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## Alkyl Nitrates during the Prophet '98 Summer Intensive

Kristi A. Ostling

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ALKYL NITRATES DURING THE PROPHET '98  
SUMMER INTENSIVE

by

Kristi A. Ostling

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  
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1999

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Kristi A. Ostling

## ALKYL NITRATES DURING THE PROPHET '98 SUMMER INTENSIVE

Kristi A. Ostling, M.A.

Western Michigan University, 1999

As part of the PROPHET intensive held at the University of Michigan Biological Station in northern Michigan, a gas chromatography system for making fast-turnaround measurements of C1 to C5 alkyl nitrates was developed and deployed from July 19 to August 21, 1998. Every 30 minutes, samples were automatically acquired on a small Tenax trap made from silicosteel column and injected on a GC column by thermal desorption prior to ECD detection. Tests performed to measure breakthrough and on-trap destruction indicated no breakthrough for C3, C4, and C5 nitrates and excellent stability for these compounds on the trap. Chromatographic resolution of C3, C4, and C5 nitrates was better than the resolution of C1 and C2 nitrates. The detection limit of the instrument was less than 1 pptv. The sum of C3-C5 alkyl nitrates measured during this intensive ranged from 3.45-65.8 pptv, with a mean of 18.6 pptv. C3-C5 alkyl nitrates contributed 1% on average to total NO<sub>y</sub>, with a range of >0.5% to 3%, but differences are found when the data are filtered according to air mass origin. The relationship of alkyl nitrate isomers from the same parent hydrocarbon was investigated. A kinetic model to describe a relationship between n-propyl nitrate and peroxypropionyl nitrate was developed.

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## CHAPTER I

### INTRODUCTION

#### Alkyl Nitrates: Background

In the troposphere, alkyl nitrates are formed through a series of reactions involving volatile organic compounds (VOC's) and  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ). Alkyl nitrates have the general formula of  $\text{RONO}_2$ , where R is any hydrocarbon chain.

Measurements of C1 to C6 alkyl nitrates are the most common in the literature.

Initial interest in alkyl nitrates arose from attempts to account for total  $\text{NO}_y$ .  $\text{NO}_y$  is the sum of all oxidized nitrogen species in the troposphere [ $\text{NO}_x$ , peroxyacyl nitrates (PANs), alkyl nitrates, nitric acid, etc.]. The sum of the individual measurements of oxidized nitrogen species (PANs, nitric acid, etc) was compared to measured values of  $\text{NO}_y$ . A significant shortfall was discovered (~20% or more; Fahey et al., 1986). Alkyl nitrates were suggested to be a possible source to make up the shortfall (Atherton and Penner, 1988). Later field studies showed that these nitrates did not contribute significantly in continental areas (Ridley et al., 1990; Buhr et al., 1990; Shepson et al., 1993), but could comprise up to 20% of  $\text{NO}_y$  in the Arctic springtime (Bottenheim et al., 1993).

Interest in these species continues for other reasons. Alkyl nitrates are relatively long-lived species (lifetimes of days, depending on the number of carbons).

They can act as reservoir and transport agents for NO<sub>x</sub> (Atlas, 1988). Because of their long lifetimes and few emission sources (minor contributions from some industrial processes (Roberts, 1990), they can indicate a photochemically processed air mass. Because the formation alkyl nitrates is slow and the lifetime is long (7 days for n-propyl nitrate, for example), high levels of alkyl nitrates would indicate a photochemically processes air mass.

### Alkyl Nitrates: Chemistry

The first step in the formation of alkyl nitrates is the abstraction of a hydrogen from an alkane by an OH radical (reaction 1).

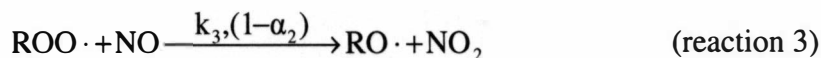


The primary source of OH radicals is from the photolysis of ozone to form an excited oxygen atom, which then reacts with water. The rate of reaction 1 increases as the number of carbons in the alkane increases. The branching ratio,  $\alpha_1$ , is the ratio between one alkyl radical isomer that can be formed from the parent alkane to the total number of alkyl radicals that can be formed from the parent alkane. For example,  $\alpha_1$  for the n-propyl radical is 0.3 and 0.7 for the 2-propyl radical.

The alkyl radical quickly reacts with O<sub>2</sub> to form an alkylperoxy radical (reaction 2).

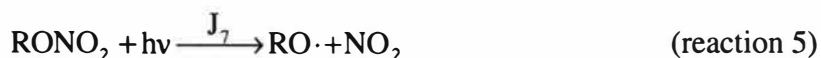


The alkylperoxy radical can then react with NO to form an alkoxy radical and NO<sub>2</sub> (reaction 3) or alkyl nitrates (reaction 4).



Another branching ratio,  $\alpha_2$ , is seen between these two reactions which increases with the number of carbons in R (0.014 for ethyl, 0.13 for pentyl). Although it would be expected that the longer carbon chain alkyl nitrates would occur in higher concentrations, the smaller alkyl nitrates (3 carbons and smaller) are the most abundant. Decomposition of larger (C4 and greater) alkoxy radicals (RO) can result in radicals that form alkyl nitrates with 3 or fewer carbons (Flocke et al., 1998a).

Alkyl nitrates can be destroyed by photolysis (reaction 5) or reaction with the OH radical (reaction 6).



Alkyl nitrates are primarily removed by photolysis. Formation of alkyl nitrates provides a sink for NO<sub>x</sub> and the potential to transport NO<sub>x</sub> to remote locations. Once transported, alkyl nitrates can decompose through reaction 5 to form NO<sub>2</sub>. Photolysis of NO<sub>2</sub> can form ozone through reactions 7 and 8.



## Previous Measurements

### Overview

Measurements of alkyl nitrates in ambient air have only been performed since the mid-1980's (Atlas, 1988). Methods that can be automated or are portable are desirable for ambient measurement of atmospheric species like alkyl nitrates. Different sampling techniques combined with different detection methods have been used for ambient measurements at field sites throughout the world. The sampling techniques that will be discussed are (a) charcoal preconcentration, (b) direct injection, (c) cryogenic sampling, and (d) Tenax adsorption. The detection techniques include (a) electron capture detection (ECD), (b) mass spectrometry (MS), and (c) chemiluminescent detection (CLD). All of these methods have been successfully employed at field research sites to measure alkyl nitrates ( $C_1$  to  $C_{14}$ ) (see Table 1 for summary of measurements).

### Sampling Techniques

#### Charcoal Adsorption Tubes (Charcoal Preconcentration)

The most common technique used to measure alkyl nitrates utilizes charcoal as a solid adsorbent or charcoal preconcentration (Atlas, 1988; Atlas and Schauffler, 1991; Beine et al., 1996, Muthuramu et al., 1994; Leaitch et al., 1994; Shepson et al., 1993; O'Brien et al., 1995; O'Brien et al., 1997). This technique concentrates the alkyl nitrates in glass tubes that are packed with a charcoal bed (typically about 5



mg). Sample volumes used are listed in Table 2. Samples can be stored on the charcoal bed for 12 to 15 hours with the glass tubes sealed.

Table 1  
Review of Ambient Measurements of Alkyl Nitrates and Methods Used

Location	Alkyl Nitrate Measured	Average Measured conc (pptv)	Range (pptv)	Method	Reference:
Poker Flat, AK	$\Sigma C_2-C_6$	34	11-66	Charcoal preconcentration, GC-ECD, GC-MS	Beine et al., 1994
N. Pacific Ocean	2-BN + 2-PeB + 3-PeN	12	0.8-37	Charcoal preconcentration GC-ECD, GC-MS	Atlas, 1999
Boulder Creek, Calif.	$\Sigma C_3-C_{12}$	53.9		Tenax/silica gel adsorbant, GC-ECD	Schneider et al., 1998
Santa Cruz, Calif.	$\Sigma C_3-C_{12}$	19.3		Tenax/silica gel adsorbant, GC-ECD	Schneider et al., 1998
Ulm, Germany	IPN	13.1		Tenax adsorbant, GC-ECD, GC-MS	Luxenhofer et al., 1994
Ulm	NPN	3.5		Tenax adsorbant, GC-ECD, GC-MS	Luxenhofer et al., 1994
Ulm	IBN + 2-BN	10.6		Tenax adsorbant, GC-ECD, GC-MS	Luxenhofer et al., 1994
Ulm,	NBN	2.7		Tenax adsorbant, GC-ECD, GC-MS	Luxenhofer et al., 1994
Location	Alkyl Nitrate Measured	Average Measured conc (pptv)	Range (pptv)	Method	Reference:
Ulm	3-PeN	3.2		Tenax adsorbant, GC-ECD, GC-MS	Luxenhofer et al., 1994
Ulm	2-PeN	4.3		Tenax adsorbant, GC-ECD, GC-MS	Luxenhofer et al., 1994
Ulm	NPeN	1.8		Tenax adsorbant, GC-ECD, GC-MS	Luxenhofer et al., 1994
Ulm	IPeN	1.0		Tenax adsorbant, GC-ECD, GC-MS	Luxenhofer et al., 1994
Alert, Northwest Territories, CA	IPN -dark -light	12.44 13.08		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	NPN -dark -light	3.33 3.14		Charcoal preconcentration, GC-ECD,	Muthuramu et al., 1994
Alert	2-BN -dark -light	18.41 13.73		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	NBN -dark -light	1.70 1.18		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	3-PeN -dark -light	4.31 2.31		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994

Table 1-Continued

Location	Alkyl Nitrate Measured	Average Measured conc (pptv)	Range (pptv)	Method	Reference:
Alert	2-PeN -dark -light NPeN	5.44 2.47		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	-dark -light 3-Me-2-BN	1.01 0.53		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	-dark -light 3-Me-1-BN	4.84 2.32		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	-dark -light 2-Me-1-BN	0.55 0.30		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	-dark -light 3-HexN	0.77 0.39		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	-dark -light 2-HexN	4.27 1.65		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	-dark -light 3-HepN	2.46 0.98		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	-dark -light 2-HepN	1.86 0.68		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	-dark -light Unknown	1.45 0.56		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert	-dark -light	18.67 8.95		Charcoal preconcentration, GC-ECD	Muthuramu et al., 1994
Alert, aircraft	IPN	12.53	9.84-14.73	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994
Alert, aircraft	NPN	3.96	3.15-5.38	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994
Alert, aircraft	2-BN	13.98	10.6-17.97	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994
Alert, aircraft	3-Me2-BN	2.65	1.64-3.43	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994
Alert, aircraft	NBN	2.05	1.1-2.75	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994
Alert, aircraft	3-PeN	3.02	1.64-4.92	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994
Alert, aircraft	2-PeN	4.18	2.42-5.42	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994
Alert, aircraft	NPeN	1.03	0.53-1.44	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994
Alert, aircraft	3-HexN	2.55	2.73-3.95	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994
Alert, aircraft	2-HexN	1.50	0.35-2.73	Charcoal preconcentration, GC-ECD	Leaitch et al., 1994

Table 1-Continued

Location	Alkyl Nitrate Measured	Average Measured conc (pptv)	Range (pptv)	Method	Reference:
Mauna Loa, HI	IPN	1.39	0.37-4.03	Charcoal preconcentration, GC-ECD	Atlas et al., 1992
Mauna Loa	NPN	0.5	0.18-1.2	Charcoal preconcentration, GC-ECD	Atlas et al., 1992
Mauna Loa	2-BN+IBN	0.96	0.19-3.81	Charcoal preconcentration, GC-ECD	Atlas et al., 1992
Mauna Loa	NBN	0.06	<0.1-0.23	Charcoal preconcentration, GC-ECD	Atlas et al., 1992
Mauna Loa	3-PeN	0.15	<0.1-1.00	Charcoal preconcentration, GC-ECD	Atlas et al., 1992
Mauna Loa	2-PeN	0.26	<0.1-1.34	Charcoal preconcentration, GC-ECD	Atlas et al., 1992
Mauna Loa	$\Sigma C_2-C_5$	3.39	0.92-11.4	Charcoal preconcentration, GC-ECD	Atlas et al., 1992
Niwot Ridge, CO	MN	2.1	1.5-4.9	Direct injection to GC-ECD	Ridley et al., 1990
Niwot Ridge	NPN+2BN				
	Easterly	2.6	0.4-11.7	Direct injection to GC-ECD	Ridley et al., 1990
	Westerly	0.94	0.2-5.1		
Juelich, Germany	MN	109		Cryotrap, GC-CLD	Flocke et al., 1991
Juelich	EN	47.7		Cryotrap, GC-CLD	Flocke et al., 1991
Juelich	IPN	27.4		Cryotrap, GC-CLD	Flocke et al., 1991
Juelich	NPN	8.4		Cryotrap, GC-CLD	Flocke et al., 1991
Juelich	2-BN+IBN	27.3		Cryotrap, GC-CLD	Flocke et al., 1991
Juelich	$\Sigma C_5+NBN$	42.0		Cryotrap, GC-CLD	Flocke et al., 1991
Juelich	$\Sigma C_6-C_8$	5.1		Cryotrap, GC-CLD	Flocke et al., 1991
Juelich	$\Sigma C_1-C_8$	198.8		Cryotrap, GC-CLD	Flocke et al., 1991
Schauinsland, Germany	MN	10.0		Cryotrap, GC-CLD	Flocke et al., 1991
Schauinsland	EN	9.5		Cryotrap, GC-CLD	Flocke et al., 1991
Schauinsland	IPN	19.7		Cryotrap, GC-CLD	Flocke et al., 1991
Schauinsland	NPN	3.2		Cryotrap, GC-CLD	Flocke et al., 1991
Schauinsland	2-BN+IBN	13.3		Cryotrap, GC-CLD	Flocke et al., 1991
Schauinsland	$\Sigma C_5+NBN$	5.9		Cryotrap, GC-CLD	Flocke et al., 1991
Schauinsland	$\Sigma C_1-C_8$	62		Cryotrap, GC-CLD	Flocke et al., 1991
S. Hemisphere Trade winds	$\Sigma C_3-C_{12}$	3.5		Tenax/silica gel adsorbant, GC-ECD, GC-MS	Schneider et al., 1999

Table 1-Continued

Location	Alkyl Nitrate Measured	Average Measured conc (pptv)	Range (pptv)	Method	Reference:
SH Westwind belt	$\Sigma C_3-C_{12}$	11.1		Tenax/silica gel adsorbant, GC-ECD, GC-MS	Schneider et al., 1999
Ulm	$\Sigma C_6-C_{12}$	13.6		Silica gel adsorbant, HRGC-ECD, GC-MS	Schneider et al., 1999
Ulm	Hexyl isomers	2.95		Silica gel/polyurethane foam, GC-ECD	Luxenhofer et al., 1996
Ulm	Heptyl isomers	1.01		Silica gel/polyurethane foam, GC-ECD	Luxenhofer et al., 1996
Ulm	Octyl isomers	0.52		Silica gel/polyurethane foam, GC-ECD	Luxenhofer et al., 1996
Ulm	Nonyl isomers	0.48		Silica gel/polyurethane foam, GC-ECD	Luxenhofer et al., 1996
Ulm	Decyl isomers	0.61		Silica gel/polyurethane foam, GC-ECD	Luxenhofer et al., 1996
Ulm	Undecyl isomers	0.48		Silica gel/polyurethane foam, GC-ECD	Luxenhofer et al., 1996
Ulm	Dodecyl isomers	0.28		Silica gel/polyurethane foam, GC-ECD	Luxenhofer et al., 1996
Ulm	Tridecyl isomers	0.15		Silica gel/polyurethane foam, GC-ECD	Luxenhofer et al., 1996
Ulm	Tetradecyl isomers	0.15		Silica gel/polyurethane foam, GC-ECD	Luxenhofer et al., 1996
Scotia, PA	$\Sigma C_2-C_5$	66		Direct injection to GC-ECD	Buhr et al., 1990
Egbert, Ontario, CA	IPN	14		Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Egbert	NPN	4.5		Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Egbert	2BN	15.5		Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Egbert	NBN	3		Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Egbert	3-PeN	6		Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Egbert	2-PeN	7		Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Egbert	NPeN	4		Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Egbert	3-HexN	2		Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Egbert	2-HexN	2		Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Egbert	$\Sigma C_3-C_6$		29-87	Charcoal preconcentration, GC-ECD	Shepson et al., 1993
Hastings, Ontario, CA	$\Sigma C_3-C_5$		10-140	Charcoal preconcentration, GC-ECD	O'Brien et al., 1995
Mauna Loa	MN	3.9		Cryotrap, GC-ECD	Walega et al., 1992
Alert to Hawaii, aircraft	MN Free troposphere Tropopause		1-5 0.1-0.5	Canisters	Flocke et al., 1998b

Table 1-Continued

Location	Alkyl Nitrate Measured	Average Measured conc (pptv)	Range (pptv)	Method	Reference:
Chebogue Point, Nova Scotia, CA	MN	1.6	<0.2-3.5	GC-ECD	Roberts et al., 1998
Chebogue Point	EN	2.4	0.75-6.8	GC-ECD	Roberts et al., 1998
Chebogue Point	NPN	1.7	<0.2-5.5	GC-ECD	Roberts et al., 1998
Chebogue Point	IPN	4.7	0.39-22	GC-ECD	Roberts et al., 1998
Chebogue Point	2-BN	3.5	0.34-19	GC-ECD	Roberts et al., 1998
Chebogue Point	$\Sigma$ RONO <sub>2</sub>	14	4.4-50	GC-ECD	Roberts et al., 1998
Schauinsland	MN	26.2	2.5-216	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	EN	11.8	2.5-75.3	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	IPN	13.9	3.1-79.4	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	NPN	3.9	0.6-19.0	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	2-BN+IBN	15.8	1.2-96.3	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	NBN	2.4	<0.6-13.6	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	2-Me-2-PN	0.35	<0.6-3.7	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	2-Me-2-BN	0.33	<0.6-3.2	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	3-Me-2-BN	5.1	<0.6-39.4	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	3-PeN	4.5	<0.6-30.3	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	2-PeN	6.5	<0.6-49	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	NPeN	1.6	<0.6-10.4	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	i-Amyl (2 isomers)	2.3	<0.6-17.4	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	$\Sigma$ C <sub>6</sub>	13.9	<2.2-79.7	Cryotrap, GC-CLD	Flocke et al., 1998a
Schauinsland	$\Sigma$ C <sub>1</sub> -C <sub>8</sub>	119.8	30.3-623.4	Cryotrap, GC-CLD	Flocke et al., 1998a
Freiburg, Germany	$\Sigma$ C <sub>1</sub> -C <sub>8</sub>	240	89-480	Cryotrap, GC-CLD	Flocke et al., 1998a
Lower Fraser Valley, British Columbia, CA	$\Sigma$ C <sub>3</sub> -C <sub>6</sub>		214 (max)	Charcoal preconcentration, GC-CLD	O'Brien et al., 1997

Table 1-Continued

Location	Alkyl Nitrate Measured	Average Measured conc (pptv)	Range (pptv)	Method	Reference:
Equatorial Pacific 15°N-10°S, 144-165°W	EN		0.3-5.4	Tenax or Charcoal Adsorbant, GC-ECD	Atlas et al., 1993
Equatorial Pacific	IPN		0.9-10.4	Tenax or Charcoal Adsorbant, GC-ECD	Atlas et al., 1993
Equatorial Pacific	NPN		0.35-4.12	Tenax or Charcoal Adsorbant, GC-ECD	Atlas et al., 1993
Equatorial Pacific	2BN+IBN		0.60-5.45	Tenax or Charcoal Adsorbant, GC-ECD	Atlas et al., 1993
Equatorial Pacific	NBN		0.1-0.83	Tenax or Charcoal Adsorbant, GC-ECD	Atlas et al., 1993
Equatorial Pacific	3-Me-2-BN		0.06-0.74	Tenax or Charcoal Adsorbant, GC-ECD	Atlas et al., 1993
Equatorial Pacific	$\Sigma C_2-C_5$	10.2	2.24-18.95	Tenax or Charcoal Adsorbant, GC-ECD	Atlas et al., 1993

MN = methyl nitrate, EN = ethyl nitrate, IPN = 2-propyl nitrate, NPN = 1-propyl nitrate, 2-BN = 2-butyl nitrate, IBN = 2-methyl-1-propyl nitrate, NBN = 1-butyl nitrate, 2-Me-2-PN = 2-methyl-2-propyl nitrate, 3-Me-2-BN = 3-methyl-2-butyl nitrate, 2-Me-1-BN = 2-methyl-1-butyl nitrate, 3-Me-1 BN = 3-methyl-1-butyl nitrate, 2-PeN = 2-pentyl nitrate, 3-PeN = 3-pentyl nitrate, NPeN = 1-pentyl nitrate.

Table 2

## Sampling Volumes Used With the Charcoal Preconcentration Technique

Volume	Reference
12 L	Atlas, 1988
500 L	Muthuramu et al., 1994
22.5 L	Leaich et al., 1994
12-20 L	Atlas et al., 1992
55-175 L	O'Brien et al., 1995
36-306 L	O'Brien et al., 1997

After adsorption, the alkyl nitrates are extracted with a solvent: benzene (Atlas and Schauffler, 1991) or cyclohexanol (Shepson et al., 1993). A frozen extracted sample can be stored in heat-sealed capillary tubes for later analysis. After extraction, the charcoal tubes are cleaned with methanol then benzene and can be re-used. The samples are typically analyzed by liquid injection into a gas chromatograph (GC) with an ECD or MS (Atlas, 1988) or a chemiluminescence detector (CLD) (Shepson et al., 1993; O'Brien et al., 1997). Quantification of C<sub>3</sub> to C<sub>7</sub> alkyl nitrates is possible with this technique. Detection limits are typically around 0.1 pptv.

Charcoal preconcentration has several advantages. By concentrating the sample prior to injection, the detection limit is lowered. Low detection limits are necessary because the levels of alkyl nitrates in ambient air are often low (see Table 1 for actual values). The set-up for ambient samples is fairly simple and can be automated. This is advantageous because most ambient air measurements are taken at a field site in coordination with measurements of a wide variety of other compounds (such as NO<sub>x</sub>, NO<sub>y</sub>, and ozone). A simple set-up makes transport to the field site more convenient and can be used for aircraft measurements (Leaitch et al., 1994). Automated sampling allows for unattended sampling. Extracted samples can be stored, if frozen, and can be analyzed multiple times using different methods. Multiple analyses are helpful for confirming the accuracy of measured concentrations.

The major disadvantages of the charcoal preconcentration sampling method are the inability to quantify methyl and ethyl nitrate, the requirement of solvents for extraction, and the large amount of air sample required. It is important to measure methyl and ethyl nitrates since they are usually the most abundant of the alkyl nitrates and can also be formed from radicals formed by other reactions than by reaction of a hydroxyl radical with an n-alkane. Although the amounts of solvents required for extraction are small, a source of solvent is required for field studies. These solvents used for extraction can interfere with hydrocarbon measurements (if being measured at the field site), so the charcoal tubes would have to be taken else where to extract and analyze. Because of large volume sample and low flow rates, a 12-L sample could take 1 hour to collect. In some cases, sampling can take up to 6 hours (Beine et al., 1996). This greatly limits the frequency of samples that can be collected in one day.

#### Direct and Cryogenic Sampling

C<sub>1</sub> to C<sub>5</sub> alkyl nitrates have been sampled by direct injection with or without cryogenic concentration into a GC (Ridley et al., 1990; Buhr, 1990). In this type of analysis, a length of Teflon tubing is used as a sample loop [1 cm<sup>3</sup> used by Ridley et al. (1990) and Buhr (1990)]. The sample loop is attached to a electronically actuated valve that serves as an injection port to the GC column. Detection is usually by ECD. This method has been used to measure C<sub>1</sub>-C<sub>4</sub> alkyl nitrates. This technique has detection limits ~2 pptv. Ambient data is shown in Table 1.



By using an electronically actuated valve directly connected to the GC, the instrument can be controlled by a computer to do routine measurements at set times. This allows for sampling and analyses to take place unattended. This feature makes it extremely attractive for field research in contrast to charcoal preconcentration which requires active participation of the researcher. Because of small sample volumes, injections can take place frequently (for example, every 30 minutes). This method can also be used to measure peroxyacyl nitrates (PAN's), which are a group of compounds that contribute significantly to the total NO<sub>y</sub> measurement, increasing the versatility of the instrument.

The major drawback with this method is the high detection limit. The high detection limit makes it difficult to measure alkyl nitrates such as n-butyl and n-pentyl nitrates because they are often measured at levels below 2 pptv. To lower the detection limit, cryogenic trapping has been used. Ridley et al. (1990) immersed a stainless steel sample loop in liquid nitrogen to condense the gases in the sample loop. The sample loop was then heated to inject the sample onto the column. Flocke et al. (1991 and 1998a) also used cyrotrapping. A glass tube filled with glass beads immersed in liquid nitrogen was used to concentrate the alkyl nitrates. Flocke et al. also used thermal desorption into a GC but used a CLD for detection. This technique allowed for quantification of C<sub>1</sub>-C<sub>8</sub> alkyl nitrates (see Table 1 for ambient measurements). Because field studies are often performed in remote locations, the necessity of liquid nitrogen makes this method less desirable.

An alternative method for cryofocusing utilizing thermoelectric coolers was offered by Bertman et al. (1993). This method achieves cryogenic temperatures (as low as  $-100^{\circ}\text{C}$ , depending on the configuration) without the need of liquid nitrogen, making it advantageous for field studies. Heating can also be accomplished using thermoelectric coolers, increasing the versatility of this method.

#### Tenax Adsorption

Recently, a solid adsorbent called Tenax has also been investigated for use in trapping alkyl nitrates (Atlas et al., 1993; Luxenhofer et al., 1994; Schneider et al., 1998; Schneider and Ballschmiter, 1999). Atlas (1993) used a  $\frac{1}{4}$ " stainless steel tube packed with 600 mg of Tenax to sample 2 L of air. Luxenhofer et al. (1994), Schneider et al. (1998), and Schneider and Ballschmiter (1999) used sampling tubes filled with 70-90 mg of Tenax to sample 30 to 80 L, usually using two traps in series (to prevent breakthrough). In both cases, the alkyl nitrates are thermally desorbed and directly injected into a GC-ECD. Ambient concentrations of  $\text{C}_3$  to  $\text{C}_6$  alkyl nitrates have been measured using this technique (see Table 1). Detection limits are usually around 0.1 pptv. Because no solvent extractions are required, this technique is faster and less labor intensive than charcoal preconcentration which requires solvent extraction. The GC can be equipped with a thermal desorber to allow for direct analysis, making routine field measurements possible.

A disadvantage of this particular system is the high air volumes required for the sample. Because air flow through the traps are limited to smaller flow rates (20-

50 ml/min), high volume samples can take hours to collect (up to 3 hours depending on flow rate) Again, the number of measurements taken in a day is limited (8 per day assuming, 3 hour sample time). Problems with detecting methyl and ethyl nitrates are due to interferences from halogenated hydrocarbons that are easily detected by an ECD.

#### Sampling of $\geq C_7$ Alkyl Nitrates

Measurements of  $\geq C_7$  alkyl nitrates are rare for a few reasons. Longer chain alkyl nitrates are less abundant in the atmosphere, primarily due to decomposition of the larger ( $\geq C_7$ ) alkylperoxy radicals. The concentrations of these alkyl nitrates will be extremely small, making them difficult to measure. The number of isomers that can form also increases with the number of carbons. Synthesis and purification of all the possible isomers becomes difficult, so that identification and quantitation of  $\geq C_7$  nitrates becomes difficult.

Despite the difficulties, some measurements have been taken of  $\geq C_7$  nitrates (Luxenhofer et al., 1996; Schneider et al., 1998; Schneider and Ballschmiter, 1999). Large volumes of air (100-500 m<sup>3</sup>) are drawn through tubes containing silica gel. Solvent extractions are used to remove the alkyl nitrates from the gel followed by liquid chromatography (LC) to separate. Both GC-ECD and GC-MS were used by Schneider and Ballschmiter to identify the components of the fractions obtained by LC. Ambient concentrations of  $C_7$  to  $C_{14}$  alkyl nitrates have been measured using this technique (see Table 1).

### Aircraft Measurements

Methyl nitrate has been measured in the lower stratosphere and upper troposphere using aircraft (Flocke et al., 1998b). Samples were collected in stainless steel canisters. The canisters were treated initially at 240°C with an oxidizing environment and then humidified so that the alkyl nitrates could be stored without decomposition. The samples are then measured using GC-MS. This technique allows for multiple samples that require no solvent extraction. This is advantageous, especially when many samples are taken.

Leaitch et al. (1994) also measured alkyl nitrates in an aircraft. Charcoal preconcentration was used to measure C<sub>3</sub> to C<sub>7</sub> alkyl nitrates (Table 1).

### Detection

#### Electron Capture Detection and Mass Spectrometry

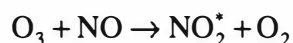
Electron capture detection (ECD) and mass spectrometry (MS) are the two most common methods of detecting alkyl nitrates. Both can be combined with a GC for separation of the components of the sample. Both detectors are transportable to a field research site. Often, an MS system is used to verify the results from an ECD, especially when validating a new sampling technique (Schneider and Ballschmiter, 1999).

The major disadvantage to using an ECD over a MS or chemiluminescent detector (CLD) are interferences due to halogenated hydrocarbons. All of the

sampling techniques discussed will trap halocarbons as well as alkyl nitrates. ECD's are more sensitive to chlorinated compounds than to alkyl nitrates. In most cases, it is very difficult to separate halocarbons from alkyl nitrates, especially methyl and ethyl nitrates, on a GC. Quantification of methyl and ethyl nitrates is difficult because of the halocarbon coelution (Schneider and Ballschmiter, 1999). This interference can be eliminated by using a GC-MS system. The MS can be tuned to look for a mass fragment at  $m/e=46$ , which suggests  $\text{NO}_2$  (Atlas, 1988).

### Chemiluminescent Detection (CLD)

The NO chemiluminescent detector only detects species with oxidized nitrogen, such as alkyl nitrates and PANs. A chemiluminescent emission occurs when NO reacts with ozone (Weiner et al., 1974):



Compounds containing an oxidized nitrogen group can be converted to NO on molybdenum or gold converters and then quantified on a per NO basis (Weiner et al., 1974). This detector can be connected to a GC to measure alkyl nitrates or can be used to measure total NOy (Flocke et al., 1998a). Calibration is performed against standard NO source. The sensitivity measured using the standard should be the same as the sensitivity to the alkyl nitrates if the conversion (to NO) efficiency is the same. Standards of NO are more available and more reliable than laboratory synthesized alkyl nitrate standards. A gas cylinder is more easily transported and kept in the field

than alkyl nitrate standards, which need to be kept frozen. Unfortunately, a CLD is one to two orders of magnitude less sensitive than an ECD, despite all its other desirable features (Flocke et al., 1991).

Another type of CLD is the  $\text{NO}_2$ -luminol chemiluminescence detector. Instead of conversion of the oxidized nitrogen to NO, a pyrolyzer (quartz tube) is used to thermally decompose the compound to  $\text{NO}_2$  (Hao et al., 1994). Then, in a detection cell, a luminol- $\text{NO}_2$  chemiluminescence reaction occurs. A photomultiplier tube is used to measure the photons emitted, and the signal is recorded. As with the other CLD, this type can be connected to a GC. This detector has a better sensitivity than the NO-CLD. Both are highly selective for oxidized nitrogen species, thereby eliminating any interferences with halocarbons. These detectors are complex, which makes them difficult to move from field site to field site.

### Summary

Because research in atmospheric chemistry relies on field studies, instruments that can easily be transported to field sites are desirable. ECD's are commercially available already integrated into a GC and can be transported as one unit. They also have enough sensitivity to detect alkyl nitrates. ECD's are more desirable than a MS or CLD because setup in the field only requires setup of a GC.

The ability to collect high frequency data is also another desirable feature of a field instrument. Direct and cryogenic trapping of alkyl nitrates allows for frequent, automated measurements. Cryogenic trapping lowers the detection limit, but requires

a source of liquid nitrogen near the field site. Solid sorbent trapping methods (charcoal and Tenax) offer the ability to trap alkyl nitrates without the use of cryogenics, but, as in the case of charcoal, can require elaborate extraction techniques which limits the ability of the researcher to collect high frequency data. Tenax, which does not require the use of liquid extraction, has the potential to allow for high frequency and automated data collection, if modifications are made.

### Research Objectives

The objectives of this work are to develop a method to measure alkyl nitrates that allows for high frequency and automated data collection. This method will use Tenax as a trapping material which is connected directly to a GC-ECD system for analysis. This method will be validated for the use in a field study. The importance of alkyl nitrates to the total NO<sub>y</sub> in a rural site will also be investigated (from data from the same field study). The relative importance of alkyl nitrates to other oxidized nitrogen species (isoprene nitrates, PANs) measured during the field study will also be explored.

## CHAPTER II

### MATERIALS AND METHODS

Measurements of alkyl nitrates were taken as part of PROPHET (Program for Research on Oxidants: Photochemistry, Emissions, and Transport) 1998 Summer Intensive at the University of Michigan Biological Station in Pellston, Michigan from July 19 to August 21, 1998. Samples were taken from above the forest canopy (110 feet above ground) through a 4-inch glass manifold. Samples were taken every thirty minutes. The following alkyl nitrates were quantified: isopropyl, n-propyl, isobutyl + 2-butyl, n-butyl, 2-pentyl, 3-pentyl, and n-pentyl. Table 3 lists abbreviations of alkyl nitrates that are used.

#### Instrumentation

##### Sample Analysis

Alkyl nitrates were measured in this work using a Varian 3500 gas chromatograph (GC) with electron capture detection (ECD) modified for gas injections. The GC was originally equipped with two syringe injector ports. For this project, one of these injector ports was removed. A six-port Teflon rotary valve (Hamilton) was used to introduce air samples into the GC. A 30-m long DB-210 (0.53 mm, megabore) column was used for separation. Helium was used as carrier



gas at a flow rate of 6 mL/min. Nitrogen was used as makeup gas to the detector at a flow rate of 12 mL/min. The column was temperature programmed as follows: initial temperature of 35°C held for six minutes, temperature increase of 3.3°C/min to a final temperature of 90°C, final temperature held for 1 minute, then cooled back to 35°C. The time for one complete injection cycle was 28 minutes, allowing for injections every 30 minutes in the field.

Table 3  
Abbreviations of Alkyl Nitrates Used

Abbreviation	Name
MN	Methyl Nitrate
EN	Ethyl Nitrate
IPN	Isopropyl Nitrate
NPN	n-Propyl Nitrate
2BN	2-Butyl Nitrate
IBN	Isobutyl Nitrate
NBN	n-Butyl Nitrate
2PeN	2-Pentyl Nitrate
3PeN	3-Pentyl Nitrate
NPeN	n-Pentyl Nitrate
NHN	n-Hexyl Nitrate

### Sampling System

A sampling trap was designed to concentrate the sample prior to injection to the GC. The sampling trap was made by packing ~3 mg of Tenax TA (80/100 mesh; Supelco) into a piece of silicosteel (Restek, 0.4" id, 1/16" o.d.) that was 22 cm long. A small amount of glass wool was inserted about 1" into one end of the silicosteel using a piece of copper wire. This end of the trap was attached to the apparatus shown in Figure 1. The vacuum tubing is attached to an aspirator vacuum. About 3 mg of Tenax was placed into a glass dish. Tenax was drawn into the silicosteel until it was full using the vacuum. The silicosteel trap was removed from the vacuum apparatus. Excess Tenax was removed from the trap through the open end. A small amount of glass wool was used to plug the open end about 1" from the end using copper wire to pack the plug into place. The weight of Tenax in the trap was determined by the difference in the weight before and after the Tenax was packed into the silicosteel. Thermocouples (30 gauge "K" type thermocouple wire; Omega) were made and welded to the trap using a spot welder. The trap was attached to the six-port valve using 1/4-28 flat bottom fittings (Upchurch). The trap was put under nitrogen flow to remove any loose Tenax. The trap was then conditioned by heating the trap at 50-80°C under nitrogen flow (30-50 sccm) for 15 min then at 200°C for 1 hour.

After conditioning with nitrogen, the trap was placed on the rotary valve and connected to the instrument. The chromatogram for a scrubbed ambient air sample after 1 hour of conditioning is shown in Figure 2. After sampling scrubbed ambient

air for 4 days (every 30 min, 2 minute trap time, 4 minute heating time), the blank chromatogram was relatively clean (Figure 2).

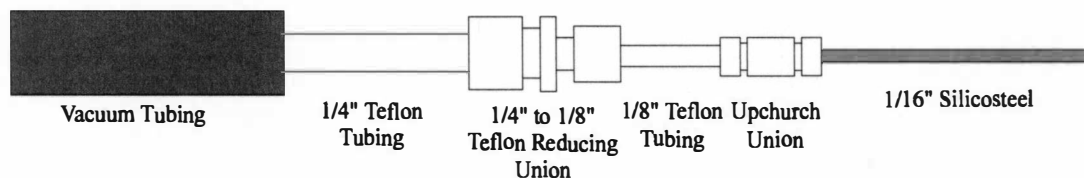


Figure 1. Diagram for Apparatus Used to Pack Tenax in Silicosteel Tubing.

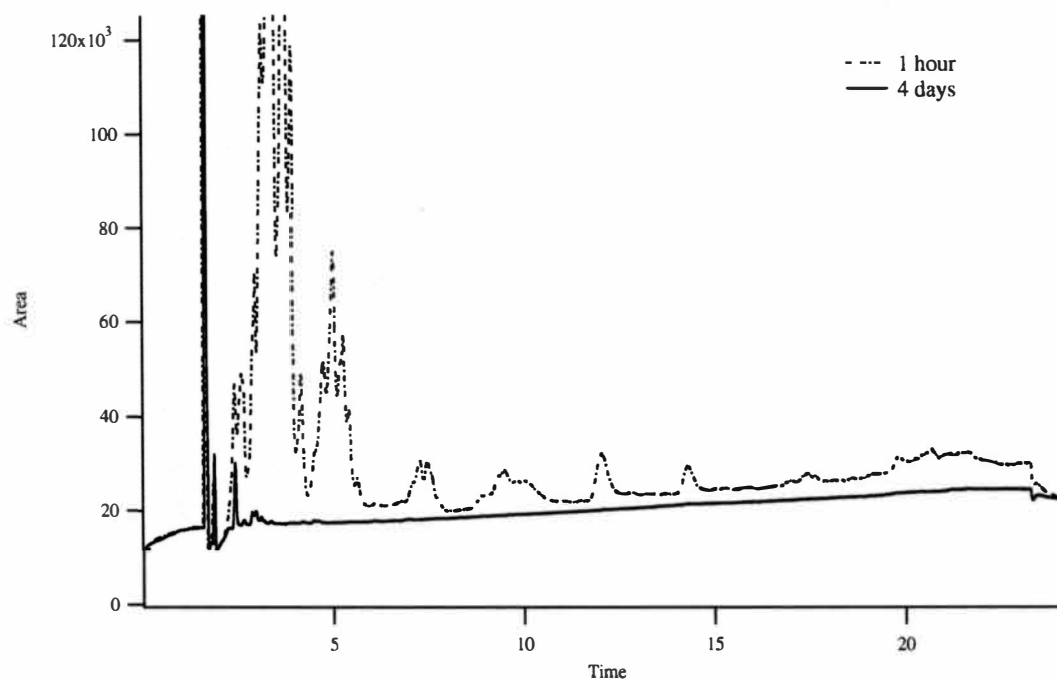


Figure 2. Blanks After Trap Conditioning.

The six-port valve was used to introduce a sample of ambient air into the GC. The valve was set up as shown (Figure 3). Ambient air was drawn through the trap (in load/powered mode) at ~20 ml/min using a 100 sccm MKS mass flow controller attached to a Teflon diaphragm pump (KNF Neuberger) (Figure 4). The trap can be loaded for variable amounts of time, which is controlled by a computer. The trap was

loaded for four minutes for field measurements. After the trap was loaded, the valve switched to the inject mode, and the trap was heated for six minutes. This process was repeated every time the system sampled air. The trap was heated to desorb the alkyl nitrates from the Tenax. A heating circuit was designed to allow rapid resistive heating of the trap. The trap was heated rapidly from ambient temperature ( $\sim 20^{\circ}\text{C}$ ) to  $175^{\circ}\text{C}$  in about 30 seconds. The temperature was controlled by a Love Temperature controller (Model # 16022-948) equipped with two temperature set-points. The temperature is controlled  $\pm 5^{\circ}\text{C}$  for the heating time. Retention times were determined using individual standards (discussed below). A standard mixture was used to verify retention times during the measurement period.

The instrument was automated using Labview software. A program in Labview was written to turn on a series of digital relays in a specific order to turn on the valve, the heating circuit, the GC, and start the data acquisition software for the chromatography (ChromPerfect, Justice Innovations). The sequence that the relays were turned on is shown in Table 4.

The Labview program was designed so that the program would start so that the sample time (the time that the valve was in the load mode) would be centered on the hour or the half hour for automatic injections. For a four minutes sample time, the program would start at two minutes before the hour or two minutes before the half hour. The program was also designed for manual injections. In the manual mode, the injection would take place when a button was pushed.

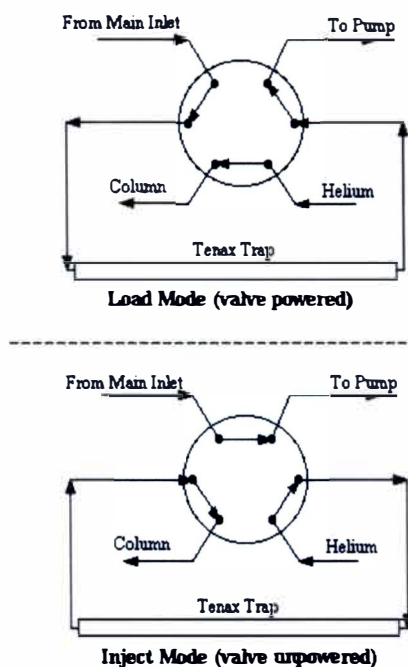


Figure 3. Diagram of the 6-Port Teflon Valve Used to Inject Samples Into the GC.

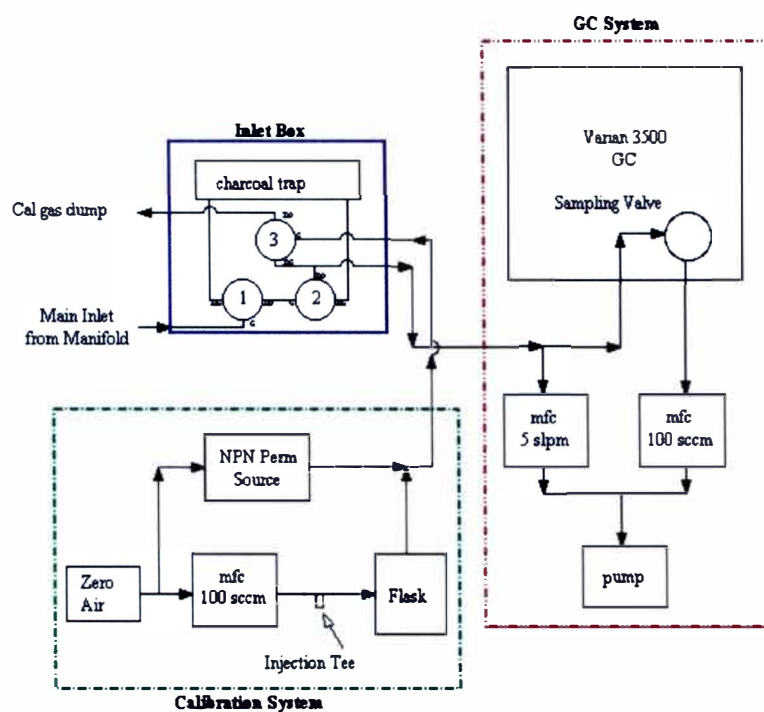


Figure 4. Flow System for the Alkyl Nitrates System Used in PROPHET 98.

Table 4

## Labview Control Program Event Sequence

Event
1 Relay #2 on – turn valve to load (powered)
2 Wait a set period of time (4 minutes, controlled by user)
3 Relay #2 off – turn valve to inject (unpowered)
4 Wait one second
5 Relays #1 and #3 on – start trap heater, start ChromPerfect, start GC temperature program
6 Wait a set period of time (6 minutes, controlled by user)
7 Relays #1 and #3 off – trap heater off
8 Wait until the program starts again, 30 minute total cycle time ( cycle time controlled by user).

Inlet Box

Ambient air was drawn to the instrument through an inlet box (Figure 4).

Three three-port solenoid valves (12 VDC; Fluoroware) were used to direct the flow of air. Valves 1 and 2 were used to direct flow through a charcoal trap to scrub the air of ambient organics including nitrates for blank and calibration runs. When these valves were powered, the normally closed (NC) port is opened, and ambient air flows through the charcoal trap, scrubbing it of alkyl nitrates (and other organic compounds). Valve 3 was used to add a calibration standard to the main inlet line when it was powered.

## Calibration

The instrument was calibrated using two different methods. The first method used a permeation device. The second method involved a Pyrex flask used as a mixing chamber. Both methods required quantification of the concentration of alkyl nitrates by use of a commercially available NO<sub>x</sub> chemiluminescence detection instrument (Thermal Environmental Instruments, model 42S). Calibrations were performed nightly (after midnight) during the PROPHET 1998 summer intensive. A calibration using n-propyl nitrate from the permeation source and another nitrate from the flask were typical. To prevent overloading of the trap, calibrations were usually run with a 30 second trap time and then scaled for a four minute trap.

### Permeation Device

A permeation device (perm source) containing n-propyl nitrate (NPN) was constructed. A stainless steel wafer device with a permeable Teflon wafer (30F3, VICI). This was filled with NPN and then placed into 3/4" Teflon tubing. Zero air was flowed through the Teflon tubing at a rate of around 23 ml/min (controlled by a Porter mass flow controller). The perm source was maintained at a temperature of 30°C using a Love temperature controller and a Kapton flexible heater (KH203/10, Omega). The source was quantified using the NO<sub>x</sub> analyzer. This provided a source of NPN of ~ 200-300 pptv.

### Flask Calibrations

A 4000 mL filter flask fitted was used as a mixing chamber for use in calibrations. A picture of the setup is shown in Figure 5. Small amounts of alkyl nitrates (>1 mL) were placed into sealed vials. Headspace from the vials was injected into the injection tee using a gas tight syringe. The injection tee consisted of a 1/8" Teflon tee with a stainless steel nut containing a Teflon septum on the center branch. Zero air was flowed through the other branches of the tee into the flask at a rate of 10 mL/min using a MKS mass flow controller (100 sccm). Flow out from the flask was teed into the flow out from the permeation source out to the inlet box.

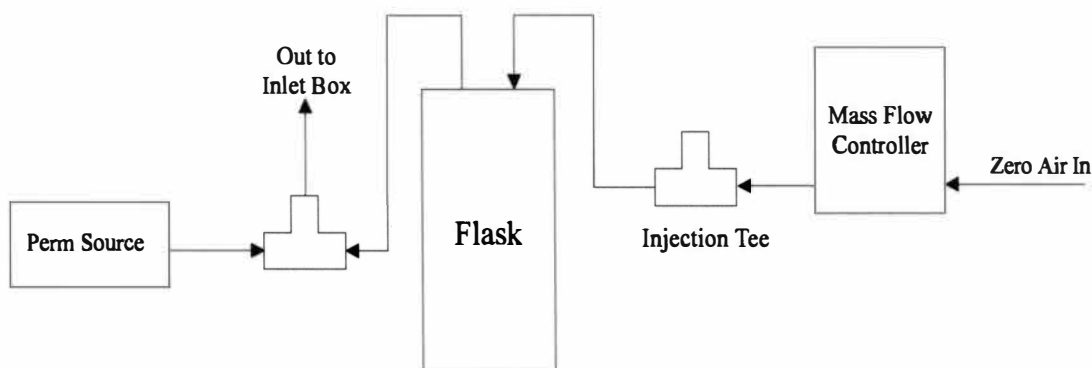


Figure 5. Flow Diagram of Flask and Permeation Source Calibration System.

### Gas Cylinder

Cylinders containing either NPN or a mixture of 6 alkyl nitrates (methyl, ethyl, isopropyl, isobutyl, 2-pentyl nitrate, and n-hexyl nitrates) in nitrogen were prepared at Purdue University. These tanks were used for laboratory tests of the instrument.



### Quantitation

Alkyl nitrate standards were quantified using a commercially available NO<sub>x</sub> chemiluminescence detection instrument (TECO Instruments, model 42S). Alkyl nitrates from one of the calibrations sources were introduced into the analyzer where they undergo a conversion to NO in a molybdenum converter at 325°C. The nitric oxide molecules react with ozone to form an excited state NO<sub>2</sub>, which emits light upon relaxation. The intensity of the light is proportional to concentration of NO that is converted to NO<sub>2</sub>. Calibration and determination of converter efficiency was performed using a known source of NO in nitrogen (NIST Traceable Std. Mixture, Scott Marin Specialty Gases). Using this calibration method, the uncertainty of the measurements is 30% for isopropyl nitrate and 50% for the remaining alkyl nitrates. The detection limit of the instrument is 0.03 pptv.

### Standard Synthesis

Standard samples of nitrates were synthesized in the lab, except for isopropyl and isobutyl nitrates, which were purchased from Aldrich and used as purchased. Methyl and ethyl nitrates were synthesized by reaction of the alcohol with nitric and sulfuric acids. The remaining nitrates were synthesized from the appropriate alkyl bromide and silver nitrate in acetonitrile (Boschan et al., 1955). The resulting alkyl nitrates were vacuum distilled.

## Chromatography

Figures 6 and 7 show chromatograms from injections of the mixture of alkyl nitrates in dodecane and ambient air, respectively. As can be seen from Figure 6, methyl, ethyl, 3-pentyl, and n-pentyl nitrates co-elute with unidentified compounds, most likely halogenated hydrocarbons. At low concentrations, the 3-pentyl and n-pentyl nitrate peaks were resolved from the unidentified peak. Throughout the PROPHET '98 intensive, these peaks were observed but not quantified.

The peaks for 2-butyl and isobutyl nitrates also co-eluted. It is expected that 2-butyl nitrate will be the major contributor to the peak, but the values are reported as the sum of 2-butyl and isobutyl nitrates.

During the 1998 PROPHET intensive, the retention times for all nine alkyl nitrates identified would fluctuate over the course of the day. This fluctuation was not seen during experiments in the laboratory at Western Michigan University. A possible explanation for the retention time fluctuation is that the nitrogen and helium gas cylinders were outside the lab. The cylinders experienced temperature fluctuations due to weather. Because the gas flowrates into the GC were controlled by a pressure regulator, variations in temperature could affect the flowrate of carrier gas through the column due to changes in the delivery pressure. The fluctuation in the retention times did not preclude identification of the alkyl nitrates, however. All the peaks in the chromatograms shifted to a later retention time together.

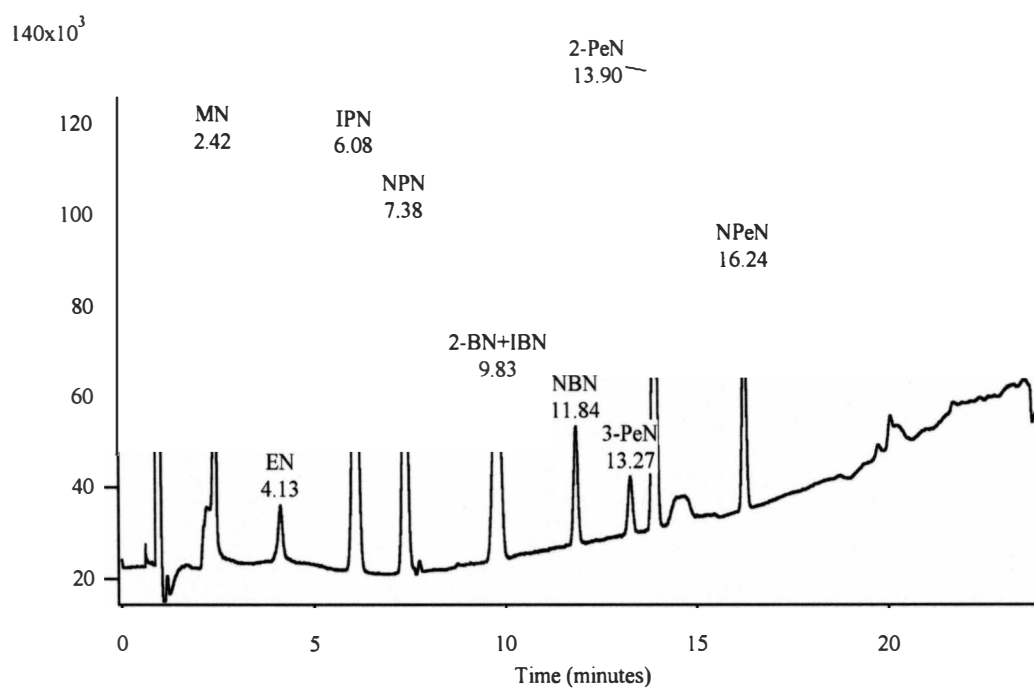


Figure 6. Chromatogram of an Injection of a Standard Mixture of Alkyl Nitrates.

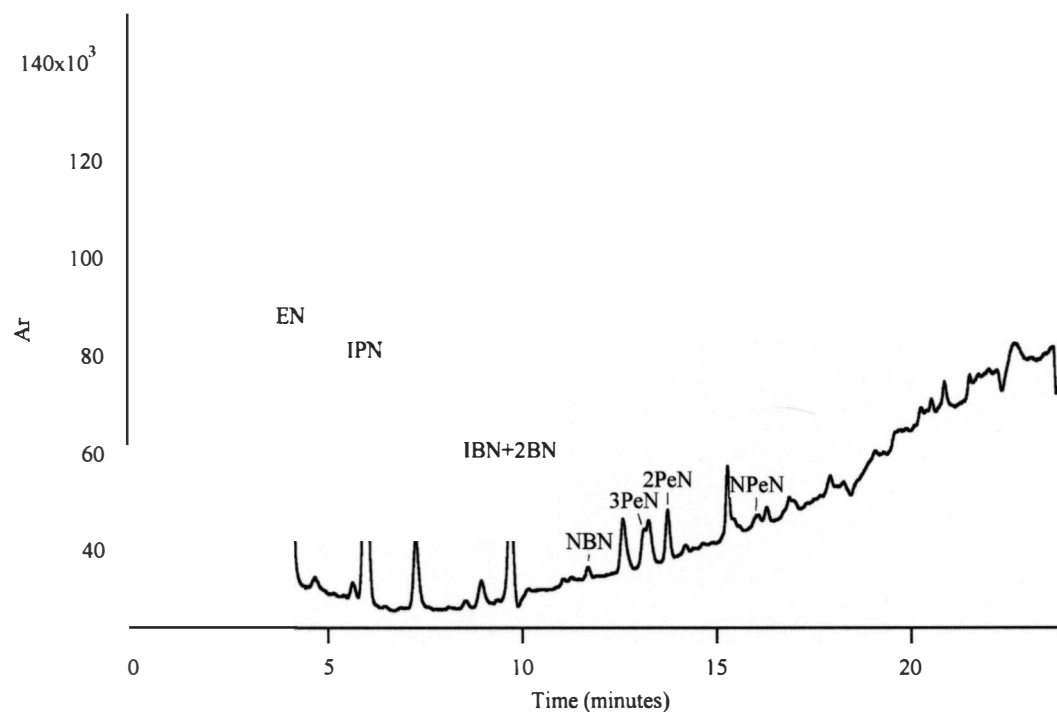


Figure 7. Ambient Alkyl Nitrate Chromatogram From the PROPHET '98 Intensive.

## System Integrity

### Breakthrough

As with all solid adsorbants, the Tenax trap has a finite capacity to trap compounds. At some point, a maximum amount of sample can be trapped. Two experiments were designed to measure to determine if this was a problem with our system. Both experiments were performed with a solution of alkyl nitrates (methyl, ethyl, isopropyl, n-propyl, isobutyl, 2-butyl, n-butyl, 2-pentyl, 3-pentyl, and n-pentyl nitrates) in dodecane. A small amount of this solution (~1 mL) was placed in a diffusion cell through the filling arm. Zero air is flowed through the inlet at ~50 ml/min. The sample was introduced in the same manner as the permeation source and flask (see calibration section).

Breakthrough Experiment 1 was designed to directly trap any material that breaks through the trap and inject it onto the column. If there is break through, a peak will be seen in the chromatogram. Breakthrough Experiment 2 measures the maximum amount in a different way. When the maximum amount of trapped material is reached, a maximum amount in the area counts from the GC should be reached. A graph of area vs. trap time should increase then plateau when the maximum amount of material is trapped.

### Breakthrough Experiment 1

For Breakthrough Experiment 1, the configuration of the valve was altered as shown in Figure 8. The Tenax trap was replaced on the valve by a silicosteel trap. The Tenax trap was placed inline with the Main Inlet. To perform this experiment, the silicosteel trap was cooled with liquid nitrogen. The valve is then switched to the Load Mode and the standard mix (C1 to C5 nitrates in dodecane) is added to the Main Inlet. After four minutes, the valve is switched to the Inject Mode and the liquid nitrogen is removed from the silicosteel trap. In this configuration, the Tenax trap should remove nitrates before the air reaches the valve, so any material that breaks through will be trapped in the liquid nitrogen. Any material trapped in the liquid nitrogen is injected into the GC for analysis. After the sample in the silicosteel trap is injected into the GC, the standard is removed from the system, leaving the system under flow with scrubbed ambient air. The Tenax trap is heated to 175°C for 6 minutes to release trapped materials.

The chromatograms from this experiment showed only one peak from methyl nitrate (Figure 9). The breakthrough of methyl nitrate was confirmed by Breakthrough Experiment 2.

### Heating Efficiency

With the valve in the configuration for Breakthrough Experiment 1, the removal efficiency of the trap was tested. After a normal run to determine breakthrough, the trap was heated for four minutes while the silicosteel trap was

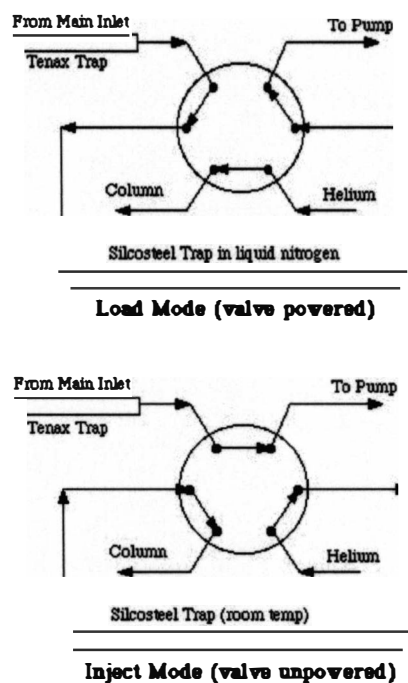


Figure 8. Injection Valve Configuration for Breakthrough Experiment 1.

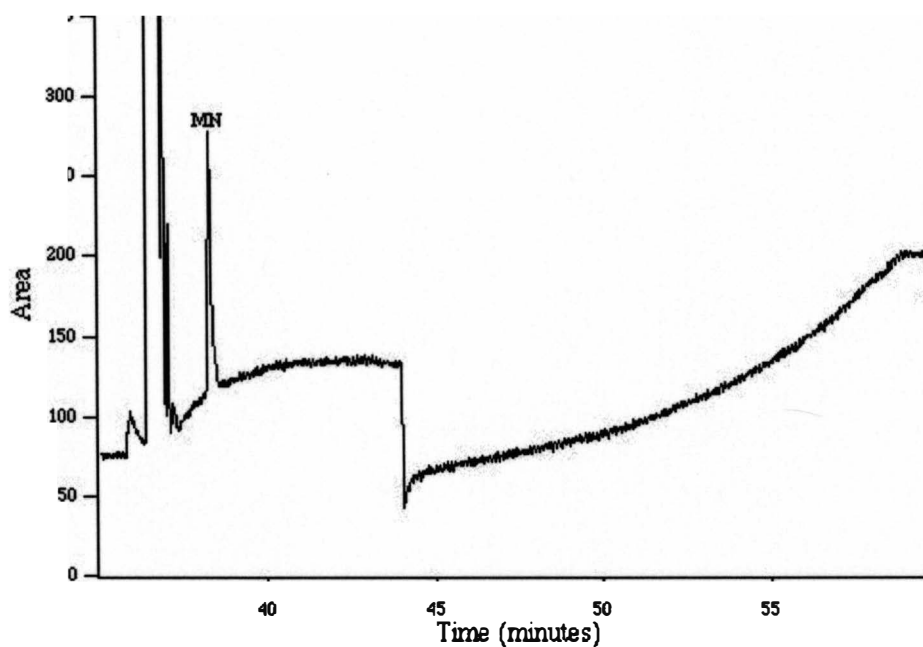


Figure 9. Chromatogram From Breakthrough Experiment 1.

placed in liquid nitrogen. If any alkyl nitrates were not removed by the heating in the previous run, they would be trapped in this run. The chromatograms showed no peaks, which indicates that the alkyl nitrates were removed.

### Breakthrough Experiment 2

For Breakthrough Experiment 2 the trap was left in its normal configuration. A standard (C1 to C5 nitrates) was added to the GC system, and the trap time was varied. Figure 10 shows a plot of peak area vs. trap time for this experiment. Methyl nitrate shows a plateau after 2 minutes of trap time. These results together with the results from Breakthrough Experiment 1 show that methyl nitrate breaks through under conditions used in the PROPHET field study. Similar results were seen for ethyl nitrate, although no peak was seen in Breakthrough Experiment 1. These experiments also show that, for the compounds that do not break through, the area increases linearly with trap time. A four minute trap was chosen as the optimal trap time to maximize the response from the GC and still allow for 30 minute sampling.

### Optimal Temperature

Experiments to determine the optimal temperature to remove the alkyl nitrates from the trap were performed prior to field experiments. The multi-nitrate cylinder was used for these experiments. The trap was heated for two minutes at different temperatures. The results are shown in Table 5. The area of the peaks increased as the temperature increased for methyl nitrate. The peak areas only increased slightly

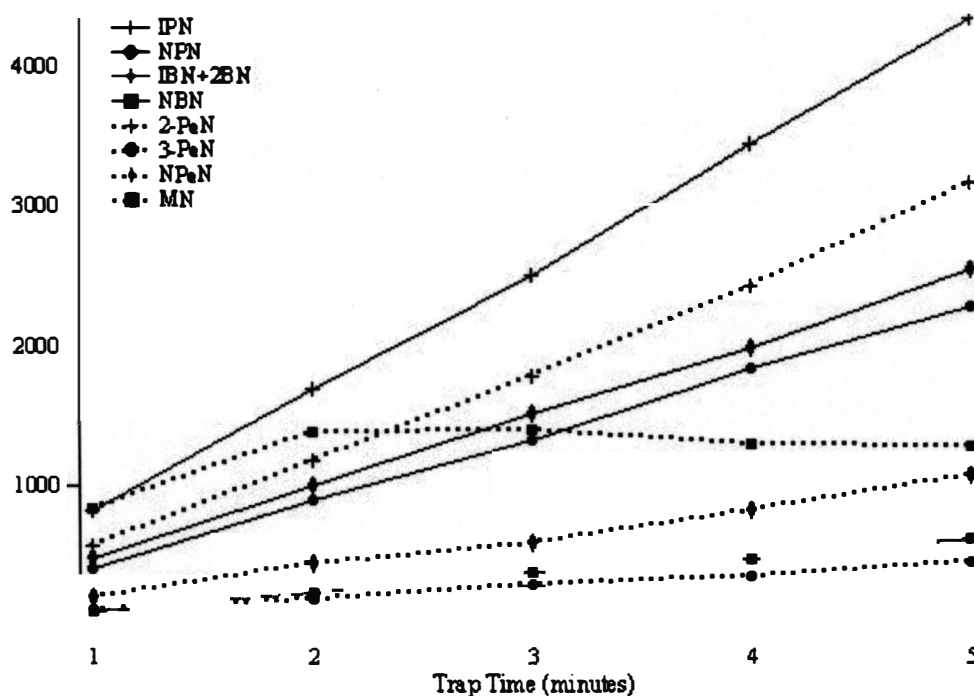


Figure 10. Results of Breakthrough Experiment 2.

for ethyl, isopropyl, and n-hexyl nitrates after 150°C. When the trap was heated to 250°C, signs of decomposition of the Tenax were seen. Figure 11 shows a chromatogram of an injection of the multi-component tank when heating the trap to 250°C. Only 6 peaks should be seen (6 alkyl nitrates in the multi-component tank). As can be seen from comparing Figure 11 and Figure 5, many unidentified peaks are seen, most likely due to some decomposition of the Tenax. A temperature of 175°C was chosen to heat the trap because the peak areas were maximized and the Tenax decomposition was minimized.



Table 5

Peak Areas of Four Alkyl Nitrates From Different Trap Heating Temperatures

Temperature (°C)	MN (area counts)	EN (area counts)	IPN (area counts)	NHN (area counts)
100	221,163	200,036	174,337	89,809
150	288,121	255,670	223,438	113,668
175	351,095	249,968	228,563	115,461

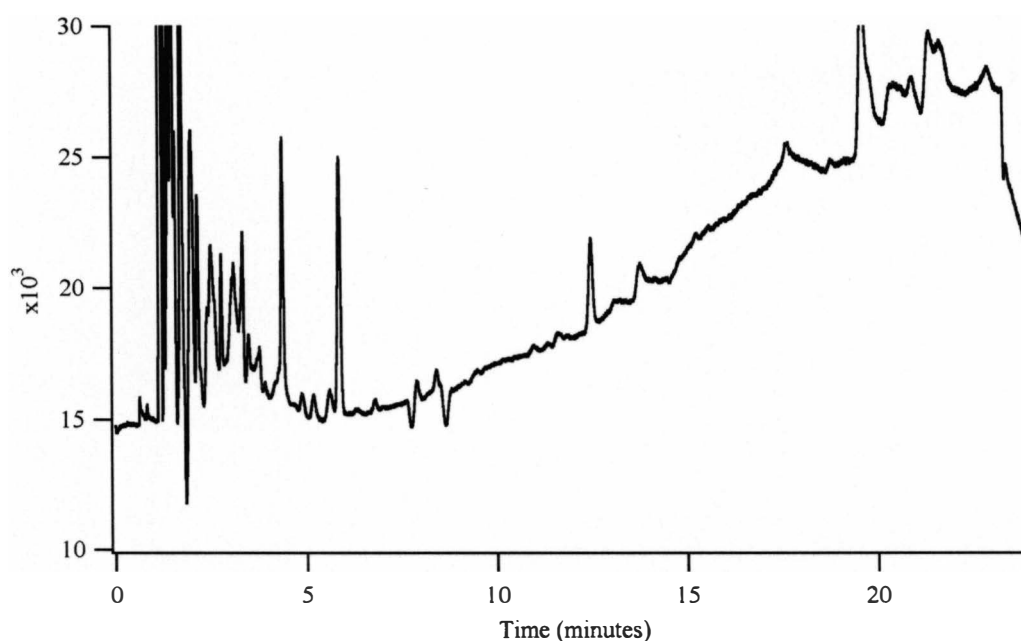


Figure 11. Injection of Multi-component Tank When Heating the Tenax Trap to 250°C.

### PAN Decomposition

One proposed mechanism of decomposition of peroxyacetyl nitrate (PAN) is through a cyclic rearrangement that results in methyl nitrate and carbon dioxide

(Roberts, 1990). Tests were done to determine if PAN decomposed to methyl nitrate when the trap was heated.

A laboratory-synthesized standard of PAN was introduced into the NO<sub>x</sub> analyzer to determine the concentration (the standard was also verified by analysis by a GC devoted to the measurement of PAN). The sample was injected to the GC in the same manner as the alkyl nitrates: trap time of 2 minutes, trap heating temperatures of 150°C, 200°C, and 250°C. At least two experiments were performed at each trap heating temperature. If the PAN standard decomposed, a peak for methyl nitrate would be seen. No methyl nitrate peak was seen in any of the experiments.

### Limitations

The method described here provides frequent simple measurements of alkyl nitrates, but is limited to C3 to C5 alkyl nitrates. The major limitation in this method lies in the chromatography. Several compounds (methyl, ethyl, 3-pentyl, and n-pentyl nitrates) coeluted with unidentified compounds. In the cases of methyl and ethyl nitrate, the unidentified compound was most likely a halocarbon. The chromatography could be improved by changing any number of variables. For example, the interference of halogenated hydrocarbons can be eliminated by using a detector, such as a CLD or an MS that can be adjusted to respond to only the nitrate group. Columns with different stationary phases could be tested to try to improve the separation. Adjusting the temperature program or the gas flow rates could also help.

The breakthrough of methyl and ethyl nitrate is another limitation of this method. Breakthrough of these compounds can be prevented by using a larger trap or by cooling the trap. Previous work on this method in our laboratory incorporated cooling a molecular sieve trap by use of thermoelectric coolers. Later work showed that cooling the molecular sieve trap was not necessary, and the cooling system was removed and not replaced when the Tenax trap replaced the molecular sieve trap. Addition of the cooling system to the method would not be difficult.

### Measurement of Other Oxidized Nitrogen Species

#### NO<sub>x</sub> and NO<sub>y</sub>

Measurements of NO, NO<sub>2</sub>, and NO<sub>y</sub> were performed by Troy Thornberry from the University of Michigan. Samples were measured via a chemiluminescence reaction and conversion using a gold converter. Samples were measured every minute. The uncertainty in the measurements is 30%.

#### Peroxyacyl Nitrates

Measurements of peroxyacyl nitrates were performed by Margaret Pippin from Western Michigan University.

#### Sample Acquisition

Samples were obtained from a large Pyrex inlet manifold through which air was drawn from the top of a 115 ft sampling tower with approximately a 2-3 second

residence time. A small ( $\sim 1$  L/min) flow of air was pulled off of this manifold at its base near the instrument lab by means of a diaphragm pump through an approximately 10 m section of 1/4" O.D. PFA Teflon tubing. The Teflon tubing was routed through a series of PFA Teflon solenoid valves used to introduce gas-phase standards immediately after the Pyrex manifold. The GC sampled air off of this Teflon tubing at a flow of about 50 standard  $\text{cm}^3/\text{min}$ .

### Sample Analysis

Peroxyacyl nitrate measurements were made using a custom GC equipped with a Shimadzu GC Mini-2 63Ni ECD maintained at 55°C. The column (J&W Scientific, DB-210, I.D.= 0.53 mm) was wrapped around an aluminum block, which was cooled using thermoelectrics to 15°C to minimize thermal decomposition. He and N<sub>2</sub> were used as carrier and make-up gases at 8  $\text{cm}^3/\text{min}$  and 1  $\text{cm}^3/\text{min}$  respectively. Whole air injections from a 2 mL sample loop composed of 1/8" PFA Teflon were made automatically in 20 minute intervals using a Hamilton Teflon 6-port rotary valve. The detection limit was 2 to 5 pptv with uncertainties with respect to PAN, PPN and MPAN of 20%, 25%, and 30%, respectively.

### Calibration

Separate calibrations for PAN, PPN, and MPAN were performed prior to and during the Summer '98 campaign using standards that were synthesized in the laboratory in dodecane and stored frozen until needed. (Nielsen et al., 1982; Gaffney

et al., 1984; Nouaime et al., 1998) Ambient peroxyacyl nitrates were first removed from ambient air by passing it through a charcoal trap. Then gaseous peroxyacyl nitrate standards were added via the Teflon solenoid valves at the glass manifold. Calibration was performed with synthetic samples of each individual analyte diluted into a variable flow in the 1/4" Teflon tubing running from the glass manifold into the laboratory. Gas-phase standards were quantified by conversion to NO followed by O<sub>3</sub>-chemiluminescence detection using a TECO Model 42S chemiluminescence NO<sub>x</sub> analyzer against a NIST traceable standard of NO (Scott Specialty Gases). A plug of nylon was used to scrub any gas-phase HNO<sub>3</sub> by placing it into the Teflon tubing that transports peroxyacyl nitrate vapors from the diffusion cell to the analyzer; and freshly synthesized peroxyacyl nitrate standards were used to avoid interference from decomposition products. Multiple-point calibrations were performed at the start, middle, and end of the intensive campaign. Spot checks of calibrations were usually performed daily. Overall uncertainty of the measurements is around 25%.

#### Nitric and Nitrous Acid

Measurements of nitric and nitrous acid were performed by Gerald Keeler from the University of Michigan. The samples were collected for 24 hours using a denuder collection system. The uncertainty of the measurements is 15%.

### Isoprene Nitrates

Measurements of isoprene nitrates were performed by John Grossenbacher from Purdue University. Sampling was carried out with preconcentration on Tenax followed by on-line chromatographic separation and selective detection of nitrate compounds via chemiluminescence reaction involving luminol. Samples were collected for thirty minutes at varying intervals throughout the intensive. The uncertainty in the measurements is 30% and a detection limit of 0.1 pptv.

## CHAPTER III

### RESULTS AND DISCUSSION

#### General Results

Alkyl nitrates were measured during the PROPHET '98 Summer intensive from July 19 to August 21, 1998. Seven alkyl nitrate isomers were identified and quantified and are presented in Figures 12 through 18. Statistics of these measurements are shown in Table 6.

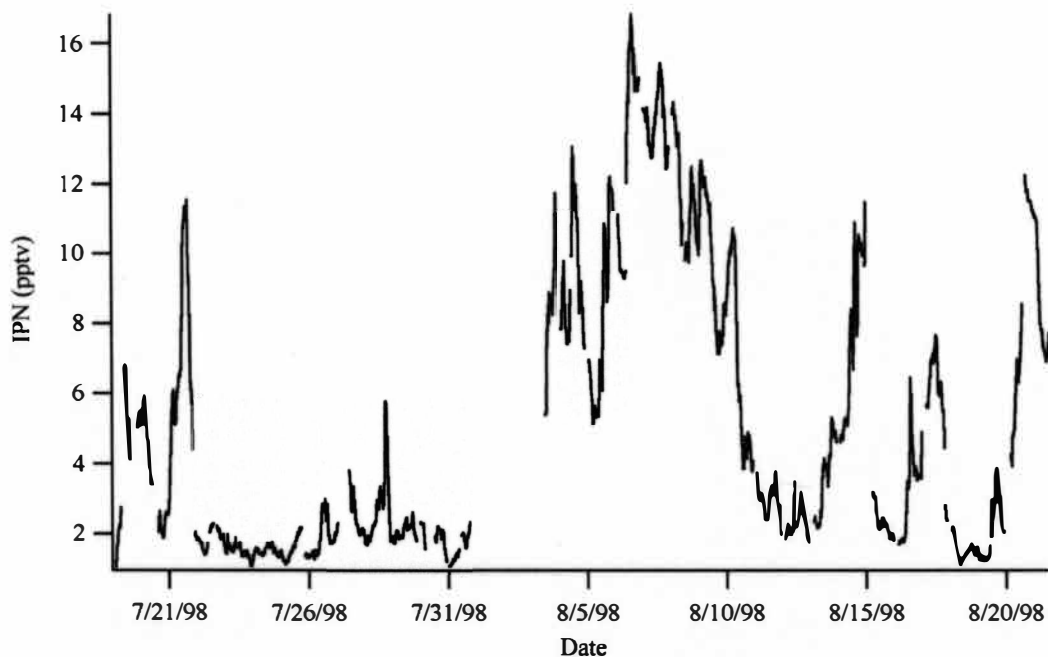


Figure 12. Time Series of Isopropyl Nitrate During the PROPHET '98 Summer Intensive.

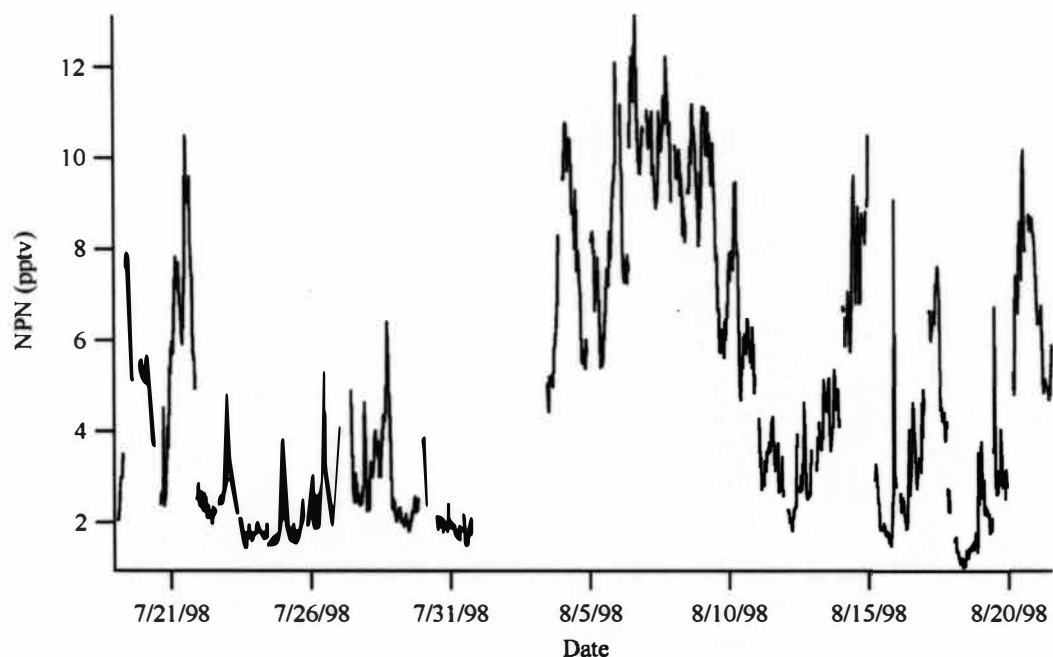


Figure 13. Time Series of n-Propyl Nitrate During the PROPHET '98 Summer Intensive.

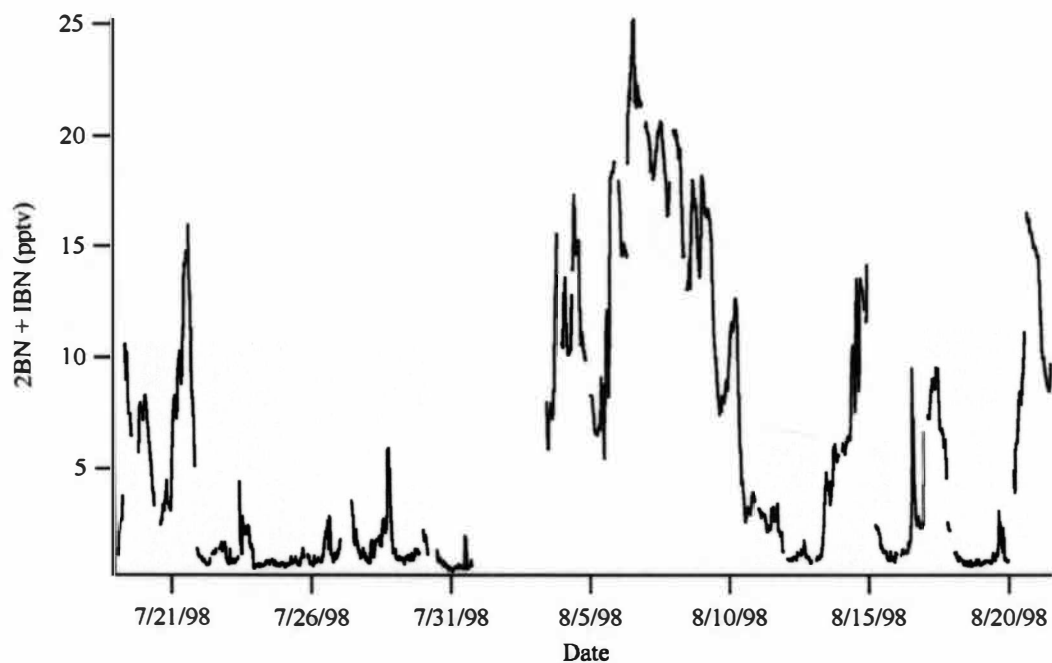


Figure 14. Time Series of the Sum of Isobutyl and 2-Butyl Nitrates During the PROPHET '98 Summer Intensive.



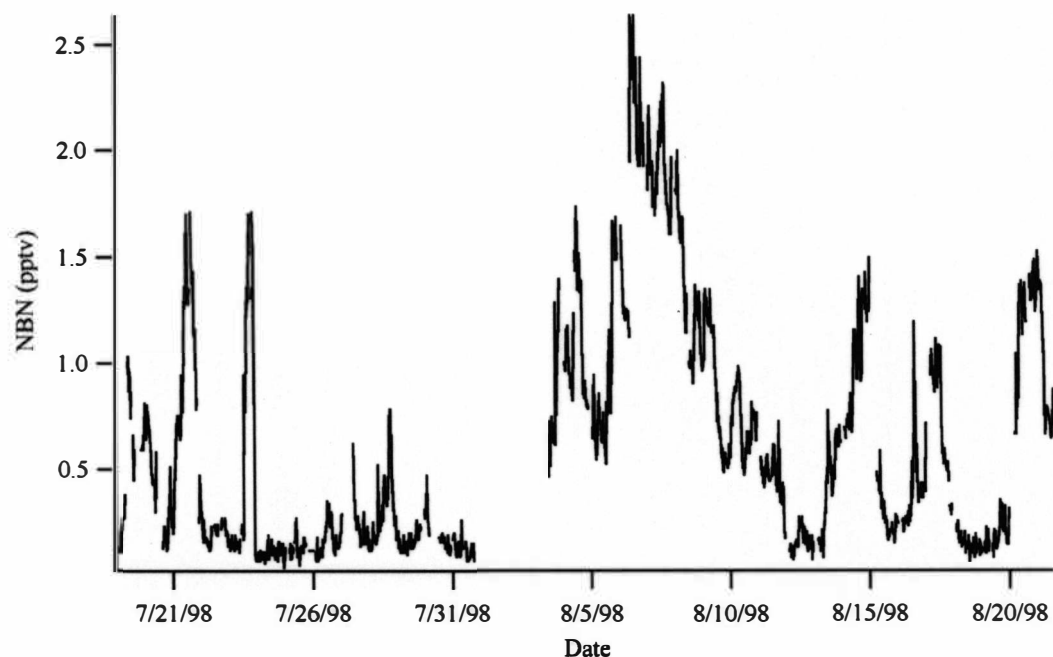


Figure 15. Time Series of n-Butyl Nitrate During the PROPHET 98 Summer Intensive.

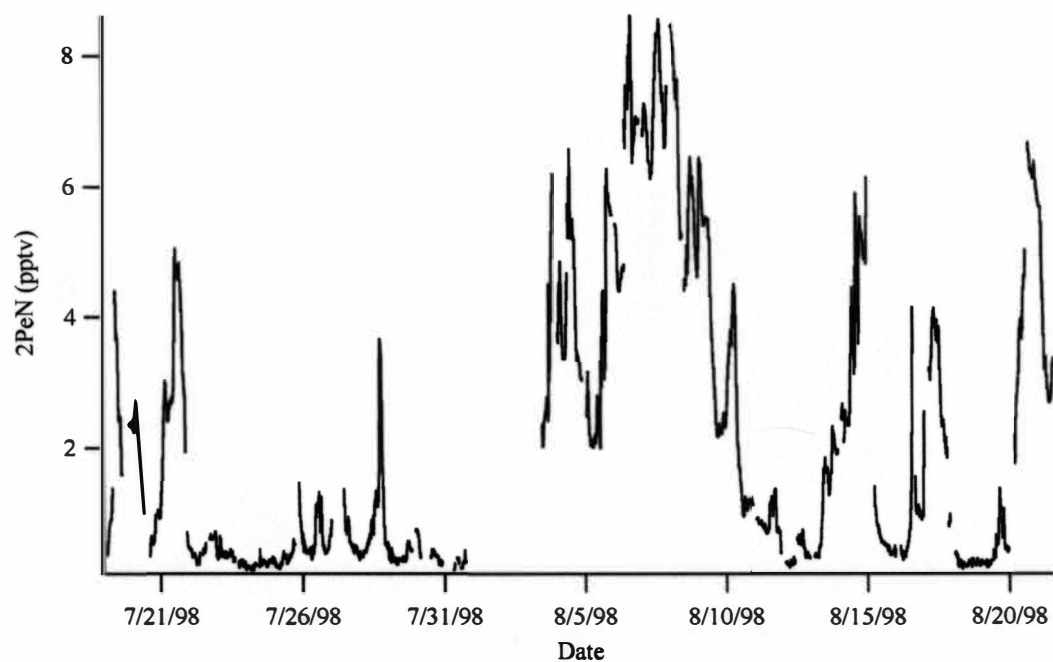


Figure 16. Time Series of 2-Pentyl Nitrate During the PROPHET 98 Summer Intensive.

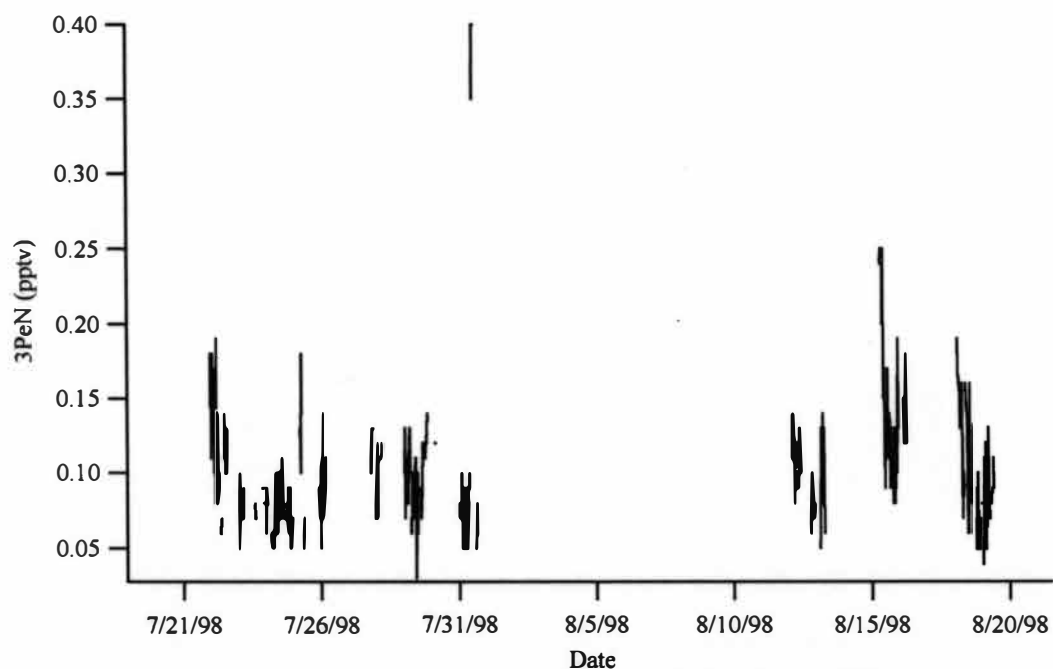


Figure 17. Time Series of 3-Pentyl Nitrate During the PROPHET '98 Summer Intensive.

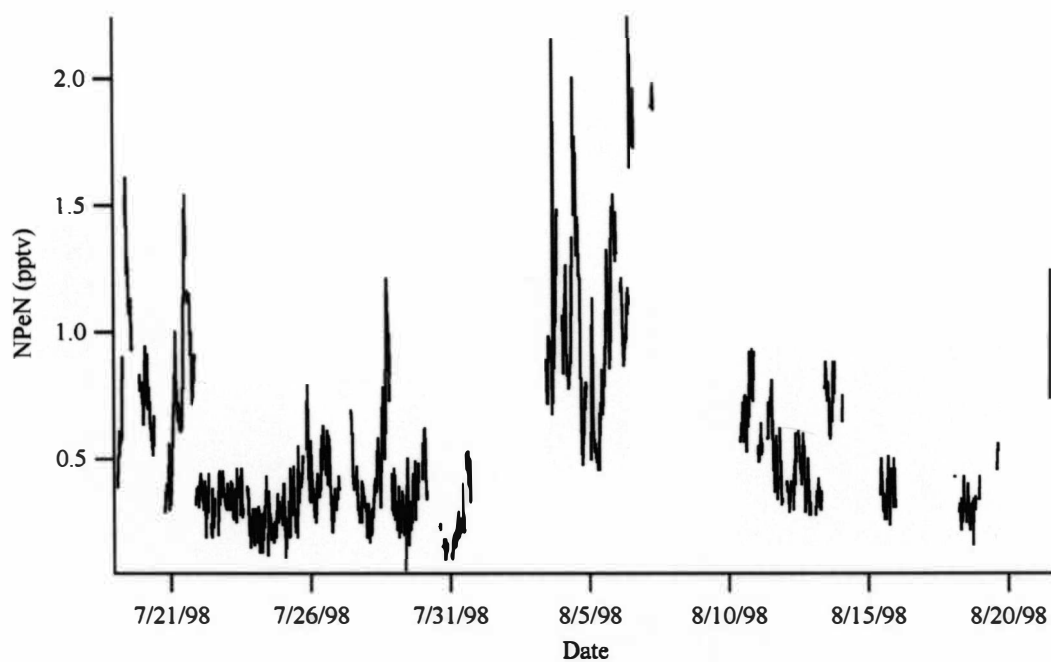


Figure 18. Time Series of n-Pentyl Nitrate During the PROPHET '98 Summer Intensive.

Table 6

## Statistics of Measured Nitrate Species From PROPHET '98

Compound	Number of Points	Average (pptv)	Minimum (pptv)	Maximum (pptv)
IPN	1239	4.97	1.04	16.84
NPN	1239	4.78	1.02	13.14
2BN+IBN	1239	5.74	0.32	25.27
NBN	1217	0.62	0.04	2.64
3PeN	303	0.10	0.03	0.40
2PeN	1213	2.10	0.12	8.61
NpeN	806	0.55	0.06	2.24
$\Sigma$ RONO <sub>2</sub>	1239	18.55	3.54	65.77
PAN	2735	188	18	943
PPN	2371	23	2	109
MPAN	748	10	2	53
NO <sub>x</sub>	15390	792	54	9624
NO <sub>y</sub>	34410	1748	183	12112
Isoprene Nitrates	249	7.27	0.32	31.01
HNO <sub>3</sub>	10	699	400	1250
HONO	10	134	90	200

Figures 12 and 13 show time series of isopropyl and n-propyl nitrates. Both nitrates were above the detection limit of the instrument and were completely resolved from any other peaks for every measurement taken (a total of 1239

measurements taken – Table 6). The highest levels of both nitrates were seen between August 5 and August 10 and the lowest in July.

Figures 14 and 15 show the time series for the sum of isobutyl and 2-butyl nitrates and n-butyl nitrate. Because isobutyl and 2-butyl nitrates coelute, the sum of the two nitrates was reported. The sum was above the detection limit for all measurements, and the mean concentration was 5.74 pptv. The mean concentration of n-butyl nitrate was lower: only 0.62 pptv. N-Butyl nitrate was occasionally below the detection limit, for about 22 measurements on July 25-26 and August 19. The butyl isomers follow the same general pattern as the propyl isomers: the highest levels in early August and the lowest in late July.

Figures 16, 17, and 18 show the concentrations of the pentyl isomers over the course of the intensive. 3-Pentyl and n-pentyl nitrates were resolved from unidentified compound when the concentrations were below 0.5 and 2 pptv, respectively. This occurred about 25% of the intensive for 3-pentyl nitrate and for about 65% of the intensive for n-pentyl nitrate. 2-Pentyl nitrate was resolved and above detection limit for 1213 of the 1239 ambient measurements. The pattern seen in both the propyl and the butyl isomers is seen in 2-pentyl and n-pentyl nitrates.

### Influence of Air Mass Origin

A useful technique in looking at data from a site is to sort the data according to wind direction. Traditionally, surface wind data is used to sector data for the different species measured at the site. By identifying sources of emissions in each

direction, the data can be filtered into different groups. For example, there is a large urban area to the south, we would expect wind from that direction to be polluted (high levels of NO<sub>x</sub> and ozone). Because of weather patterns, surface wind data from the south does not always indicate an air mass from the south; a more in depth determination of the source of the air is necessary.

Air mass trajectories for the PROPHET '98 Summer Intensive were determined from back trajectories and weather patterns by Owen Cooper, a meteorologist from the University of Virginia. Four distinct trajectories were determined: (1) northwest (NWN), (2) center of high (CoH), (3) southwest (SW), and (4) southeast (SES). The northwest trajectory brought rural air from Canada to the site. The center of high trajectory refers to periods of time when a high pressure system was centered near or on the site. During this period, the site would be influenced primarily by local sources. The air from these two trajectories, northwest and center of high, were expected to be relatively clean. The southwest and southeast trajectories were influenced by urban sources – Chicago in the southwest and Detroit in the southeast, for example. This air was expected to be polluted.

Figure 19 shows a plot of total alkyl nitrates over the PROPHET 1998 summer intensive from July 19, 1998 to August 21, 1998. The sum of resolved C3 to C5 alkyl nitrates was used to calculate the total alkyl nitrates shown in Figure 19. The highest levels were from the southeast and southwest trajectories. Because precursors of alkyl nitrates are primarily anthropogenic (human-made) source, high levels of alkyl nitrates are expected in air from urban areas, which would be from the

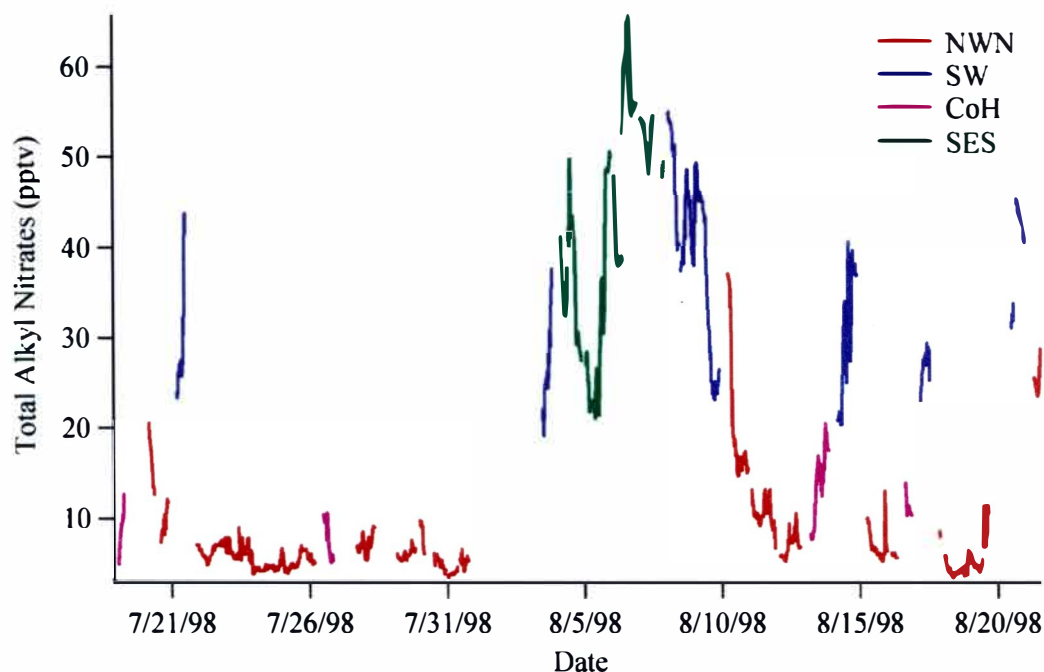


Figure 19. Time Series of Total Alkyl Nitrates From July 19, 1998 to August 21, 1998 During the PROPHET 1998 Summer Intensive.

southwest and southeast. The lowest levels of alkyl nitrates were seen from the northwest and center of high trajectories. The low levels are expected because there should be fewer sources anthropogenic sources in these two trajectories.

Table 7 shows the statistics of the ratio of total RONO<sub>2</sub> to NO<sub>y</sub> in different air flow regimes. The contribution of alkyl nitrates to NO<sub>y</sub> was highest during the period when the site experienced air from southwest (Table 7). Alkyl nitrate contribution to NO<sub>y</sub> is higher in air from the southwest and southeast than from the northwest and center of high trajectories. Again, this is expected because air from the northwest and center of high should be cleaner (fewer sources of alkyl nitrates) than the southwest and southeast.

Table 7

Statistics of RONO<sub>2</sub>/NO<sub>y</sub> During Different Air Mass Flow Regimes

Flow Direction	Average RONO <sub>2</sub> /NO <sub>y</sub>	Minimum	Maximum	Standard Deviation
Northwest	0.010	0.0018	0.025	0.005
Center of High	0.0080	0.0023	0.014	0.003
Southwest	0.014	0.0031	0.030	0.005
Southeast	0.014	0.0050	0.027	0.004

During this intensive, isoprene nitrates were measured. These compounds are formed in a similar manner as alkyl nitrates, starting from isoprene rather than alkanes. Because the Pellston site is influenced by local biogenic chemistry, isoprene nitrates can contribute significantly to NO<sub>y</sub>. Both types of compounds have similar contributions to NO<sub>y</sub> (average ~1%, for alkyl nitrates, there are 7 compounds contributing, but isoprene nitrates, there are only one). Isoprene nitrates contribute more to NO<sub>y</sub> than alkyl nitrates during a period of sustained northwest flow from July 21 to July 26 and again on July 31. Because the contribution of isoprene nitrates is higher than alkyl nitrates, and the air from this trajectory is influenced by primarily rural areas, the site was most likely influenced by biogenic sources during this time. This is contrasted to a period of southwesterly flow on August 4 when the site experienced polluted air. Isoprene nitrates contribute less than 0.5% to NO<sub>y</sub>, while alkyl nitrates contribute 1% and start to rise, indicating an air mass dominated by

anthropogenic sources because alkyl nitrates are formed primarily from anthropogenic compounds.

### NO<sub>y</sub> Shortfall

At the Pellston site, a wide range of oxidized nitrogen species was measured: NO<sub>x</sub>, catalytic NO<sub>y</sub>, nitric acid, peroxyacyl nitrates, alkyl nitrates, and isoprene nitrates. The NO<sub>y</sub> is the sum of all oxidized nitrogen species in the troposphere [NO<sub>x</sub>, peroxyacyl nitrates (PANs), alkyl nitrates, nitric acid, etc.]. The sum of these individual measurements of oxidized nitrogen species can be compared to catalytically measured values of NO<sub>y</sub> to determine if all the NO<sub>y</sub> species have been measured. Previous attempts to account for NO<sub>y</sub> have shown a significant shortfall was discovered (~20% or more; Fahey et al., 1986). Alkyl nitrates were suggested as the source of the shortfall but were later shown to only contribute from 1-2% in continental regions (Shepson et al., 1993).

Measurements of nitric acid and nitrous acid were made for a short period during the intensive from August 5 to August 14. Measurements of nitric acid and nitrous acid are important because both acids can contribute significantly to NO<sub>y</sub> in the troposphere. The absence of nitric and nitrous acid concentrations can hinder attempts to account for the total NO<sub>y</sub>. Measurements of nitric and nitrous acid are difficult because they can easily partition into water and be removed from the atmosphere.



The measurements of nitric and nitrous acid were 24-hour averages. Because the other nitrogen species were measured at more frequent rates, 24-hour averages for these compounds (from midnight to midnight) were computed. These averages greatly limit the interpretation of the data because differences between the day and night are lost. Figure 20 shows the sum of all the oxidized nitrogen species measured from August 5 to August 14, 1998 compared to catalytically determined NO<sub>y</sub> (24-hour averages) and Figure 21 shows the individual averages.

The biggest shortfall in the speciated measurements to NO<sub>y</sub> occurred on 8/7 and 8/8/98. This time period was a transition from air coming from the southeast to the southwest. This shortfall (22-27%) occurs when the site was receiving polluted air from urban areas (Detroit in the southeast and Chicago in the southwest, for example). Although isoprene nitrates were not measured on 8/7 and 8/8 (Figure 21), they are not expected to contribute to NO<sub>y</sub> more than alkyl nitrates in air from the southwest and southeast because the levels of alkyl nitrates were higher than isoprene nitrates on 8/4 when the southwest flow started. During the period from 8/10/98 to 8/13/98, the site was influenced by cleaner air from the northwest. The shortfall on during these days ranges from 13% on 8/10 to 4% on 8/13.

#### Relationship Between Alkyl Nitrate Isomers

The ratio between two alkyl nitrate isomers derived from the same parent compound can be determined by (Flocke et al., 1998):

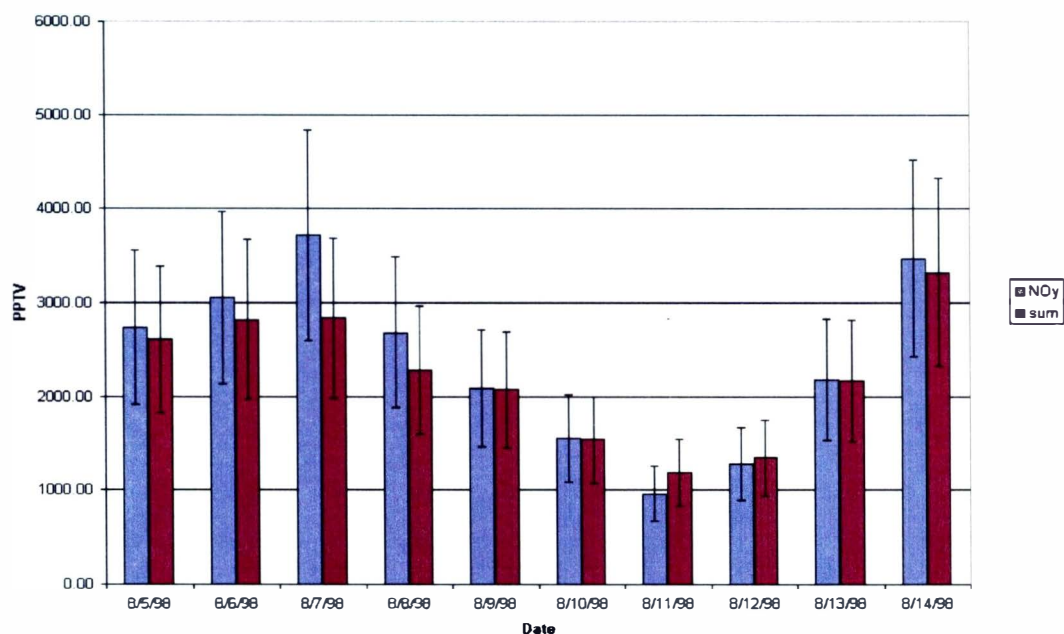


Figure 20. Sum of Oxidized Nitrogen Species ( $\text{NO}_x$ ,  $\text{HNO}_3$ , HONO, PANs,  $\text{RONO}_2$ , and Isoprene Nitrates; 24 Hour Averages) Compared to  $\text{NO}_y$  (24 Hour Averages) From August 5 to August 14, 1998.

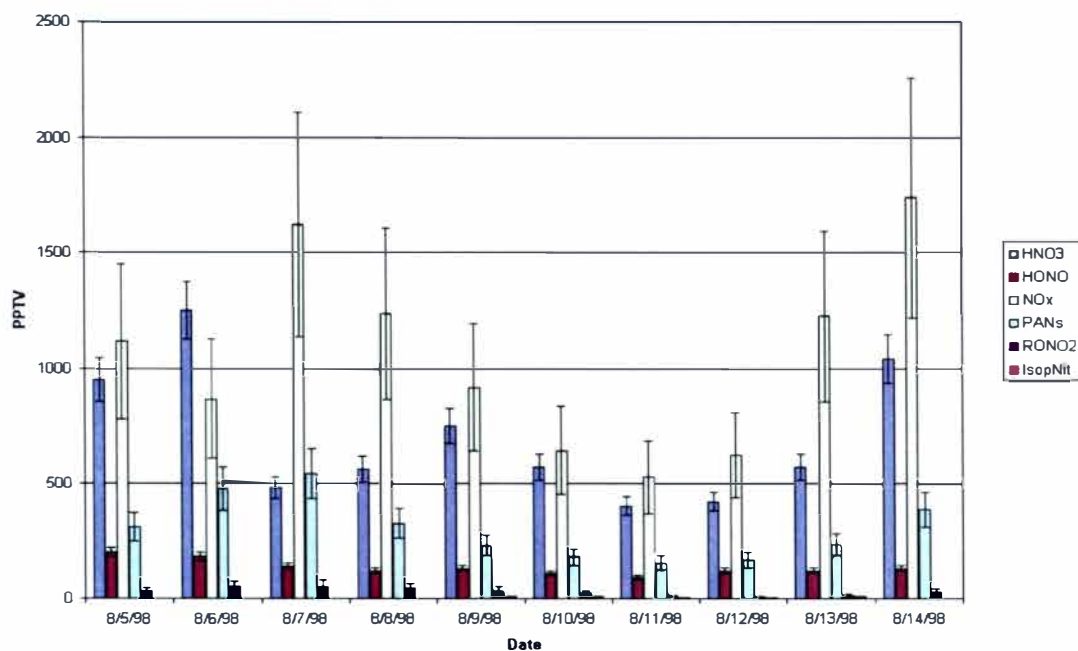


Figure 21. Individual 24 Hour Average Concentrations of Oxidized Nitrogen Species From August 5 to August 14, 1998.

$$\frac{\text{RONO}_{2,1}}{\text{RONO}_{2,2}} = \frac{\alpha_{1,1}\alpha_{2,1}}{\alpha_{1,2}\alpha_{2,2}}$$

where  $\alpha_{1,1}$  and  $\alpha_{1,2}$  are the branching ratios forming the alkyl radical from the parent hydrocarbon and  $\alpha_{2,1}$  and  $\alpha_{2,2}$  are the branching ratios to form the alkyl nitrate (see Table 8 for branching ratios). This ratio assumes that both isomers come from the same source, the parent alkane. Table 9 lists the predicted slopes for different RONO<sub>2</sub> isomers.

Table 8  
Branching Ratios

Compound	$\alpha_1^a$	$\alpha_2^b$
IPN	0.70	0.042
NPN	0.30	0.020
2BN	0.86	0.09
NBN	0.14	0.044
2PeN	0.55	0.13
NPeN	0.10	0.057

<sup>a</sup>Atkinson, 1987; <sup>b</sup>Roberts, 1990

Figure 22 shows plots of NPN vs. IPN, NBN vs. 2BN + IBN, and NPeN vs. 2PeN. Each plot shows a good correlation.

The predicted ratio for NBN/2BN [Figure 22(b)] from n-butane and the observed ratio are in agreement. The measured values of 2BN are believed to be a combination of 2BN and IBN because laboratory experiments showed that the two

Table 9

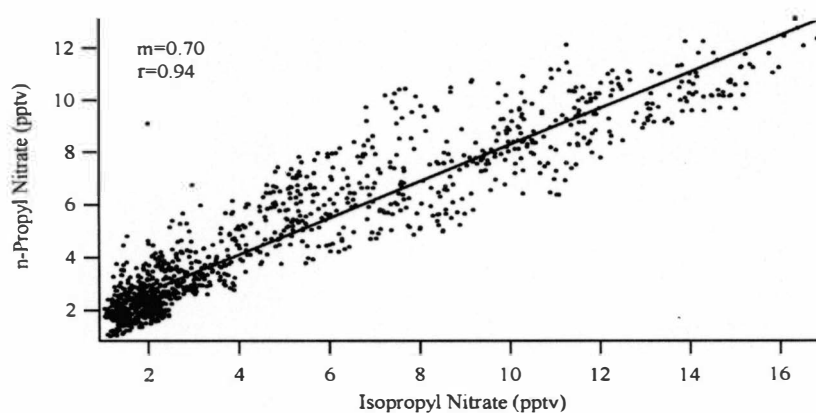
Predicted and Observed Ratios of RONO<sub>2</sub> Isomers

RONO <sub>2</sub> Ratio	Predicted Slope	Observed Slope
NPN/IPN	0.20	0.70
NBN/2BN	0.08	0.084
NPeN/2PeN	0.08	0.21

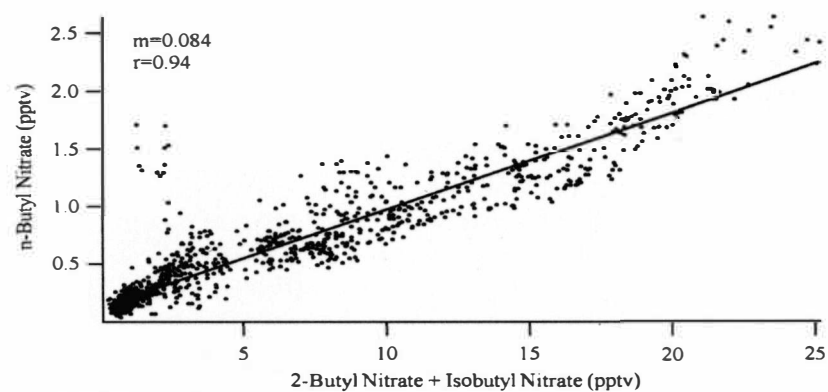
compounds coeluted. Because the predicted slope of NBN vs. 2BN agrees with the observed slope of  $\Sigma(2BN \& IBN)$ , it would appear that the observed  $\Sigma(2BN \& IBN)$  concentrations were mostly 2BN. IBN is formed from a different parent hydrocarbon (i.e. isobutane) which would have a different ratio when compared to NBN.

The predicted ratio for NPN/IPN does not agree with the observed ratio.

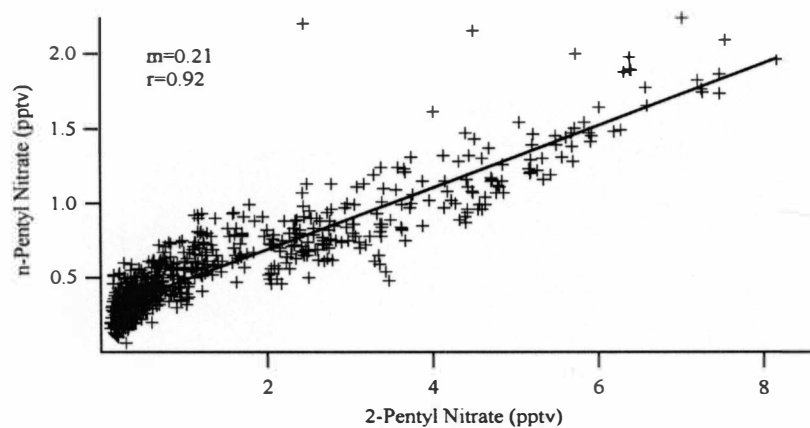
Again, this ratio assumes that the only source of NPN and IPN is from propane. A significant source of RO<sub>2</sub> radicals to form NPN and IPN are from decomposition of larger alkoxy radicals (Flocke et al., 1998, Atkinson, 1997). Unusually high levels of NPN were observed during the course of the PROPHET 1998 intensive. As seen in Table 6, the average concentration of NPN was almost the same as that for IPN. It is unclear as to whether this was an instrumentation problem or actually occurring. Calibrations on the instrument performed during and after the intensive consistently showed a sensitivity for IPN that was about half that of NPN. It is possible that this was a systematic error in the calibration system. When the same calibration factor is



(a) NPN vs. IPN



(b) NBN vs.  $\Sigma$ 2BN + IBN



(c) NPeN vs. 2PeN

Figure 22. Plots of (a) n-Propyl Vs. Isopropyl Nitrate, (b) n-Butyl vs.  $\Sigma$ 2-Butyl & Isobutyl Nitrates, and (c) n-Pentyl vs. 2-Pentyl Nitrate.

used for IPN and NPN, the observed slope is 0.31.

Like NPN/IPN, the predicted ratio for NPeN/2PeN did not agree with the observed ratio. Difficulties in resolving NPeN may have contributed to the deviation from the predicted ratio. Flocke et al. (1998) also reported a significant deviation from the predicted slope. They reported that an interference with n-pentyl nitrate may have caused some of the deviation.

### Relationship Between NPN and PPN

The composition of an air mass is dependent upon its chemical and transport history. Transport history can be determined from back trajectories, but they do not indicate the chemical processes that occur as the air mass moves through the atmosphere. Photochemical reactions take place as the air mass moves from the an initial point (for example, an emissions from an urban area into an air mass) to the measurement point, which is often referred to as photochemical age. Since the atmosphere is an open system, exchanging mass and energy, the process is not as simple as a contained parcel of air moving from point A to point B; and some species are removed and some are introduced. Ratios of two photochemical products from the same parent species with known formation and destruction pathways are useful in determining photochemical age because knowledge of the concentration of the parent species as the air mass evolves is often unnecessary. Ratios are also unaffected by dilution.

Both n-propyl nitrate (NPN) and peroxypropionyl nitrate (PPN) can be formed from propane as shown in Figure 23. If the only source of both PPN and NPN is propane, a relationship between NPN and PPN should be seen in the ambient data which could be modeled. By simplifying the reactions in Figure 23, a model for NPN and PPN over time can be derived, which could potentially be used to determine if propane is the only source of NPN and PPN and to predict photochemical age when compared to ambient data.

#### Kinetic Model Assumptions

Table 10 shows the rate constants used in the kinetic model. This model assumes a constant  $\text{NO}_2/\text{NO}$ , a constant OH concentration, no mixing or dilution, and constant sunlight for the entire time range used. These conditions do not adequately reflect processes in the atmosphere because the air mass is constantly changing through either chemical processes or by addition of new species from new sources. A more adequate model of the atmosphere would also have reactions to compete for  $\text{NO}_x$ . Powerful computer models can be developed to include addition of new compounds to the air mass and changes in OH concentration and  $\text{NO}_2/\text{NO}$ . The kinetic model described in this paper was developed to obtain a simple relationship between NPN and PPN that does not require complicated computer programming which can be useful in determining how processed the air measured at the PROPHET site were and if propane is the primary source of NPN and PPN.

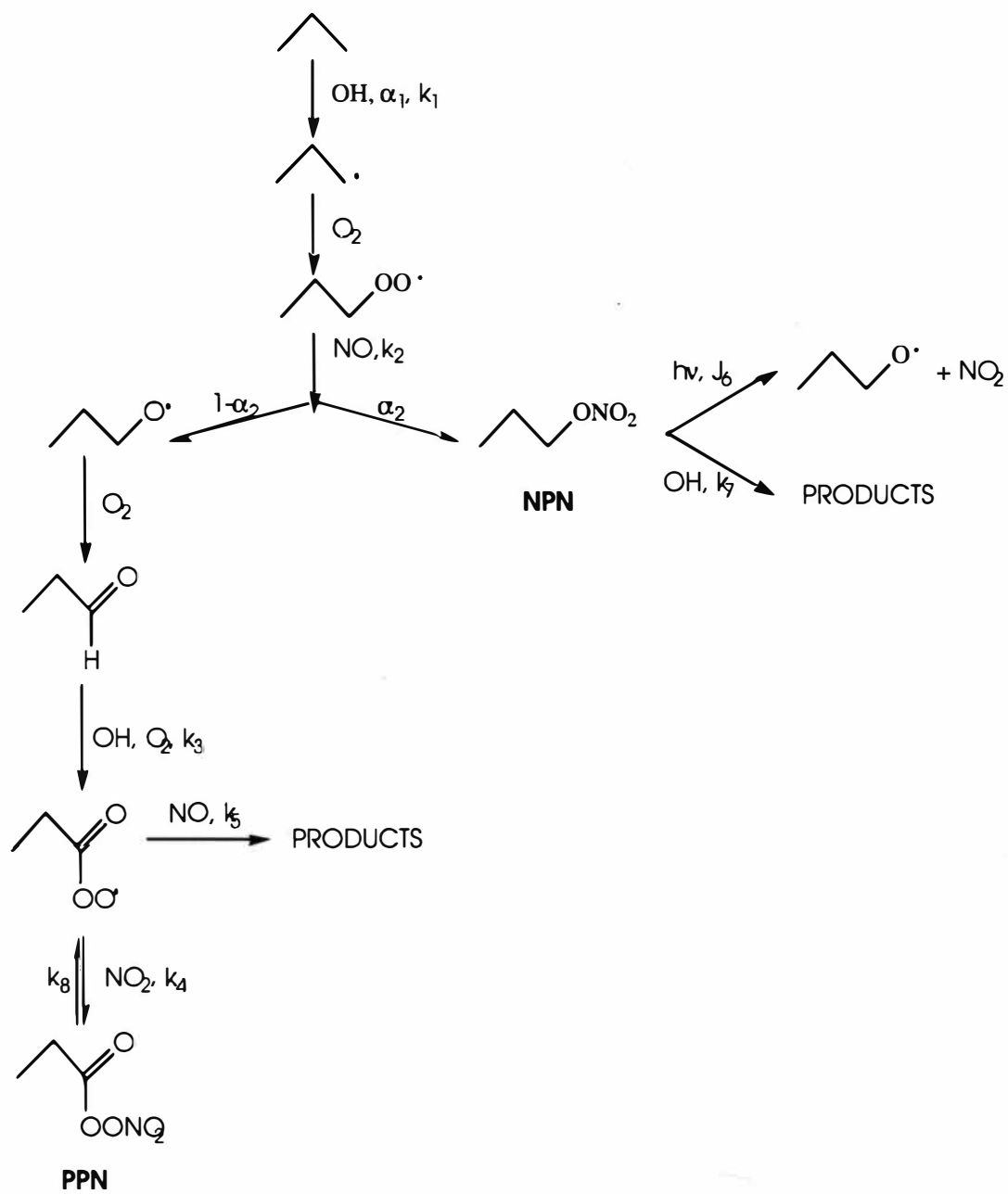


Figure 23. n-Propyl Nitrate and Peroxypropionyl Nitrate Formation From Propane.



Table 10

## Rate Constants and Branching Ratios Used in Model

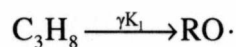
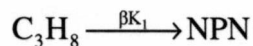
Constant	Value	Reference
$\alpha_1$	0.3	Atkinson, 1987
$\alpha_2$	0.02	Roberts, 1990
$k_1$	$1.14\text{e-}12 \text{ cm}^3\text{*molec}^{-1}\text{*s}^{-1}$	Atkinson et al., 1992
$k_3$	$2.00\text{e-}11 \text{ cm}^3\text{*molec}^{-1}\text{*s}^{-1}$	Atkinson et al., 1992
$k_4$	$1.2\text{e-}11 \text{ cm}^3\text{*molec}^{-1}\text{*s}^{-1}$ <sup>a</sup>	Atkinson et al., 1992
$k_5$	$2.00\text{e-}11 \text{ cm}^3\text{*molec}^{-1}\text{*s}^{-1}$ <sup>a</sup>	Atkinson et al., 1992
$J_6$	$15.6\text{e-}7 \text{ s}^{-1}$	Clemmshaw et al., 1997
$k_7$	$7.3\text{e-}13 \text{ cm}^3\text{*molec}^{-1}\text{*s}^{-1}$	Clemmshaw et al., 1997
$k_8$	$4.77\text{e-}4 \text{ s}^{-1}$	Schurath and Wipprecht, 1980
[OH]	$4.5\text{e}6 \text{ molec*cm}^{-3}$	Pennsylvania State Univ. <sup>b</sup>

<sup>a</sup>These rate constants are for peroxyacetyl nitrate (PAN).

<sup>b</sup>Average daytime value measured by Ian Faloona from Pennsylvania State University.

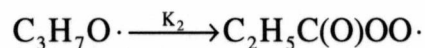
### Kinetic Model

The reaction of propane with the OH radical is assumed to be the rate limiting step for the formation of either NPN or the propoxy radical:

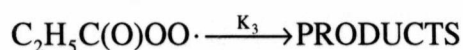


where  $K_1 = k_1[\text{OH}]$ ,  $\beta = \alpha_1\alpha_2$ , and  $\gamma = \alpha_1(1-\alpha_2)$ . The rate limiting step in the formation of the peroxypropionyl radical from the propoxy radical is assumed to be

the reaction of propanal with the OH radical, which can be simplified into the following reaction:



where  $K_2 = k_3[\text{OH}]$ . The ratio of  $\text{NO}_2/\text{NO}$  strongly influences the fate of the peroxypropionyl radical – the reaction with  $\text{NO}_2$  forms PPN or the reaction with NO destroys the radical:

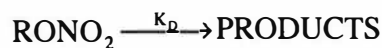


where  $K_3 = k_5[\text{NO}]$  and  $K_4 = k_4[\text{NO}_2]$ .

PPN can thermally decompose to the peroxypropionyl radical and  $\text{NO}_2$ :



The decomposition of NPN can be simplified:



where  $K_D = J_6 + k_7[\text{OH}]$ .

Assuming steady state in the radicals  $\text{C}_3\text{H}_7\text{O}$  and  $\text{C}_2\text{H}_5\text{C}(\text{O})\text{OO}\cdot$ , the time differentials for PPN, NPN, and  $\text{C}_3\text{H}_8$  are as follows:

$$\frac{d[\text{PPN}]}{dt} = \left( \frac{K_4 k_8}{K_3 + K_4} - k_8 \right) [\text{PPN}] + \frac{\gamma K_4 K_3}{K_3 + K_4} [\text{C}_3\text{H}_8]$$

$$\frac{d[\text{NPN}]}{dt} = \beta K_1 [\text{C}_3\text{H}_8] - K_D [\text{NPN}]$$

$$\frac{d[\text{C}_3\text{H}_8]}{dt} = -\alpha_1 K_1 [\text{C}_3\text{H}_8].$$

Using LaPlace Transforms, the time differentials for PPN and NPN integrate to the following equations:

$$[\text{PPN}] = \frac{K_3 K_4 [\text{C}_3\text{H}_8]_0 \gamma}{\alpha_1 K_3 - k_8 K_3 + \alpha_1 K_4} \left[ \exp\left(\frac{-k_8 K_3}{K_3 + K_4} t\right) - \exp(-\alpha_1 t) \right]$$

$$[\text{NPN}] = \frac{K_1 [\text{C}_3\text{H}_8]_0 \beta}{\alpha_1 - K_D} [\exp(-K_D t) - \exp(-\alpha_1 t)].$$

By dividing the equation for NPN by the equation for PPN, a time dependent function of the model NPN/PPN ratio can be calculated that is independent of the initial concentration of propane.

#### NPN vs. PPN

A plot of ambient NPN vs. ambient PPN is shown in Figure 24. A higher slope (0.2) is seen in the data from the NWN and COH trajectories than from the SW and SES (0.1). Comparing this plot to the model (Figure 25), both show a similar curvature. The model has a much steeper slope at low PPN concentrations than the ambient data, which has a more gradual slope.

Two different lines through the ambient data are shown in Figure 24. The data from the NWN and CoH trajectories show a lower intercept than the data from the SW and SES. The high intercept in the SW and SES data suggest that there is NPN when there is no PPN, which can occur in air that has much more NO than NO<sub>2</sub>. As the air mass is transported, NO and NO<sub>2</sub> can be introduced to the air mass at any time. NO and NO<sub>2</sub> are also rapidly interconverted. Ambient measurements of NO and NO<sub>2</sub> at the PROPHET site showed higher NO<sub>2</sub> than NO in the air from the SW

and SES trajectories. The kinetic model is unable to adjust for changing  $\text{NO}_2/\text{NO}$  ratios over time; future work on the model is needed to address changing  $\text{NO}_2/\text{NO}$  ratios.

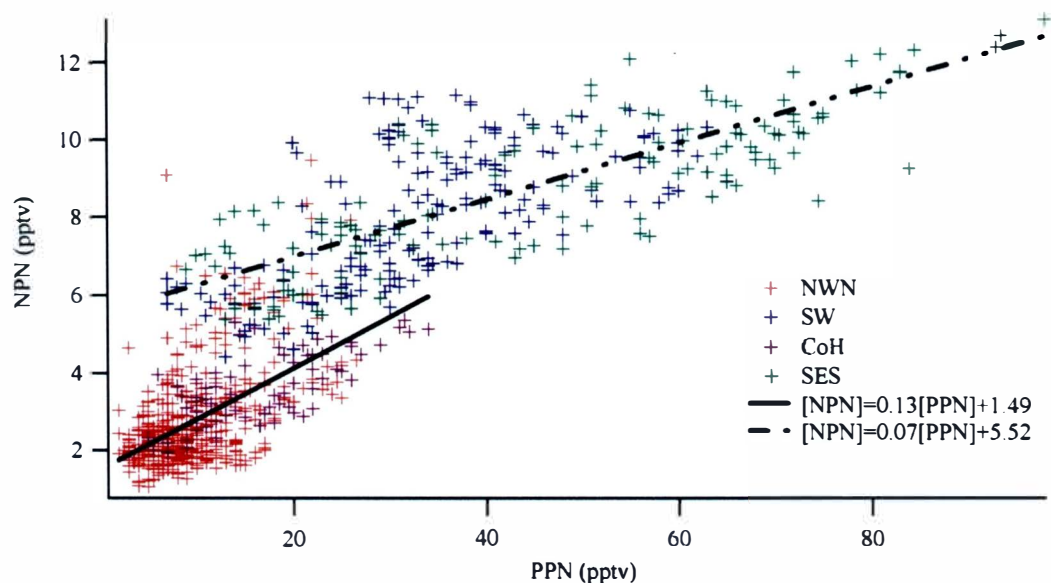


Figure 24. n-Propyl Nitrate Vs. Peroxypropionyl Nitrate Sorted by Air Mass Trajectory.

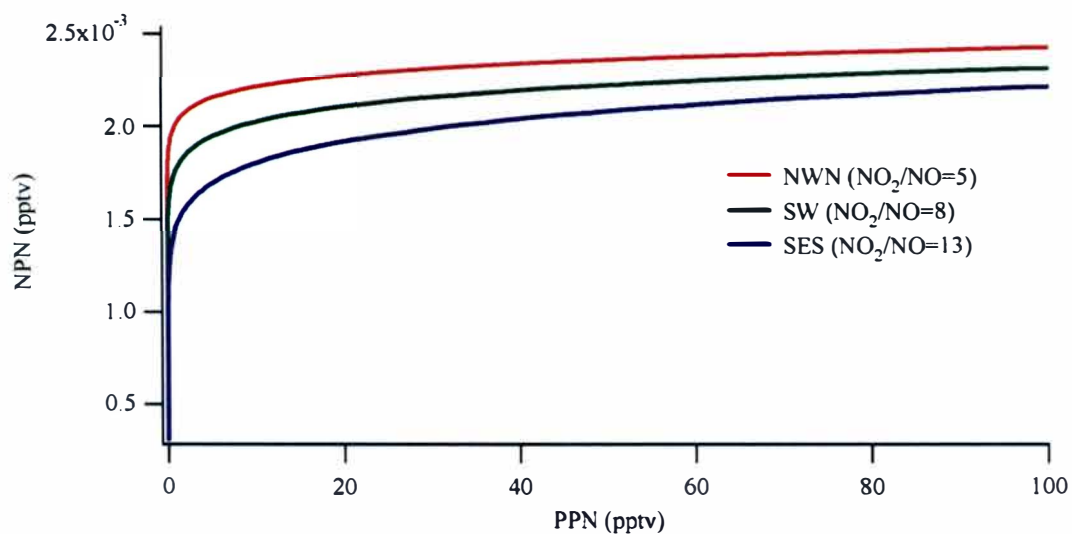


Figure 25. Model NPN vs. Model PPN.

It is important to note that the scale for NPN in Figure 25 is 3 orders of magnitude lower than the scale for NPN in Figure 24. The kinetic model does not predict concentrations of NPN that were actually seen during the PROPHET '98 intensive which could indicate that the model does not include all possible sources of NPN. The model needs to be further developed to address the under predicted NPN concentrations.

### Model Ratio

Although the kinetic model does not accurately predict the absolute concentrations, the model ratio can still be valid. In Figure 26, the model NPN/PPN ratio over time is shown. The different lines for the model correspond to different  $\text{NO}_2/\text{NO}$  ratios (0.01 to 20). The model shows that the age of the air mass is dependent upon the  $\text{NO}_2/\text{NO}$  ratio (Figure 27). The higher the  $\text{NO}_2/\text{NO}$  ratio, the longer it takes for the NPN/PPN ratio to become the same value as for a lower  $\text{NO}_2/\text{NO}$  ratio because the formation of PPN is dependent upon the  $\text{NO}_2/\text{NO}$  ratio. If there were high levels of  $\text{NO}_2$ , then higher levels of PPN would be seen than in air high levels NO. The peroxypropionyl radical is destroyed when it reacts with NO, so that when the NO concentrations are higher than the  $\text{NO}_2$  concentrations, the peroxypropionyl radical will be destroyed faster than PPN is formed.

Figure 28 shows the formation rate NPN and PPN for different  $\text{NO}_2/\text{NO}$  ratios and Figure 27 shows the lifetime of PPN vs.  $\text{NO}_2/\text{NO}$  ratio. The formation rate and the lifetime (~92 hrs) of NPN are independent of the  $\text{NO}_2/\text{NO}$  ratio. As can be seen

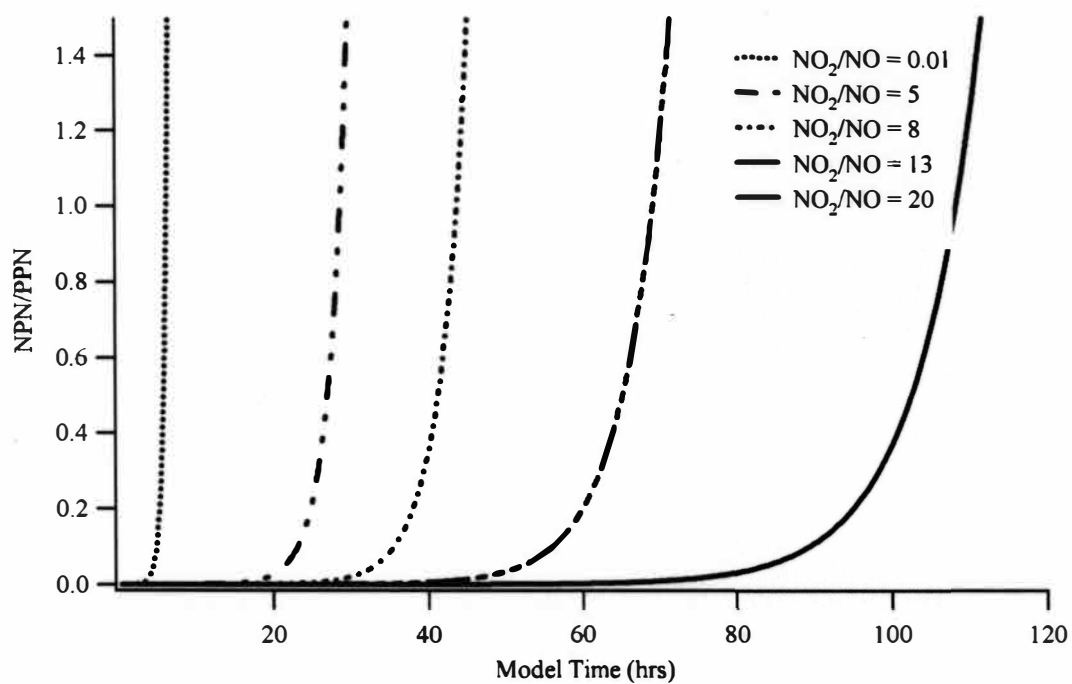


Figure 26. Model NPN/PPN Ratio for Different  $\text{NO}_2/\text{NO}$  Ratios.

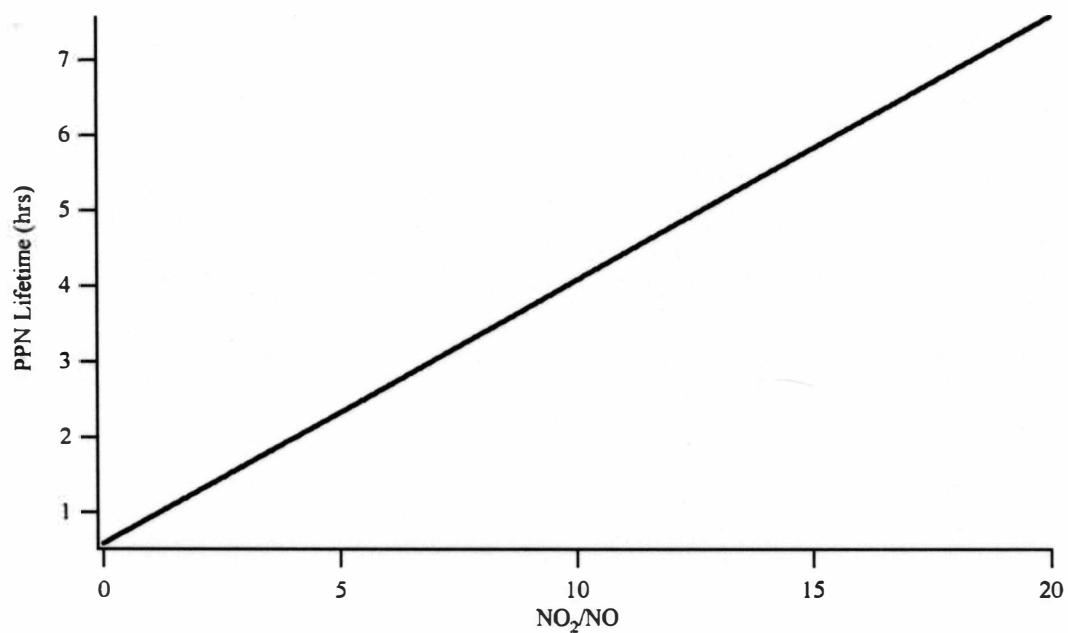


Figure 27. Lifetime of PPN Vs.  $\text{NO}_2/\text{NO}$  Ratio From Model.

in both plots, the PPN is formed faster and has a shorter lifetime than NPN, according to this model. The rate of formation of PPN increases as the  $\text{NO}_2/\text{NO}$  ratio increases.

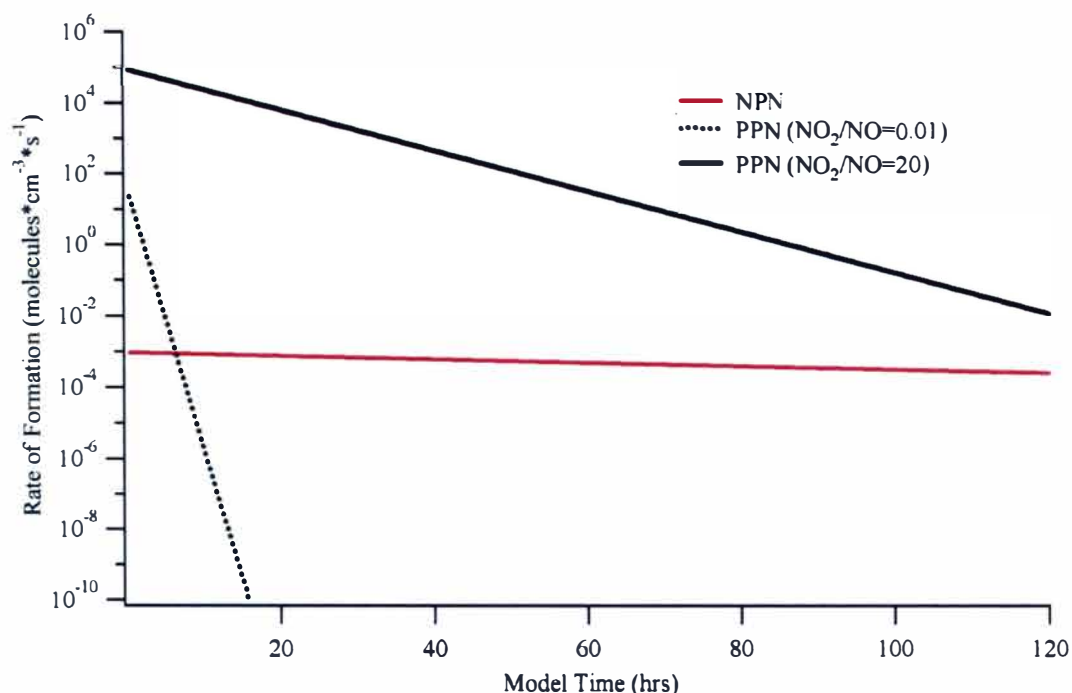


Figure 28. Rate of Formation of NPN and PPN for Different  $\text{NO}_2/\text{NO}$  Ratios.

One of the more curious features of this model is the induction period seen in Figure 26. The  $\text{NO}_2/\text{NO}$  ratio of 0.01 is essentially zero until a time of ~5 hours. Similar trends are seen for the other ratio. The ratio is essentially zero because the formation of PPN at early times in the model is much greater than the formation rate of NPN (Figure 28) and the lifetime of PPN is much shorter, resulting in greater amounts of PPN relative to NPN. Although the rate of formation of NPN is much slower than for PPN, the lifetime is significantly longer, resulting in a slow build-up of NPN. After the rate of formation of PPN reaches zero, destruction of PPN becomes dominant, and the ratio quickly increases.

Ambient NPN/PPN ratios are shown in Table 11 for different air mass trajectories. The average ratio from the NWN trajectory is 0.33 and 0.27 for the SW and 0.24 for the SES trajectories. Comparing this to the model ratio, the air from the NWN and COH trajectories would be slightly older than the air from the SW and SES trajectories, assuming that all four trajectories had the same  $\text{NO}_2/\text{NO}$  ratio. The midafternoon  $\text{NO}_2/\text{NO}$  ratios for the different trajectories as measured at the site are shown in Table 11. If these  $\text{NO}_2/\text{NO}$  ratios are assumed to be constant from the point of origin to the site, then the air from the NW trajectory would probably be younger than the SW than the SE (Figure 26). In the atmosphere, the  $\text{NO}_2/\text{NO}$  ratio is constantly changing, so it is difficult to make any definite conclusions about the air mass age using this model.

Table 11

$\text{NO}_2/\text{NO}$  Ratios in Different Air Mass Trajectories

Trajectory	NPN/PPN	$\text{NO}_2/\text{NO}$	Total $\text{NO}_x$
Northwest	0.33	5	250
Southwest	0.27	8	500
Southeast	0.24	13	650



## CHAPTER IV

### CONCLUSIONS

A sampling system using Tenax for routine fast-turnaround gas chromatograph-electron capture detection of C3-C5 alkyl nitrates was developed. With some improvements in trapping efficiency and chromatography, this system would be capable of measuring methyl and ethyl nitrate as well. The system was successfully deployed during the PROPHET '98 Summer Intensive from July 19 to August 21, 1998. The highest concentrations of alkyl nitrates measured during the intensive were from air that was influenced by urban areas.

The average contribution of C3-C5 alkyl nitrates to NO<sub>y</sub> was about 1%, which is consistent with previous measurements in continental areas and was slightly higher in polluted air. The contribution of alkyl nitrates to NO<sub>y</sub> was compared to the contribution of isoprene nitrates to NO<sub>y</sub>. The isoprene nitrate contribution was higher in air influenced by rural sources, and the alkyl nitrate contribution higher in air influenced by urban sources. Although both alkyl nitrates and isoprene nitrates were measured at the site, a shortfall in comparing speciated NO<sub>y</sub> measurements to catalytic NO<sub>y</sub> measurements was seen.

The ratio of alkyl nitrate isomers from the same parent hydrocarbon were compared. The observed ratio and the predicted ratio for n-butyl to  $\Sigma$ 2-butyl & isobutyl nitrates agreed, suggesting that the sum is mostly 2-butyl nitrate. The

observed and predicted ratios of n-propyl to isopropyl nitrate deviated which could be the result of a calibration problem. The observed and predicted ratios of n-pentyl to 2-pentyl nitrates deviated, which may be the result of interferences with the resolution of n-pentyl nitrate.

A simple model of the ratio n-propyl nitrate to peroxypropionyl nitrate was developed to use to predict photochemical age. The model ratio of NPN/PPN is dependent upon the  $\text{NO}_2/\text{NO}$  ratio. Because the model does not predict observed levels of NPN, further development of the kinetic model is needed. The model also needs to be developed to include varying  $\text{NO}_2/\text{NO}$  ratios in order to predict photochemical age.

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