

**YIELDS AND REACTIONS OF  
INTERMEDIATE COMPOUNDS FORMED  
FROM  
THE INITIAL ATMOSPHERIC REACTIONS  
OF SELECTED VOCs**

California Air Resources Board Contract No. 96-306

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August 9, 2002

PROJECT ELEMENT NO. 1:

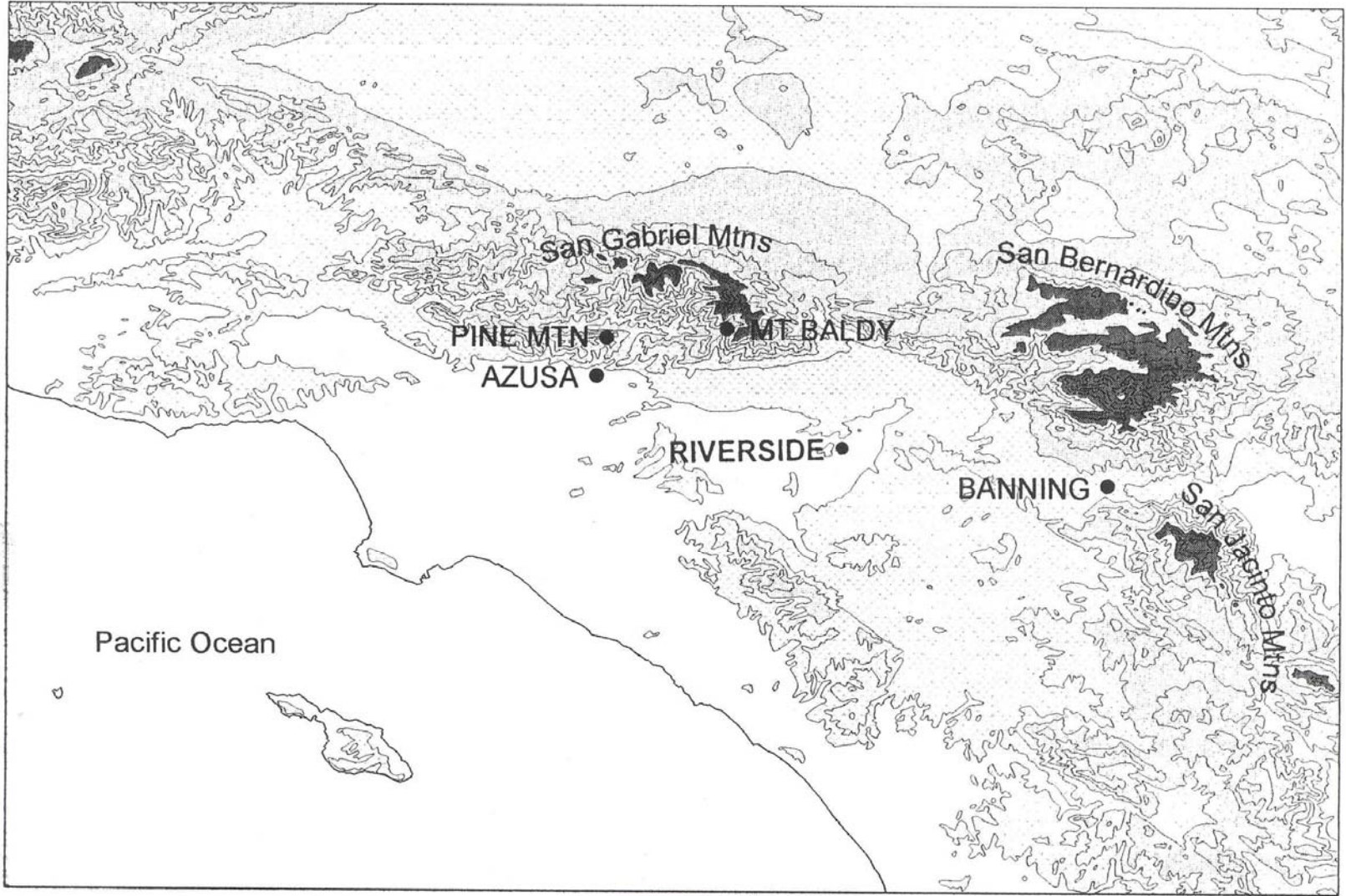
**INVESTIGATION OF  
AMBIENT NO<sub>3</sub> RADICAL LEVELS  
IN THE LOS ANGELES AIR BASIN  
DURING THE SCOS97 STUDY**

PROJECT ELEMENT NO. 2:

**CRC DATA REVIEW PANEL FOR  
ATMOSPHERIC CHEMISTRY OF VOCS**

PROJECT ELEMENT NO. 3:

**CRITICAL REVIEW PAPERS ON  
ATMOSPHERIC CHEMISTRY  
AND  
CHEMICAL KINETIC MECHANISMS  
FOR THE  
1998 NARSTO OZONE ASSESSMENT**

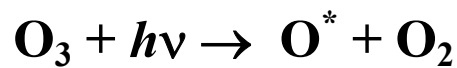


# GAS-PHASE CHEMICALS

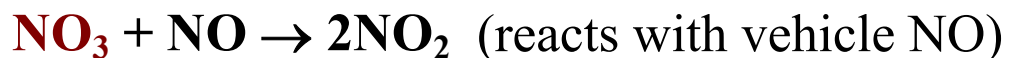
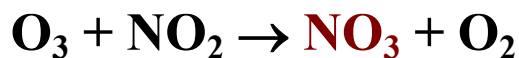
Major Atmospheric Loss Processes Are:

- Photolysis
- Reaction with Hydroxyl (OH) Radical  
(during daylight hours)
- Reaction with Nitrate (NO<sub>3</sub>) Radical  
(during nighttime hours)
- Reaction with Ozone (O<sub>3</sub>)

## **OH Radical - Daytime ubiquitous**



## **NO<sub>3</sub> Radical - Nighttime, no NO**

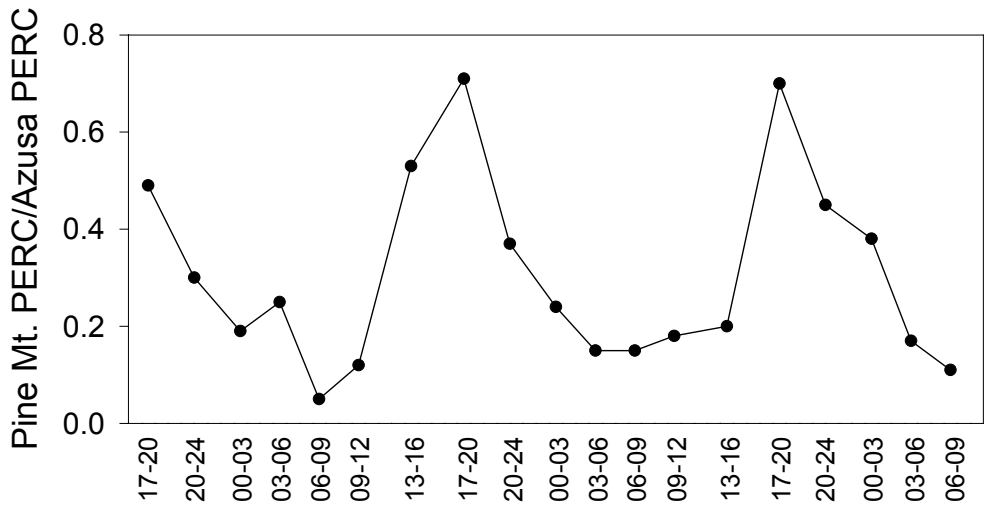
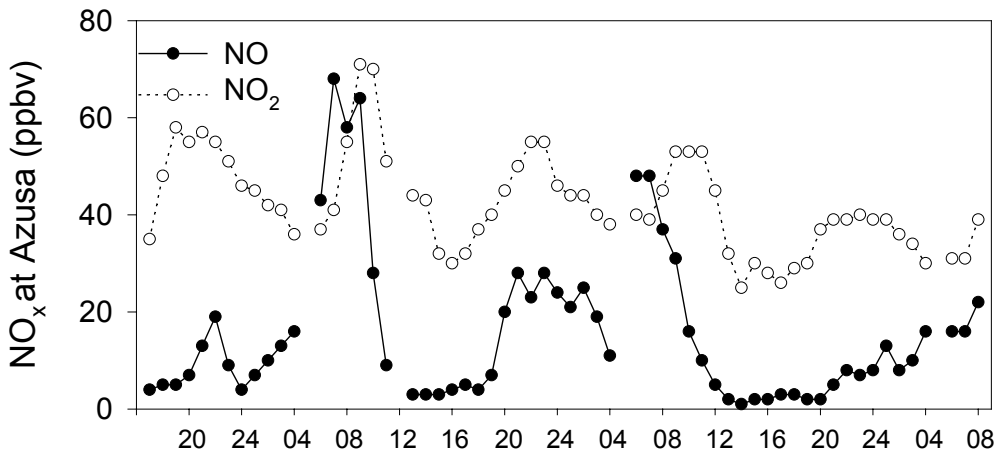
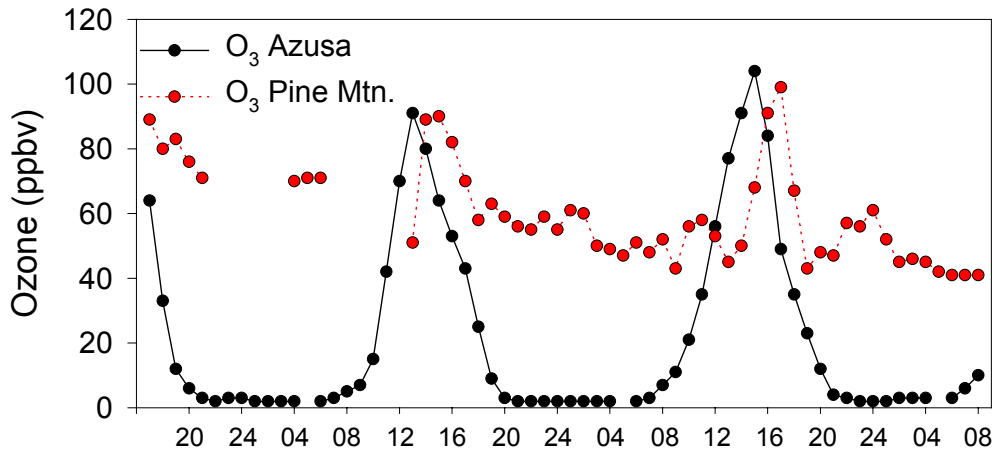


Coastal plain bounded by inland mountains in the presence of a strong temperature inversion.

From: Lu and Turco (1994) J. Atmos. Sci., Vol.

51, p. 2306.

# Sept. 4-7, 1997



PDT

NO<sub>x</sub> and O<sub>3</sub>  
transported  
to elevated  
site

Elevated site  
isolated  
from NO

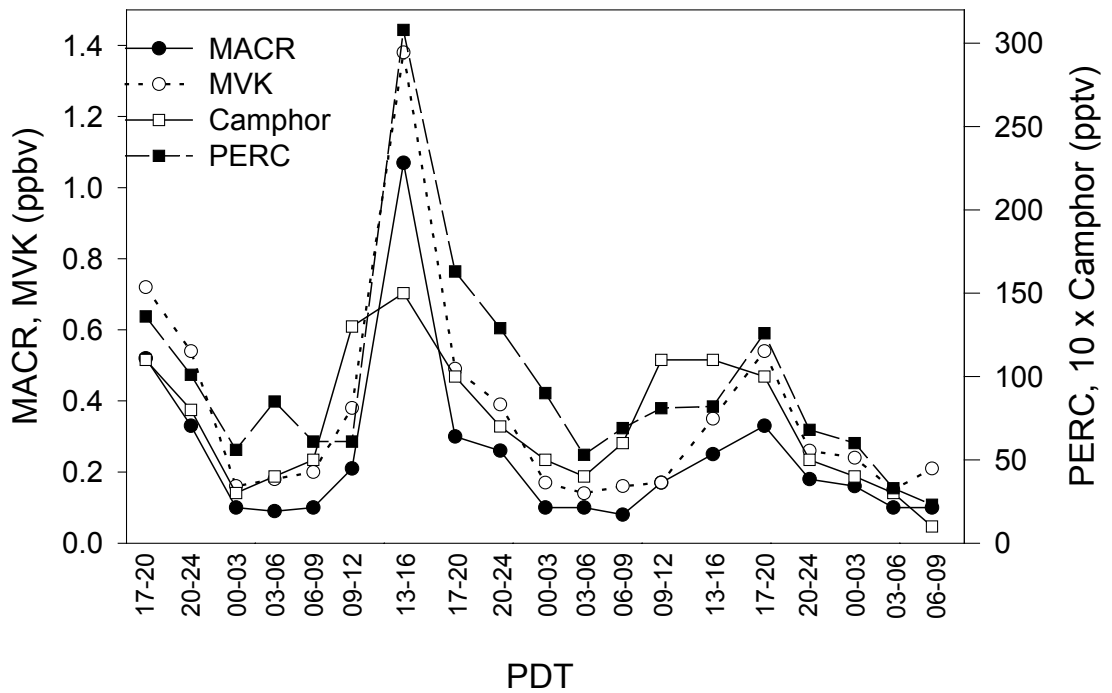
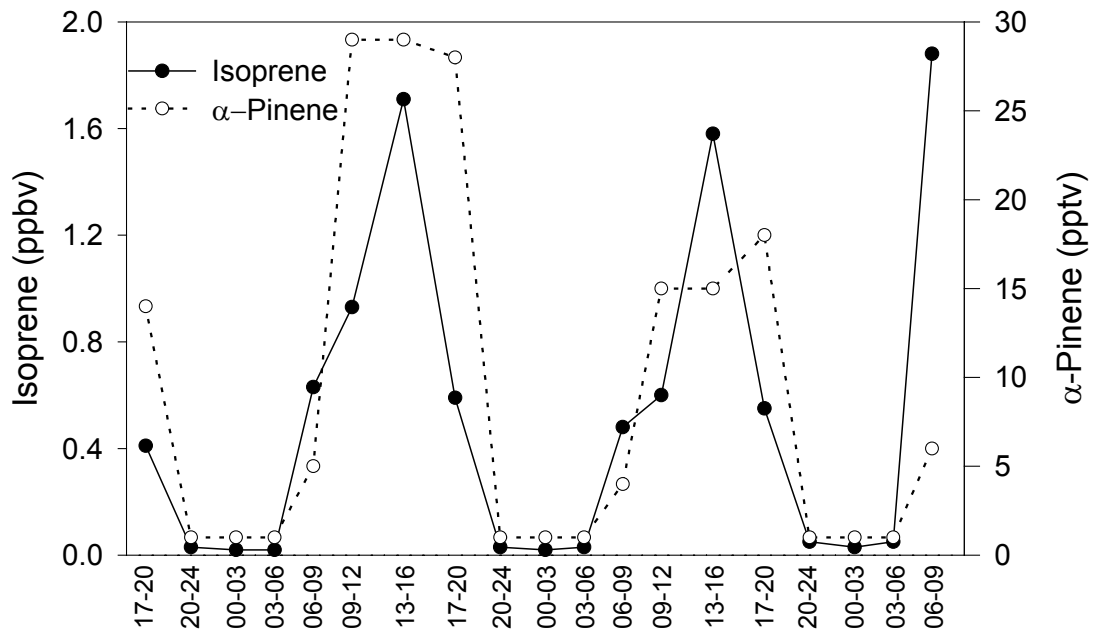
Evening:

At Azusa:  $O_3 + NO \rightarrow NO_2 + O_2$

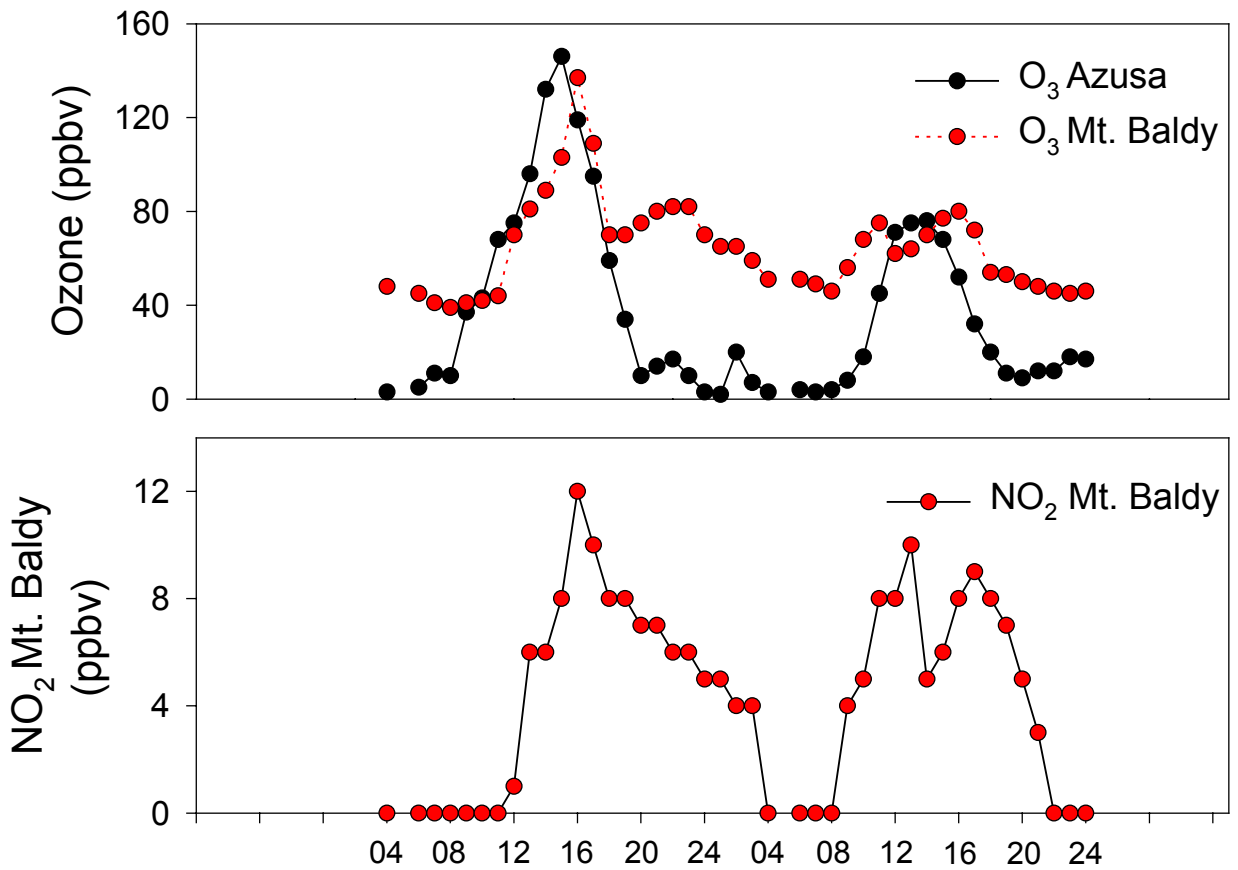
In Inversion layer:  $NO_2 + O_3 \rightarrow NO_3 + O_2$



## Pine Mountain - Sept. 4-7, 1997



# Sept. 28-29, 1997



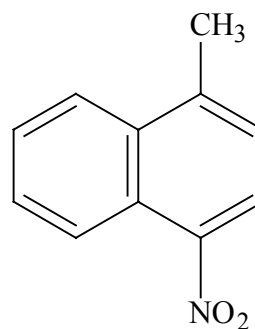
## Gas-Phase Polycyclic Aromatic Compounds

Major Atmospheric Loss Processes Are:

- **Photolysis**

Important for nitro-PAHs

MNNs:  $\tau = 0.1 - 3$  hrs



- **Reaction with OH Radical**

$\tau < 1$  day for most PAHs

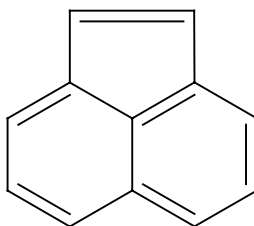
C<sub>1</sub>- and C<sub>2</sub>- Alkyl naphthalenes  $\tau = 2-4$  hrs

- **Reaction with NO<sub>3</sub> Radical**

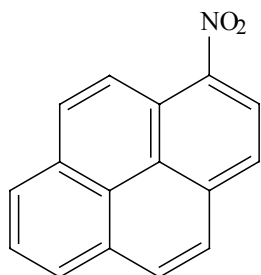
Forms nitro-PAHs in high yields

- **Reaction with O<sub>3</sub>**

only for *e.g.*,  
 $\tau = 2.5$  hrs

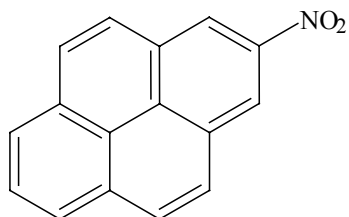


# Nitro-PAH can serve as unique markers of **OH** radical and **NO<sub>3</sub>** radical reactions.



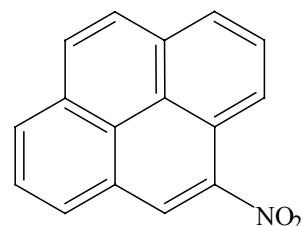
**1-NP**

electrophilic



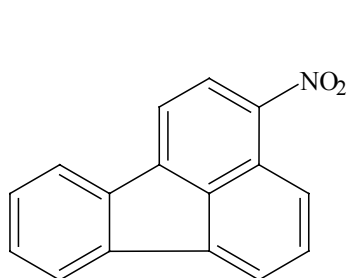
**2-NP**

**OH** rxn. (0.5% yield)



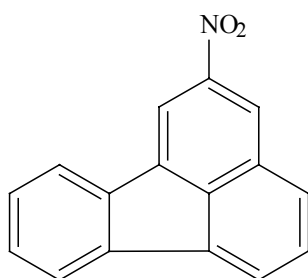
**4-NP**

**NO<sub>3</sub>** rxn. (trace)



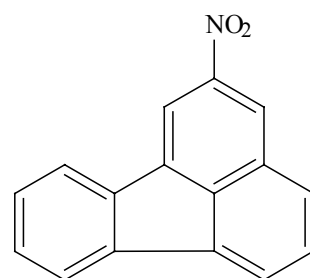
**3-NF**

electrophilic



**2-NF**

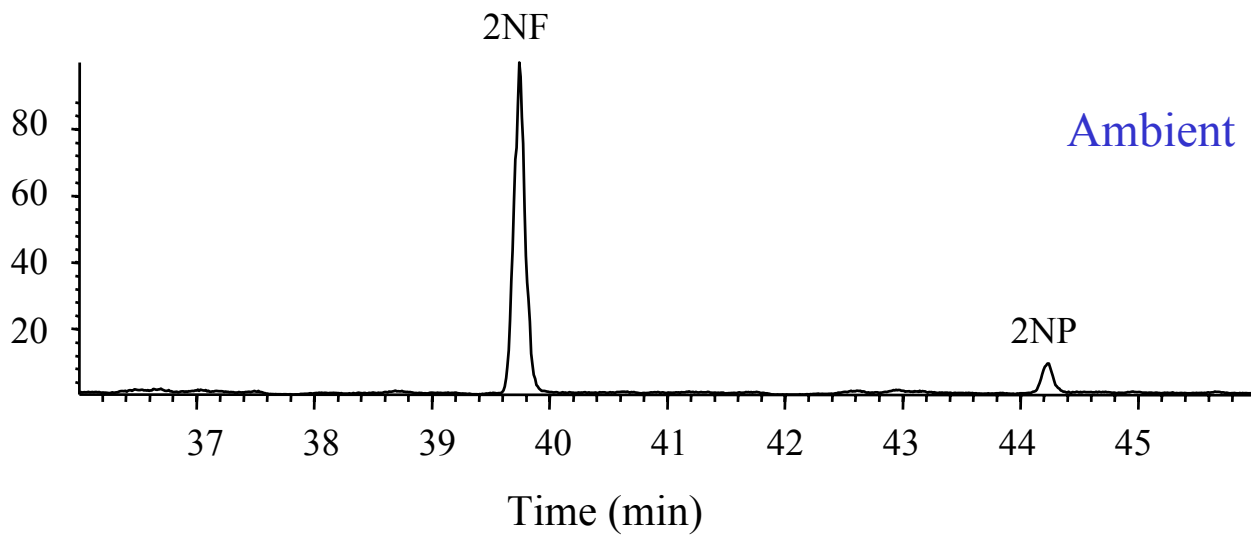
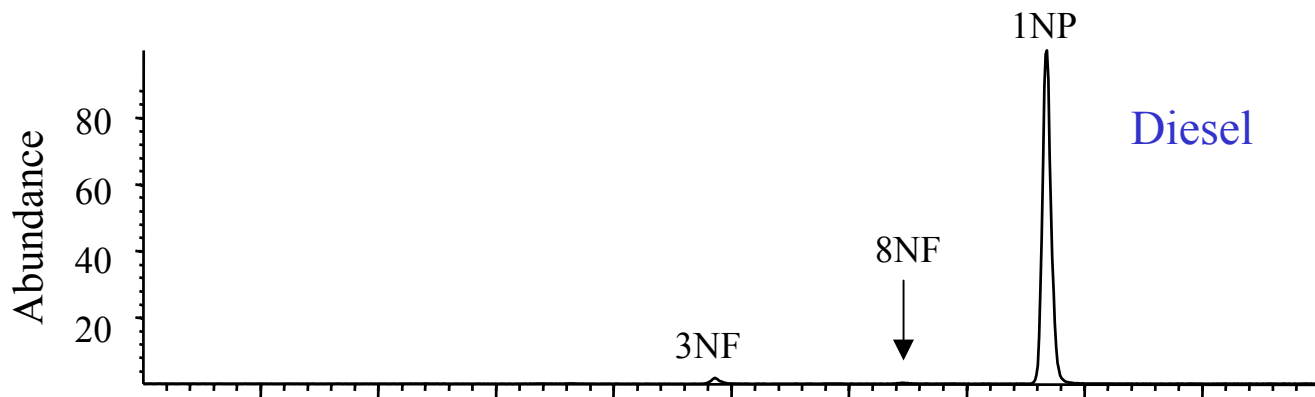
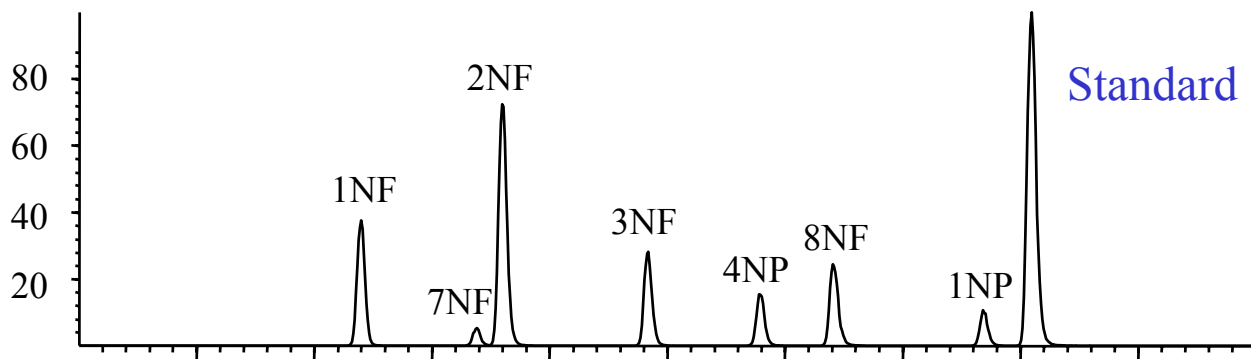
**OH** rxn. (3% yield)

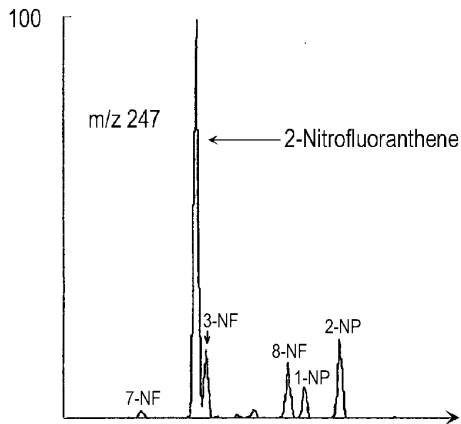


**2-NF**

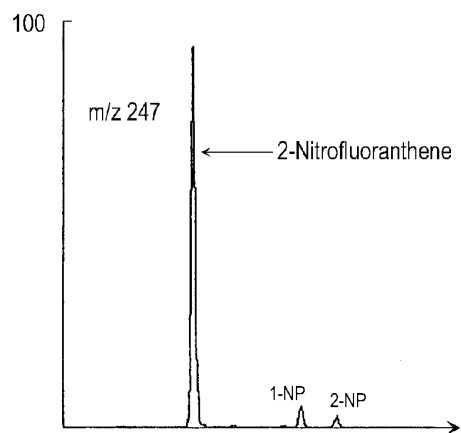
**NO<sub>3</sub>** rxn. (24% yield)

$[M]^+ = 247$

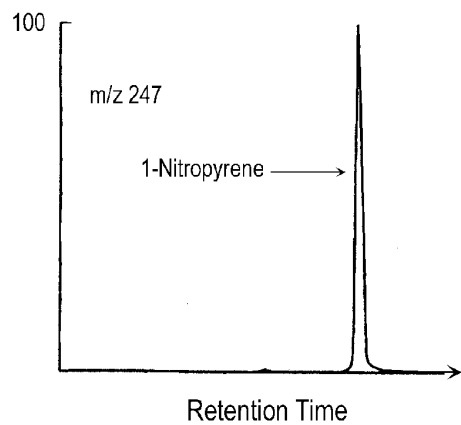




OH Radical Chemistry  
Daytime  
Torrance, CA



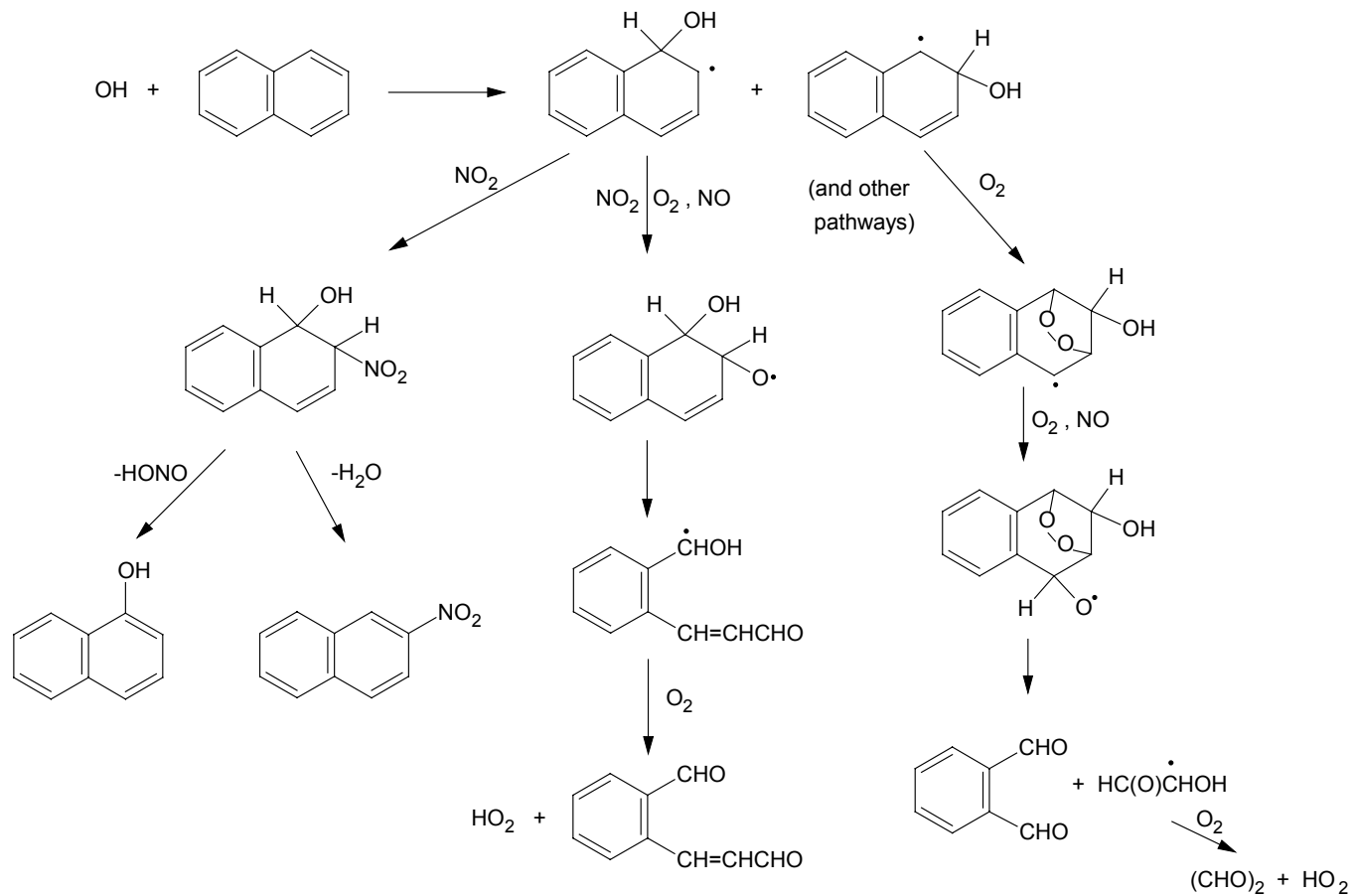
$\text{NO}_3$  Radical Chemistry  
Nighttime  
Claremont, CA



Diesel Particles

## Ambient PAH Concentrations (ng/m<sup>3</sup>)

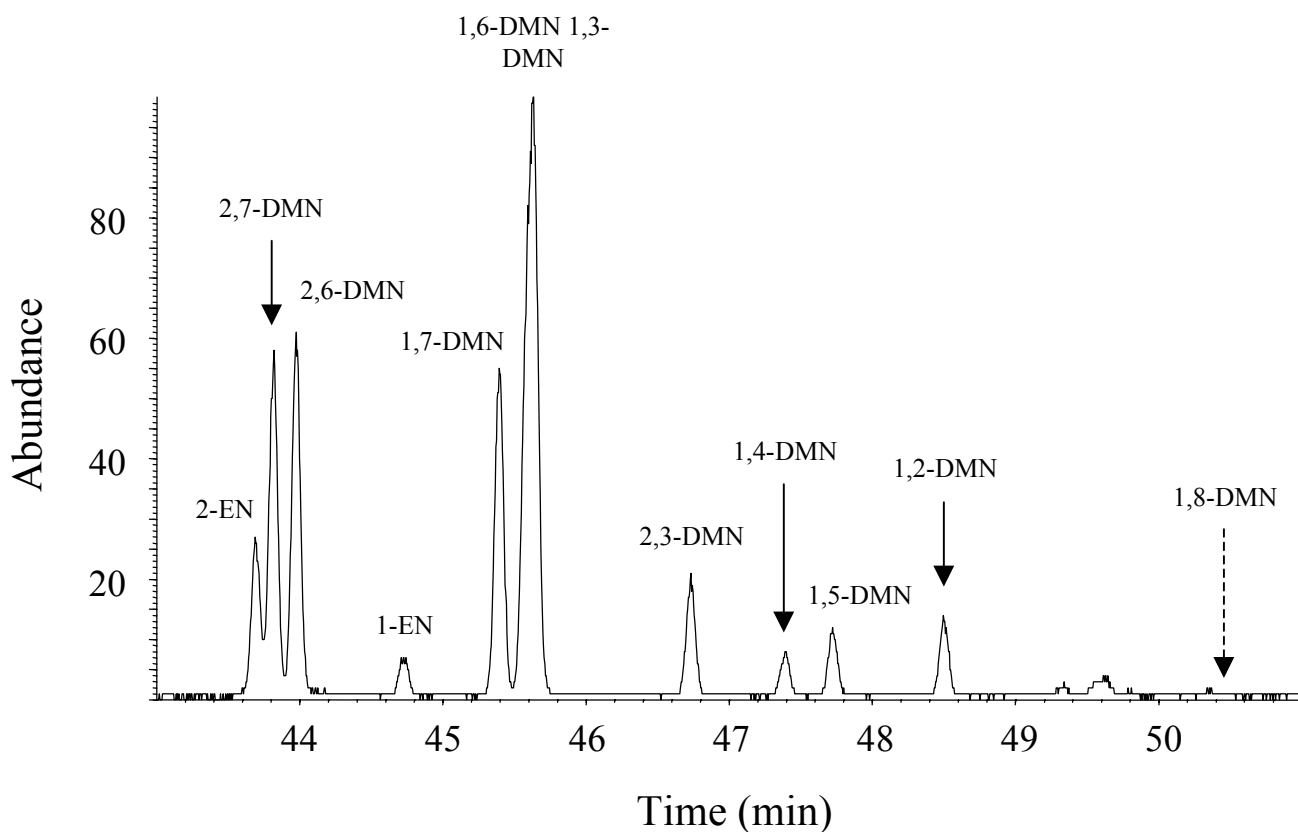
<b>PAH</b>	<b>Sampling Media</b>	<b>Vehicle Traffic Impacted</b>	<b>Wood Smoke Impacted</b>	<b>Industrial Emissions</b>
Naphthalene	Tenax	4,800	1,400	4,600
1-Methylnaph.	Tenax	390	210	370
2-Methylnaph.	Tenax	730	340	780
Phenanthrene	Tenax	51	230	79
Fluoranthene	PUF(filter)	6.2 (0.3)	16 (30)	18 (0.5)
Pyrene	PUF(filter)	5.5 (0.3)	12 (30)	16 (0.6)
B[a]P	Filter	1.5	8	4.2
B[e]P	Filter	0.6	12	6.2

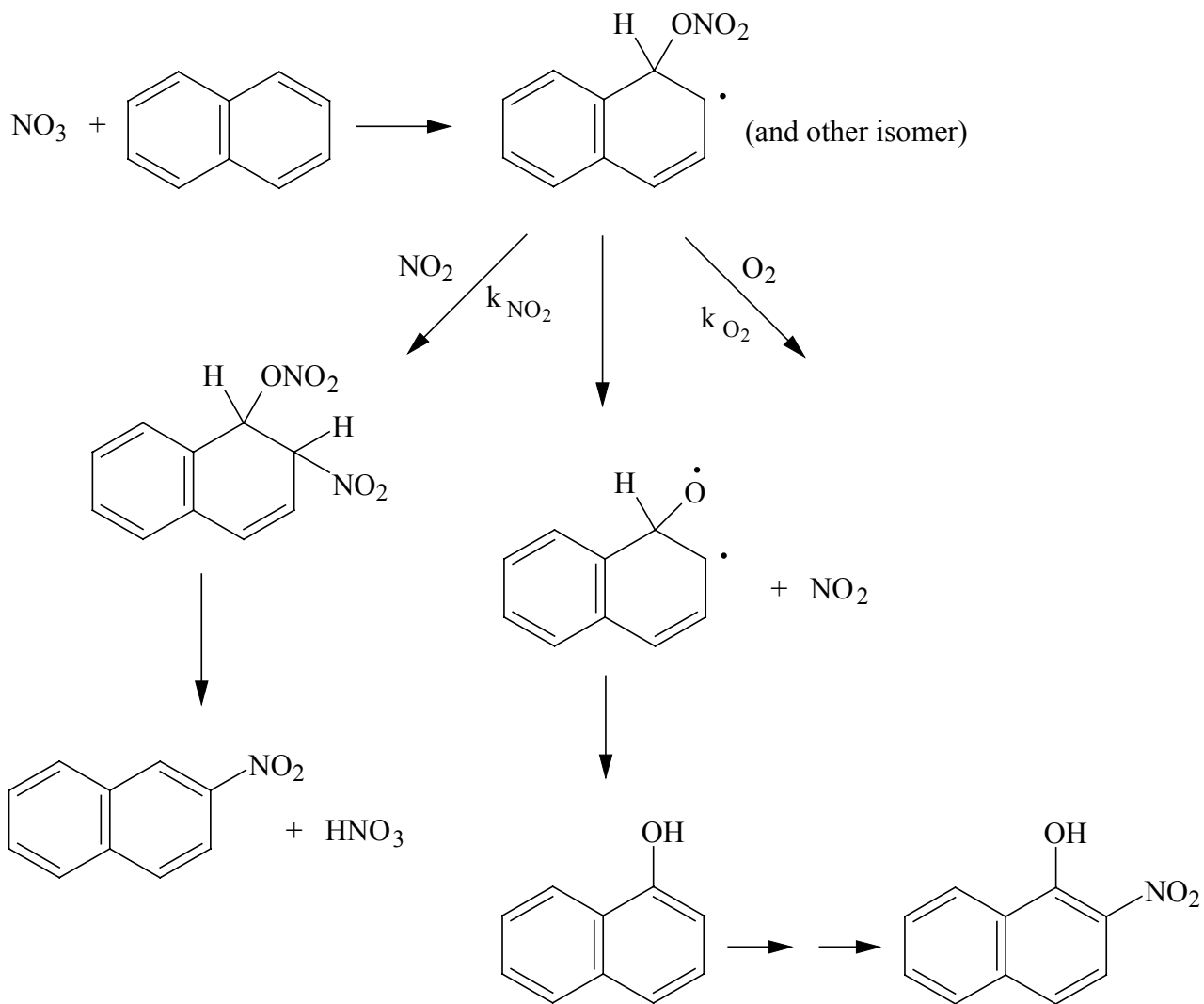




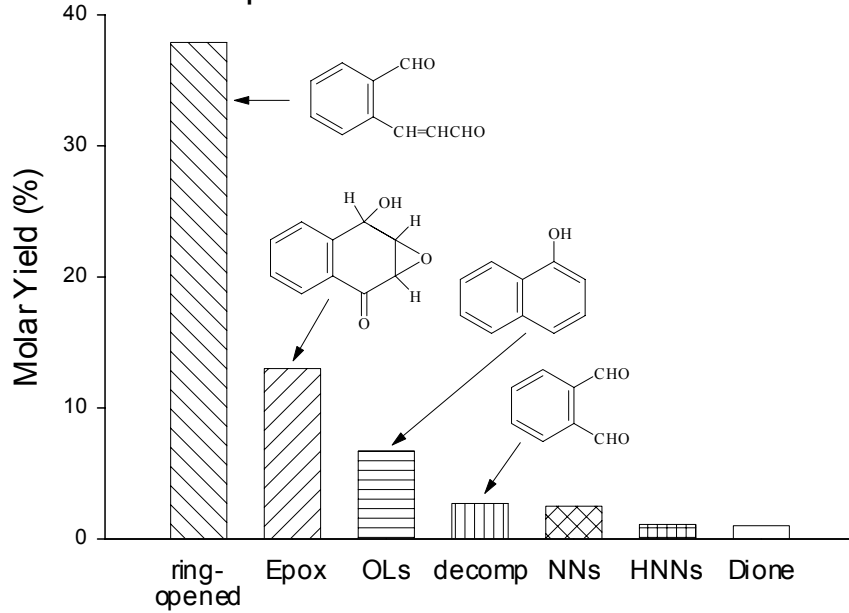
# Riverside, CA Nighttime Tenax Sample

## GC/MS-SIM Analysis for Dimethyl- and Ethyl-naphthalenes

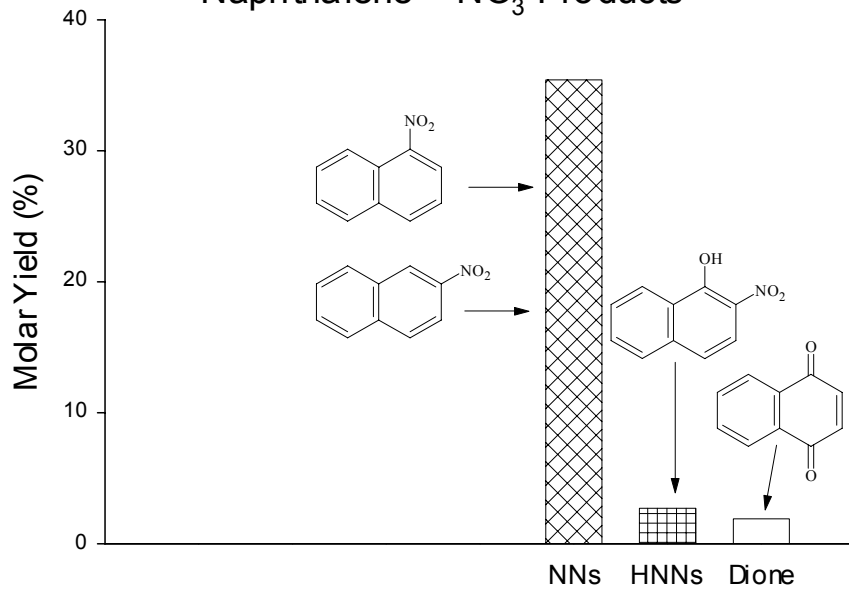




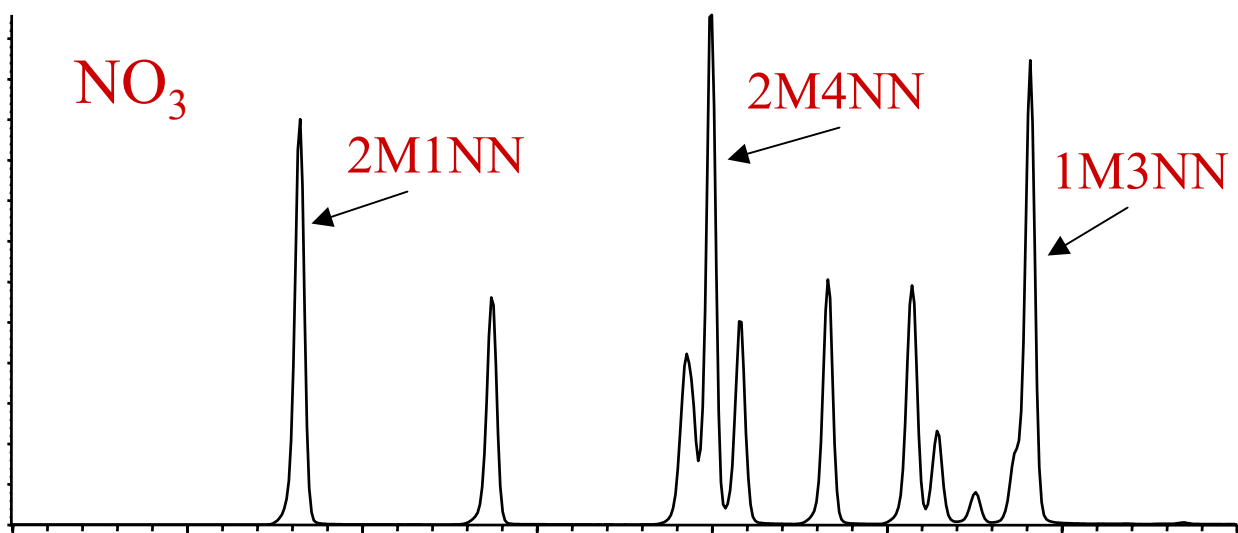
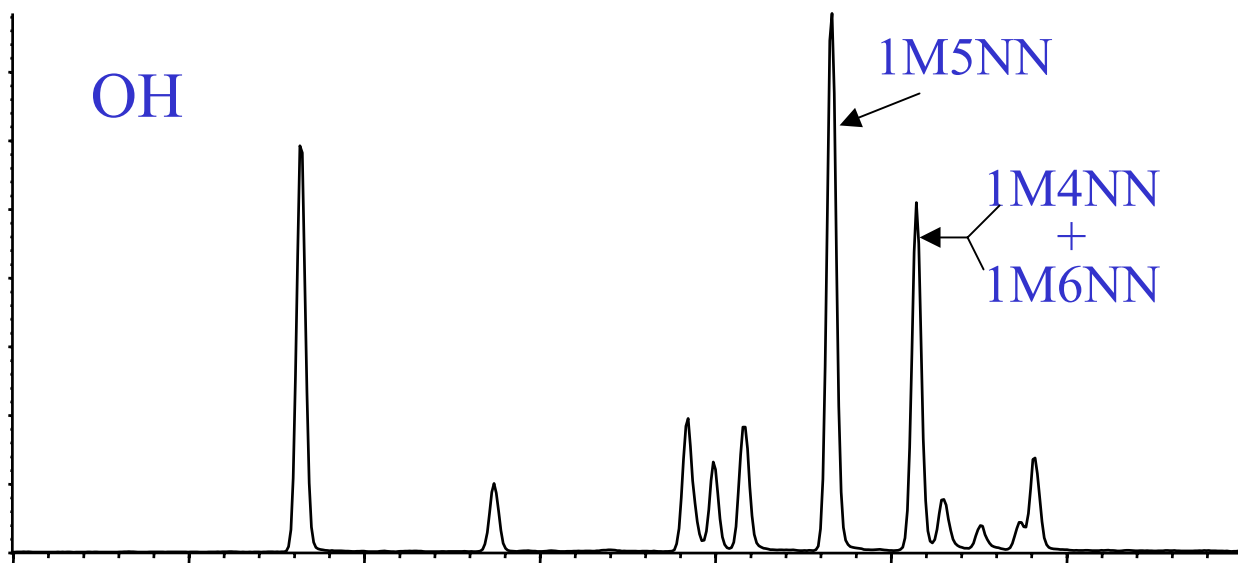
### Naphthalene + OH Products



### Naphthalene + NO<sub>3</sub> Products

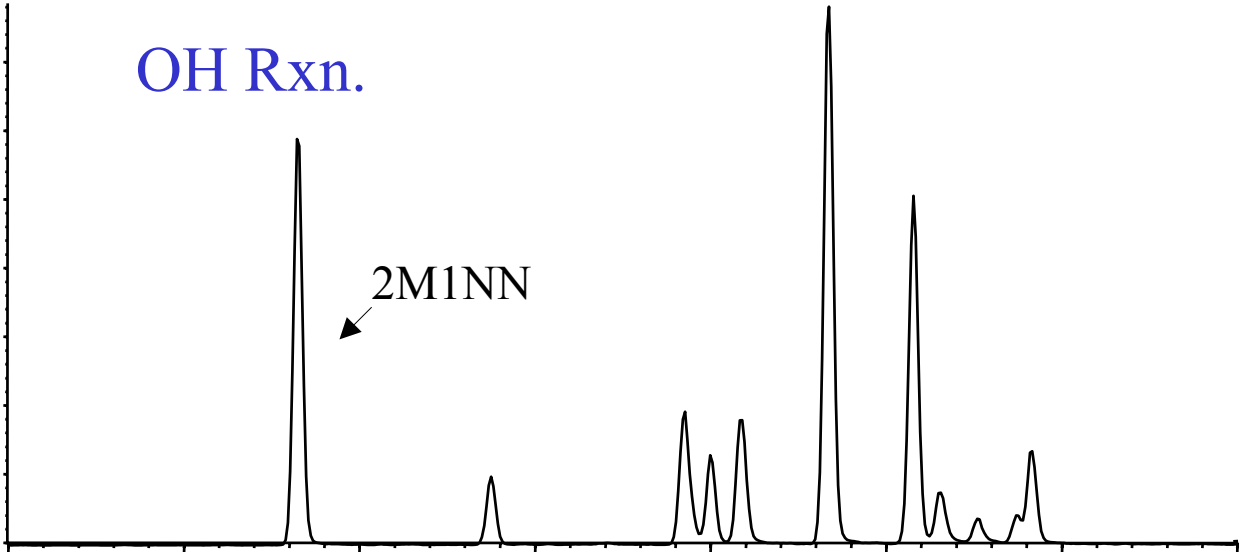


# Methylnitronaphthalenes (MNNs) from OH and NO<sub>3</sub> Radical Reactions

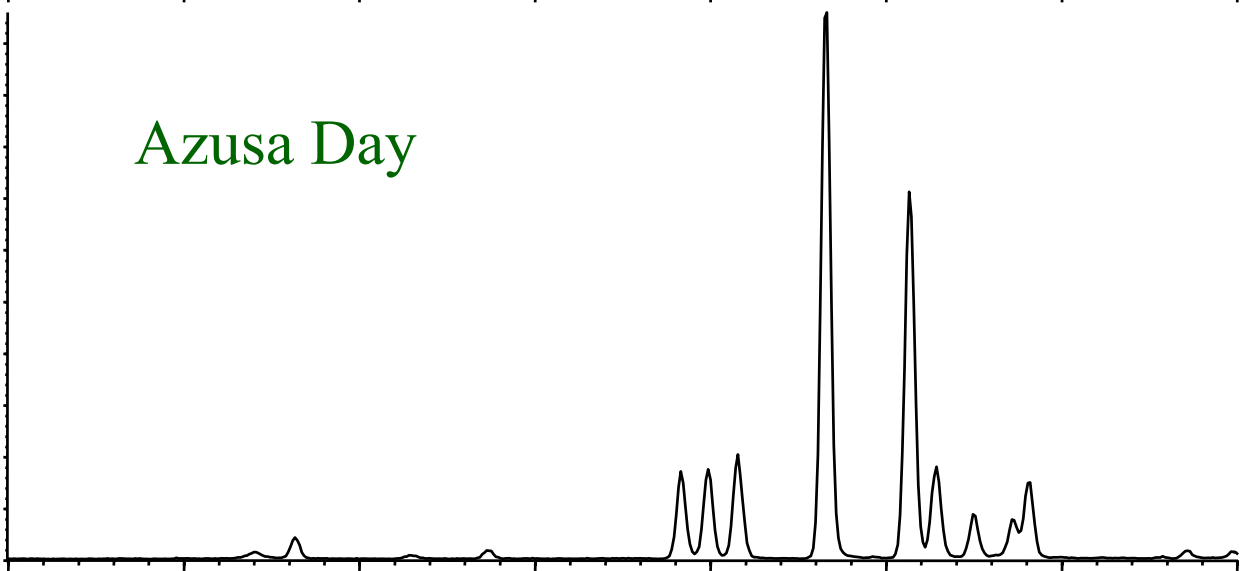


OH Rxn.

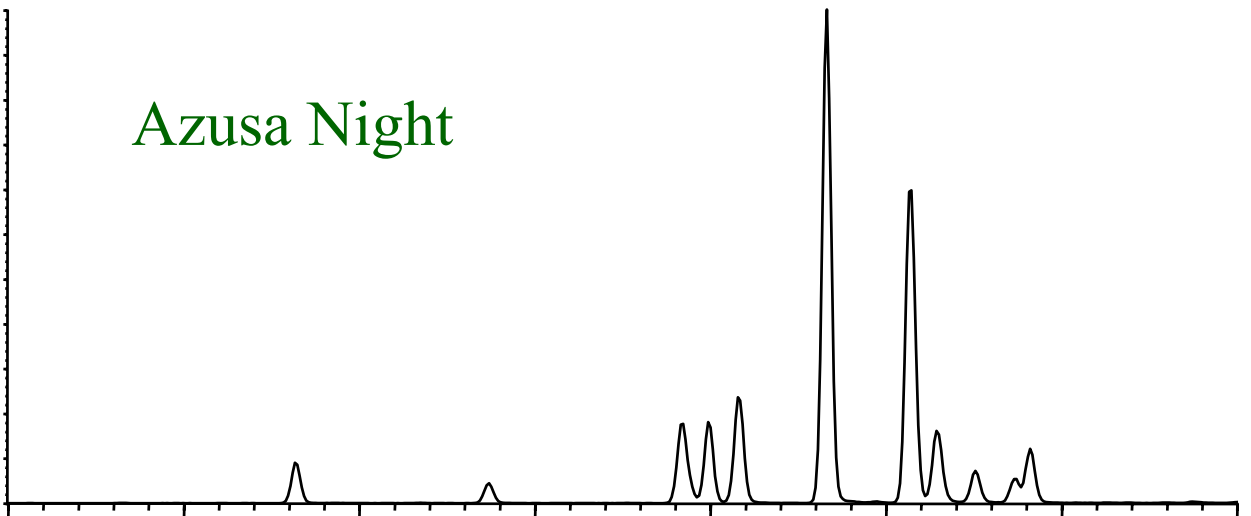
2M1NN



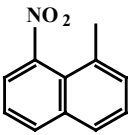
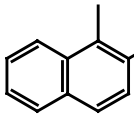
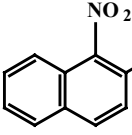
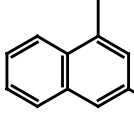
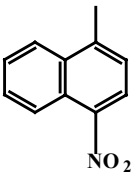
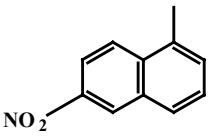
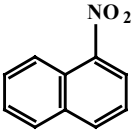
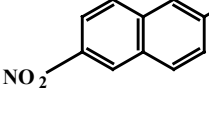
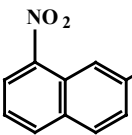
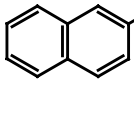
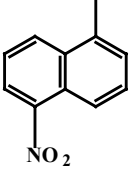
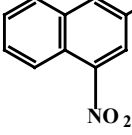
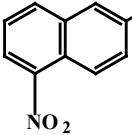
Azusa Day



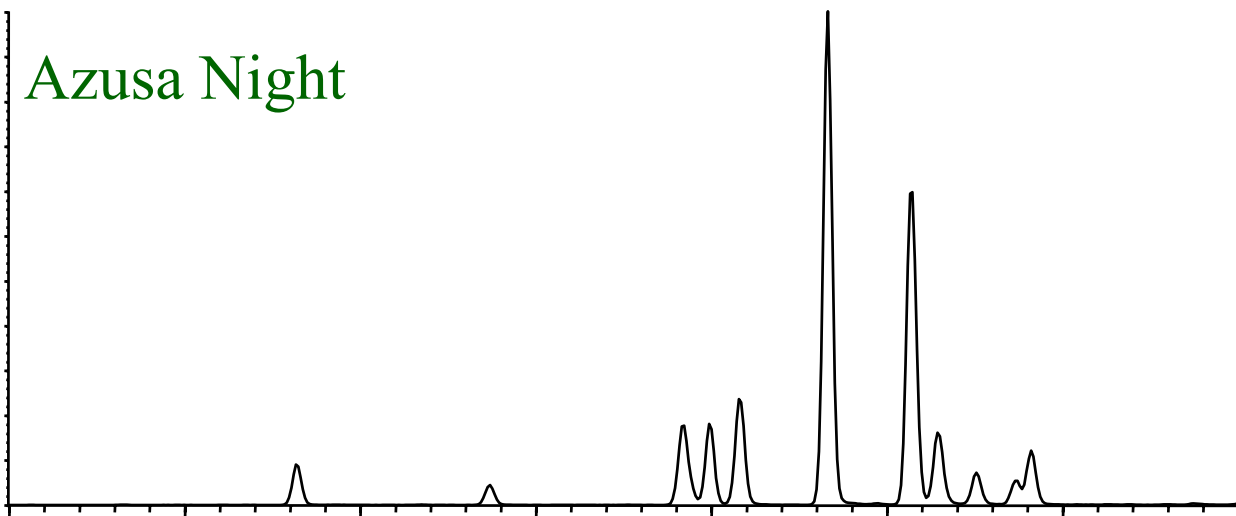
Azusa Night



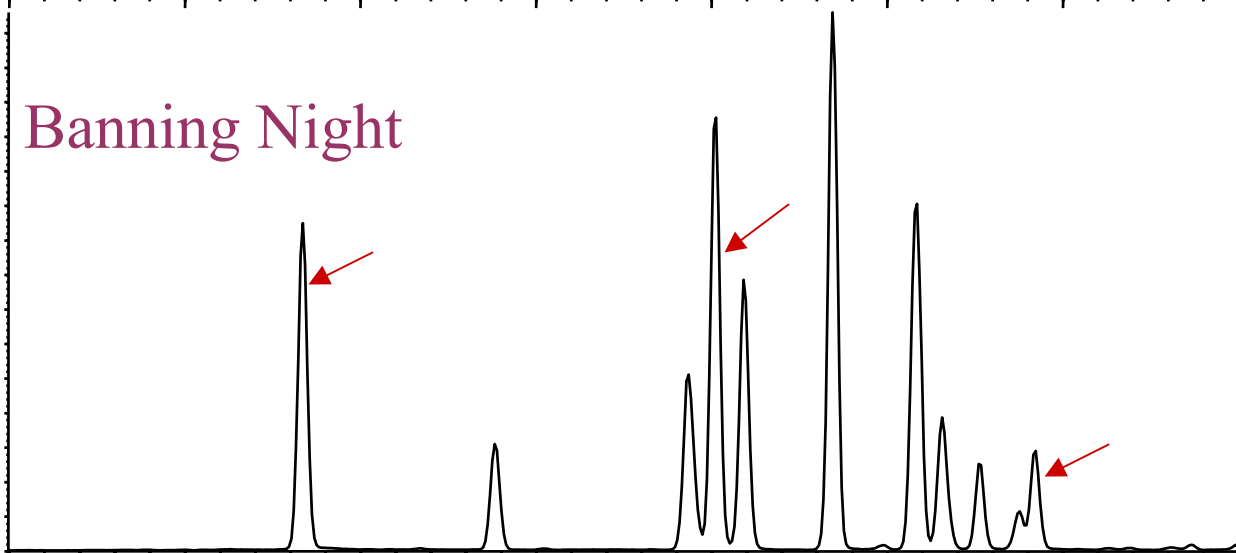
# Calculated Photolysis Lifetimes (min) of Nitronaphthalenes & Methylnitronaphthalenes

NO <sub>2</sub> on C <sub>1</sub>	Lifetime (min)	NO <sub>2</sub> on C <sub>2</sub>	Lifetime (min)	
	1M8NN	6	 1M2NN	31
	2M1NN	10	 1M3NN	71
	1M4NN	22	 1M6NN	88
	1NN	24	 2M6NN	133
	2M8NN	31	 2NN	177
	1M5NN	38		
	2M4NN	41		
	2M5NN	49		

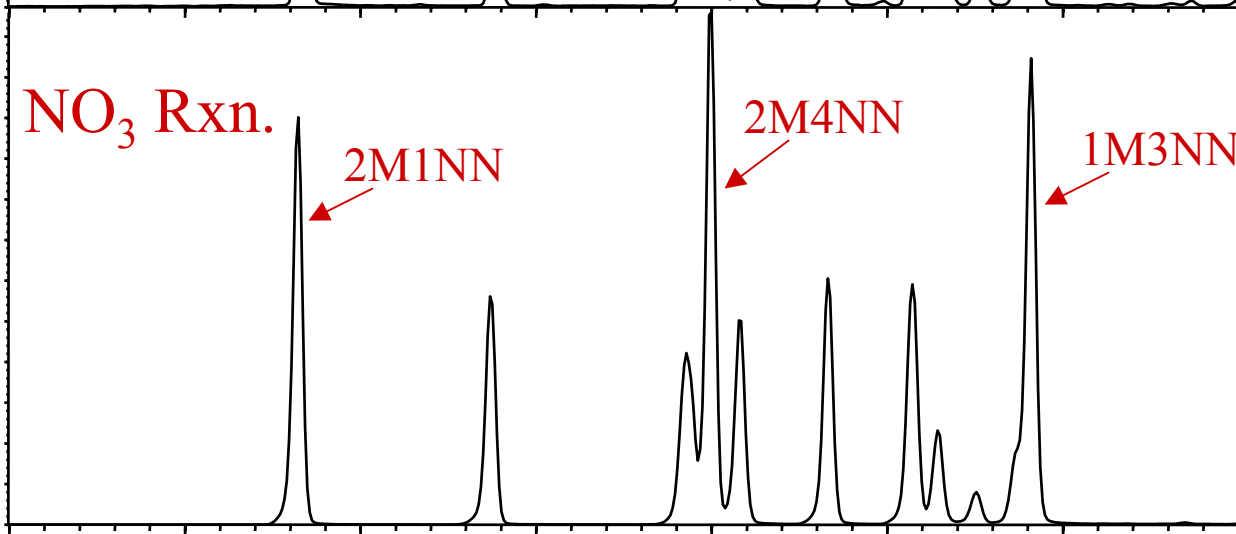
Azusa Night



Banning Night



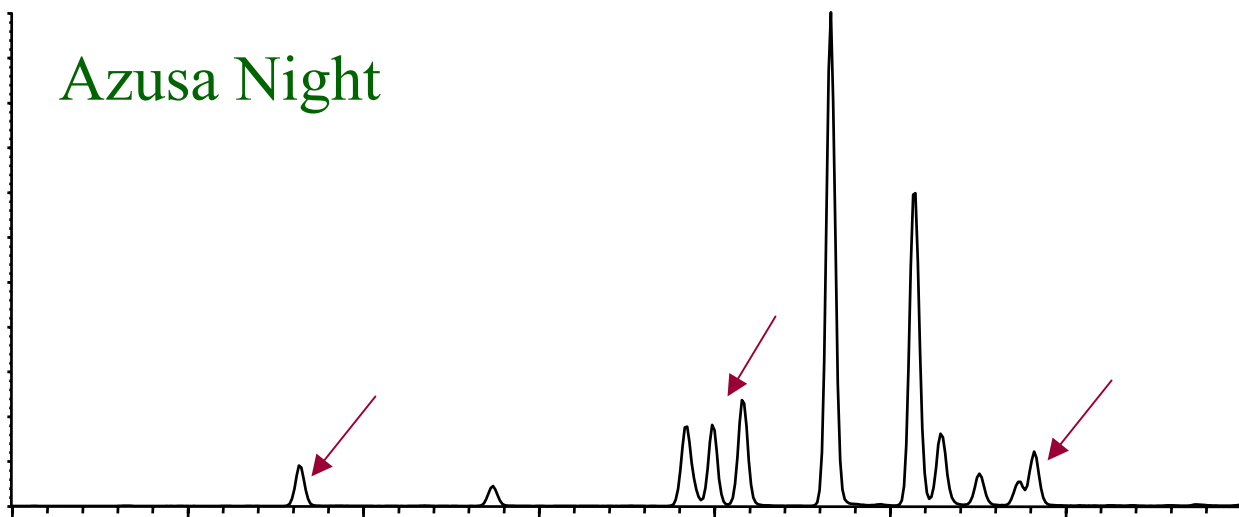
NO<sub>3</sub> Rxn.



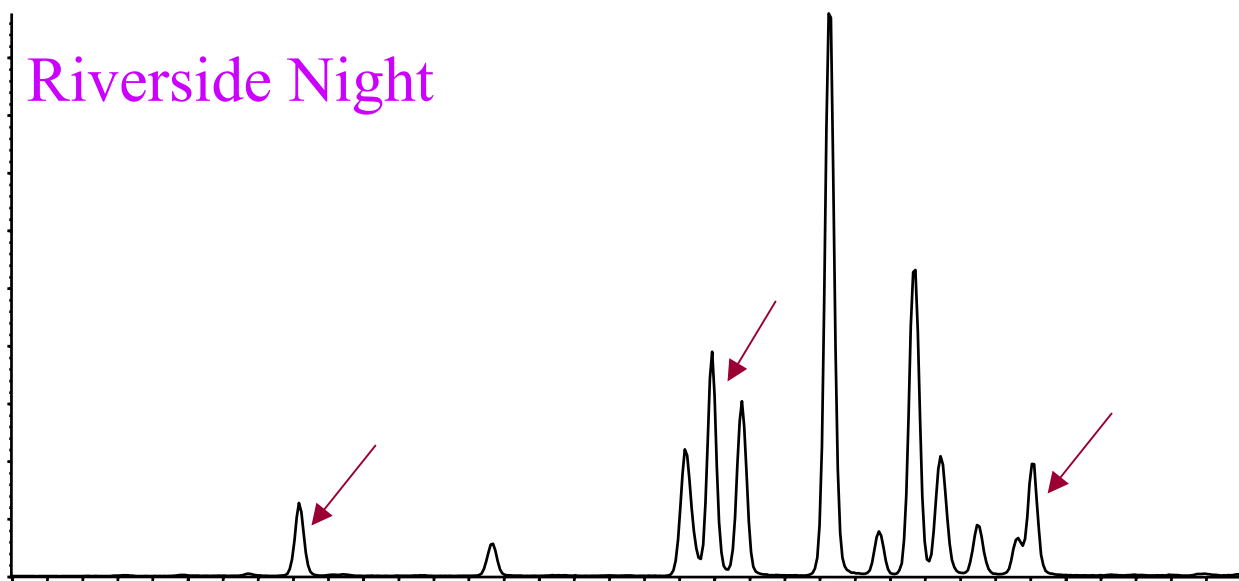
MAP SHOWING AZUSA,  
RIVERSIDE, MOUNTAIN SITES  
AND BANNING



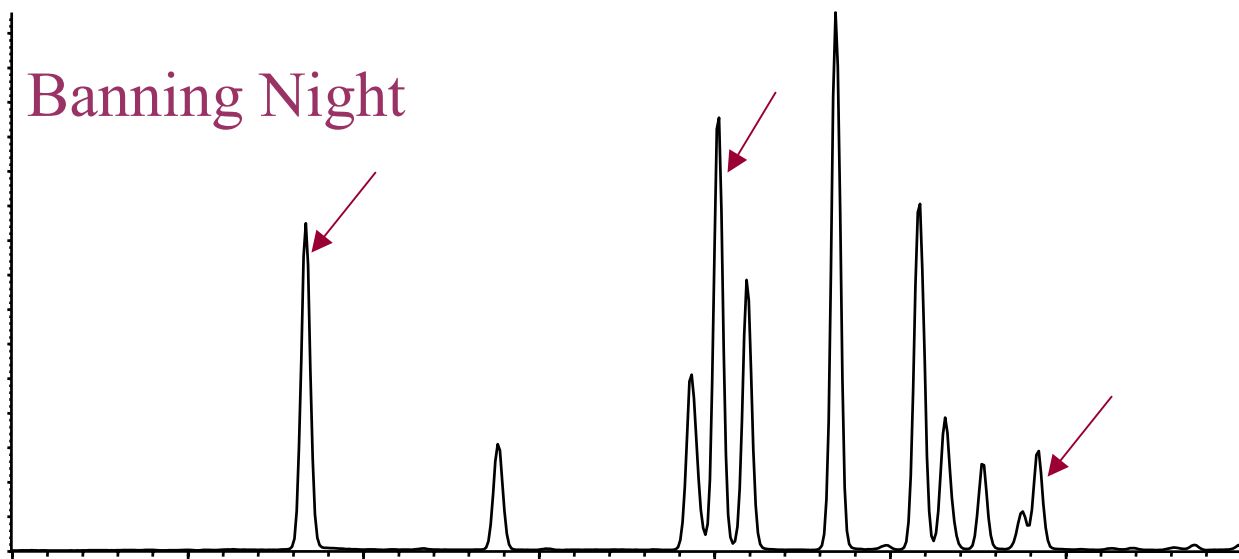
Azusa Night



Riverside Night



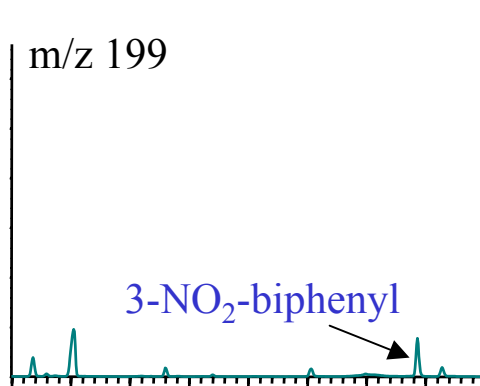
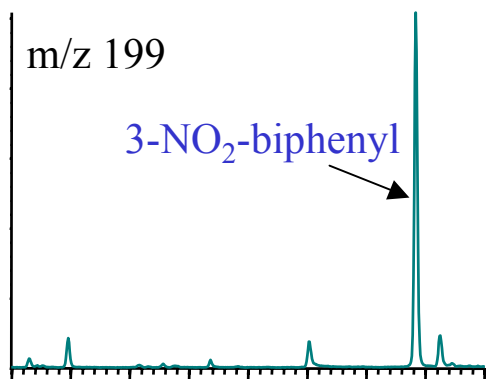
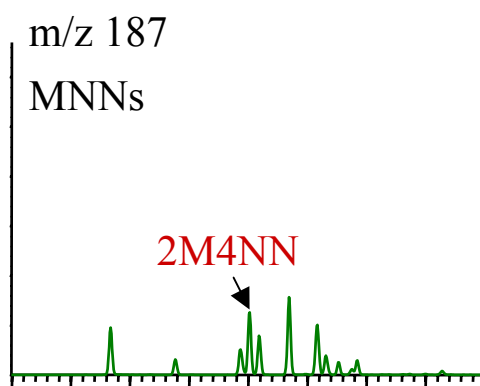
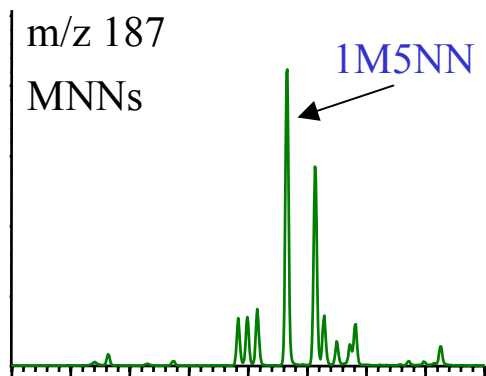
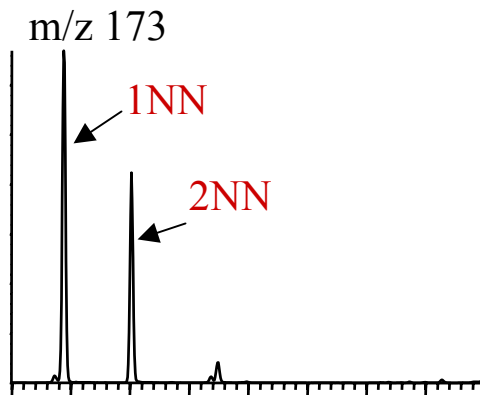
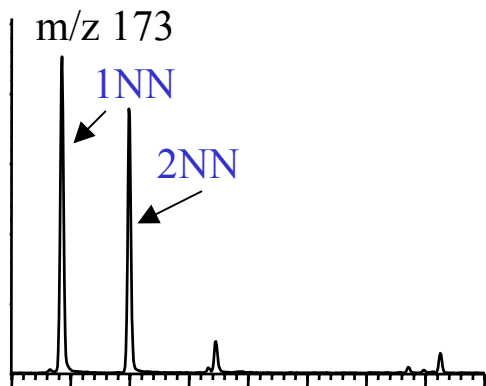
Banning Night

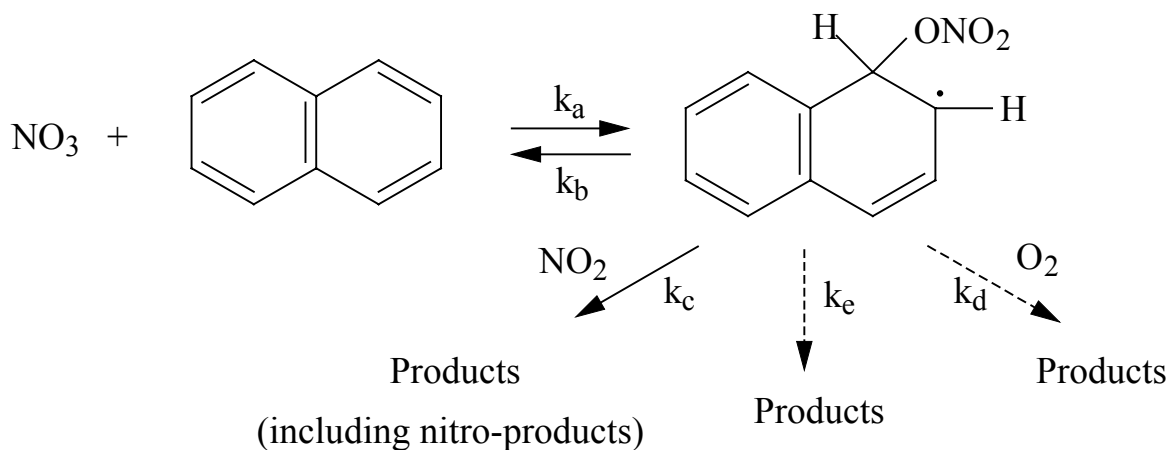


# Nitro-PAH Markers of **OH** Radical and **NO<sub>3</sub>** Radical Reactions

PAH	OH Rxn.	NO <sub>3</sub> Rxn.
Naphthalene	1-NN (1%) 2-NN (1%)	1-NN (24%) 2-NN (11%)
1-Methyl- Naphthalene	1M5NN 1M4+6NN Σ MNNs 0.4%	1M3NN Σ MNNs 30%
2-Methyl- Naphthalene	2M5NN Σ MNNs 0.2%	2M4NN 2M1NN Σ MNNs 30%
Biphenyl	3-NBPh (5%)	No rxn.

## Azusa Day





$$k_{\text{obs}} = k_a k_c [\text{NO}_2] / (k_b + k_c [\text{NO}_2])$$

$$= \frac{k_a k_c [\text{NO}_2]}{k_b} \quad \text{when } k_b \gg k_c [\text{NO}_2]$$

2-MN  $k_{\text{obs}} = 1 \times 10^{-27} \text{ cm}^{-6} \text{ molecule}^{-2} \text{ s}^{-1} \quad [\text{NO}_2]$

Yield 2M4NN = 0.1

$[\text{2-MN}] = 60 \text{ ng/m}^3$

$[\text{2M4NN}] = 0.3 \text{ ng/m}^3$

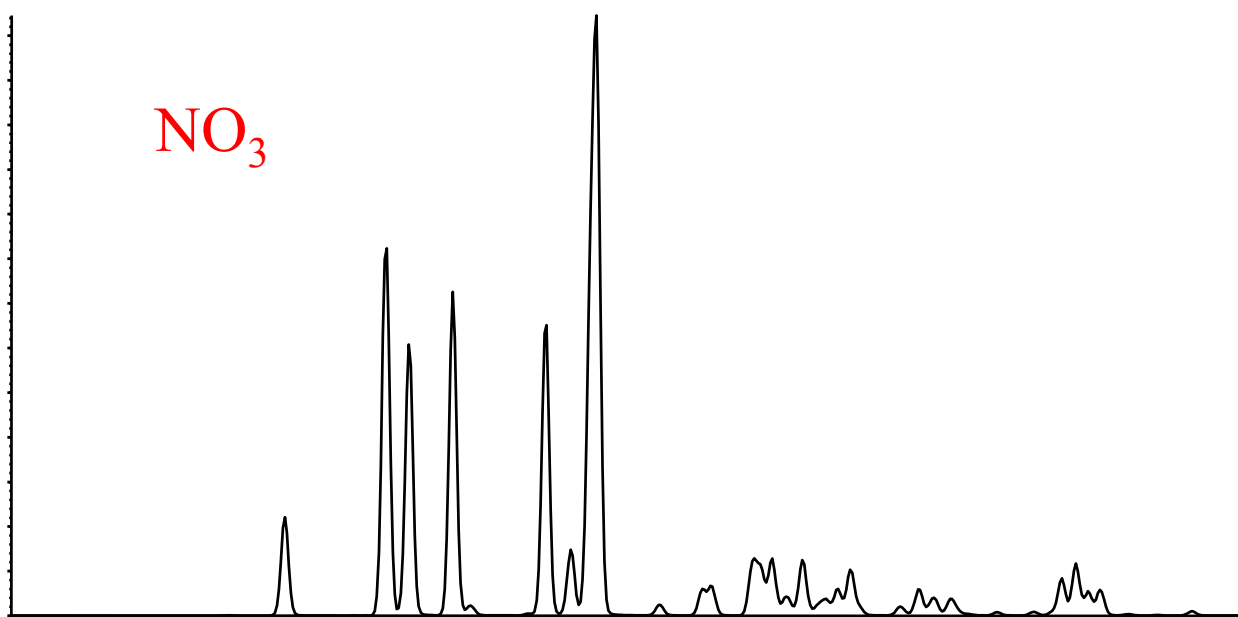
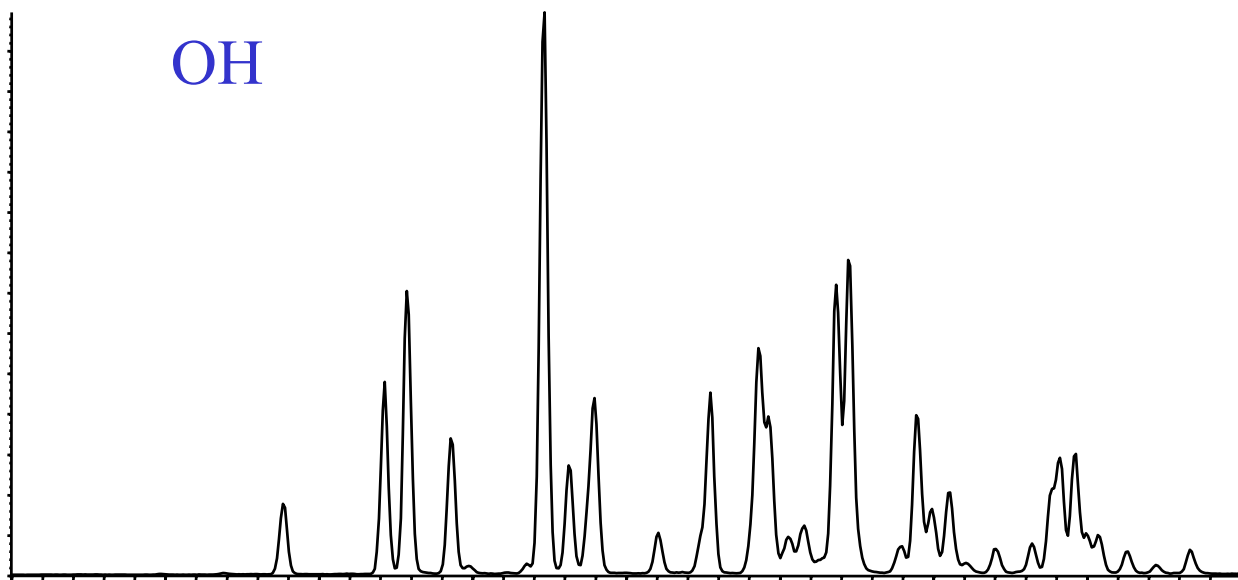
$t = 2.2 \times 10^4 \text{ s}$

$$[\text{2M4NN}] = \frac{k_a k_c [\text{NO}_2]}{k_b} \text{ Yield } [\text{NO}_3] [\text{2-MN}] t$$

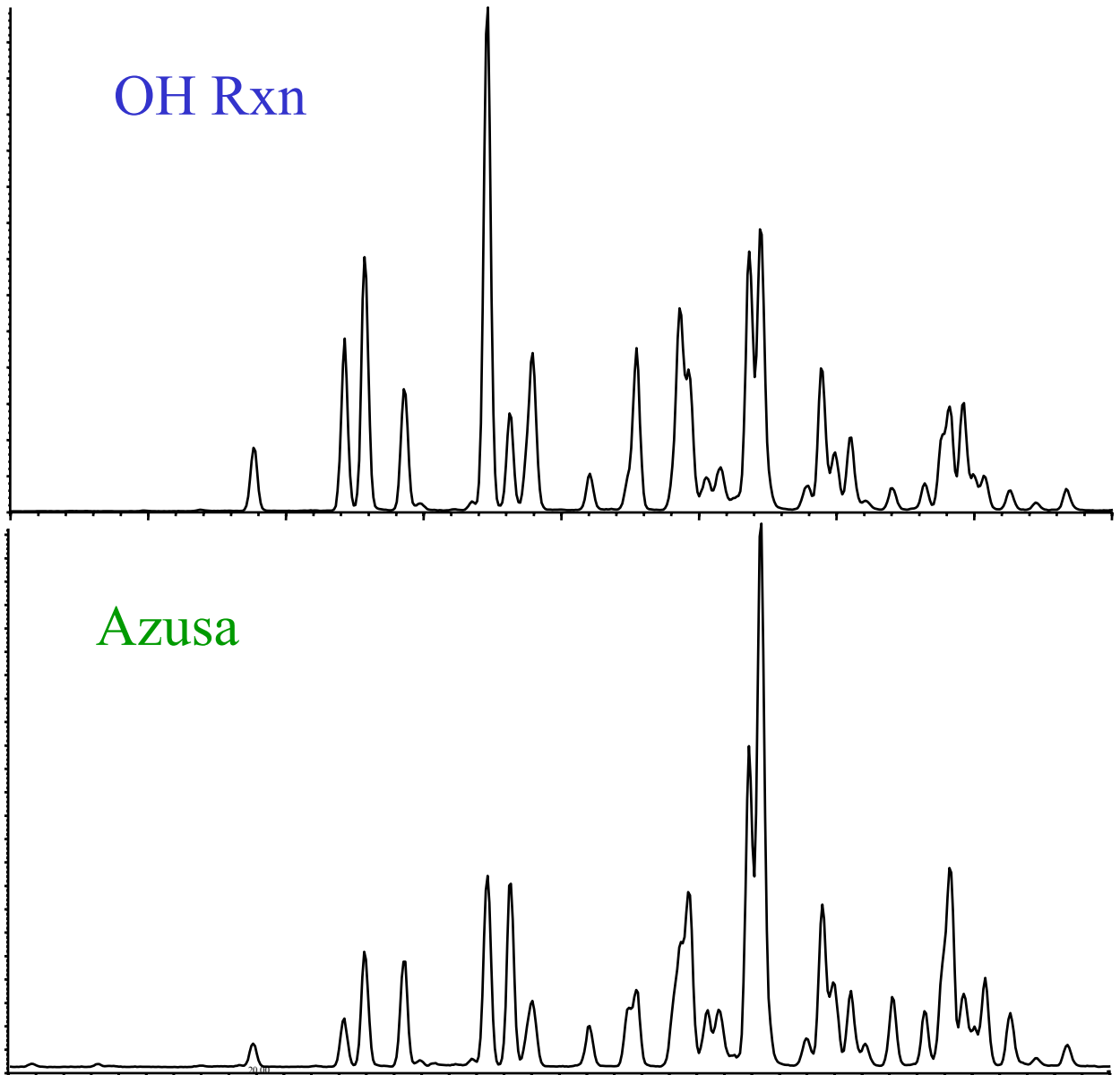
$$[\text{NO}_2] [\text{NO}_3] = 2.3 \times 10^{21} \text{ molecule}^2 \text{ cm}^{-6}$$

Assume  $[\text{NO}_2] = 10 \text{ ppbv}$ , then  $[\text{NO}_3] = 1 \times 10^{10} \text{ molecule cm}^{-3}$

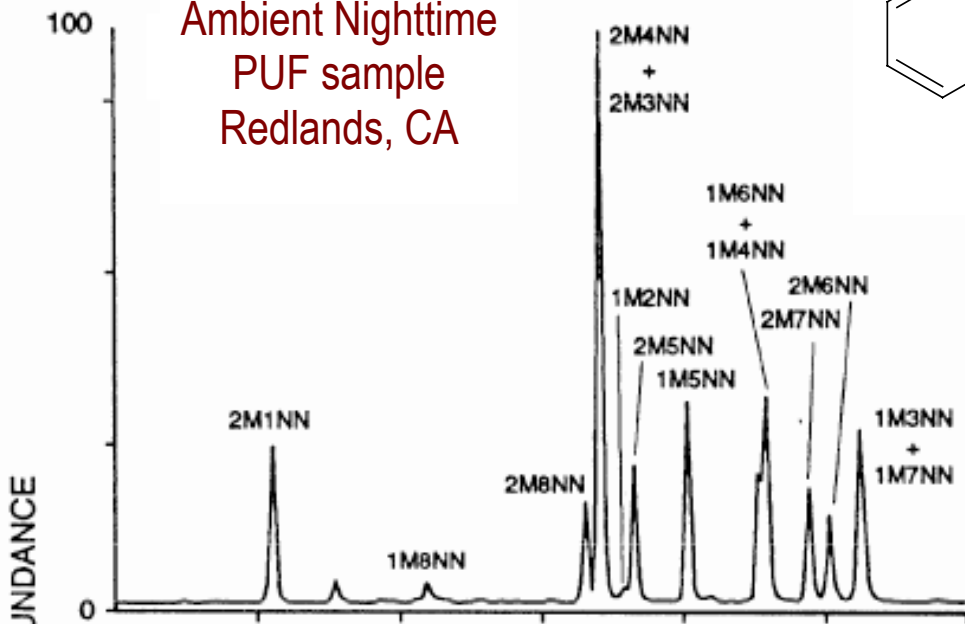
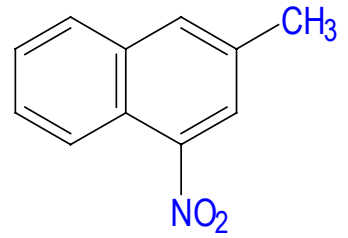
Dimethylnitronaphthalenes (DMNNs)  
from OH and NO<sub>3</sub> Radical Reactions  
of Volatilized Diesel Fuel



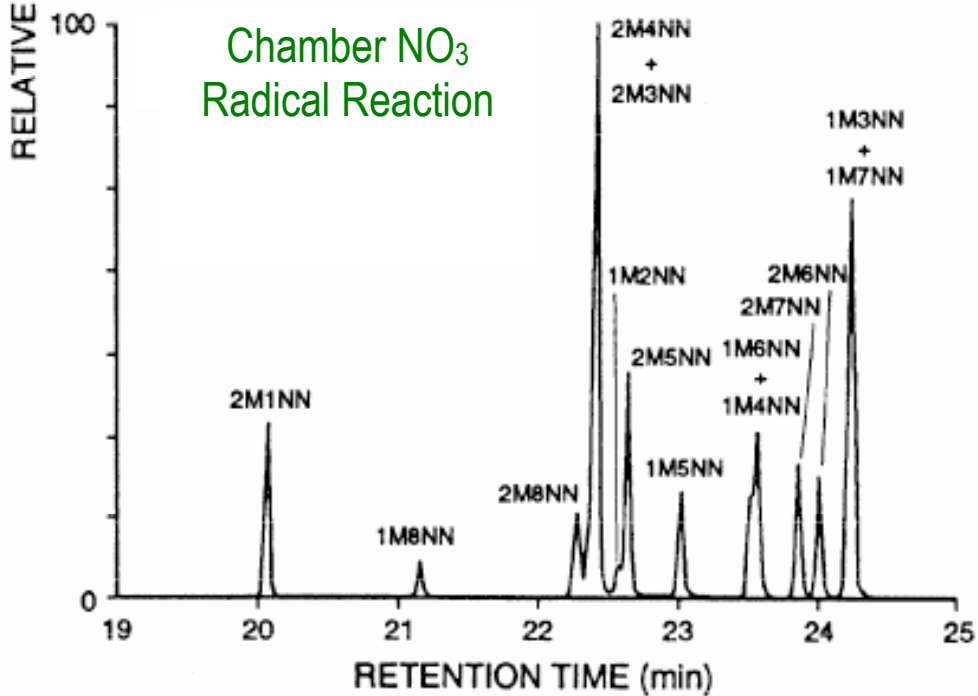
Dimethylnitronaphthalenes (DMNNs)  
from OH Reaction of Volatilized Diesel Fuel  
and Ambient Sample from Azusa



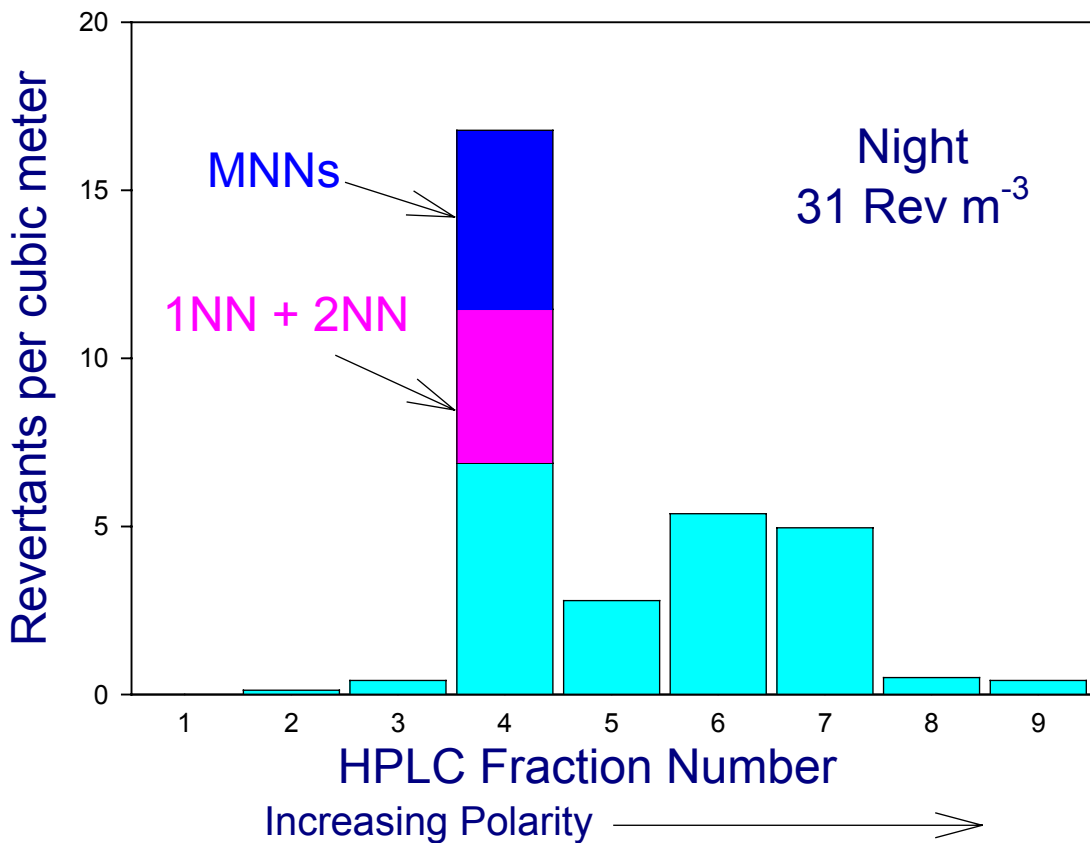
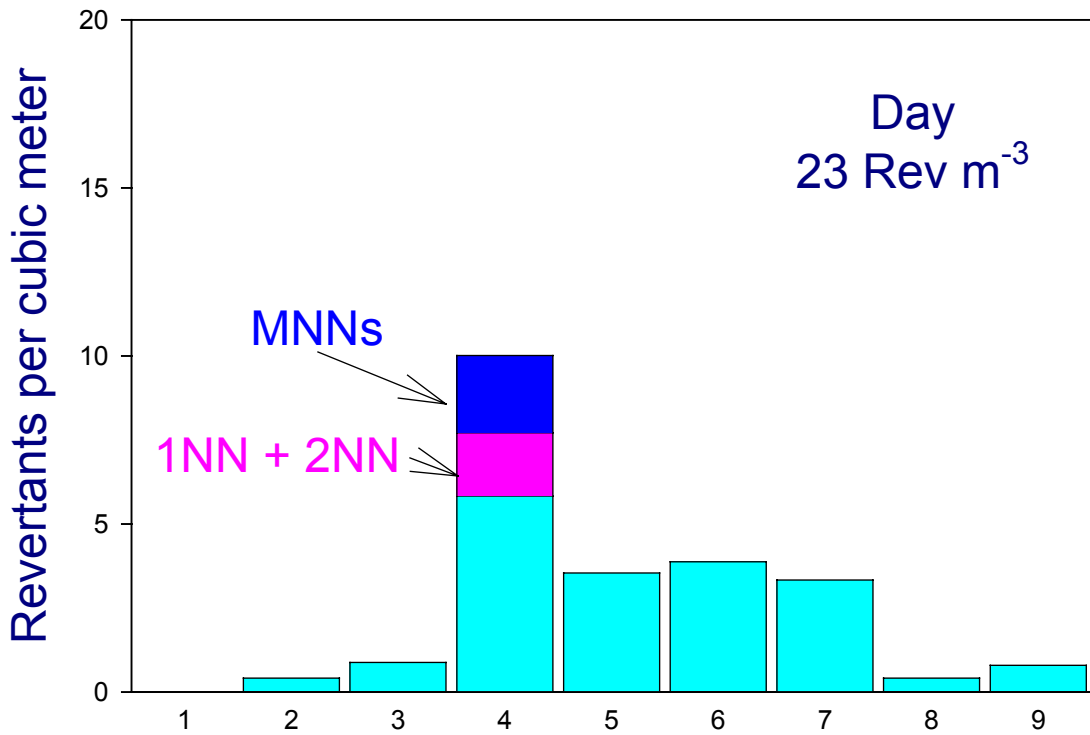
Ambient Nighttime  
PUF sample  
Redlands, CA



Chamber NO<sub>3</sub>  
Radical Reaction



# Vapor Phase Mutagrams - Redlands, CA





# **ACKNOWLEDGEMENTS**

Patricia Phousongphouang

Fabienne Reisen

Pamela Gupta

Jennifer Sasaki

Eric Kwok

EPA SUPERSITE

DOE

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