPN and alkyl nitrates by chemical reactions (Finlayson-Pitts and Pitts, 2000).

Therefore the model can provide a link between the starting compounds and the changes in pollutant concentration levels. The model output can be used to generate a series of time-dependant concentrations of O_3 and concentrations of other secondary species of interest, which result from simulated chemistry (Finlayson-Pitts and Pitts, 2000).

Photochemical box models have been used in many studies to address different issues in atmospheric chemistry. Jin and Demerjian (1993) built a PBM to study the relationship of O_3 with NO_x and CO; Pippin (1999) set up a PBM to explore the chemistry of the family of peroxyacyl nitrates (PANs) in the atmosphere. However, little study has been done on alkyl nitrates- O_3 chemistry with models. Ostling (1999) derived a simple analytical model to predict the ratios of n-propyl nitrate and peroxypropionyl nitrate under different NO_2/NO ratios, but the model was too simplified to do further study on alkyl nitrates. Therefore a photochemical box model was developed for this study and discussed below.

Testing Photochemical Box Model

The photochemical box model for alkyl nitrates used in this study is ChemK, which was developed by Whitten and Hogo (1980), and modified by J. Barker (Personal communication). To verify the photochemical box model (ChemK) works properly, a simplified model, including the basic photochemical cycle of NO_2 , NO and O_3 , was set up. The reactions for this NO_x and O_3 cycle are:



If consider only these reactions are taking place in a small chamber, assume initial concentrations of NO and NO_2 have been given, O_2 concentration is constant, M

is a third body. After the irradiation begins, the rate of change in NO_2 concentration is determined by:

$$\frac{d[\text{NO}_2]}{dt} = -J[\text{NO}_2] + k_3[\text{O}_3][\text{NO}] \quad \text{R14}$$

similar calculations apply to the rate of change in $[\text{O}]$, $[\text{NO}]$ and $[\text{O}_3]$ as follows:

$$\frac{d[\text{O}]}{dt} = J[\text{NO}_2] - k_2[\text{O}][\text{O}_2][\text{M}] \quad \text{R15}$$

$$\frac{d[\text{NO}]}{dt} = J[\text{NO}_2] - k_3[\text{O}_3][\text{NO}] \quad \text{R16}$$

$$\frac{d[\text{O}_3]}{dt} = -k_3[\text{NO}][\text{O}_3] + k_2[\text{O}][\text{O}_2] \quad \text{R17}$$

Since there are no other incoming species or emission sources of NO_x , the pseudo-steady state approximation can be achieved after few seconds. At steady-state (ss), the concentration of O_3 is given by:

$$[\text{O}_3]_{\text{ss}} = \frac{J[\text{NO}_2]}{k_3[\text{NO}]} \quad \text{R18}$$

The expression R18 indicates that the steady state O_3 concentration is proportional to the $[\text{NO}_2]/[\text{NO}]$ ratio.

If the above three reactions are put into a box model, the simulated results should be in agreement with the equation R18 if the model runs properly. Therefore it is worthwhile to examine the behavior of the model as a function of initial concentrations of NO_x .

Figure 28 shows the mixing ratio as a function of time for the following initial conditions that correspond to very polluted conditions:

$$[\text{NO}_2]_0 = 406.5 \text{ ppb} \quad [\text{NO}]_0 = 20.3 \text{ ppb} \quad [\text{O}_3]_0 = 40.6 \text{ ppb}$$

As can be seen, NO_2 , NO and O_3 achieved steady state very quickly. At steady state, the ratio of $[\text{NO}_2]/[\text{NO}]$ was 5 and the O_3 concentration was 90.8 ppbv. If $[\text{NO}_2]/[\text{NO}]$ ratio of 5 is applied to $[\text{O}_3]_{\text{ss}}$ equation R18, the calculated O_3

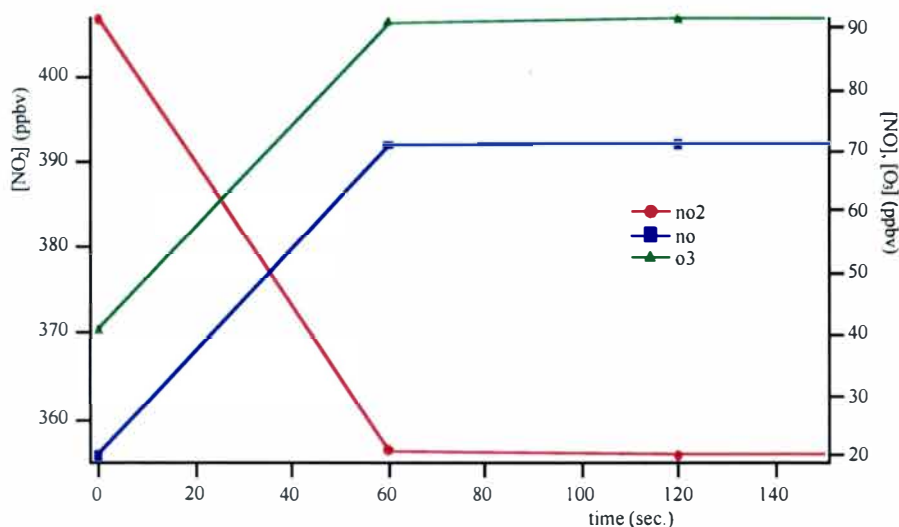


Figure 28. Simulation of O_3 Formation at Initial $[\text{NO}_2]/[\text{NO}]$ Ratio of 20.

concentration is 91.3 ppbv, indicating good agreement between the model simulated O_3 concentration and the analytical solution.

Figure 29 shows the mixing ratio versus time for the initial conditions:

$$[\text{NO}_2]_0 = 20.3 \text{ ppb} \quad [\text{NO}]_0 = 406.5 \text{ ppb} \quad [\text{O}_3]_0 = 40.6 \text{ ppb}$$

In this case, the initial ratio of $[\text{NO}_2]/[\text{NO}]$ is 0.05, and at steady state, the $[\text{NO}_2]/[\text{NO}]$ ratio is 0.16. The O_3 concentration changed to 2.87 ppbv. The calculated O_3 concentration at steady state is 2.74 ppbv, which is also in accord with the simulated concentration.

The simulated results from the above model runs show good agreement with analytical solutions, therefore the box model (ChemK) worked properly, and the simulated results can be used on analysis of O_3 chemistry theoretically.

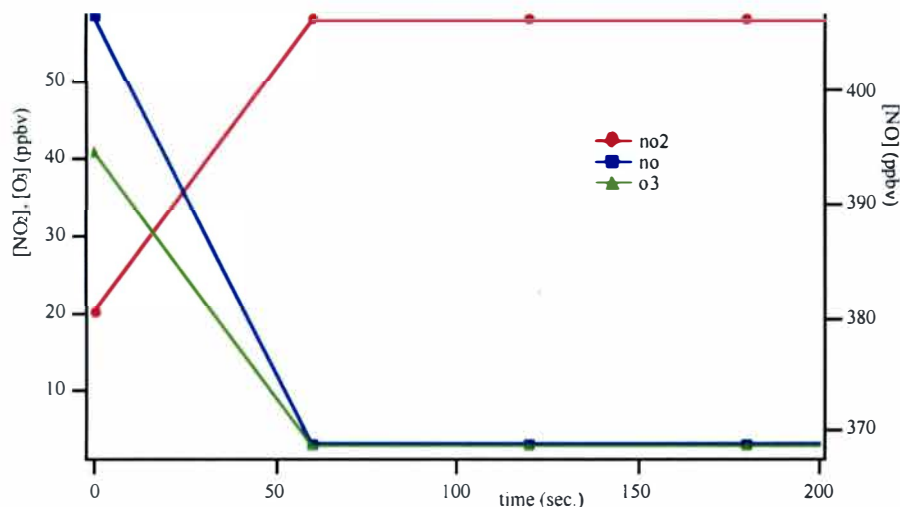


Figure 29. Simulation of O₃ Formation at Initial [NO₂]/[NO] Ratio of 0.05.

Box Model for Alkyl Nitrates in Dickson

The photochemical box model for studying O₃ chemistry in Dickson was set up to be a simple box, with no emission sources. The scheme in this model included not only the formation of O₃ (Figure 30), the formation of propyl nitrates, butyl nitrates and PPN, but also the loss of these species from the atmosphere (Figure 21, 24 and 32). In this model, a series of photolysis rate constants (*J*), which were calculated hourly specifically for Dickson, were used in photolysis reactions (Figure 31 and 33). All reactions were assumed to take place at 298K and 70% relative humidity. No dilution factors and no meteorological effects were included in the model. The model was simulated with only chemistry under different initial conditions, such as different NO_x levels.

The chemical mechanism of the model which contains reactions and corresponding rate constants were listed in Appendix C. The key to the abbreviation of chemical species is listed in Appendix D.

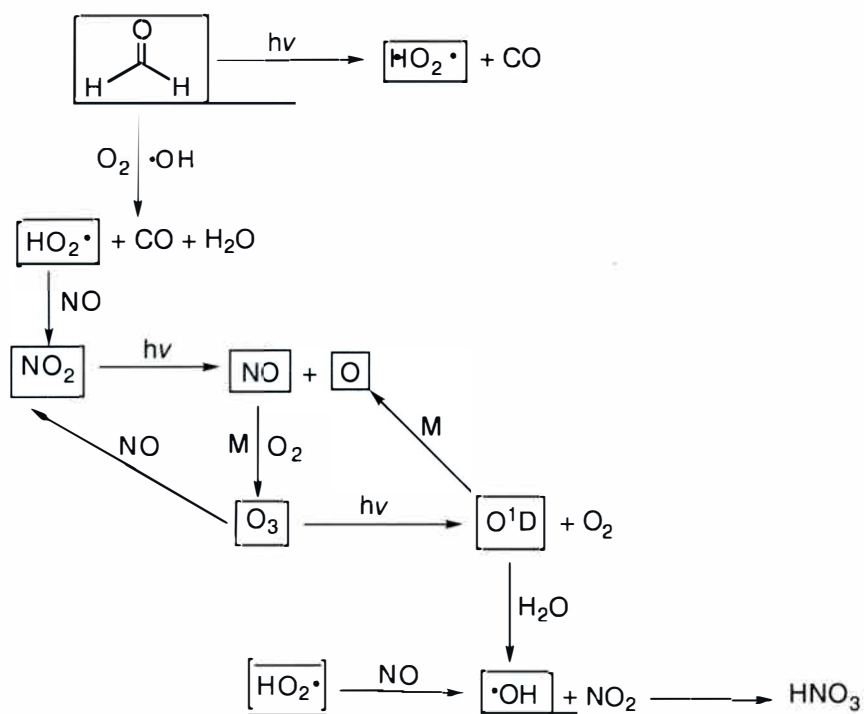


Figure 30. Formation of O_3 in Troposphere.

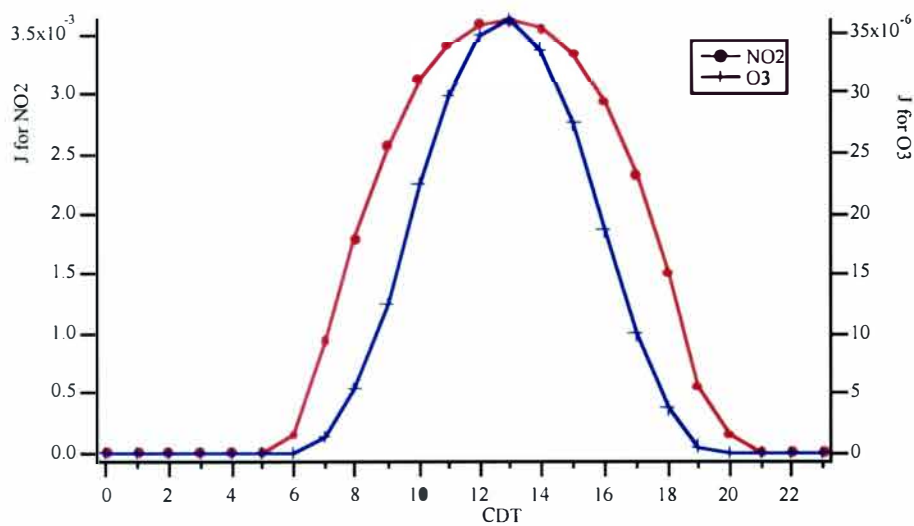


Figure 31. J Values for NO_2 and O_3 in Dickson

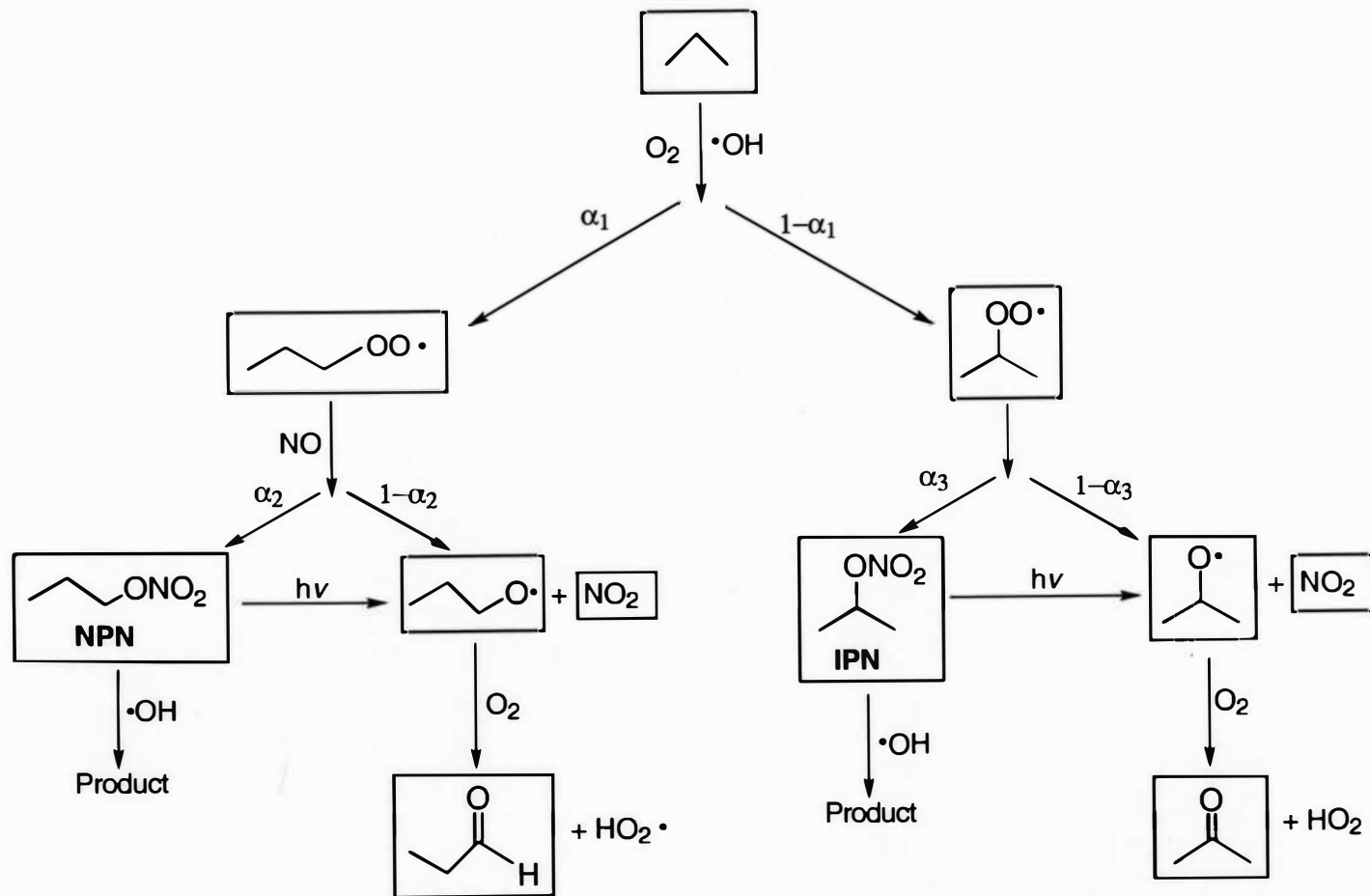


Figure 32. Formation of Propyl Nitrates in Troposphere

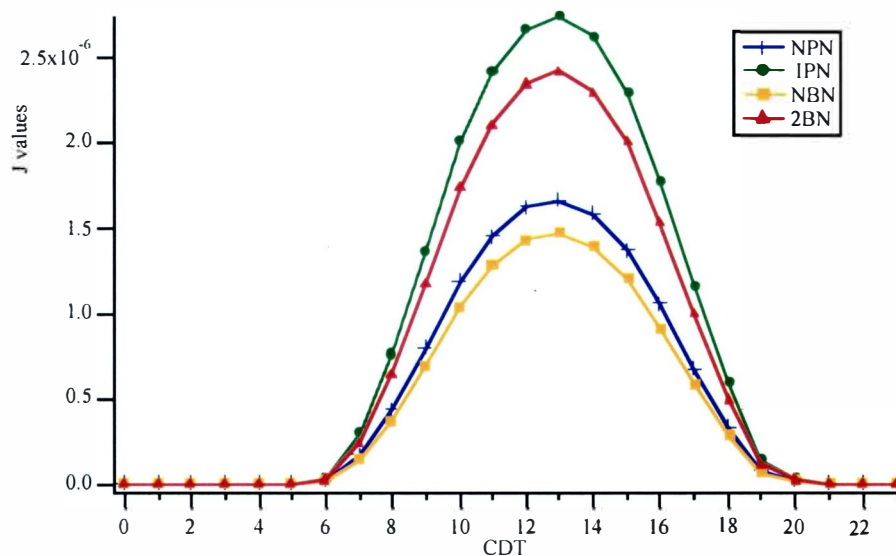


Figure 33. J Values for Alkyl Nitrates in Dickson.

The species with initial concentrations are listed below (Table 4). Propane and butane were put excess for initial concentrations to ensure not to run out during the simulations. The other initial concentrations were chosen based on the ambient air conditions.

Table 4

Species and Initial Concentrations

| Compound | Mixing ratio (molecules/cm ³) |
|--------------------------------|---|
| NO ₂ | vary |
| NO | vary |
| O ₃ | 1.97×10 ¹² |
| HCHO | 8.76×10 ¹⁰ |
| C ₃ H ₈ | 1.23×10 ¹¹ |
| C ₄ H ₁₀ | 1.23×10 ¹¹ |

Table 4-Continued

| Compound | Mixing ratio (molecules/cm ³) |
|-------------------------------|---|
| Isoprene | 2.46×10^{11} |
| O ₂ | 5.0×10^{18} |
| N ₂ | 1.92×10^{19} |
| H ₂ O ^a | 5.34×10^{17} |

a. concentration was calculated under pressure at 70% of saturated vapor pressure at 298K.

Verification of the Model for Alkyl Nitrates

To test the efficiency of the box model built for alkyl nitrates in Dickson, a more complex photochemical box model developed by Sillman (1991) was also employed. Unlike the box model for alkyl nitrates, this complex model includes emissions from the NAPAP 1990 inventory (Environmental Protection Agency, 1993) and BEIS2 inventory (Geron et al., 1994) for Nashville area. The species with initial concentrations are listed in Appendix E. The key to abbreviations of chemical species used in this model is shown in Appendix F. The chemical mechanism of this complex model is based on Lurmann et al. (1986), Paulson and Seinfeld (1992), Kirchner and Stockwell (1996), Stockwell et al. (1995) and Pippin (1999), but was modified to speciate the n-propyl nitrate and isopropyl nitrate.

The complex model was run under different emission conditions, which are listed in Table 5. The selected emissions from Nashville area were used in Case I to compare with the model for alkyl nitrates. The emissions in Case II represent the Nashville area.

Table 5
Emission Sources for the Complex Model

| Chemical Species* | Case I | Case II |
|-------------------------------|-----------------------|-----------------------|
| NO ₂ | 2.19×10^{10} | 2.19×10^{10} |
| NO | 2.30×10^{11} | 2.30×10^{11} |
| CO | 2.52×10^{12} | 2.52×10^{12} |
| C ₃ H ₈ | 5.67×10^{10} | 5.67×10^{10} |
| ALK ₄ | 2.27×10^{11} | 2.27×10^{11} |
| ALK ₇ | 0.00 | 7.29×10^{10} |
| HCHO | 4.43×10^9 | 4.43×10^9 |
| ETHE | 0.00 | 2.58×10^{10} |
| PRPE | 0.00 | 8.66×10^{10} |
| BUTE | 0.00 | 5.00×10^{10} |
| ISOP | 1.55×10^{11} | 1.55×10^{11} |
| TOLU | 0.00 | 3.42×10^{10} |
| XYLE | 0.00 | 2.41×10^{10} |
| MOH | 0.00 | 1.05×10^9 |
| EOH | 0.00 | 9.14×10^9 |

*. Unit is molecule/cm². The key to the abbreviation of chemical species is listed in Appendix E .

Results from the Models

The model for alkyl nitrates did simulations under different initial NO_x levels and constant initial concentrations for other species for 3 days. Table 6 listed the

concentrations of NO_x and other selected species for each simulation under the chemical mechanism listed in Appendix B.

O₂ and OH Change in the Model for Alkyl Nitrates

O₃ levels with different initial NO_x concentrations were shown in Table 6. The O₃ was seen to decrease with the increase of initial NO_x concentrations. This is because the loss of O₃ was faster than its formation when the NO_x concentrations increased. But the amount of O₃ under different initial NO_x levels are still reasonable to compare to the ambient data, and enough to complete the simulations.

OH radicals, however, are relatively lower than those in polluted area, but they are still at the average level in ambient air (Figure 34). Since only the ratios of alkyl nitrates isomers were considered rather than the amount of individual species in the simulations, the OH level would not affect the relationship of those isomers.

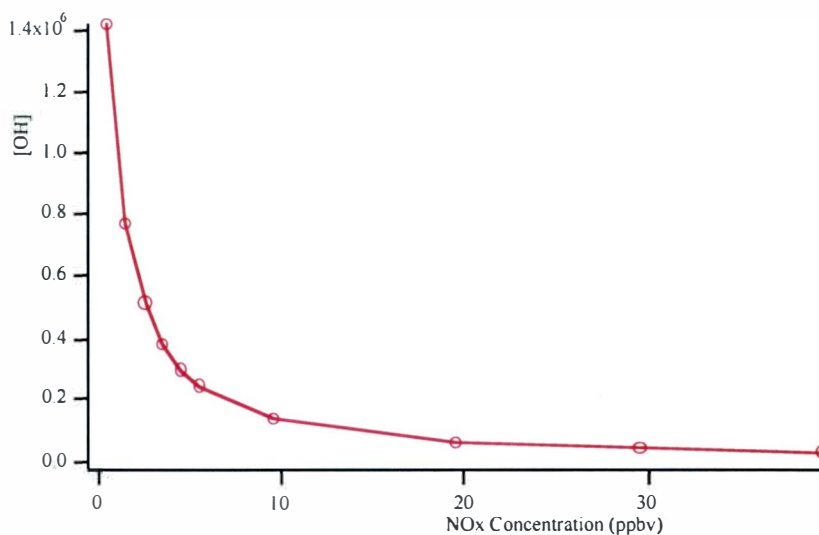


Figure 34. OH with NO_x Concentrations in the Model for Alkyl Nitrates.

Table 6

Concentrations of NO_x and Other Selected Species for Each Simulation. ⁴

| Trial | Initial NO _x ¹ | NO _x ¹ | $\frac{\text{NO}_2}{\text{NO}}$ | O ₃ ¹ | OH ² | HNO ₃ ¹ | PPN ³ | NPN ³ | IPN ³ | NBN ³ | 2BN ³ | $\frac{\text{NPN}}{\text{PPN}}$ | $\frac{\text{IPN}}{\text{NPN}}$ | $\frac{2\text{BN}}{\text{NBN}}$ |
|-------|---|------------------------------|---------------------------------|-----------------------------|----------------------|-------------------------------|------------------|------------------|------------------|------------------|------------------|---------------------------------|---------------------------------|---------------------------------|
| 1 | 1.0 | 0.469 | 11.34 | 81.71 | 1.41×10 ⁶ | 0.258 | 2.850 | 0.339 | 3.752 | 0.658 | 9.472 | 0.119 | 11.07 | 14.39 |
| 2 | 2.0 | 1.462 | 10.33 | 78.86 | 7.64×10 ⁵ | 0.370 | 1.000 | 0.208 | 2.289 | 0.411 | 5.813 | 0.208 | 11.00 | 14.14 |
| 3 | 3.0 | 2.479 | 9.92 | 76.83 | 5.12×10 ⁵ | 0.405 | 0.480 | 0.145 | 1.594 | 0.287 | 4.065 | 0.302 | 10.99 | 14.16 |
| 4 | 4.0 | 3.497 | 9.57 | 76.02 | 4.78×10 ⁵ | 0.406 | 0.423 | 0.136 | 1.496 | 0.270 | 3.821 | 0.322 | 11.00 | 14.15 |
| 5 | 5.0 | 4.504 | 9.26 | 72.76 | 2.96×10 ⁵ | 0.419 | 0.171 | 0.0873 | 0.959 | 0.174 | 2.459 | 0.511 | 10.98 | 14.13 |
| 6 | 6.0 | 5.508 | 9.03 | 71.14 | 2.41×10 ⁵ | 0.419 | 0.115 | 0.0724 | 0.793 | 0.144 | 2.033 | 0.630 | 10.95 | 14.12 |
| 7 | 10.0 | 9.552 | 8.40 | 66.26 | 1.34×10 ⁵ | 0.411 | 0.037 | 0.0419 | 0.459 | 0.0837 | 1.179 | 1.132 | 10.95 | 14.09 |
| 8 | 20.0 | 19.60 | 7.60 | 60.16 | 5.98×10 ⁴ | 0.385 | 0.0074 | 0.0195 | 0.214 | 0.0392 | 0.549 | 2.635 | 10.97 | 14.01 |
| 9 | 30.0 | 29.64 | 7.08 | 56.10 | 3.71×10 ⁴ | 0.363 | 0.0028 | 0.0123 | 0.135 | 0.025 | 0.347 | 4.456 | 10.97 | 14.05 |
| 10 | 40.0 | 39.63 | 6.68 | 52.84 | 2.63×10 ⁴ | 0.343 | 0.0013 | 0.0088 | 0.096 | 0.018 | 0.247 | 6.600 | 10.93 | 14.03 |

1. Species unit is ppbv.
2. Species unit is molecules/cm³.
3. Species unit is pptv.
4. Data was collected at noon at day 2 from each simulation.

Total NOy in the Model for Alkyl Nitrates

To verify that the mechanism used in the model for alkyl nitrates correct, one of the effective ways is comparing the NOy levels before and after the simulations. Since only NO₂ and NO were input as starting oxidized nitrogen species, the NOy before model run should be the sum of NO₂ and NO. The corresponding NOy at the end of simulation would be the sum of NOx and other oxidized nitrogen species, which, in this case, are HNO₃, propyl nitrates, butyl nitrates, peroxypropionyl nitrate, and the products of the photolysis of these alkyl nitrates. Table 7 lists the comparison of NOy for each simulation.

Table 7
Comparison of NOy in Each Simulation *

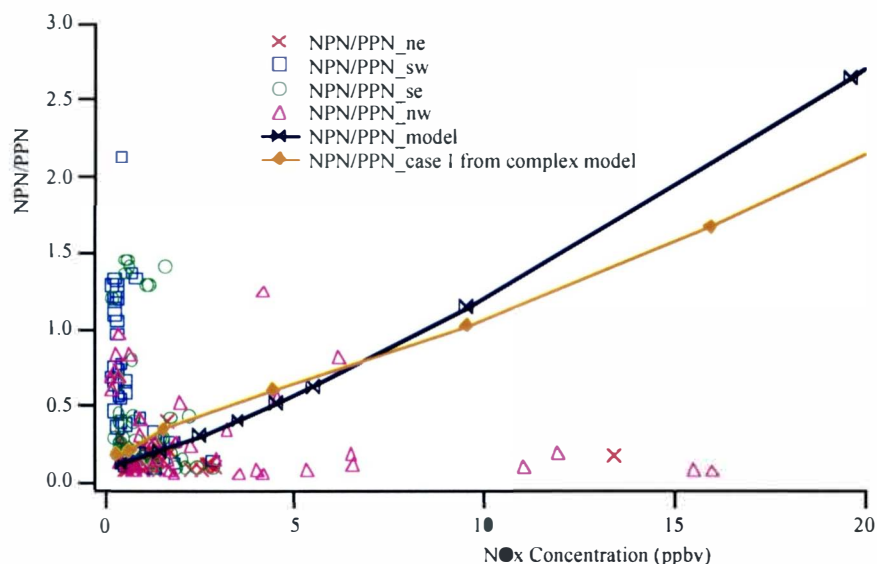
| Trial | Initial NOx (ppbv) | Initial NOy (ppbv) | Total NOy after simulation(ppbv) | | |
|-------|-----------------------|-----------------------|----------------------------------|---------------|---------------|
| | | | Day 1 at noon | Day 2 at noon | Day 3 at noon |
| 1 | 1.0 | 1.0 | 0.977 | 0.744 | 0.534 |
| 2 | 2.0 | 2.0 | 1.970 | 1.841 | 1.727 |
| 3 | 3.0 | 3.0 | 2.972 | 2.884 | 2.815 |
| 4 | 4.0 | 4.0 | 3.978 | 3.916 | 3.849 |
| 5 | 5.0 | 5.0 | 4.984 | 4.923 | 4.892 |
| 6 | 6.0 | 6.0 | 5.893 | 5.907 | 5.933 |
| 7 | 10.0 | 10.0 | 9.976 | 9.963 | 9.939 |
| 8 | 20.0 | 20.0 | 19.98 | 19.98 | 19.98 |
| 9 | 30.0 | 30.0 | 30.00 | 30.00 | 29.96 |
| 10 | 40.0 | 40.0 | 39.98 | 39.98 | 39.97 |

*. Models were simulated with time step of 30 minutes.

Table 7 shows that under very low initial NO_x concentrations, the discrepancy between final NO_y and initial NO_y is bigger than those with high initial NO_x levels, especially at day 2 and day 3. The possible reason is propagation of truncation error when doing numerical integration for model output. To verify this assumption, the time step was changed from 30 minutes to 1 minute. The discrepancy of NO_y increased up to 1.59% under very low NO_x levels.

NPN/PPN Sensitivity to NO_x

The model ratios and ambient ratios of NPN and PPN under different NO_x levels are shown in Figure 35.



* Each marker on the line corresponds to a simulation listed in Table 5.

Figure 35. Model Ratios vs Ambient Ratios of NPN/PPN with NO_x Concentration.

As can be seen, the model ratios of NPN/PPN increased with NO_x concentrations. This is because PPN decreased with NO_x concentrations faster than

NPN did in the simulations (Figure 36). The ratios of NPN/PPN from Case I of the

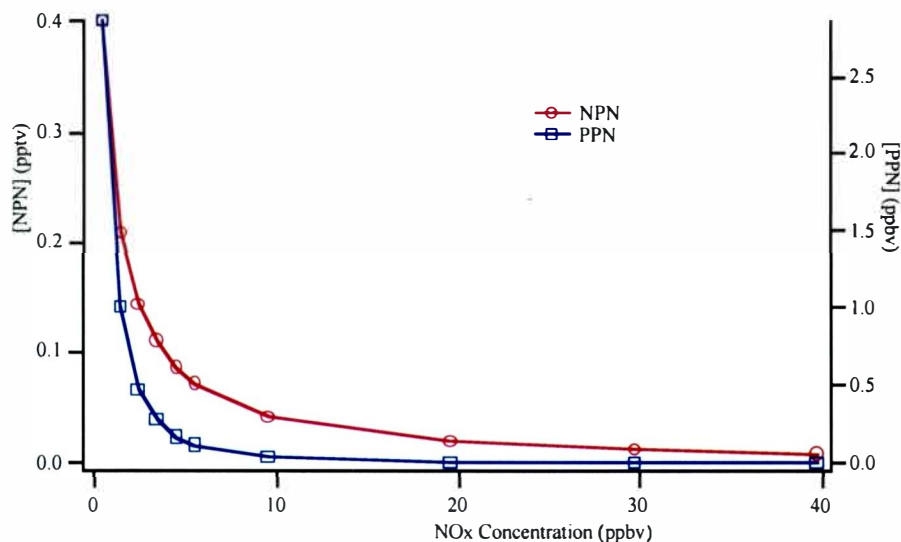


Figure 36. NPN and PPN with NOx Concentrations in the Model for Alkyl Nitrates.

complex model also showed increase with NOx. However the ambient ratios of NPN/PPN have different behaviors. Under air flow from the southwest, NOx levels are mostly less than 1 ppbv, and most of ambient NPN/PPN ratios are between 0.36 and 1.32, the model ratios are less than 0.20. In the photochemically aged rural air brought to the measurement site in southwesterly flow, the ambient ratio of NPN/PPN should be higher in air due to the short lifetime of PPN. When NOx levels are above 4 ppbv, mainly in air from the northwest which can bring large amount of NOx released from the Cumberland power plant to the site, most of ambient ratios of NPN/PPN stayed below 0.18, and did not change too much with the NOx levels, while the model ratios are above 0.5.

Although PPN and NPN were assumed to originate solely from the same anthropogenic hydrocarbons, i.e., propane in the model for alkyl nitrates, the complex model contains more anthropogenic hydrocarbons as the precursors of PPN. The

different behaviors of ambient NPN/PPN from the model implied that there could be more precursors of NPN, as well as for PPN. The studies of alkyl nitrates with less than 5 carbons indicated that the assumption that alkane is the only source of RO_2 radicals for alkyl nitrates is not always true when large alkoxy radicals are present in the atmosphere (Flocke et al., 1998; Atkinson, 1997), so more sources other than propane could form NPN. Studies (Grosjean et al., 1993, Konig et al., 1995) has shown that a biogenic source, the unsaturated alcohol *cis*-3-hexen-1-ol ($\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{OH}$), could be a precursor of PPN. *cis*-3-hexen-1-ol, which is known as leaf alcohol, has been identified as emissions from some plants including grass, trees and agricultural crops. It can be oxidized in the atmosphere initiated by O_3 or OH radicals (Arey et al., 1991) to give propanal, which is then oxidized by O_2 and reacted with NO_2 to form PPN. Since the measurement site in Dickson is a rural place which has trees, grass and many crops, the emission of *cis*-3-hexen-1-ol could occur during the summers, thus providing a biogenic source of PPN in Dickson. Since no measurement of *cis*-3-hexen-1-ol and large RO radicals were made in this study, future investigation should be done to verify the above assumption.

IPN/NPN Sensitivity to NO_x

The ratios of IPN/NPN as a function of NO_x levels was shown in Figure 37. It is interesting to see that the model ratios of IPN/NPN have no significant change under any NO_x level. The same trend can also be seen from the complex model. Since the complex model does not contain loss of NPN and IPN while the model for alkyl nitrates does, the ratios of IPN/NPN from the complex model are higher than those in the model for alkyl nitrates. The ambient ratios of IPN/NPN were much lower than the model ratios, and varied with different NO_x concentrations. Since propane was the only source of IPN and NPN formation in the model, the difference of the relationship of

IPN/NPN with NO_x in the model with that in ambient air implied that there could be more precursors of IPN and NPN in Dickson.

As discussed above, the large alkoxy radicals could be another kind of precursor of alkyl nitrates with under 5 carbons due to their decomposition, but the model did not include this possibility. In addition, alkyl nitrates have been known to have relatively long life times, and are not impacted much by dry or wet deposition during transport

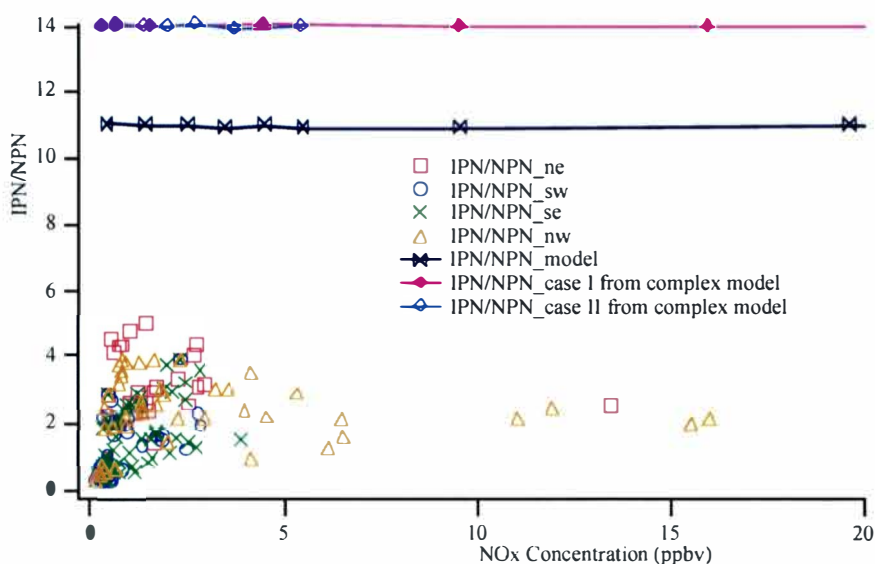


Figure 37. Model Ratios vs Ambient Ratios of IPN/NPN with NO_x Concentration.

(Roberts et al., 1989; Bertman et al., 1995). Alkyl nitrates not only could be formed locally, but also could be accumulated from transport. The measured alkyl nitrates *in situ* should be composed of these two parts in ambient air. Therefore the relationship of IPN/NPN with NO_x in ambient air is not as simple as that in the model.

2BN/NBN Sensitivity to NO_x

The behavior of 2BN/NBN as a function of NO_x in the model for alkyl nitrates was very similar to that of IPN/NPN, with no significant change in the model ratios of

2BN/NBN with different NO_x levels as shown in Figure 38. The ratios of 2BN/NBN were not explored in the complex model due to their similarity with IPN/NPN ratios.

Under air flow from southwest, even though NO_x levels in ambient air did not change significantly, the ratios of 2BN/NBN did change over 4-5 orders of magnitude.

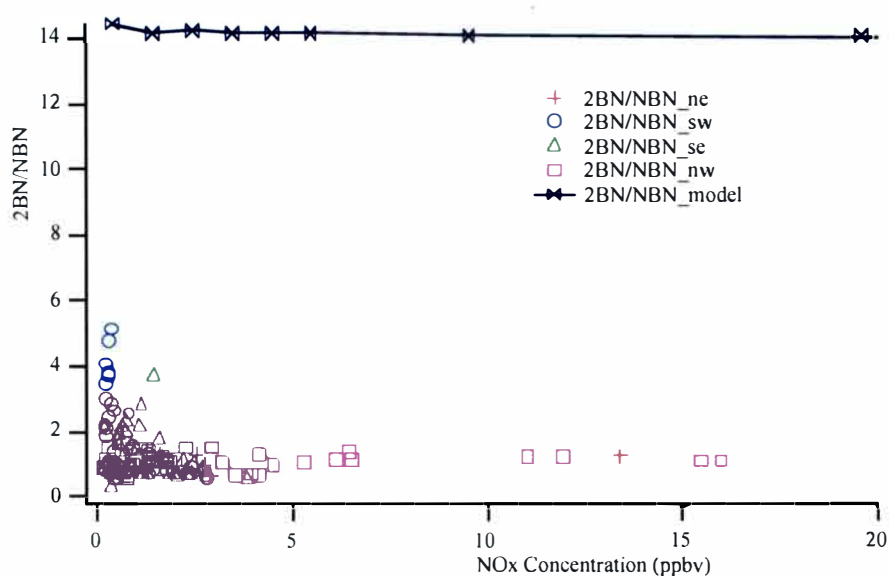


Figure 38. Model Ratios vs Ambient Ratios of 2BN/NBN with NO_x Concentration.

Under northwesterly wind, however, 2BN/NBN ratios did not change much (0.51 to 1.50), although the NO_x level changed a lot (0.16 to 15.98). The behavior of 2BN/NBN ratios in ambient air illuminated further that not only the chemistry is important to alkyl nitrates formation but the transport of air could also be contributive to the accumulation of alkyl nitrates.

Conclusions

The photochemical box model was built based on pure chemistry conditions for this study. Tests of the model for alkyl nitrates showed it simulated chemistry correctly.

The comparison with the complex model also showed the model for this study was efficient. The model was simulated under different NO_x levels, and the relationships of alkyl nitrates isomers with NO_x were found. The model ratios of NPN/PPN, IPN/NPN and 2BN/NBN showed different behaviors from those in ambient air under different NO_x levels. Since only chemistry of O₃ and alkyl nitrates was put into the model for alkyl nitrates, and only parent hydrocarbons as the source to contribute to alkyl nitrates formation, the difference between the model and the ambient behaviors of alkyl nitrates isomers implied that more variables, such as other possible precursors, and transport history could affect on alkyl nitrates and other organic nitrates in the ambient air.

CHAPTER V

CONCLUSIONS AND FUTURE WORK

Conclusions

The developed measurement method was tested and used in Dickson during the 1999 SOS Field Campaign. Measurement of standards and ambient air samples showed that the method was successfully used in the field study, and it could separate and detect nine alkyl nitrates, which are MN, EN, IPN, NPN, 2BN, NBN, 3PeN, 2PeN and NpeN. Due to the amount of alkyl nitrates in Dickson, only the first six was quantified. The alkyl nitrate with the largest mixing ratio measured in Dickson was methyl nitrate, while the smallest was 2-butyl nitrate.

The measured alkyl nitrates except methyl nitrate showed higher mixing ratios under northeasterly and southeasterly wind, which came from urban areas, and brought anthropogenic sources to the measurement site. The alkyl nitrates except methyl nitrate have lower mixing ratios when wind came from the northwest and the southwest, which brought considerable amount of NO_x and clean air, respectively. The mixing ratio of methyl nitrate did not show a significant difference under any wind direction. This phenomenon requires further investigation.

The contribution of the measured alkyl nitrates to the total oxidized nitrogen species, NO_y, ranged from 1.1% and 1.9%, indicating that alkyl nitrates account for a small part of NO_y in Dickson. The diurnal variations of $\sum \text{RONO}_2/\text{NO}_y$ and $\sum \text{RONO}_2$ showed similar trends while different from that of NO_y. However, the ratios of $\sum \text{RONO}_2/\text{NO}_y$ did not have diurnal trends under the four designated wind directions, but the highest ratios of $\sum \text{RONO}_2/\text{NO}_y$ were seen under southwesterly air flow.

The observation of the ratios of alkyl nitrates from the same parent hydrocarbons in Dickson indicated that the ratio of propyl nitrates isomers, IPN/NPN showed different behaviors from that of butyl nitrates isomers, 2BN/NBN. The IPN/NPN had the highest ratios under wind from urban areas, while the 2BN/NBN showed the highest when air flow came from rural areas. This observation may imply that some other sources other than parent hydrocarbons could affect alkyl nitrates formation in Dickson. The relationship of NPN and PPN was also studied. The ratio of NPN/PPN may be used to determine the photochemical age of an air mass, but further study should be done.

A simple photochemical box model was developed for studying the relationship of alkyl nitrates and NO_x. The mechanism of the model for alkyl nitrates is based on pure chemical reactions. The test and comparison with a complex model indicated that the output of both models were consistent, and the model for alkyl nitrates was sufficient to simulate the chemistry of alkyl nitrates in troposphere. Under different NO_x levels, the model ratios of IPN/NPN and 2BN/NBN showed little change, while the ambient ratios varied significantly. The model ratios of NPN/PPN were also investigated. Simulations showed that the model ratios of NPN/PPN increased with the increase of NO_x, however, the ambient ratios of NPN/PPN have different behaviors. Since the parent hydrocarbons of alkyl nitrates and PPN were only sources for their formation in the model, the results of the model suggested that the alkyl nitrates formation could be affected by more variables other than parent hydrocarbons in ambient air.

Future Work

In order to analyze the different behaviors of the model ratios of alkyl nitrates isomers from those of the ambient ratios, and the different behaviors of the model ratios

of NPN/PPN, more work should be done in the future.

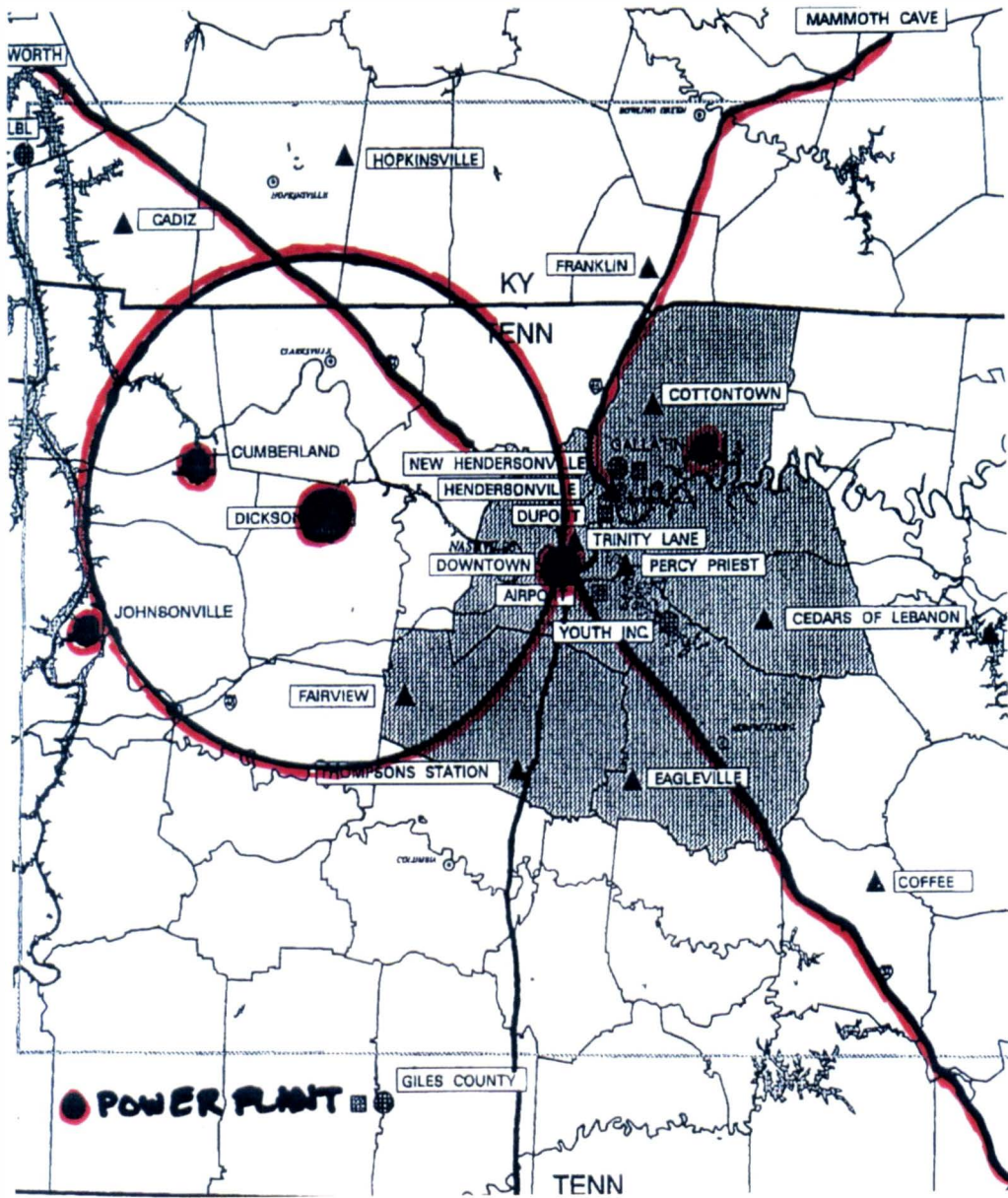
Since large alkoxy radicals could be sources of $<C_5$ alkyl nitrates as a result of cleavage, measurements of larger alkoxy radicals need to be performed. The effect of alkoxy radical decomposition on the formation of alkyl nitrates also should be explored in the future studies.

N-propoxy radical, which is the precursor of PPN, is formed both from n-propyl peroxy radical and photodecomposition of n-propyl nitrate (Figure 27), the light intensity could affect the amount of n-propoxy radical. Future modeling study on the relationship of light intensity with n-propoxy radical could help to study the NPN/PPN ratio difference under the degree of cloudiness from different flow regimes. Biogenic emissions from plants, grass and agricultural crops need to be considered as possible sources of PPN, which can affect the NPN/PPN ratio in ambient air, but was not included in models developed in this study.

Since the photochemical box model for alkyl nitrates built in this study was just based on pure chemistry, meteorological parameters, emissions and dilution factors should be put in future models to perform simulations closer to the real world.

Appendix A

The Map of Measurement Site in Dickson



Appendix B

The Sensitivity of NO_x Analyzer and The Calibration Factors of Alkyl Nitrates

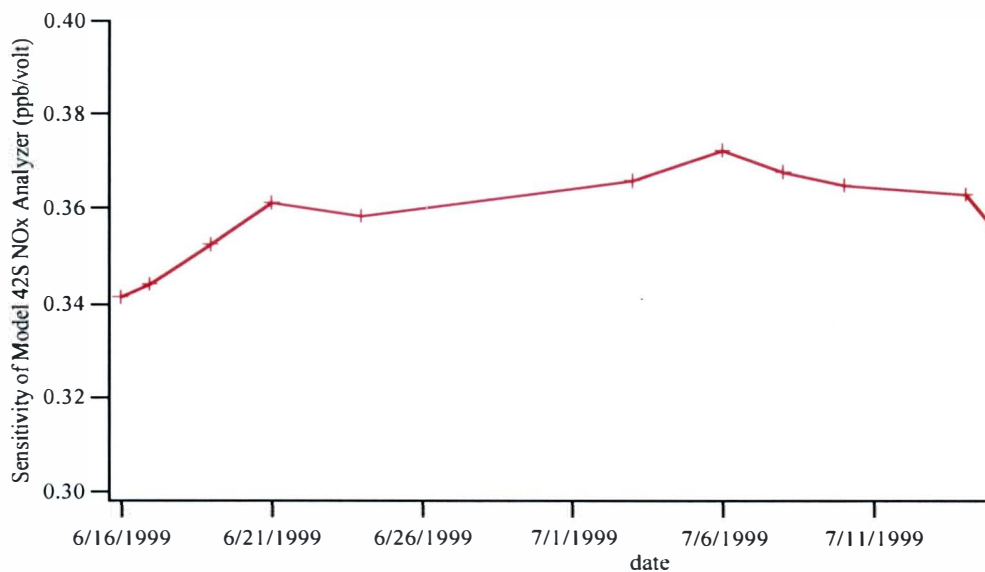


Figure I. The Sensitivity of NOx Analyzer During the SOS Field Campaign.

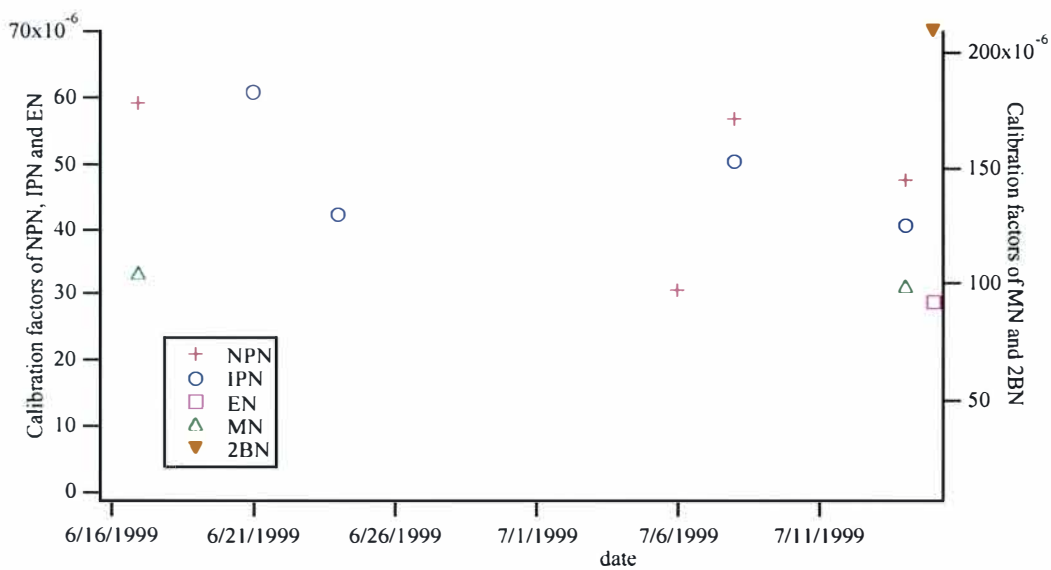


Figure II. Calibration Factors with Time During the SOS 1999 Field Campaign.

Appendix C

Reactions and Rate Constants in the Model for Alkyl Nitrates

| # | Chemical Reaction | Rate Constant** | note |
|------|---|------------------------|------|
| 1 * | $\text{NO}_2 \rightarrow \text{NO} + \text{O}$ | 3.62×10^{-3} | a |
| 2 | $\text{O} + \text{O}_2 \rightarrow \text{O}_3$ | 1.50×10^{-14} | a |
| 3 * | $\text{O}_3 \rightarrow \text{O}(^1\text{D}) + \text{O}_2$ | 3.60×10^{-5} | a |
| 4 | $\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2$ | 1.80×10^{-14} | a |
| 5 | $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH}$ | 2.20×10^{-10} | b |
| 6 | $\text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O} + \text{N}_2$ | 2.60×10^{-11} | a |
| 7 * | $\text{HCHO} \rightarrow 2 \text{HO}_2 + \text{CO}$ | 2.92×10^{-5} | a |
| 8 | $\text{HCHO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO} + \text{H}_2\text{O}$ | 1.00×10^{-11} | a |
| 9 | $\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$ | 8.10×10^{-12} | a |
| 10 | $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$ | 8.83×10^{-12} | a |
| 11 * | $\text{HNO}_3 \rightarrow \text{OH} + \text{NO}_2$ | 4.13×10^{-7} | a |
| 12 | $\text{C}_3\text{H}_8 + \text{OH}\cdot \rightarrow \text{A}_3\text{O}_2\cdot$ | 1.67×10^{-13} | b |
| 13 | $\text{C}_3\text{H}_8 + \text{OH}\cdot \rightarrow \text{B}_3\text{O}_2\cdot$ | 9.34×10^{-13} | b |
| 14 | $\text{A}_3\text{O}_2\cdot + \text{NO} \rightarrow 0.02 \text{NPN}$ | 8.50×10^{-12} | b |
| 15 | $\text{A}_3\text{O}_2\cdot + \text{NO} \rightarrow 0.98 \text{PLD} + 0.98 \text{NO}_2 + 0.98 \text{HO}_2$ | 8.50×10^{-12} | b |
| 16 | $\text{B}_3\text{O}_2\cdot + \text{NO} \rightarrow 0.04 \text{IPN}$ | 8.50×10^{-12} | b |
| 17 | $\text{B}_3\text{O}_2\cdot + \text{NO} \rightarrow 0.96 \text{ACT} + 0.96 \text{NO}_2 + 0.96 \text{HO}_2$ | 8.50×10^{-12} | b |
| 18 * | $\text{NPN} \rightarrow \text{PLD} + \text{NO}_2 + \text{HO}_2$ | 1.66×10^{-6} | c |
| 19 | $\text{NPN} + \text{OH}\cdot \rightarrow \text{Product}$ | 0.62×10^{-12} | d |
| 20 * | $\text{IPN} \rightarrow \text{ACT} + \text{NO}_2 + \text{HO}_2$ | 2.74×10^{-6} | c |
| 21 | $\text{IPN} + \text{OH}\cdot \rightarrow \text{Product}$ | 0.41×10^{-12} | d |
| 22 | $\text{PLD} + \text{OH}\cdot \rightarrow \text{PPR}$ | 2.00×10^{-11} | b |
| 23 | $\text{PPR} + \text{NO}_2 \rightarrow \text{PPN}$ | 8.66×10^{-12} | e |
| 24 | $\text{PPR} + \text{NO} \rightarrow \text{EPR} + \text{NO}_2 + \text{CO}_2$ | 2.16×10^{-11} | b |

Table-----Continued

| # | Chemical Reaction | Rate Constant** | note |
|------|---|-------------------------|------|
| 25 | $\text{PPN} \rightarrow \text{PPR} + \text{NO}_2$ | 4.40×10^{-4} | b |
| 26 | $\text{C}_4\text{H}_{10} + \text{OH}\cdot \rightarrow \text{E}_4\text{O}_2\cdot$ | 1.67×10^{-13} | b |
| 27 | $\text{C}_4\text{H}_{10} + \text{OH}\cdot \rightarrow \text{F}_4\text{O}_2\cdot$ | 1.15×10^{-12} | b |
| 28 | $\text{E}_4\text{O}_2\cdot + \text{NO} \rightarrow 0.04 \text{ NBN}$ | 8.50×10^{-12} | b |
| 29 | $\text{E}_4\text{O}_2\cdot + \text{NO} \rightarrow 0.96 \text{ BTA} + 0.96 \text{ NO}_2 + 0.96 \text{ HO}_2$ | 8.50×10^{-12} | b |
| 30 | $\text{F}_4\text{O}_2\cdot + \text{NO} \rightarrow 0.083 \text{ 2BN}$ | 8.50×10^{-12} | b |
| 31 | $\text{F}_4\text{O}_2\cdot + \text{NO} \rightarrow 0.917 \text{ MEK} + 0.917 \text{ NO}_2 + 0.917 \text{ HO}_2$ | 8.50×10^{-12} | b |
| 32 * | $\text{NBN} \rightarrow \text{BTA} + \text{NO}_2 + \text{HO}_2$ | 1.47×10^{-6} | c |
| 33 | $\text{NBN} + \text{OH}\cdot \rightarrow \text{Product}$ | 1.78×10^{-12} | d |
| 34 * | $\text{2BN} \rightarrow \text{MEK} + \text{NO}_2 + \text{HO}_2$ | 2.42×10^{-6} | c |
| 35 | $\text{2BN} + \text{OH}\cdot \rightarrow \text{Product}$ | 0.92×10^{-12} | d |
| 36 | $\text{ISOP} + \text{OH}\cdot \rightarrow \text{APR}$ | 101.0×10^{-12} | b |
| 37 | $\text{APR} + \text{NO} \rightarrow \text{NO}_2 + \text{HO}_2 + \text{HCHO}$ | 8.50×10^{-12} | b |

*. Photolysis reaction. Listed photolysis rate constant is the biggest one in a day.

**. Units are: first order, s^{-1} ; second order, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

***. The key to the abbreviation of chemical species is listed in Appendix B .

- Rate constants were taken from DeMore et al., 1997.
- Rate constants were taken from Finlayson-Pitts and Pitts, 2000.
- Rate constants were taken from Reborts and Fajer, 1989.
- Rate constants were taken from Atkinson, 1990.
- Rate constants were taken from Stockwell et al., 1997.

Appendix D

Abbreviations of Chemical Species in the Model for Alkyl Nitrates

| Abbreviation | Chemical species |
|-------------------------------|---|
| O ₃ | ozone |
| NO ₂ | nitrogen dioxide |
| NO | nitric oxide |
| O | ground state oxygen atom |
| O ¹ D | excited singlet oxygen atom |
| OH | hydroxyl radical |
| HO ₂ | hydroperoxyl radical |
| H ₂ O | water vapor |
| HCHO | formaldehyde |
| CO | carbon monoxide |
| HNO ₃ | nitric acid |
| C ₃ H ₈ | propane |
| A ₃ O ₂ | n-propyl radical ($\text{CH}_3\text{CH}_2\text{CH}_2(\text{OO}\cdot)$) |
| B ₃ O ₂ | secondary propyl radical ($\text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}_3$) |
| NPN | primary propyl nitrate ($\text{CH}_3\text{CH}_2\text{CH}_2\text{ONO}_2$) |
| IPN | isopropyl nitrate ($\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_3$) |
| PLD | propionaldehyde ($\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{H}$) |
| PPR | peroxy propionyl radical ($\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OO}\cdot$) |
| EPR | ethyl peroxy radical ($\text{CH}_3\text{CH}_2\text{OO}\cdot$) |
| PPN | peroxypropionyl nitrate ($\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OONO}_2$) |
| ALK ₄ | n-butane (C_4H_{10}) |
| E ₄ O ₂ | primary butyl radical ($\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OO}\cdot$) |
| F ₄ O ₂ | 2-butyl radical ($\text{CH}_3\text{CH}_2(\text{OO}\cdot)\text{CH}_2\text{CH}_3$) |

Table-Continued

| Abbreviation | Chemical species |
|--------------|--|
| NBN | n-butyl nitrate ($\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{ONO}_2$) |
| 2BN | 2-butyl nitrate ($\text{CH}_3\text{CH}_2(\text{ONO}_2)\text{CH}_2\text{CH}_3$) |
| BTA | butyl aldehyde ($\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{H}$) |
| MEK | methyl ethyl ketone ($\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$) |
| ISOP | isoprene ($\text{CH}_2\text{CHC}(\text{CH}_3)\text{CH}_2$) |
| APR | alkenylperoxy radical (isoprene ROO) |
| Pro | product from the photolysis of alkyl nitrates |

Appendix E

Species with Initial Concentrations in the Complex Model

| Species Name * | Case I | Case II |
|-------------------------------|-----------------------|-----------------------|
| O ₃ | 9.8×10 ¹¹ | 9.8×10 ¹¹ |
| NO ₂ | 6.0×10 ⁹ | 6.0×10 ⁹ |
| NO | 6.0×10 ⁸ | 6.0×10 ⁸ |
| NO ₃ | 6.0×10 ⁷ | 6.0×10 ⁷ |
| N ₂ O ₅ | 5.0×10 ⁷ | 5.0×10 ⁷ |
| HONO | | 2.0×10 ⁷ |
| HNO ₄ | | 2.0×10 ⁷ |
| OH | 2.0×10 ⁵ | 2.0×10 ⁵ |
| HO ₂ | 2.0×10 ⁸ | 2.0×10 ⁸ |
| H ₂ O ₂ | | 2.5×10 ¹⁰ |
| SO ₂ | | 2.0×10 ⁵ |
| H ₂ O | 5.34×10 ¹⁷ | 5.34×10 ¹⁷ |
| CO | | 4.7×10 ¹² |
| CH ₄ | | 4.0×10 ¹³ |
| C ₂ H ₆ | | 2.4×10 ¹⁰ |
| C ₃ H ₈ | 1.1×10 ¹⁰ | 1.1×10 ¹⁰ |
| ALK ₄ | 1.38×10 ¹⁰ | 1.38×10 ¹⁰ |
| ALK ₇ | | 9.6×10 ⁹ |
| HCHO | 1.73×10 ¹⁰ | 1.73×10 ¹⁰ |
| ALD ₂ | | 5.0×10 ⁹ |
| RCHO | | 5.0×10 ⁹ |
| ACET | | 2.4×10 ⁹ |

Table ----Continued

| Species Name | Case I | Case II |
|-----------------|-------------------|------------------------|
| MEK | | 1.0×10^9 |
| ETHE | | 6.9×10^9 |
| PRPE | | 1.44×10^9 |
| BUTE | | 7.2×10^9 |
| ISOP | 2.0×10^9 | 2.0×10^9 |
| BENZ | | 2.8×10^9 |
| TOLU | | 3.5×10^9 |
| XYLE | | 1.08×10^9 |
| PAN | | 2.0×10^9 |
| MO ₂ | | 8.0×10^7 |
| MVK | | 2.5×10^{10} |
| MACR | | 2.5×10^{10} |
| HAC | | 2.5×10^{10} |
| H ₂ | | 1.233×10^{13} |

*. The unit is molecules/cm³

Appendix F

Key to Chemical Species Abbreviations in the Complex Model

| Abbreviation | Chemical Species |
|-------------------------------|--|
| NO ₃ | NO ₃ radical |
| N ₂ O ₅ | dinitrogen pentoxide |
| HONO | nitrous acid |
| HNO ₄ | pernitric acid |
| H ₂ O ₂ | hydrogen peroxide |
| CO | carbon monoxide |
| SO ₂ | sulfur dioxide |
| CH ₄ | methane |
| C ₂ H ₆ | ethane |
| C ₃ H ₈ | propane |
| ALK ₄ | C ₄ -C ₅ alkanes |
| ALK ₇ | C ₆ -C ₈ alkanes |
| ALD ₂ | acetaldehyde |
| RCHO | propanal |
| ACET | acetone |
| MEK | methyl ethyl ketone |
| ETHE | ethene |
| PRPE | propene |
| BUTE | trans-2-butene |
| ISOP | isoprene |
| BENZ | benzene |
| TOLU | toluene |
| XYLE | xylene |

Table ----Continued

| Abbreviation | Chemical Species |
|-----------------|---|
| MOH | CH ₃ OH |
| EOH | CH ₃ CH ₂ OH |
| PAN | peroxyacetyl nitrate |
| MO ₂ | CH ₃ O ₂ |
| MVK | methyl vinyl ketone |
| MACR | methacrolein |
| HAC | hydroxyacetaldehyde (HOCH ₂ CHO) |
| H ₂ | hydrogen |

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