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# **ANALYSIS OF ORGANIC NITRATES IN ARCTIC OUTFLOW**

by

**Deanna Elyea-Piper**

**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  
April 1997**

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1997

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Deanna Elyea-Piper

## ANALYSIS OF ORGANIC NITRATES IN ARCTIC OUTFLOW

Deanna Elyea-Piper, M.A.

Western Michigan University, 1997

The Arctic Outflow Study (AOS) was a project funded by the National Science Foundation to assess the impact of tropospheric ozone concentrations by the measurement of oxidized nitrogen. Measurements of arctic outflow were made to assess the seasonal cycle of compounds in arctic air and the partitioning of NO<sub>y</sub> during transport to the North Atlantic region. These photochemically active compounds are elevated in the arctic during the winter and spring because of the lack of photochemical processes to destroy them.

Measurements of PAN, Alkyl nitrates, NO<sub>y</sub>, NO, NO<sub>2</sub>, CO, HNO<sub>3</sub>, O<sub>3</sub>, and particulate nitrate were made at a rural site in Cape Norman, Newfoundland from February 1996 to May 1996. The focus of this thesis will be on the analysis of PAN and alkyl nitrates. The measured PAN concentration varied from below 2 pptv to a maximum of 783 pptv. The lack of a diurnal trend in the PAN data shows that PAN was transported to the Cape Norman site during the campaign. PAN/NO<sub>y</sub> ratios were determined to be 40 % in arctic air masses, and the thermal decomposition of PAN was not determined to occur faster over open water versus over land. The measured Alkyl nitrate concentration varied from 3 pptv to 101 pptv. Alkyl nitrates were determined to be transported to the site by comparison to an analytical expression.

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## CHAPTER I

### INTRODUCTION

The atmosphere is a mixture of compounds, primarily nitrogen and oxygen, extending to approximately 110 kilometers above surface. Ninety-nine percent of the mass of the atmosphere is below 30 kilometers and half of that mass is below 5.5 kilometers. The atmosphere is divided into different layers by altitude and temperature, as a result of several inversion layers at vertical intervals, as seen in Figure 1.

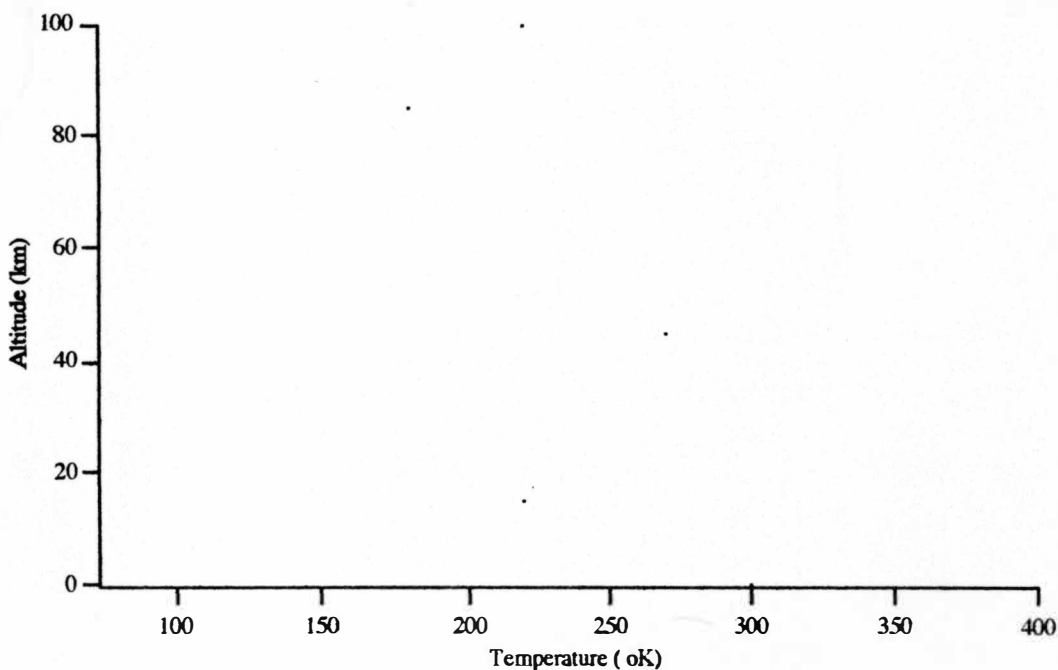


Figure 1. Altitude vs Temperature Graph (Finlayson-Pitts, 1986).

The bulk of the atmosphere is in the first two layers, the stratosphere and the troposphere. This is where most of the chemistry occurs.

The layer closest to the surface up to approximately 18 kilometers is the troposphere. Initially temperature decreases with an increase in altitude due to heating from the absorption of visible and near ultraviolet solar radiation by the earth's surface. The troposphere is characterized by strong vertical mixing. Molecules can move the entire depth of this layer in a few days in calm air and a few minutes during large thunderstorms (Wayne, 1993).

The stratosphere is the layer above the troposphere extending to about 50 kilometers. In the stratosphere the temperature increases with increasing altitude due to photochemical reactions involving ozone ( $O_3$ ) and molecular oxygen ( $O_2$ ) (Finlayson-Pitts, 1986). Ozone strongly absorbs radiation from 210-290 nm and molecular oxygen absorbs at  $\leq 200$  nm. The absorption of light by  $O_3$  is also responsible for filtering radiation which is detrimental to life. The filtering by  $O_3$  and  $O_2$  sets limits on tropospheric photochemistry, enabling only molecules that absorb radiation  $> 290$  nm to undergo photodissociation.

The stratosphere is characterized by little vertical mixing. It may take molecules years to be transported vertically through this layer. Since the temperature within the stratosphere is warmer than the air within the troposphere, as seen in Figure 1, an inversion layer occurs. An inversion layer is when warm air flows over a cold surface or colder air, causing a shallow mixing layer topped by a more stable layer (Seinfeld, 1986). The inversion layer, referred to as the tropopause, is the boundary between the troposphere and the stratosphere. The air below the tropopause is continually mixing within the troposphere and has minimal contact with the air in the stratosphere, therefore, the majority of the chemistry in the atmosphere occurs in the troposphere.

## Tropospheric Chemistry

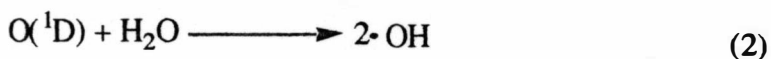
The chemistry in the troposphere is characterized by radical chain reactions initiated by sunlight (Finlayson-Pitts, 1986). Since the upper atmosphere acts as a filter to remove short-wavelength radiation, the photochemistry is driven by the lower energy photons that reach the surface, particularly the near-ultraviolet. According to Seinfeld, SO<sub>2</sub>, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, nitrogen dioxide (NO<sub>2</sub>), and aldehydes absorb in the near-ultraviolet (Seinfeld, 1986). Ozone and nitrogen dioxide are the most abundant of these molecules found in the troposphere and are a main source of radicals.

### Ozone

Ozone plays different roles in the troposphere than in the stratosphere where ozone is primarily decomposed by ultra-violet absorption. In the troposphere, ozone can absorb a photon of radiation  $\leq 310$  nm to give O<sub>2</sub> and an excited oxygen atom O(<sup>1</sup>D).



The excited oxygen atom reacts with water present in the atmosphere to form hydroxyl radicals (OH). The reactions of OH radicals drives the daytime chemistry of the troposphere. About 10 % of the O(<sup>1</sup>D) in Reaction 1 will react with water to form the hydroxyl radical (Wayne, 1993). The majority of the O(<sup>1</sup>D) is deactivated by water to the ground state oxygen atom O(<sup>3</sup>P). The O(<sup>3</sup>P) can react with O<sub>2</sub> to reform O<sub>3</sub> thus there is not a net loss of O<sub>3</sub>.



Reaction 2 is the major source of the OH radical, but OH radical can also be formed from the photolysis of HONO, H<sub>2</sub>O<sub>2</sub>, and HCHO.



The photolysis of HCHO requires more than one step to form the OH radical.



The hydroxyl radical propagates chain reactions by attack on organic compounds or CO. These reactions produce additional radicals, preventing the radical production to reach steady state.

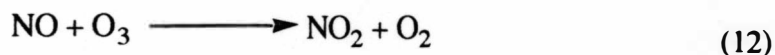


Reaction 8 is responsible for converting CO to CO<sub>2</sub>, a greenhouse gas, which traps radiation in the troposphere causing a rise in atmospheric temperature. The product radicals propagate the chain by forming peroxy radicals via reaction with O<sub>2</sub>. These peroxy radicals play a critical role in tropospheric chemistry.

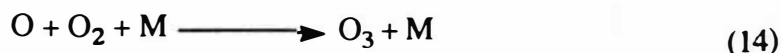


## NO<sub>x</sub>

Nitric oxide and nitrogen dioxide are grouped together into a category called NO<sub>x</sub>. Nitric oxide (NO) is formed in the atmosphere from biological processes (microbial actions in soil and the oxidation of ammonia (NH<sub>3</sub>) by OH radicals) and from anthropogenic processes (biomass burning and high temperature combustion). NO is readily oxidized by ozone in the atmosphere to NO<sub>2</sub>.

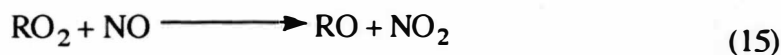


The photolysis of NO<sub>2</sub> is responsible for the production of O<sub>3</sub> in the troposphere. NO<sub>2</sub> photodissociates at wavelengths  $\leq 400$  nm.



(M is an inert molecule)

The formation of peroxy radicals, reaction 11, can regenerate NO<sub>2</sub>.



Reactions 12, 13, and 14 are referred to as the photostationary state, where the steady state ozone concentration is proportional to the [NO<sub>2</sub>]/[NO] ratio.

NO<sub>x</sub> is a component of an even larger oxidant group, NO<sub>y</sub>, the total oxidized nitrogen in the atmosphere. NO<sub>y</sub> consists of NO, NO<sub>2</sub>, nitric acid (HNO<sub>3</sub>), HONO, alkyl nitrates, and PAN. Figure 2 shows the major processes of the NO<sub>y</sub> system.

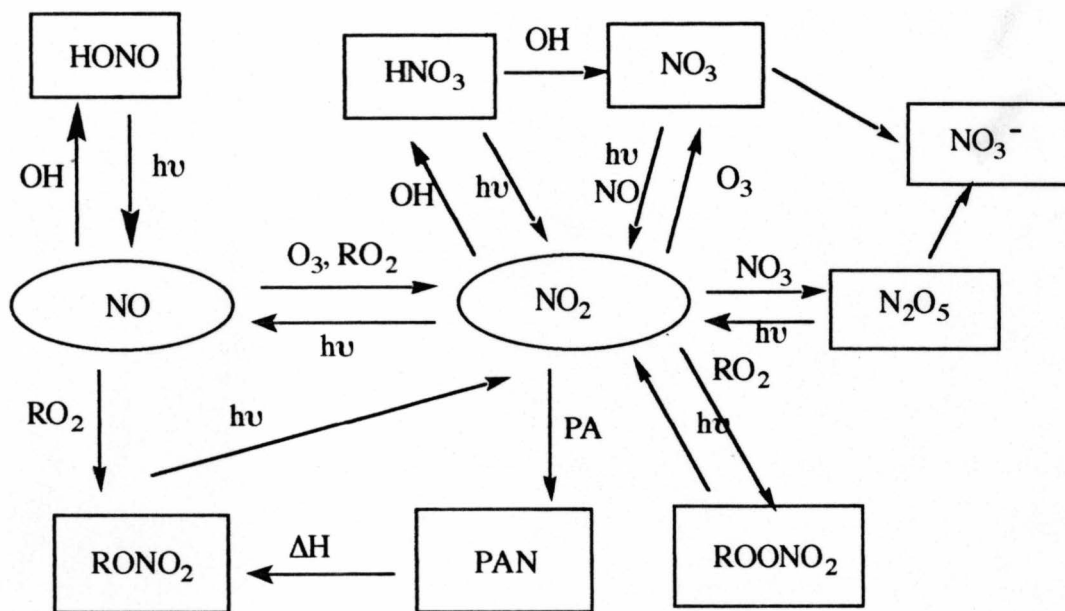


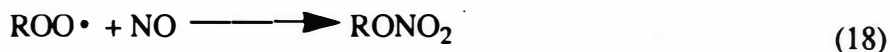
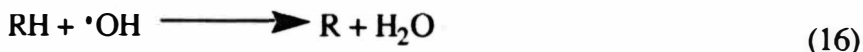
Figure 2. Reactive Nitrogen Species (Roberts, 1990).

NO<sub>x</sub> is processed through a variety of chemical reactions. Among these are reactions with organic compounds. The organic compounds can sequester NO<sub>x</sub> from the atmosphere, affecting the formation of ozone. The secondary products that are formed from the reaction of NO<sub>x</sub> with the organic compounds are a part of NO<sub>y</sub>. The NO<sub>y</sub> products are less reactive and allow for the transport of NO<sub>x</sub> to other areas. Knowing the partitioning of NO<sub>y</sub> gives information on the potential of NO<sub>x</sub> available to form ozone.

### Role of Organic Carbon

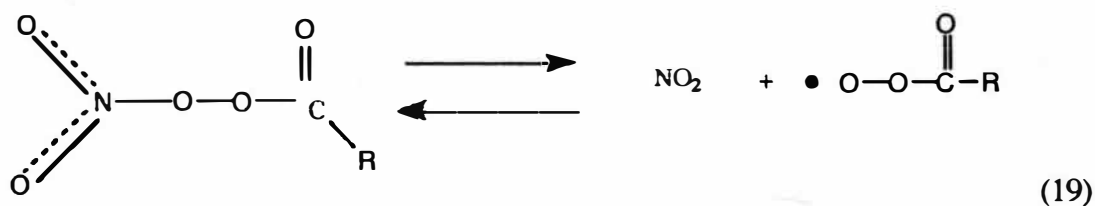
Organic compounds enter the atmosphere via release from natural sources, chemical manufacturing, and auto exhaust, which contains large amounts of partially burned and unburned gasoline. The reaction of organic compounds in the atmosphere

with  $\text{NO}_x$ , as seen in Figure 2, can form stable compounds through reactions with radicals or through photolysis.



For instance, alkane will react with OH radicals to form alkyl radicals. Smaller alkane radicals, carbon chain length of four or less, will follow the pathway of oxidation of NO to  $\text{NO}_2$  (Finlayson-Pitts, 1986). Larger chain length radicals will form the organic nitrate compounds due to more carbon-hydrogen bonding. Organic nitrates are quite stable and allow for the transport of  $\text{NO}_x$  to different geographical locations and provides a reservoir for  $\text{NO}_x$  in areas where sources of  $\text{NO}_x$  are scarce.

An important sub category of organic nitrate compounds is peroxyacyl nitrates or PANs, whose general structure is shown below. PANs form from the reversible reaction of acyl peroxy radicals with  $\text{NO}_2$ .



The reverse reaction is quite facile and temperature dependent.

The decomposition of PAN occurs according to the Arrhenius expression  $k = 10^{17.4 \pm 0.4} e^{(-28.5 \pm 0.5/RT)}$  with temperatures measured between 302-323 °K (Roberts and Bertman, 1992). The decomposition of PAN releases NO<sub>2</sub> into the troposphere.

The measurement of known NO<sub>y</sub> species in field studies, NO<sub>x</sub>, HNO<sub>3</sub>, PAN and particulate nitrate is less than the total measured NO<sub>y</sub>. The missing fraction of NO<sub>y</sub> has been as much as 45 % measured at Niwot Ridge, Colorado (Fahey, 1987) and as low as 10 % at Scotia, Pennsylvania (Hubler, 1987). This deficit is likely due to some organic nitrate species (Roberts, 1990).

Organic nitrates, including PAN, comprise a large fraction of NO<sub>y</sub> in the troposphere and constitute an important category of atmospheric compounds. Another class of important organic nitrates is the alkyl nitrates. Alkyl nitrate sources and sinks represent a large potential for interaction between the nitrogen and carbon cycles in the atmosphere. Alkyl nitrates have a relatively long lifetime and are an important reservoir for NO<sub>y</sub> in the troposphere. Shepson, et al., showed that at low NO<sub>y</sub> levels, alkyl nitrates can contribute 3-4 % of the total NO<sub>y</sub> at a continental site (Shepson, 1993), and Bottenheim, et al., showed alkyl nitrates contributed up to 20 % of NO<sub>y</sub> in arctic air masses (Bottenheim, 1993). Multi-functional nitrates may contribute even more to the total NO<sub>y</sub>.

### Alkyl Nitrates

Alkyl nitrates are formed in the troposphere by the oxidation of hydrocarbons. The rate determining step is the hydrogen abstraction by the hydroxyl radical to form a carbon-centered radical, as seen in reactions 16, 17, and 18. The alkyl radical quickly reacts with O<sub>2</sub> to form a peroxy radical which reacts with NO to form NO<sub>2</sub> and RO. The peroxy radical can also react with NO to form an alkyl nitrate. Atkinson, et al.,

showed that the branching ratio in alkyl nitrate formation varies from 0.08 for a two carbon chain length to 0.30 for an eight carbon chain length; larger chain length the greater chance of directly forming an alkyl nitrate (Atkinson, 1982).

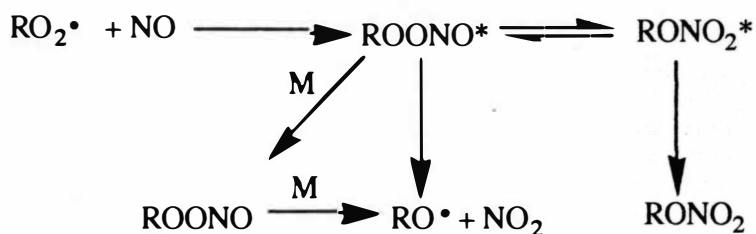


Figure 3. Mechanism for the Formation of Alkyl Nitrates.

Atkinson, et al., hypothesized a mechanism for the formation of alkyl nitrates, as seen in Figure 3 (Atkinson, 1983). The mechanism has the reaction of ROO with NO as a multi-step process. The first step is the formation of an unstable vibrationally excited peroxy nitrite (ROONO\*). The excited peroxy nitrite, suggested by Atkinson but not proven, goes through a rearrangement to form an excited nitrate (RONO<sub>2</sub>\*) by formation of a three-membered ring transition state, Figure 4. The excited species can decompose to form RO + NO<sub>2</sub> or can collisionally deactivate.

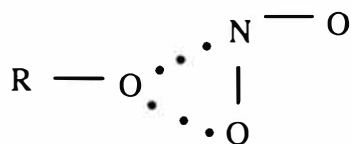


Figure 4. Transition State of an Alkyl Peroxynitrite to an Alkyl Nitrate.

#### Removal of Alkyl Nitrates

Alkyl nitrates can be removed from the atmosphere through three processes, dry and wet deposition, reaction with OH, or photolysis at wavelengths above 300 nm

(Taylor, 1980). Measurements of the Henry's Law constants has shown that the alkyl nitrates are not very water soluble, so wet deposition is insignificant (Luke, 1989). Atkinson (1982), et al., determined that the first-order rate loss due to dry deposition is small except for 2-propyl nitrate. The main removal processes of alkyl nitrates are photolysis and reaction with OH radicals.

The rate of removal of alkyl nitrates in the atmosphere by photolysis and OH radical is similar for lighter nitrates,  $C_2$ - $C_4$ , (Atkinson, 1982). For heavier alkyl nitrates, carbon chains longer than four carbons, the contributions of the OH radical become more significant. Kerr and Stocker experimentally determined the lifetimes of methyl nitrate, ethyl nitrate, and n-propyl nitrate to be 31 days, 24 days, and 17 days respectively at a temperature of 305 °K (Kerr and Stocker, 1986). Experiments like this have shown that the alkyl nitrates have long lifetimes, making the compounds important nitrogen reservoirs, (Roberts and Fajer, 1989).

## CHAPTER II

### PURPOSE

The purpose of this thesis is to present the analysis of organic nitrates, including PAN, and alkyl nitrate data from the Arctic Outflow Study. The PAN data was measured by GC-ECD and the alkyl nitrate data was measured using the technique developed by Atlas and Schauffler, (Atlas and Schauffler, 1991 and modified by Shepson, (Shepson, 1993).

The North Atlantic coastal rim of the United States and Canada contain industrial regions which are major global sources of pollutants. The pollutants emitted from these areas are transported over the North Atlantic Ocean, a relatively pollutant-free environment. The North Atlantic region thus gives an excellent opportunity to study the mechanisms of chemical processing of the emitted compounds. One of the field studies to take place in the North Atlantic was the Arctic Outflow Study.

The Arctic Outflow Study (AOS) was a project funded by the National Science Foundation to assess the impact of tropospheric ozone concentrations by the measurement of oxidized nitrogen.  $\text{NO}_y$  compounds,  $\text{HNO}_3$ ,  $\text{NO}_x$ , PAN, particulate nitrate and alkyl nitrates were measured from the end of February through April of 1996 in a lighthouse in Cape Norman, Newfoundland. The organizations that participated in this study and the data they measured is in Table 1.

It was originally thought that air masses originating from the arctic should be clean since there are no forms of pollution, cars or factories, in the arctic. However, this is not true. Air masses from Asia and Europe are transported to the Arctic region and

trapped during the winter period (Honrath, 1996). Without photolysis, there is no way to break down the pollutants, so the concentrations build up. Once spring arrives

Table 1  
Arctic Outflow Study Participants

<b>Organization</b>	<b>Measurements</b>
Michigan Technological University	NO, NO <sub>2</sub> , NO <sub>y</sub> , Eppley UV - project organizers
National Oceanic and Atmospheric Administration	CO, O <sub>3</sub> , meteorological parameters, HNO <sub>3</sub>
Purdue University	Alkyl Nitrates
York University	C <sub>2</sub> -C <sub>6</sub> non-methane hydrocarbons
University of Virginia	Meteorological data
University of Rhode Island	Forecasts and archival of forecasts
Western Michigan University	PAN, PPN, and alkyl nitrates

and the sunlight returns to the Arctic, the compounds can be photolyzed and transported to an area like the North Atlantic region. The measurement of air masses in the Arctic has been the focus of many studies, such as the Polar Sunrise Experiment and the Arctic Boundary Layer Expedition. However, there has never been a study to measure the concentrations of the pollutants being transported out of the Arctic. The Arctic Outflow Study is the first study to measure the effect of transported Arctic air masses on the North Atlantic region (Honrath, 1996).

The purpose of the Arctic Outflow Study is to provide a clear picture of the winter-spring change of the compounds in outflowing arctic air and the processes which decay arctic NO<sub>y</sub> and non-methane hydrocarbon concentrations during transport to the south. These photochemically active compounds are elevated in the arctic troposphere during winter and spring because of the reduced removal rates and an increase in transport from the source areas. The transport from the arctic provides a flux of the total NO<sub>y</sub> and non-methane hydrocarbons to the North Atlantic. This flux can contribute to the ozone budget in remote regions.



Figure 5. Map of Canada and Newfoundland.

The measurements of PAN, alkyl nitrates, and  $\text{NO}_x$  provides information on the release of  $\text{NO}_x$  from the PAN and alkyl nitrate reservoirs. When PAN and alkyl nitrates decompose,  $\text{NO}_x$  is released into the atmosphere. The non-methane hydrocarbon measurements provide information on the pathways of the decay of alkyl nitrates and non-methane hydrocarbons. The data for the measurement and analysis of organic nitrates will be given in this thesis.

The organic nitrates are analyzed to try to address three particular questions. The first is to show that PAN and alkyl nitrates are transported from the arctic. The second is to show that PAN decomposes during Arctic outflow. The last aspect of this thesis is to compare the PAN concentrations transported over land versus open water.

## CHAPTER III

### METHODS AND MATERIALS

The methods and materials section describes the measurement and analysis of organic nitrates, PAN and alkyl nitrates, in Canada as part of the Arctic Outflow Study. The Arctic Outflow Study was a field study from February 1996 to May 1996. The measurements were made in a lighthouse, at Cape Norman, Newfoundland, the northern tip of Newfoundland. Cape Norman is located at 55 ° 54.5' West and 51 ° 37.75' North and the lighthouse is approximately 50 feet above sea level. The closest town to the site is a small fishing village, Cook's Harbour, where there is no industry and minimal pollution from automobiles. The lighthouse has four levels, (see Figure 6). The PAN and alkyl nitrate systems were situated on the second floor. The sample inlet box was attached to the outside catwalk of the lighthouse, facing north-northwest towards the ocean.

#### Measurement and Analysis of Organic Nitrates

##### PAN System

PAN was measured using a modified gas chromatograph with electron capture detection. The Shimadzu Mini-2 ECD detector was set at a temperature of 55 °C. Two cc samples of whole air were injected onto the column for 20 seconds every 15 minutes with a Hamilton teflon valve. The GC column was a twenty meter J&W DB210 0.53 mm i.d. Megabore column and the column temperature was set at 15 °C by means of

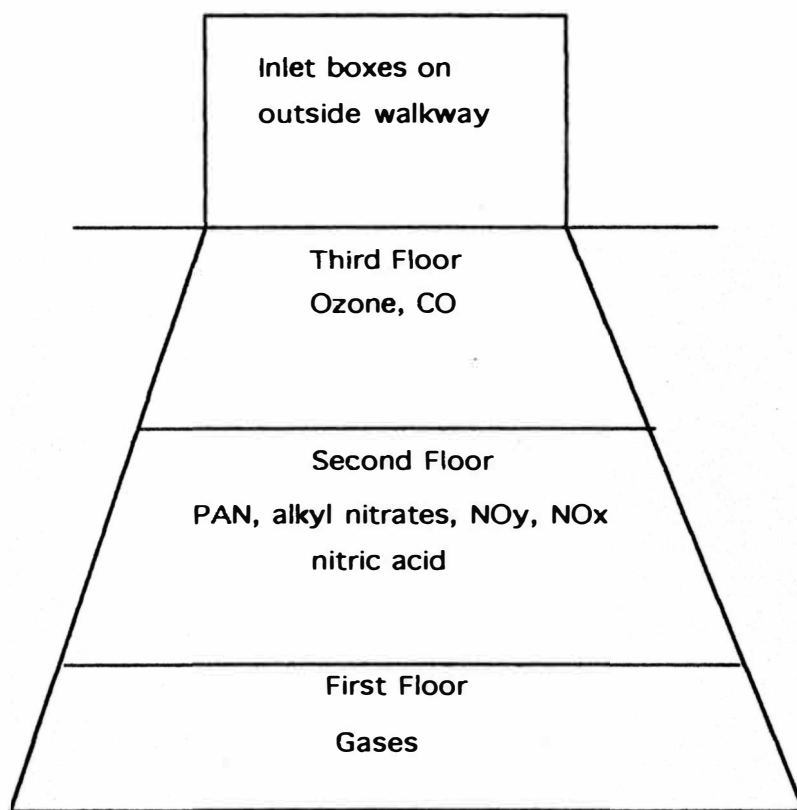


Figure 6. Schematic Diagram of Experiments Performed in the Various Lighthouse Levels.

Thermoelectrics controlled by a Love programmable temperature controller. Helium was used as the carrier gas set at a flowrate of 15 cc/min. Nitrogen was used as the make-up gas and was set at a flowrate of 2 cc/min.

The air samples were drawn through the system, Figure 7, through a teflon inlet at 1000 sccm (standard cc per minute). Valves 1, 2, and 3 are unpowered for ambient runs and powered for calibrations. Flows for the GC sample loop, set at 35 sccm, and the alkyl nitrate system, set at 300 sccm, were taken off the main inlet.

The chromatograms were collected and analyzed by the chromatography program Chromperfect and a Data Translations 20 bit A/D PC Board. The PAN chromatograms were integrated and the peak areas were recorded. The concentrations

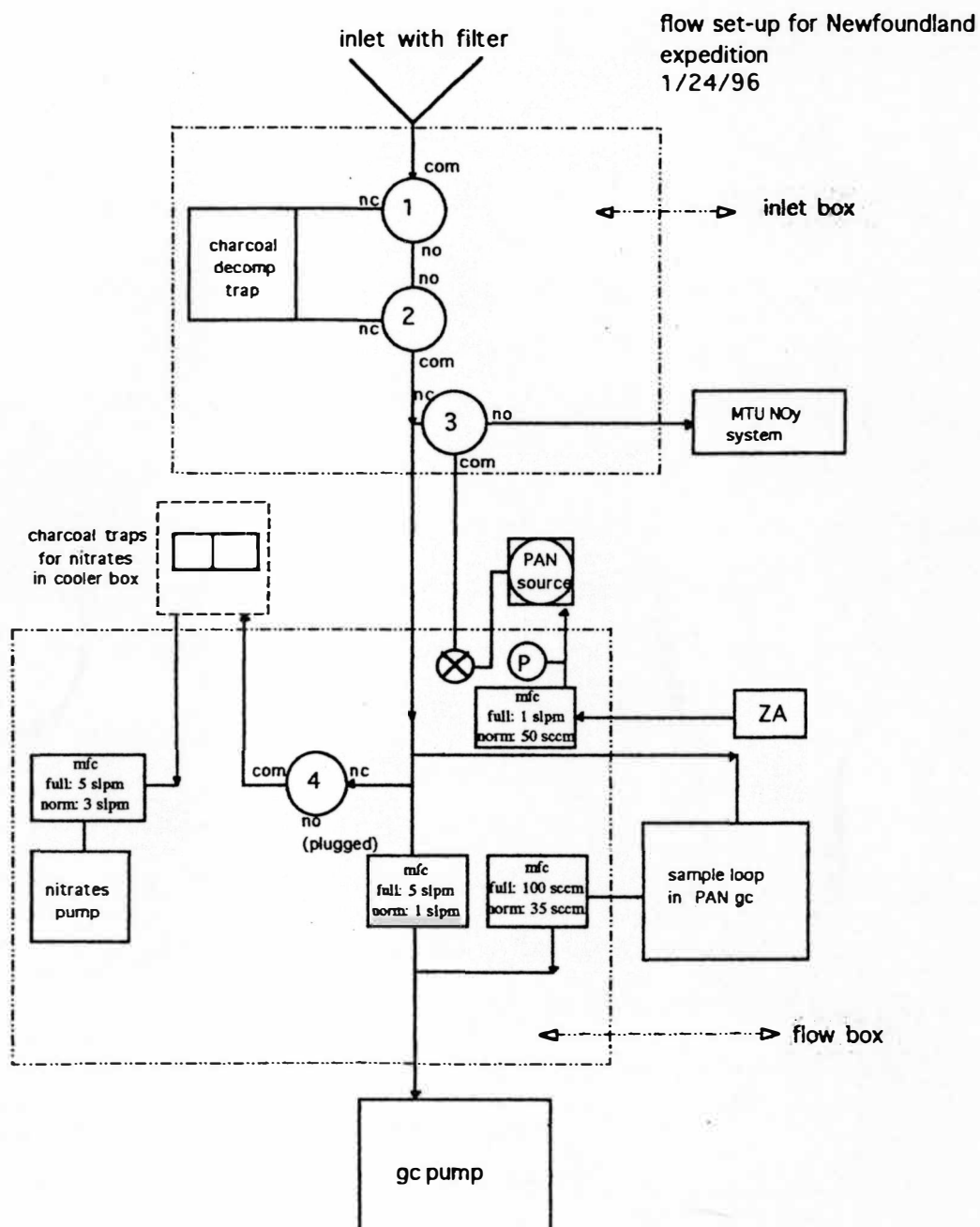


Figure 7. Sampling System for the Organic Nitrates.

of the PAN peak areas were obtained from a calibration curve of PAN concentration versus PAN area.

### PAN Calibrations

Approximately 1 mL of a dilute PAN standard in tridecane solvent was placed into a diffusion cell under flow of 50 sccm Zero Air, (ultra pure air). The PAN vapor flowed to valve 3 where the concentration was measured by Michigan Technological University's catalytic NOy system. To calibrate the PAN GC, valves 1, 2, and 3 were powered and ambient air was scrubbed of ambient organics through a charcoal decomposition trap. The air was then mixed with the PAN standard and sampled by the GC. A multi-point calibration curve was prepared by changing the dilution flow.

### Sampling System for Alkyl Nitrates

The sampling technique for the alkyl nitrates was developed by Atlas and Schauffler 1988 and modified by Shepson 1995. The technique involved pumping air, approximately 300 cc/min, through a 1/4 inch glass tube containing 5 mg of charcoal held in place by a foil (Paxton Scientific Glass, Loveland, OH). Two of the glass tubes were connected in series, with the front tube and back tube labeled accordingly, using stainless steel unions with teflon ferrules (see Figure 8).

The unions were only fingertight to make sure the glass tubes did not break. The glass tubes were kept below 10 °C, the normal ambient room temperature in the lighthouse with little temperature fluctuations. The front tube was connected to a section of 1/4 inch teflon tubing which was split off from the main inlet line of the PAN-GC system with a Fluoroware series 211 inline teflon filter in the nitrate sampling line. The back tube was connected to a section of 1/4 inch teflon tubing running to a mass flow meter and to a pump.

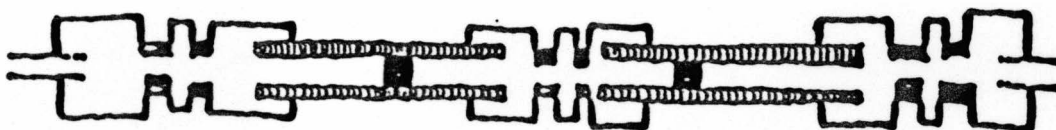


Figure 8. Schematic Diagram of Charcoal Traps.

The samples were collected daily from 10:00 am to 4:00 pm, unless the winds were out of the north. Winds out of the north were considered outflow weather and the samples were collected for four hours, the minimum sampling time necessary to achieve concentrations above the detection limit. The four hour samples were continually sampled throughout the outflow weather period. The alkyl nitrates were sampled at the same time and interval as the nitric acid filters. After the collection of the samples, the tubes were capped and kept cooled below 10 °C until the charcoal beds could be extracted, preferably within 24 hours.

#### Extraction of Charcoal

The extraction procedure is the source of most of the human error in this technique, so the extraction was practiced on blank traps first. The glass tubes were extracted with benzene and placed in glass capillary tubes, labeled with the tube number, date of extraction, and which charcoal tubes were used.

The front tube was extracted twice. 50  $\mu$ L of benzene was used for the first extraction, adding 20  $\mu$ L, 15  $\mu$ L, and 15  $\mu$ L aliquots. The benzene was added to the tube using a 100  $\mu$ L Dynatech precision sampling syringe (2-0953). After each

addition of benzene, the tube was held horizontally and a rubber bulb was placed on one end of the tube. Gently touching the bulb, the benzene was pushed back and forth through the charcoal bed approximately 30 times. It was easy to lose solvent by being impatient and forcing the solvent out of the tube. After the extraction, a 25  $\mu\text{L}$  Dynatech precision sampling syringe (2-0951), with the point of the needle cut off to leave a flat tip, was used to remove the extract from the traps. The flat tip was necessary so the gold foil holding the charcoal in the traps did not get punctured by the syringe.

The above procedure was repeated for the second extraction of the front tube using 30  $\mu\text{L}$  of benzene. The rear trap was then extracted using 50  $\mu\text{L}$  of benzene. Each of the three extracts was placed in its own capillary tube. The capillary tube was labeled with the sample name, date, and extract identity. The tubes were sealed with a propane torch and kept frozen until analysis could be performed.

The charcoal tubes were re-usable and were washed after each use with 100  $\mu\text{L}$  portions of methanol, then with two 50  $\mu\text{L}$  portions of benzene. The charcoal tubes were dried by blowing zero air through the tubes for a few seconds.

### Storage and Shipment

After the sampling and extraction procedure, the capillary tubes were stored in a glass jar, which was kept frozen. At the end of the campaign, the capillary tubes were wrapped in bubble wrap and placed in a styrofoam cooler with dry ice packed around the samples and on top. The styrofoam cooler was placed in a plastic commercial cooler to be shipped to York University in Toronto, Ontario.

### Analysis at York University

The samples, once received at York University, were kept wrapped in bubble wrap and placed in a freezer. The samples were analyzed in the order of importance, outflow samples and blanks were run first. Standards were used often to account for drift in the luminol baseline.

The alkyl nitrates were analyzed from the end of April through mid-May by George Nouaime of Western Michigan University. The samples were analyzed according to a procedure from Atlas and Schauffler and modified by Hao (Hao,1994). The samples were analyzed by capillary gas chromatography using an electron capture detector (ECD) in series with a pyrolysis/luminol chemiluminescence detector. A 3300 Varian GC equipped with a  $^{63}\text{Ni}$  ECD heated to 180 °C was used. The sample was separated using a 30 m X 0.53 mm id DB-1701 capillary column with nitrogen as carrier gas, 6.5 ml/min, and make-up gas, 20 ml/min. The GC-ECD is sensitive to electronegative species, like alkyl nitrates. However, halogens interfere with the measurements, so a luminol-based chemiluminescence detector was used in series with the ECD. The luminol-based chemiluminescence detector responds only to compounds that thermally decompose to yield  $\text{NO}_2$ . Five  $\mu\text{L}$  of the samples was injected on the GC. After the sample goes through the ECD, the sample is pyrolyzed at 350 °C, which quantitatively produces  $\text{NO}_2$ . The  $\text{NO}_2$  reacts with the luminol and a chemiluminescent signal is recorded (Hao, 1994).

### Calibration

Before the samples were run, three different concentrations of standards were made, 0.1 picomolar, 0.2 picomolar, and 0.5 picomolar. The standards contain 19 alkyl nitrates which elute in the following order and retention time:

Peak 1	2-propyl nitrate	4.76 min
Peak 2	1-propyl nitrate	5.52 min
Peak 3	2-butyl nitrate and isobutyl nitrate	6.62 min
Peak 4	1-butyl nitrate	7.94 min
Peak 5	3-methyl-2-butyl nitrate	8.25 min
Peak 6	3-pentyl nitrate	8.70 min
Peak 7	2-pentyl nitrate	8.90 min
Peak 8	2-methyl-1-butyl nitrate	9.34 min
Peak 9	3-methyl-1-butyl nitrate	9.48 min
Peak 10	1-pentyl nitrate	10.47 min
Peak 11	3-hexyl nitrate	10.84 min
Peak 12	2-hexyl nitrate	11.29 min
Peak 13	1-nitrooxy-2-propanol	12.90 min
Peak 14	2-nitrooxy-ethanol	13.14 min
Peak 15	2-nitrooxy-1-propanol	13.57 min
Peak 16	3-nitrooxy-2-butanol	13.77 min
Peak 17	1-nitrooxy-2-butanol	14.81 min
Peak 18	2-nitrooxy-1-butanol	16.857 min
Peak 19	1,2-dinitrooxy butane	18.121 min

The standards were prepared from a 5 picomolar stock solution which was prepared on November of 1994 by Jason O'Brien. The stock solution was compared to a freshly prepared isopropyl nitrate solution, made on May 14, 1996 by Dr. Paul Shepson, to determine the concentration decay of the stock solution. The stock solution concentration was determined to be 90 % of the original solution. The 0.1, 0.2, and 0.5 picomolar solutions were remade periodically, when the peak area of the standard was significantly less, this varied with how often the solutions were used and refrozen. These solutions decay faster because of the low concentration, therefore, the decay was more noticeable than in the stock solution.

#### Data Analysis and Calculations for Alkyl Nitrates

The data analyses and calculations were divided into two categories, results from the ECD detector and results from the Luminol detector. The luminol data was analyzed by comparing the retention times of peaks in a sample to the retention time of peaks in a standard. Any other peaks that did not match up with the retention times of the standards were labeled as unknown nitrates. The ECD data was analyzed by

comparing the retention times of peaks in a sample to the retention times of peaks in a standard.

The following data was obtained for the calculations.

1. The time the traps were under flow- obtained from the nitrate log book
2. The flow through the traps/volume of air sampled- obtained from summing the recorded voltage from a Mass Flow Meter. The voltage was recorded as one-minute averages. The volume was obtained from a calibration curve.
3. The moles of air = (Flowrate x Volume Sampled).
4. The volume of the sample capillaries- 50  $\mu\text{L}$  for volume of Fa and R, and 30  $\mu\text{L}$  for Fb.

5. Picomoles of the standards used- (Std.conc.)(injection vol = 5 $\mu\text{L}$ ).
6. Average standard area- Standards were run between extract runs, the peak areas of the standards were averaged.
7. The sample concentration [ppt] was calculated by the following:

$$(\text{Sample area} / \text{Std. area}) \times (\text{picomoles of Std.}) \times (\text{Vol. in capillary} / \text{Vol. injected}) \times (1 / \text{moles of air})$$

The nitrate concentrations for each compound were added together to get a total concentration. The precision in the alkyl nitrate samples was approximately 20 %. The large error in the precision is due to the sampling technique, extraction procedure, and the error of averaging the standard areas in the calculation of the alkyl nitrate calculation.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### PAN Analysis

Peroxyacetyl nitrate (PAN) is prevalent over continental sites of NO<sub>x</sub> emissions, mainly over midlatitudes in the northern hemisphere. PAN is distributed relatively zonally throughout the troposphere of the northern hemisphere, with the maximum levels found in the coldest regions, as calculated by Moxim (Moxim, 1996) and measured by Bottenheim (Bottenheim, 1993). Moxim found that PAN is uniformly spread, with values in the 200 - 500 pptv range during the coldest periods. This is a result of strong midlatitude winter circulation mixing PAN northward and eastward from industrial regions of the United States, Europe, China, and Japan. The spring maximum in PAN concentration in the northern high latitudes is related to, and partly responsible for, the observed spring maximum in tropospheric ozone (Penkett and Brice, 1986). This section will give evidence to support the hypothesis that organic nitrates, especially PANs, have relatively long lifetimes during the northern hemisphere winter and through transport to lower latitudes, can affect local and regional ozone budgets in the spring.

In order to analyze for air masses from the arctic, the origins of the air masses that reached Cape Norman were needed. Air mass back trajectories were calculated by John Merrill from the University of Rhode Island. The trajectories were calculated twice a day, at midnight and noon, for the entire period of the campaign. The air masses were tracked, by analysis of different air mass potential temperatures in the atmosphere, for ten days previously from when the air mass reached Cape Norman,

Newfoundland. The trajectories were interpreted with day zero being the day the air mass reached Newfoundland, day one was where the air mass was the day before, and so on. With the aid of these trajectories, the data collected throughout the campaign, especially the organic nitrates, can be discussed.

The PAN data measured throughout the campaign, shown in Figure 9, shows that a variety of air masses reached Newfoundland. The original hypothesis was that the arctic outflowing PAN concentration should be relatively constant. This hypothesis was based on the fact that arctic PAN measurements are at a relatively constant concentration (Worthy, 1994). However, the variability in PAN concentrations, as seen in Figure 9, was quite large. The variability in the PAN concentrations was due to different types of air masses measured at the site.

On February 25 through February 27, the PAN concentration was at the lowest concentration seen throughout the campaign. The PAN concentration was less than 2 pptv. In contrast, there were periods of high PAN concentrations during the middle of March. The PAN concentration reached a maximum for the campaign on March 23 of 783 pptv. This maximum is comparable to the daily average PAN concentration measured during the Southern Oxidants Study, (SOS) July of 1995, in Nashville, Tennessee. The Southern Oxidants Study is a long term study to assess the accumulation of ozone concentrations in the southeastern United States. The SOS study will be used as a comparison to contrast the arctic outflow data because the measurements of PAN were made at a site close to large emission sources (Nouaime, 1997). The high PAN concentration suggests that the North Atlantic region is affected by the continental industries.

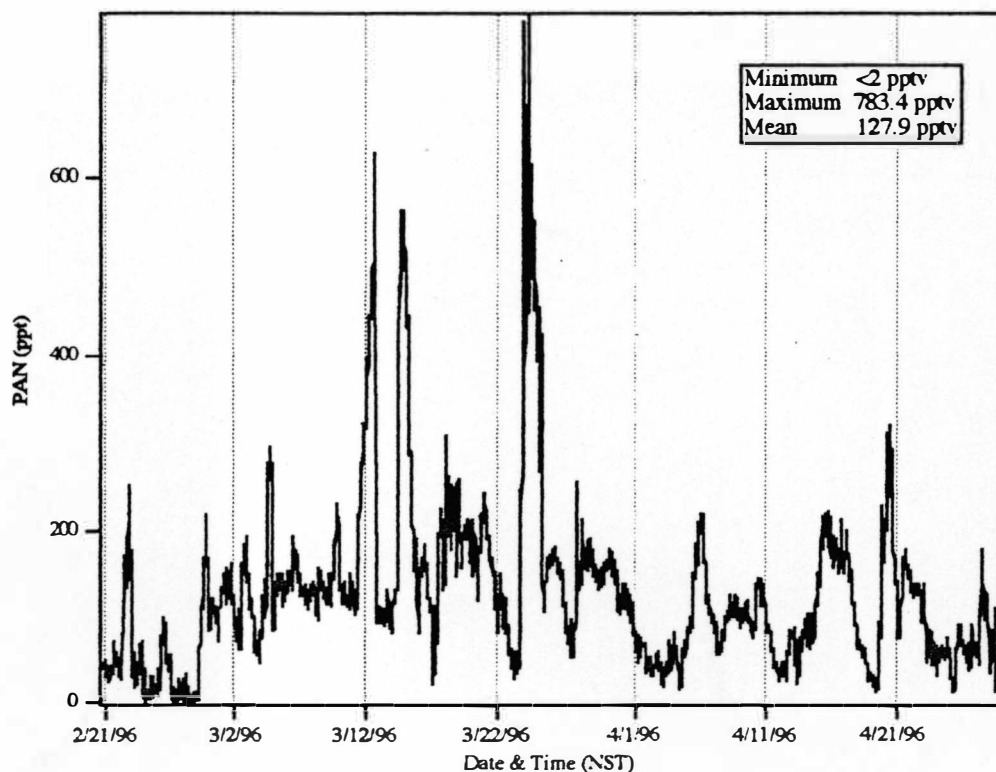


Figure 9. PAN Data for the Arctic Outflow Study. The PAN data in parts per trillion per volume (pptv) is graphed versus date and time in Newfoundland standard time.

### Alkyl Nitrate Analysis

As noted previously, alkyl nitrates have relatively long lifetimes, on the order of days, with the main removal mechanism being reaction with hydroxyl radical and photolysis (Kerr and Stocker, 1986). Alkyl nitrates, besides being a reservoir for  $\text{NO}_x$ , can be used to estimate how long a polluted air mass has been transported. This is determined by the amount of photochemical processing of the alkyl nitrates. The alkyl nitrate data will be presented as the total nitrate concentration with the individual alkyl nitrate concentrations added up for the given timeperiod. Figure 10 shows the total alkyl nitrate concentration data and the data for n-butane for the campaign.

N-butane is graphed with the alkyl nitrates as a representative sample of the hydrocarbon data analyzed by Valerie Young from Ohio University.

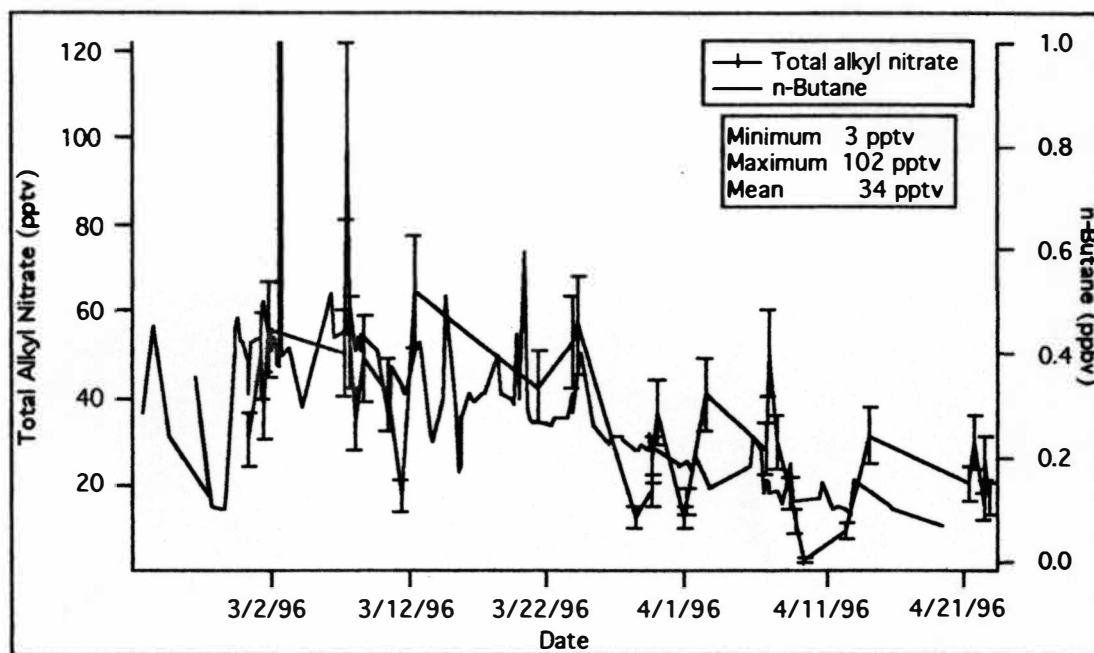


Figure 10. Total Nitrate and n-Butane Data

The absolute alkyl nitrate concentration is similar to what has been measured in the arctic, 34-128 pptv (Shepson, 1993, Bottenheim, 1993, Muthuramu, 1994). An interesting trend seen in Figure 10 is the slow decrease in the total alkyl nitrate concentration and the n-butane concentration. The slope of a linear regression of the data is  $-7.89 \times 10^{-8}$  with an R value of -0.57. This weak trend shows that as Spring progressed, the concentration of the hydrocarbons and the alkyl nitrates decreased. This could be due to an increase in photochemical activity. With the increase in photochemical activity, the hydrocarbon concentrations decrease, and with a lack of NO<sub>x</sub>, the formation of the alkyl nitrates decreases.

## Transport of PAN

In order to answer the question of transport, diurnal trends for the PAN data from the Arctic Outflow Study, Figure 11, are compared to the diurnal trends for the PAN data from the Southern Oxidant Study, Figure 12, which is an example of an urban continental sites. Figures 11 and 12 are daily averages of the PAN data for the entire campaign periods for each hour of the day.

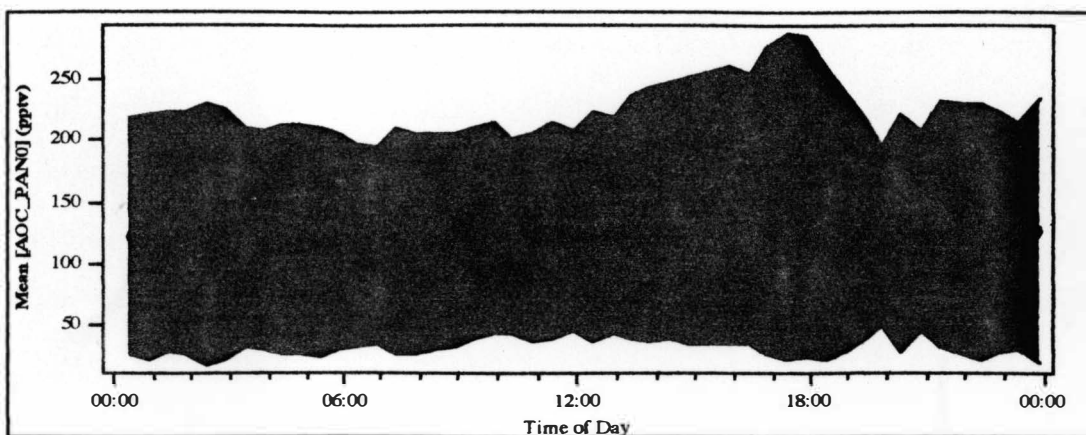


Figure 11. Arctic PAN Diurnal Graph.

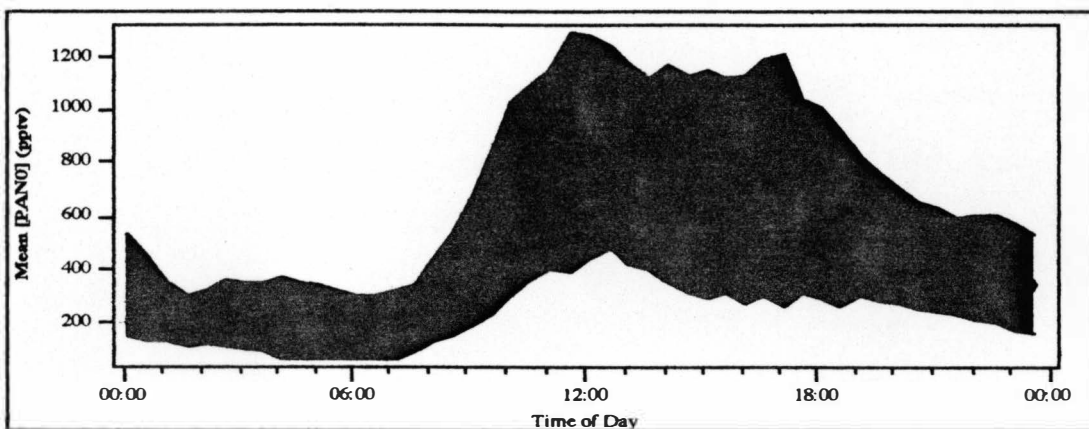


Figure 12. Southern Oxidants Study's PAN Diurnal Graph.

In Figure 12, the average Southern Oxidants Study PAN data started out at a relatively low concentration of approximately 300 pptv in the early morning, but started to increase in concentration around 8:00 am. This increase in concentration continued until reaching a maximum at noon and stayed high throughout the afternoon. The PAN concentration started to decrease again after 6:00 pm. Having a diurnal trend suggested that the field site where PAN was being measured, was close to the origin of pollution, Nashville. Being close to the origin of pollution allowed the instrumentation at the site to measure rapid changes in the concentrations. The increase in the PAN early in the morning was possibly due to rush hour traffic emitting fresh NO<sub>x</sub> and the break up of nocturnal inversion that brings elevated concentrations from aloft, since the trend was seen consistently. These pollutants built up during the day, giving a higher PAN concentration. The decrease in the evening was due to the lack of photochemistry at night and dry deposition (O'Brien, 1995).

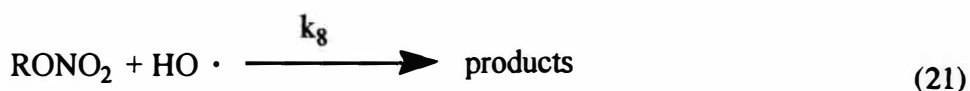
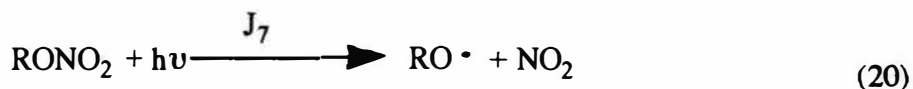
In contrast to the Nashville data, Figure 11 shows no diurnal trend in the Arctic Outflow Data. The average PAN concentration over the campaign was quite consistent. There were no consistent varying trends in the arctic outflow data, as in the Nashville data. The lack of an average diurnal trend in the arctic data suggested that the air masses were well-mixed averaging out short-term fluctuations. There was no local source of pollution for the instrumentation to measure, just transported air masses, so rapid fluctuations in the concentrations were observed.

### Transport of Alkyl Nitrates

A way to determine if alkyl nitrates have been transported is to determine the photochemical processing time of the alkyl nitrates, as previously described (Bertman, et al, 1995). An analytical expression can be developed relating the ratio of alkyl nitrate to its corresponding hydrocarbon precursor as a function of time. This analytical

expression can be plotted along with the ambient data to determine relative processing time.

Alkyl nitrates can be removed from the atmosphere by two photochemical processes, photolysis and reaction with OH. The rate of the reaction depends on the size of the alkyl nitrate, as previously discussed.



Bertman, et al. assumed that OH reaction with an alkane is the rate-limiting step in the formation of alkyl nitrates, and simplified the formation and destruction of alkyl nitrates into two sequential reactions.



An assumed diurnally averaged OH concentration is used to arrive at pseudo first order rate constants for the formation and destruction of the alkyl nitrate,  $k_A = k_{16}[\text{OH}]$ ,  $k_B = J + k_{16}[\text{OH}]$ . Factor  $\beta$  takes into account branching ratios, the fraction of H atom abstraction at the particular carbon and the fraction of peroxy radicals that react with NO. This leads to the differential rate law:

$$d[\text{RONO}_2]/dt = \beta k_A [\text{RH}] - k_B [\text{RONO}_2] \quad (24)$$

which integrates to

$$[\text{RONO}_2]/[\text{RH}] = (\beta k_A/(k_B - k_A))(1 - e^{(k_A - k_B)t}) + [\text{RONO}_2]_0/[\text{RH}]_0 e^{(k_A - k_B)t} \quad (25)$$

Assuming there are no initial concentrations of hydrocarbons and alkyl nitrates, equation 25 becomes

$$[\text{RONO}_2]/[\text{RH}] = (\beta k_A/(k_B - k_A))(1 - e^{(k_A - k_B)t}) \quad (26)$$

Figure 13 shows this analytical expression graphed with ambient data ratios [2-propyl nitrate]/[propane] vs [2-butyl nitrate]/[n-butane]. The ratios are plotted versus each other to compare the ambient data with the kinetic data without needing an absolute timescale for the ambient data. The theoretical line is also approximately linear in the range plotted.

The data points falling on the upper right section of the theoretical line are more processed. If the hydrocarbon concentration is depleted as the alkyl nitrate is being formed, then the ratio of alkyl nitrate/hydrocarbon increases with time. Therefore, ambient data with a higher alkyl nitrate to hydrocarbon ratio has a longer processing time.

The ambient data seen in the graph falls above the line with some of the points falling on the line. This graph does show that the alkyl nitrates are being transported to the site with the longer processing time since the points fall on the upper right side of the theoretical line. However, some of the points do fall above the theoretical line. This can be attributed to experimental error or an error in the assumption that propane is the only precursor to the formation of 2-propyl nitrate.

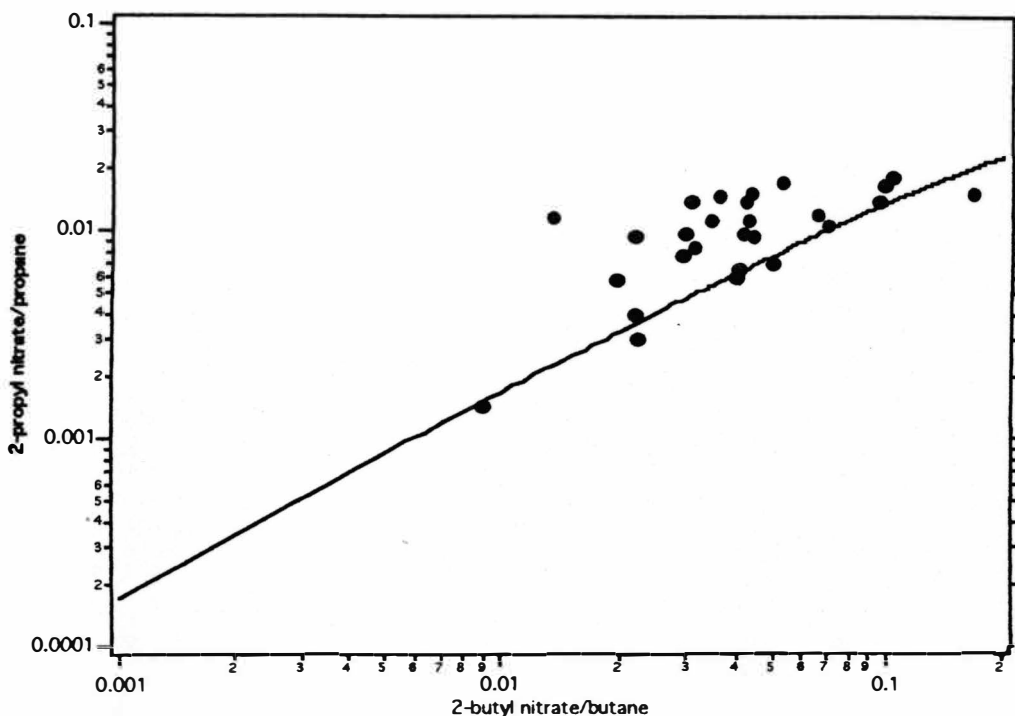


Figure 13. Comparison of Ambient [2-Propyl Nitrate]/Propane] and [2-Butyl Nitrate]/Butane] Ratios With the Predicted Kinetic Results.

#### PAN Decomposition in Transit

The previous sections have provided evidence to support PAN and alkyl nitrates transport during the Arctic Outflow Study. The second goal is to find evidence that PAN decomposes in transport from the Arctic. Air mass trajectories for the timeperiod of the study can provide information for the transport of PAN.

The trajectories can be separated into three arbitrary categories which help classify the air masses: CA - Continental/Arctic, A - Arctic, and MA - Marine/Arctic. Figure 14 shows an example of the trajectories.

The "Continental/Arctic" trajectory has air masses originating from the arctic and passing over the continental sections of Canada and the United States, allowing for influences from industrial cities to affect the arctic air mass. The "Arctic" air masses

originate from the arctic and pass over Greenland and other smaller islands. The "Marine/Arctic" air masses originate in the arctic, travel over the Atlantic Ocean, and have minimum contact with land masses.



Figure 14. Trajectory Sketch Describing General Origins of Air Masses.

In comparing the data from the three trajectory periods, ratios of the components, PAN, alkyl nitrates, NO<sub>x</sub>, and nitric acid with NO<sub>y</sub> will be used instead of absolute concentrations. The ratios are used to show the distribution of the NO<sub>y</sub>. Using this analysis, the air masses can be characterized by a signature pattern. Air masses from the arctic have a high PAN/NO<sub>y</sub> ratio even if the absolute concentrations of the PAN were low, since the NO<sub>y</sub> concentration is also lower. For example, during one arctic outflow period, PAN was 105 pptv and NO<sub>y</sub> was 269 pptv. In contrast, in continental air masses PAN/NO<sub>y</sub> ratios are lower even though the absolute

concentration of PAN is higher. For example, in one continental air mass, PAN was 533 pptv and NO<sub>y</sub> was 1252 pptv. This is because the absolute NO<sub>y</sub> concentration has also increased making the fraction of PAN with respect to NO<sub>y</sub> smaller.

Figure 15 shows the average ratios for each type of air mass measured at the site. Continental/Arctic air masses were seen 55 % of the time during the campaign, Arctic air masses 19 % of the time, and Marine/Arctic air masses 17 % of the time.

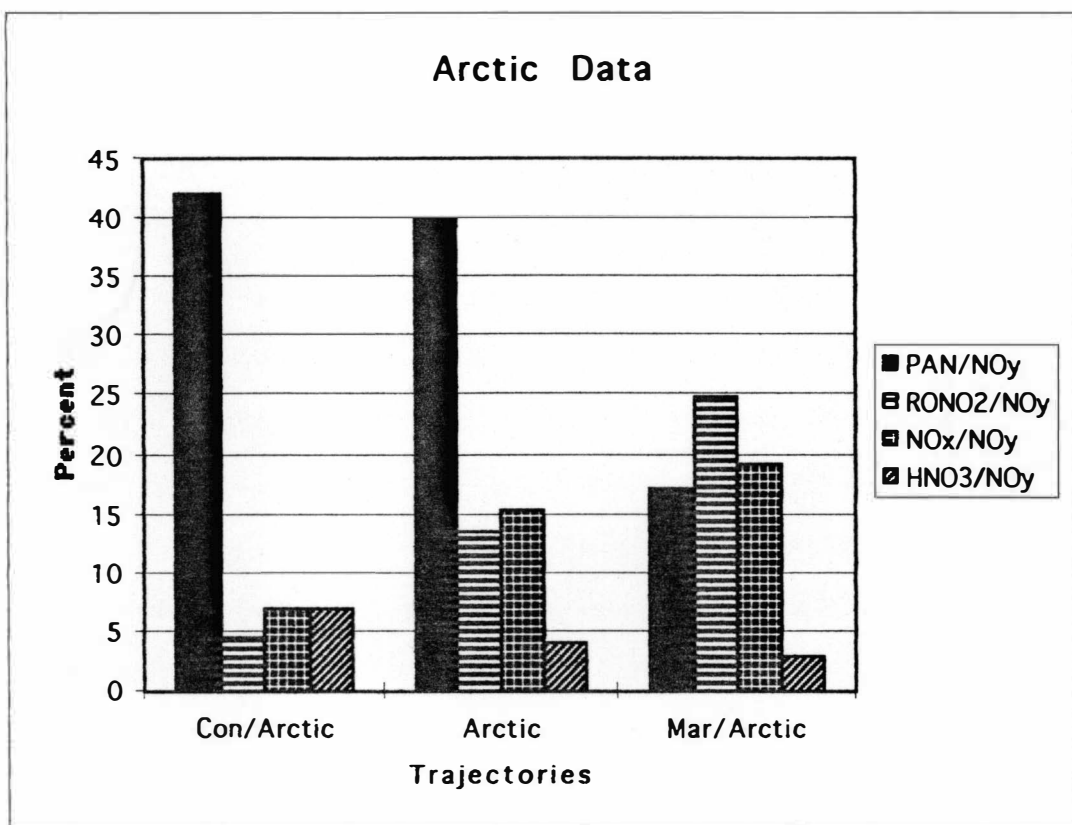


Figure 15. Comparison of Arctic Air Mass Composition for Different Trajectory Classes.

The hypothesis was that air masses traveling out of the arctic have a high PAN/NO<sub>y</sub> ratio due to the low temperatures encountered in the arctic. The low

temperatures cause a buildup of PAN in the arctic during the winter. In the arctic from March to April, the average PAN/NO<sub>y</sub> is 70 % (Bottenheim, 1993).

In the Continental/Arctic air masses, PAN/NO<sub>y</sub> ratio was 42 %, RONO<sub>2</sub>/NO<sub>y</sub> ratio was 4.5 %, NO<sub>x</sub>/NO<sub>y</sub> ratio was 7 %, and HNO<sub>3</sub>/NO<sub>y</sub> was 7 %. The ratios are average calculated values from the different trajectory classes. As the air masses travel out of the arctic, the PAN/NO<sub>y</sub> ratio is high, as expected. However, in transit the air masses were mixed with other air masses containing industrial and urban pollution. These continental air masses are relatively new, not having much time for the compounds in the air mass to be photochemically processed. For example, there was not enough time for alkyl nitrates to be formed from the reaction of hydrocarbon radicals with NO<sub>2</sub>. Therefore, there is a low RONO<sub>2</sub>/NO<sub>y</sub> ratio.

The arctic air mass with the continental influence showed an increase in the absolute NO<sub>y</sub> concentration. This increase does not affect the PAN/NO<sub>y</sub> ratio as much because PAN is abundant in urban areas. However, the RONO<sub>2</sub>/NO<sub>y</sub> ratio dramatically decreased. RONO<sub>2</sub>/NO<sub>y</sub> ratios in the arctic can be up to 20 %, as compared to 2-3 % measured in rural sites in August (Shepson, 1993, O'Brien, 1995). This decrease in the RONO<sub>2</sub>/NO<sub>y</sub> ratio could be due to the lack of photochemical processing in the continental air mass. Thus the NO<sub>y</sub> concentration increases but the RONO<sub>2</sub> concentration remained the same, due to the long lifetime of alkyl nitrates, causing the RONO<sub>2</sub>/NO<sub>y</sub> ratio to decrease.

In the Arctic air masses, PAN/NO<sub>y</sub> ratio was 40 %, RONO<sub>2</sub>/NO<sub>y</sub> was 14 %, NO<sub>x</sub>/NO<sub>y</sub> ratio was 15.5 %, and HNO<sub>3</sub>/NO<sub>y</sub> ratio was 4 %. The RONO<sub>2</sub>/NO<sub>y</sub> ratio was expected for arctic outflowing air masses, but the PAN/NO<sub>y</sub> ratio was slightly lower than expected. The lower ratio could be due to the decomposition of PAN with the increase in temperatures in transit. The lower absolute PAN concentration could explain why the NO<sub>x</sub>/NO<sub>y</sub> ratio was higher with the release of NO<sub>2</sub> into the atmosphere

from the decomposition of PAN. The absolute alkyl nitrate concentration was relatively unchanged from the arctic due to the long lifetime of the alkyl nitrates.

In Marine/Arctic air masses, PAN/NO<sub>y</sub> ratio was 17 %, RONO<sub>2</sub>/NO<sub>y</sub> ratio was 25 %, NO<sub>x</sub>/NO<sub>y</sub> ratio was 19 %, and HNO<sub>3</sub>/NO<sub>y</sub> ratio was 3 %. One reason for the lower PAN/NO<sub>y</sub> in the Marine/Arctic air masses in comparison to the Continental/Arctic and Arctic air masses could be due to the fact that Marine/Arctic air masses were transported over the ocean where temperatures could be higher than over the land. This higher temperature would cause PAN to decompose faster releasing NO<sub>2</sub>, thus increasing the NO<sub>x</sub>/NO<sub>y</sub> ratio. Another reason for the lower PAN/NO<sub>y</sub> ratio in the Marine/Arctic air masses could be due to the uptake of the peroxyacetyl radicals by fog droplets (Roberts, et al., 1996). The uptake of the peroxyacetyl radical would inhibit the reformation of PAN.

Nitric acid would also be formed from the release of NO<sub>2</sub>. However, the nitric acid is water soluble and can be removed from the atmosphere by wet deposition. The removal of HNO<sub>3</sub> from the atmosphere lowers the absolute concentration of NO<sub>y</sub>, causing the RONO<sub>2</sub>/NO<sub>y</sub> ratio to increase. The concentration of the alkyl nitrates remained constant in transport since they are thermally labile, as PAN is, nor are they water soluble, like nitric acid. The previous analysis gives evidence to support the hypothesis that PAN decomposes in air masses originating in the arctic.

### Comparison of PAN Concentrations

The final section is to compare the relative PAN concentrations, which may have decomposed in transport. The main focus will be on comparison of air masses containing PAN transported over land versus PAN transported over the Atlantic Ocean. The time period that will be discussed occurred from March 30, 1996 to April 6, 1996. During this period, a Continental/Arctic air mass on March 30-31, was replaced by an

air mass transported over the Atlantic Ocean and was followed by another Continental/Arctic air mass. Figure 16 shows the data graphed from this time period. The PAN/NO<sub>y</sub>, RONO<sub>2</sub>/NO<sub>y</sub>, HNO<sub>3</sub>/NO<sub>y</sub>, and NO<sub>x</sub>/NO<sub>y</sub> are graphed versus the specified time periods.

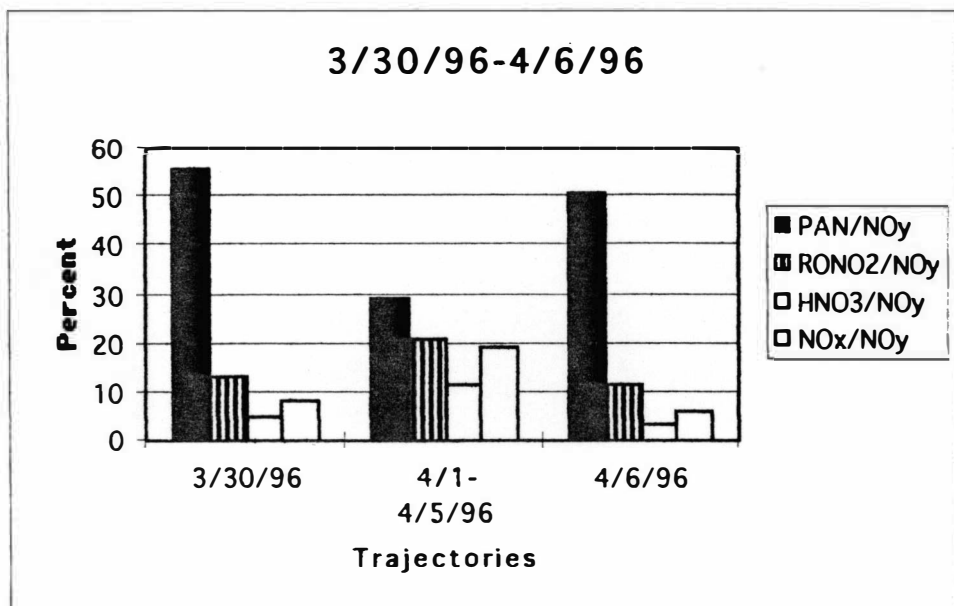


Figure 16. Air Mass Composition for Three Separate Air Masses From March 30, 1996 Through April 6, 1996.

On March 30-31, the Continental/Arctic air mass resulted in a PAN/NO<sub>y</sub> ratio of 55 %, a RONO<sub>2</sub>/NO<sub>y</sub> ratio of 11 %, a HNO<sub>3</sub>/NO<sub>y</sub> ratio of 5 %, and NO<sub>x</sub>/NO<sub>y</sub> of 9 %. This air mass was replaced with a Marine air mass. The air mass consisted of a lower PAN/NO<sub>y</sub> ratio of 30 %, which resulted in a higher HNO<sub>3</sub>/NO<sub>y</sub> and NO<sub>x</sub>/NO<sub>y</sub> ratios. The marine air masses remained around Newfoundland until being replaced by another Continental/Arctic air mass. The ratios returned to the similar levels to those seen previously on March 30-31.

To compare the decomposition of PAN, only thermal decomposition of PAN will be considered. The reformation of PAN will not be considered. Thus a simple

first order rate expression, as seen on page 7, can be used to calculate the decomposition of PAN (Roberts and Bertman, 1992). The temperatures used to calculate the rate constant were obtained from the air mass trajectories. For each trajectory, there were different categories of temperature potentials, 265 K - 295 K, depending on the atmospheric pressure. The temperatures at the 295 K temperature potential was used for these calculations, since this category is based on the highest atmospheric pressure and hence should be closest to measured site. The rate constant can be used to calculate the PAN concentration at each point in the air mass trajectories by using the following first order rate equation.

$$[\text{PAN}] = [\text{PAN}]_0 e^{(-kt)} \quad (27)$$

The PAN concentrations were calculated based on an initial Arctic PAN concentration of 350 pptv. This initial concentration is an average PAN concentration measured at Alert (Bottenheim 1993). Only a two day trajectory will be compared because the marine trajectories are approximately two days in length.

The continental/arctic air mass starting on 3/30 at 0:00 was comparable to what was seen from the continental/arctic air mass on 4/6. However, the air mass on 3/30 at 12:00 and 3/31 at 0:00 shows a dramatic decrease in PAN concentration. This could be due to a higher atmospheric temperature, but realistically the dramatic drop does not occur since the ambient data does not show such a low PAN concentration. The higher ambient PAN concentration is due to the mixing of PAN from urban air masses in Canada and the United States. There was not a drastic difference in the temperature between the Continental/Arctic air masses and the Marine air mass, as seen in Figures 17, 18, and 19, with similar decomposition in the theoretical PAN concentration.

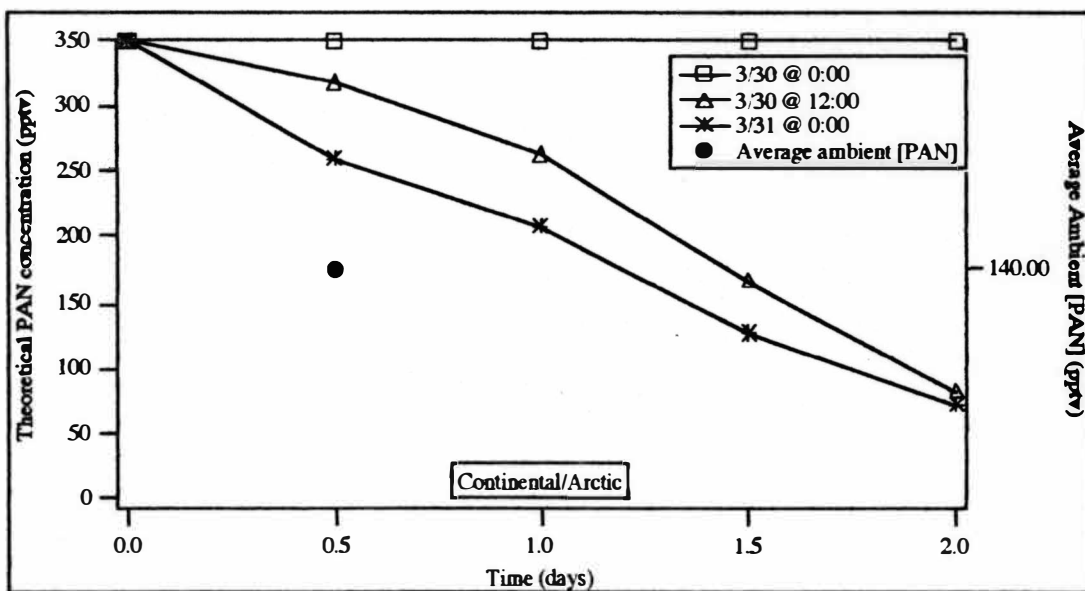


Figure 17. Theoretical PAN Decomposition in a Continental/Arctic Air Mass Graphed With the Average Measured PAN Concentration From the Timeperiod of March 30 to March 31, 1996.

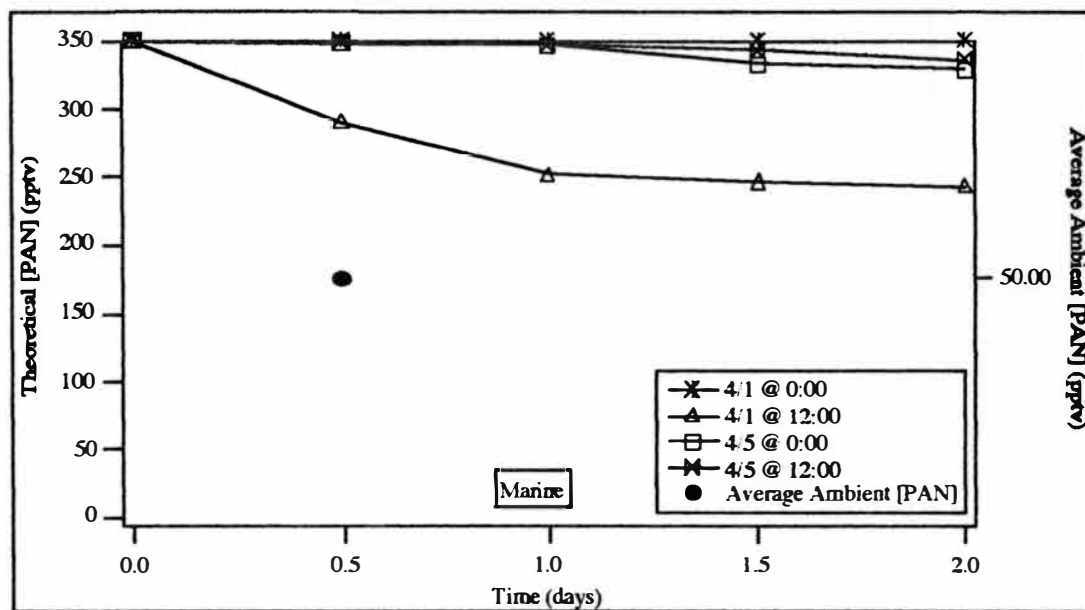


Figure 18. Theoretical PAN Decomposition in a Marine Air Mass Graphed With the Average Measured PAN Concentration From the Timeperiod of April 1 to April 5, 1996.

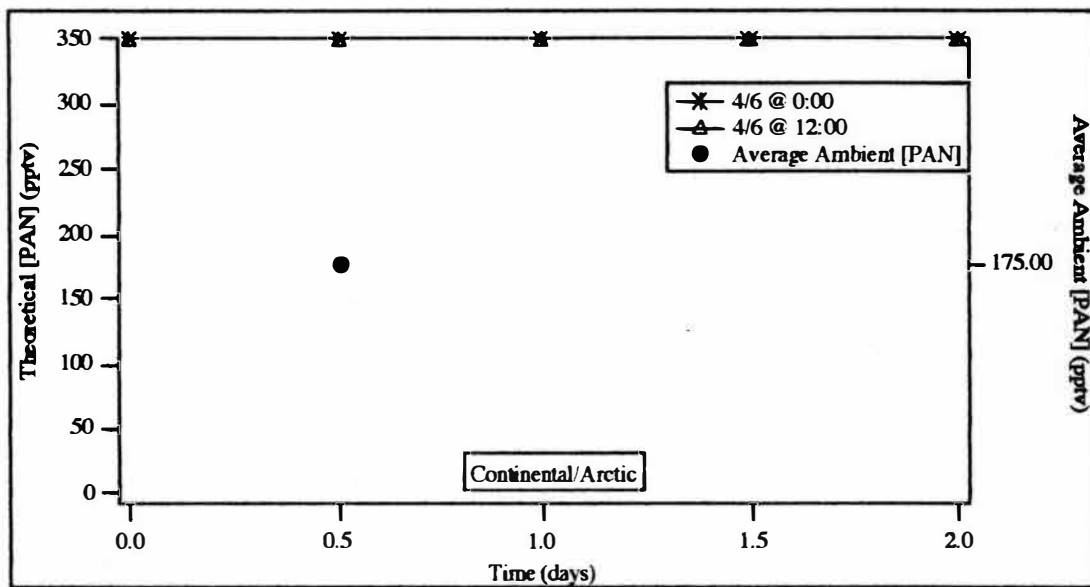


Figure 19. Theoretical PAN Decomposition in a Continental/Arctic Air Mass Graphed With the Average Measured PAN Concentration From the Timeperiod of April 6, 1996.

The previous calculation of the PAN decomposition was a simple comparison of PAN decomposition over land versus PAN decomposition over the ocean. The calculation does not take into account dilution of air masses, reformation of PAN, contributions of additional PAN from continental influences, or uptake of peroxyacetyl radicals by fog droplets. No conclusions can be drawn from the previous comparison, since the PAN decomposition over the ocean was not significantly lower than the PAN decomposition over the land.

## CHAPTER V

### CONCLUSIONS

The present work provides analysis to investigate specific experimental ideas: (a) organic nitrates, PAN and alkyl nitrates are transported in arctic outflowing air masses; (b) PAN decomposed during the transport out of the arctic, and finally; (c) If PAN in a simplistic comparison, decomposed faster over the ocean.

PAN was shown to be transported by the lack of a daily diurnal trend. This indicated that the PAN measurements were not performed close to the origin of the air masses as was inferred from the daily diurnal trend from the Southern Oxidants Study. The alkyl nitrates were shown to be transported by comparing ambient measured ratios of [2-propyl nitrate]/[propane] and [2-butyl nitrate]/[butane] versus an analytical expression. The graph indicated that the air masses had undergone significant photochemical processing.

PAN was shown to decompose during transport out of the arctic by comparing PAN/NO<sub>y</sub> ratios of arctic air masses to continental/arctic and marine/arctic air masses. The PAN/NO<sub>y</sub> ratio was lower in the arctic air masses suggesting PAN decomposition in transit. The PAN/NO<sub>y</sub> ratio was lower in the marine/arctic air masses than the arctic air masses due to a warmer temperature over the ocean and the uptake of the peroxyacetyl radical by fog droplets inhibiting the reformation of PAN in transport (Roberts, 1996).

A simplistic comparison of the thermal decomposition of PAN over land and over the ocean was inconclusive. There was not a significant difference between the PAN decomposition rates of continental/arctic air masses versus a marine air mass.

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