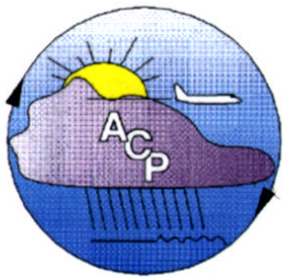
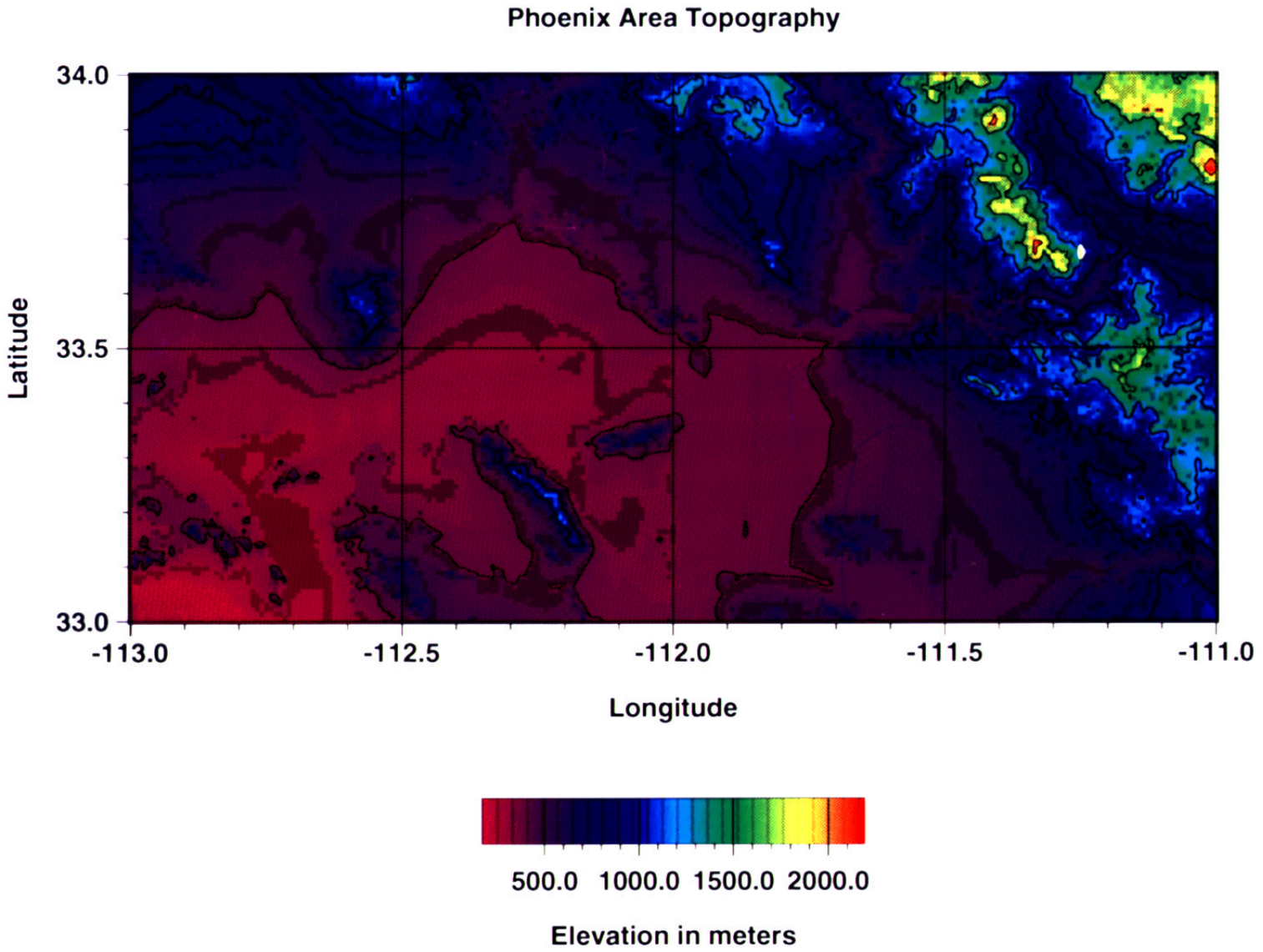


Atmospheric Chemistry of Organic Oxidants: Phoenix, AZ and G-1 Aircraft Studies

Jeffrey S. Gaffney and Nancy A. Marley
Atmospheric Sciences Section
Environmental Research Division
Argonne National Laboratory

ABSTRACT

As part of the recent DOE Atmospheric Chemistry Program (ACP) Phoenix field study, approx. four weeks of one-minute time resolved data for NO_2, peroxyacyl nitrates (PANs), ozone, UV-B, and temperature were measured at a site near Usery Mountain in the Phoenix, Arizona located above the nearby urban Phoenix air basin in May-June 1998. Size fractionated aerosol samples were also collected at the site. Aerosol samples were examined for optical properties, and for natural radionuclides as a means of estimating the fine aerosol lifetimes. Presented here are preliminary results for ozone, nitrogen dioxide, total oxides of nitrogen, PAN, UV-B, NO_3 production rates, and temperature.


Phoenix Area Topography
34.0
33.5
33.0
Latitude
-113.0
-112.5
-112.0
-111.5
-111.0
Longitude
500.0
1000.0
1500.0
2000.0
Elevation in meters

Phoenix Results

Ozone Background variable – 40 to 60 ppb

Implications for 80 ppb control strategies

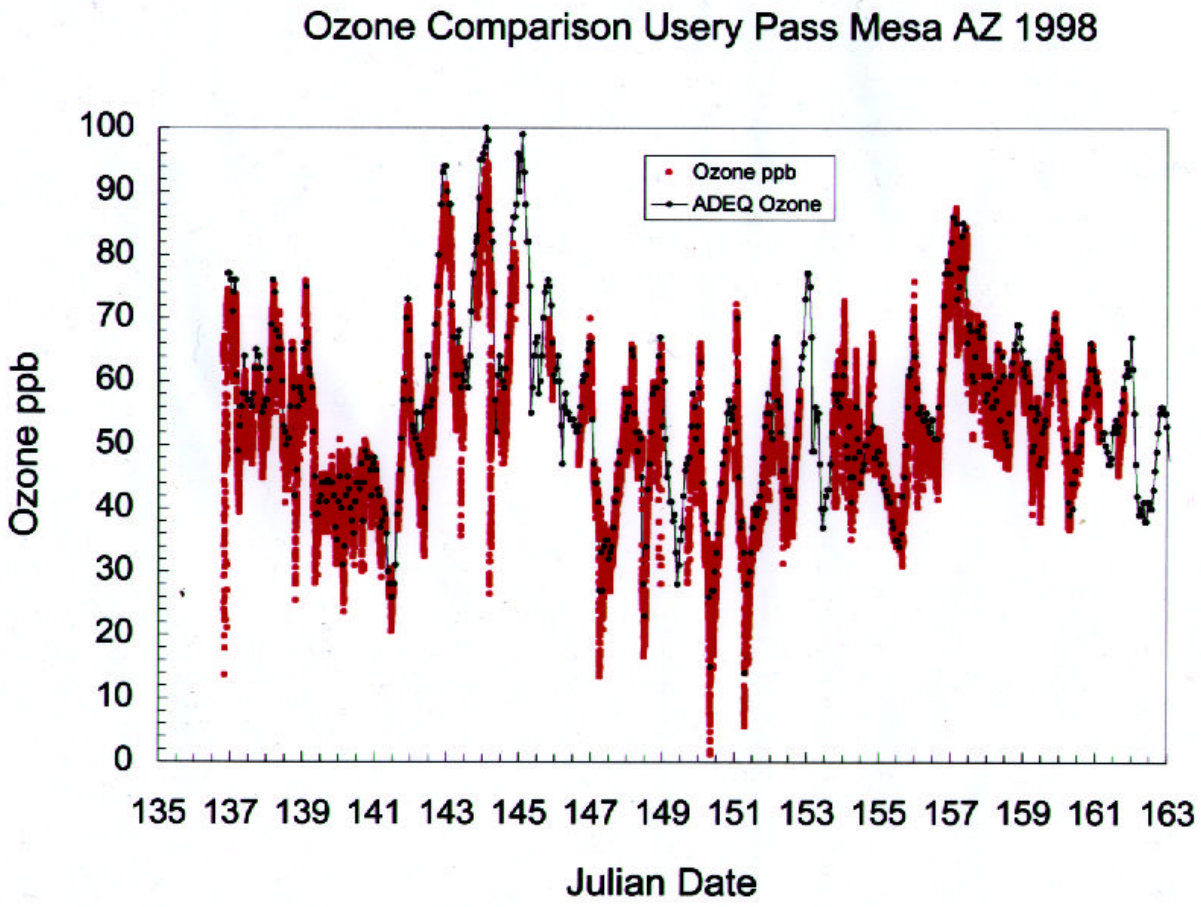
O_3, NO_2 minimum associated with Smoke

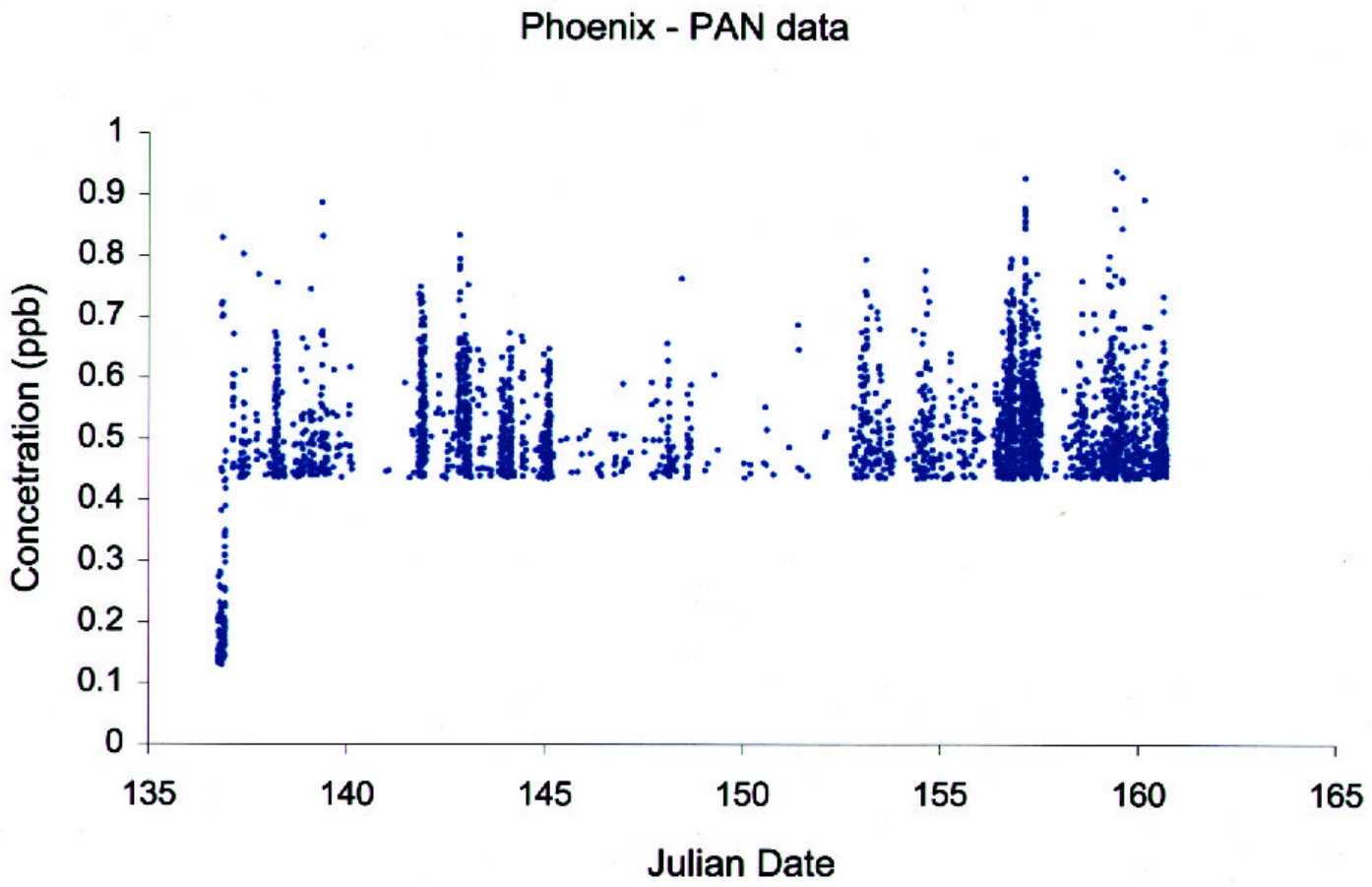
PAN levels very low… 1ppb or less

Consistent with high temperatures

NO_2 plumes at nighttime lead to NO_3 production

Production on the plume edges very large


Ozone Comparison Usery Pass Mesa AZ 1998
Ozone ppb
ADEQ Ozone
Ozone ppb
100
90
80
70
60
50
40
30
20
10
0
135 137 139 141 143 145 147 149 151 153 155 157 159 161 163
Julian Date

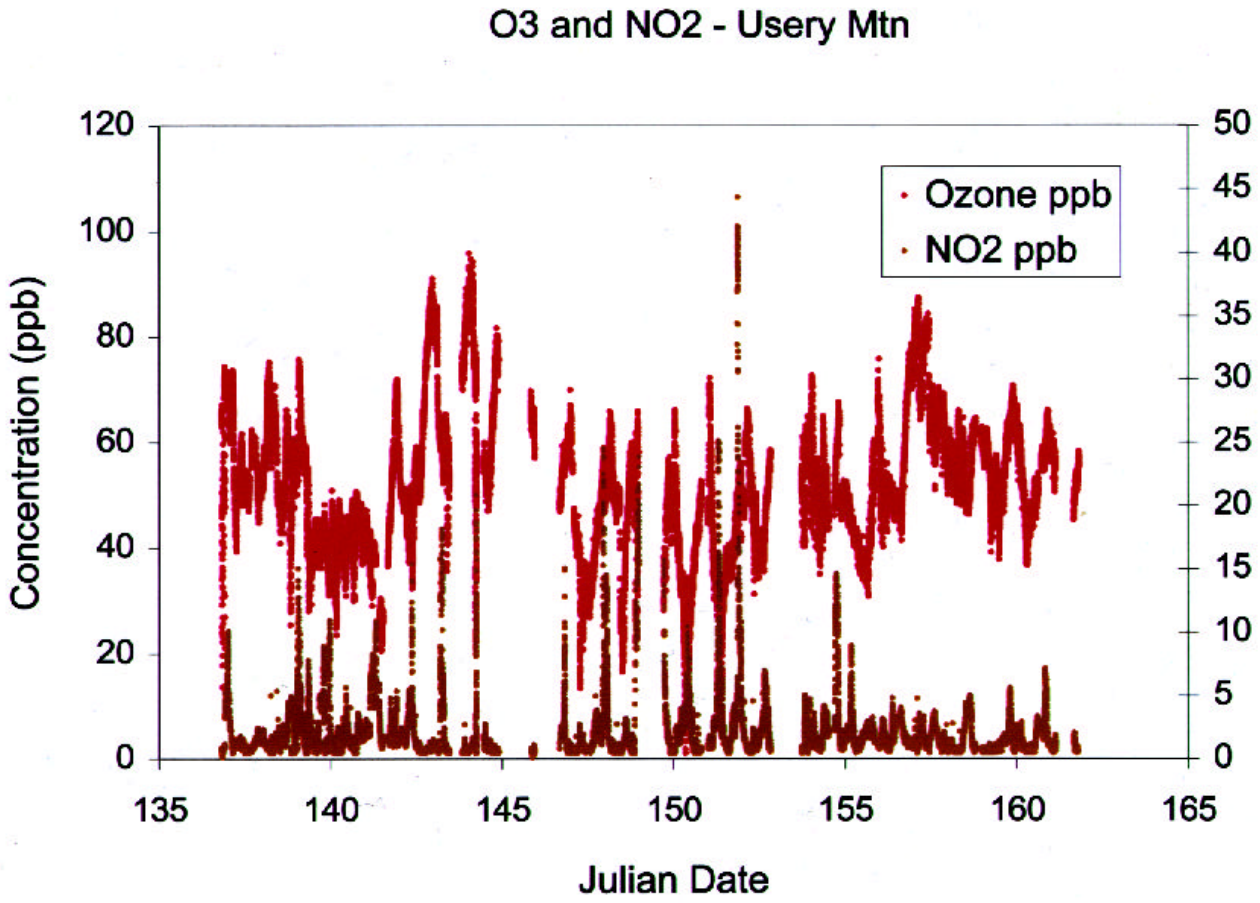

Phoenix - PAN data
Concetration (ppb)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
135
140
145
150
155
160
165
Julian Date

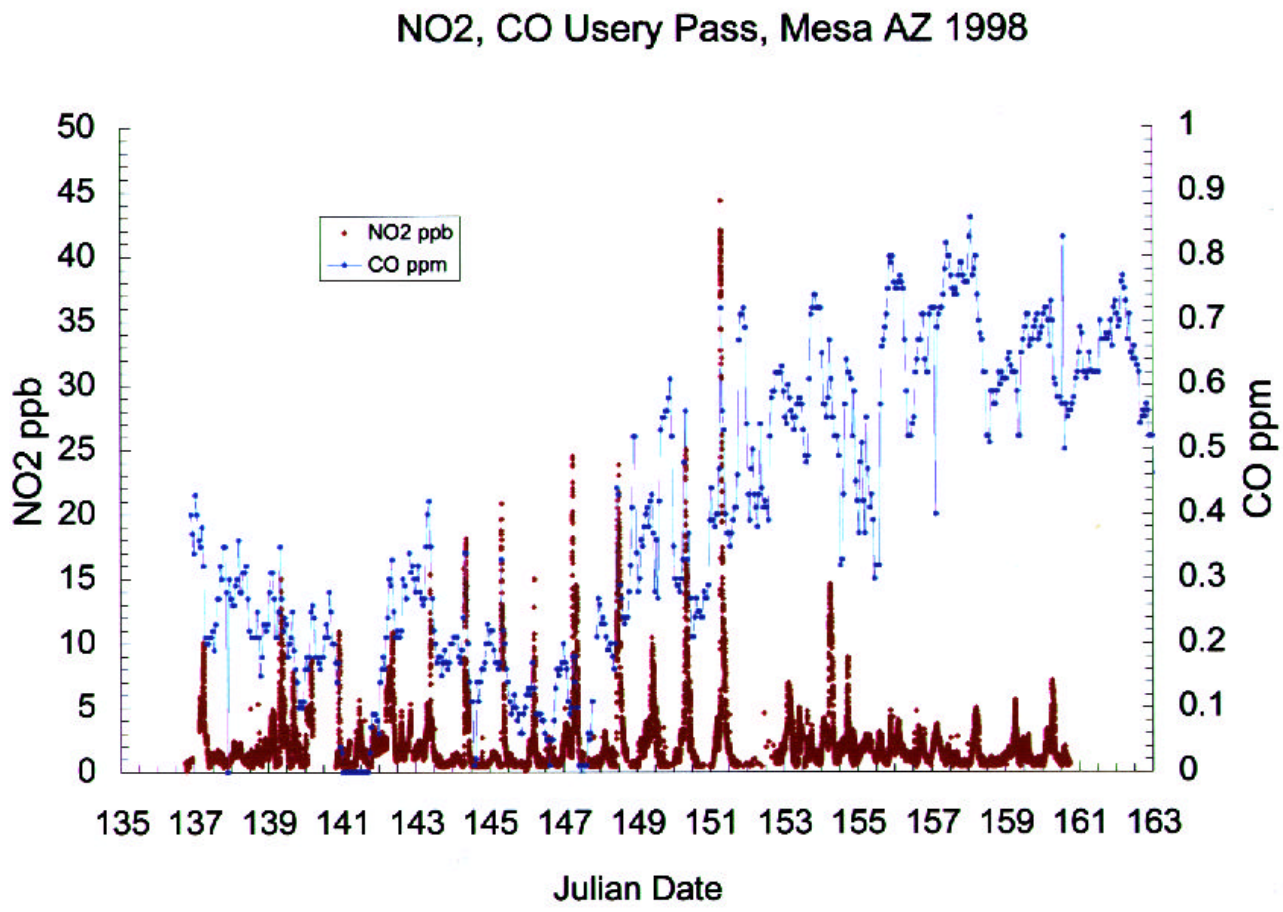
A Plume Blows at Midnight

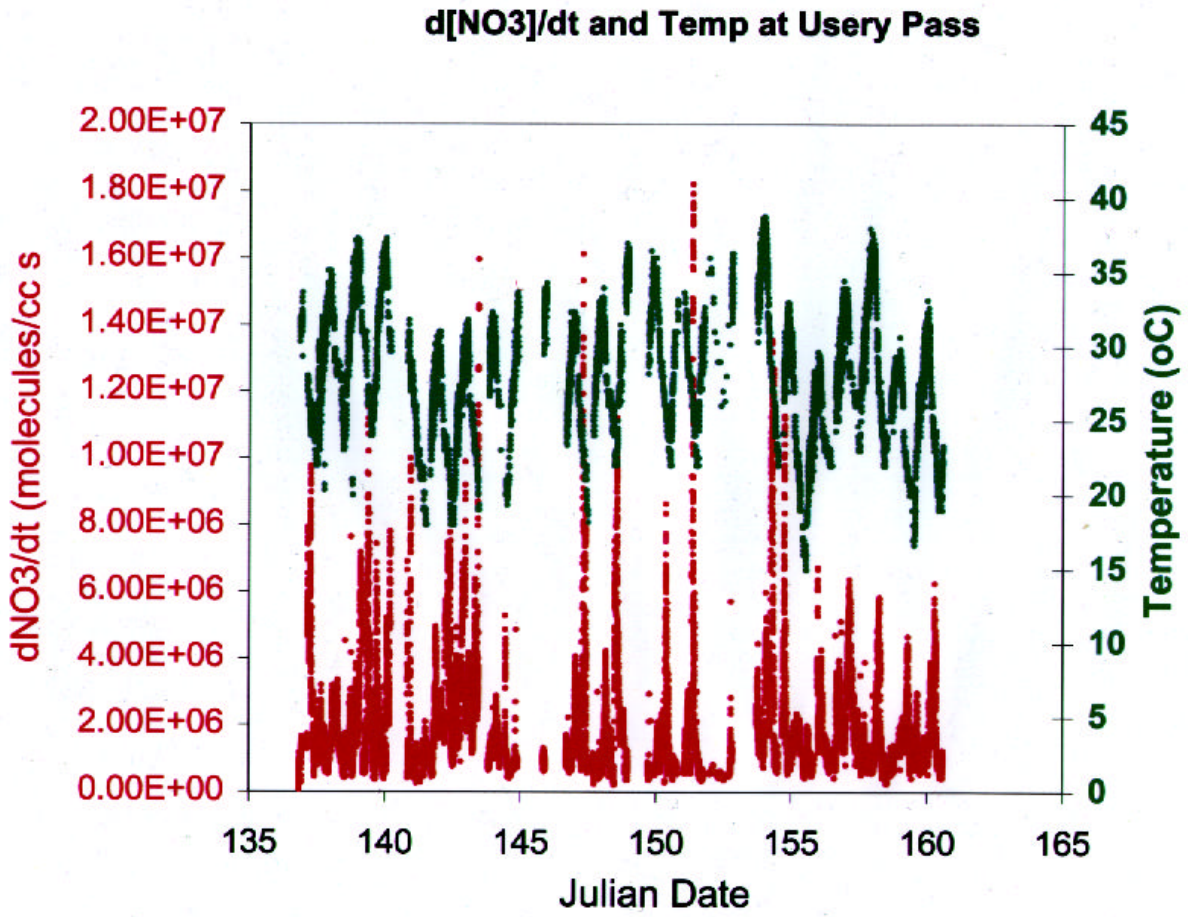
Several nights very high NO_2 was observed during the study. These plumes were associated with low O_3, CO, and hydrocarbons. This is due to local NO emissions titrating ozone to produce nitrogen dioxide by thermal oxidation at night.

$$NO + O_3 \rightarrow NO_2 + O_2$$

NO_3 production rate calculations using NO_2, O_3 and T indicate very large production rates on the edges of these urban plumes. Thus, both meteorology and chemistry are key to nighttime NO_3 radical production.

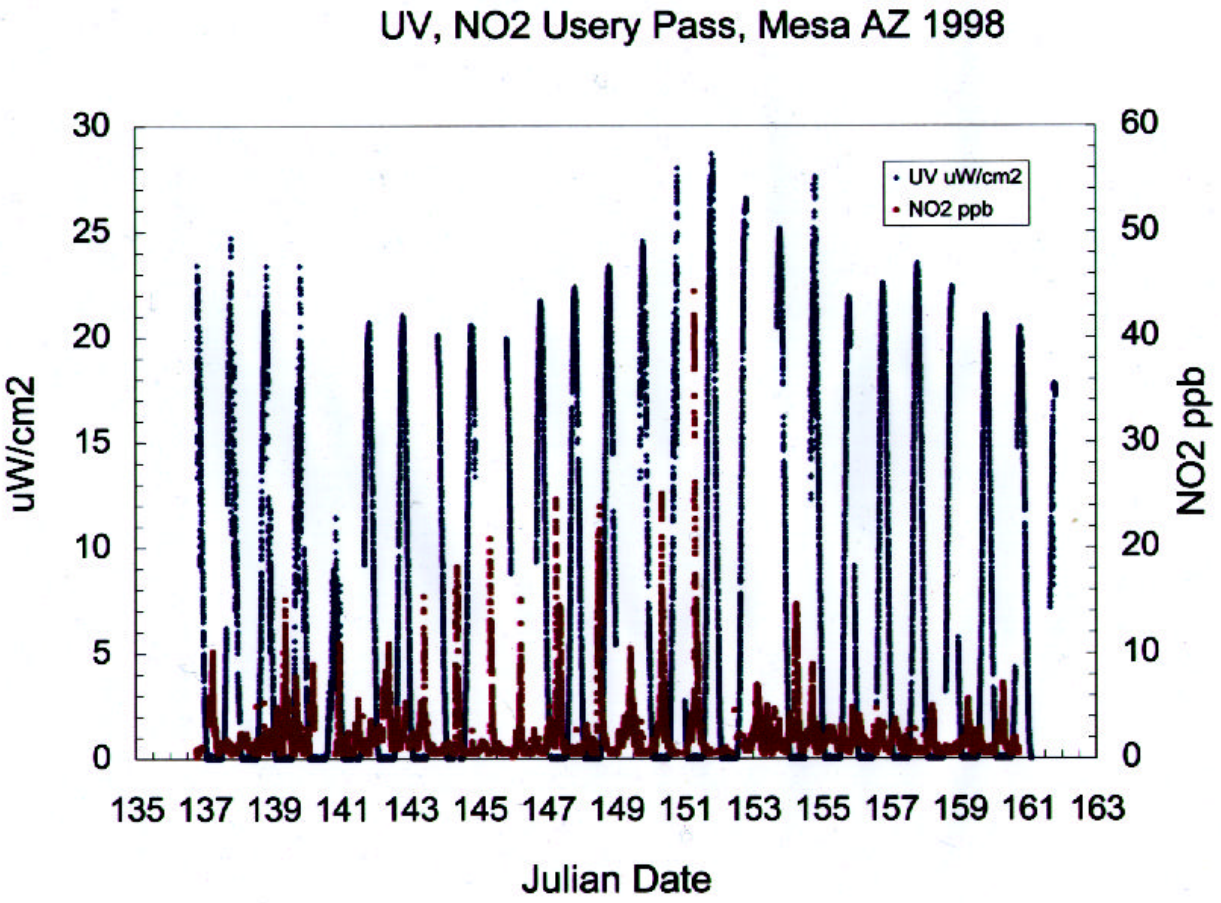

O3 and NO2 - Usery Mtn
Concentration (ppb)
120
100
80
60
40
20
0
50
45
40
35
30
25
20
15
10
5
0
135
140
145
150
155
160
165
Julian Date
Ozone ppb
NO2 ppb


NO2, CO Usery Pass, Mesa AZ 1998
NO2 ppb
CO ppm
50
45
40
35
30
25
20
15
10
5
0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
135 137 139 141 143 145 147 149 151 153 155 157 159 161 163
Julian Date


d[NO3]/dt and Temp at Usery Pass
dNO3/dt (molecules/cc s
2.00E+07
1.80E+07
1.60E+07
1.40E+07
1.20E+07
1.00E+07
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
135
140
145
150
155
160
165
Julian Date
Temperature (oC)
45
40
35
30
25
20
15
10
5
0

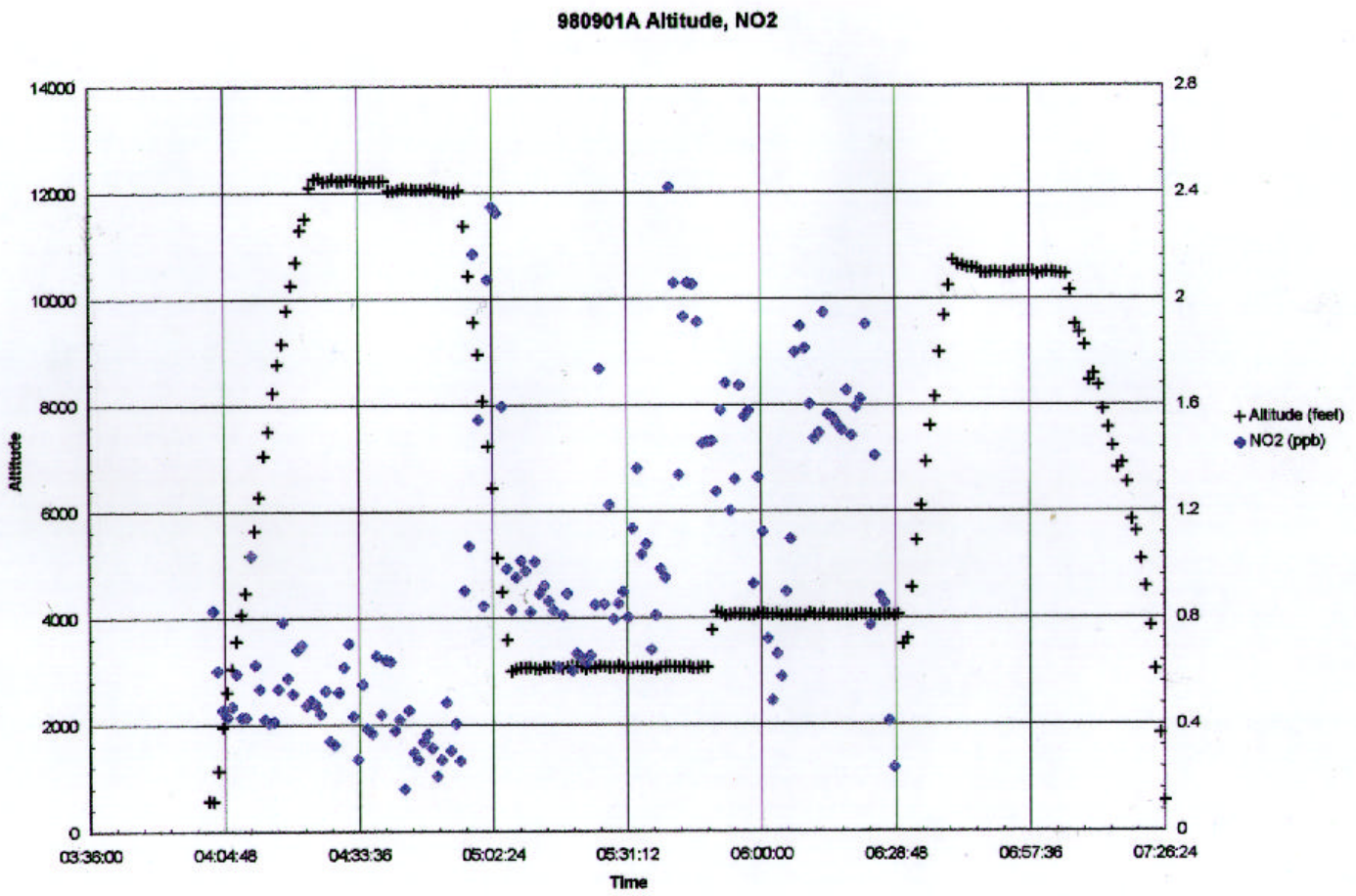
Smoke Event and Long-Range Transport

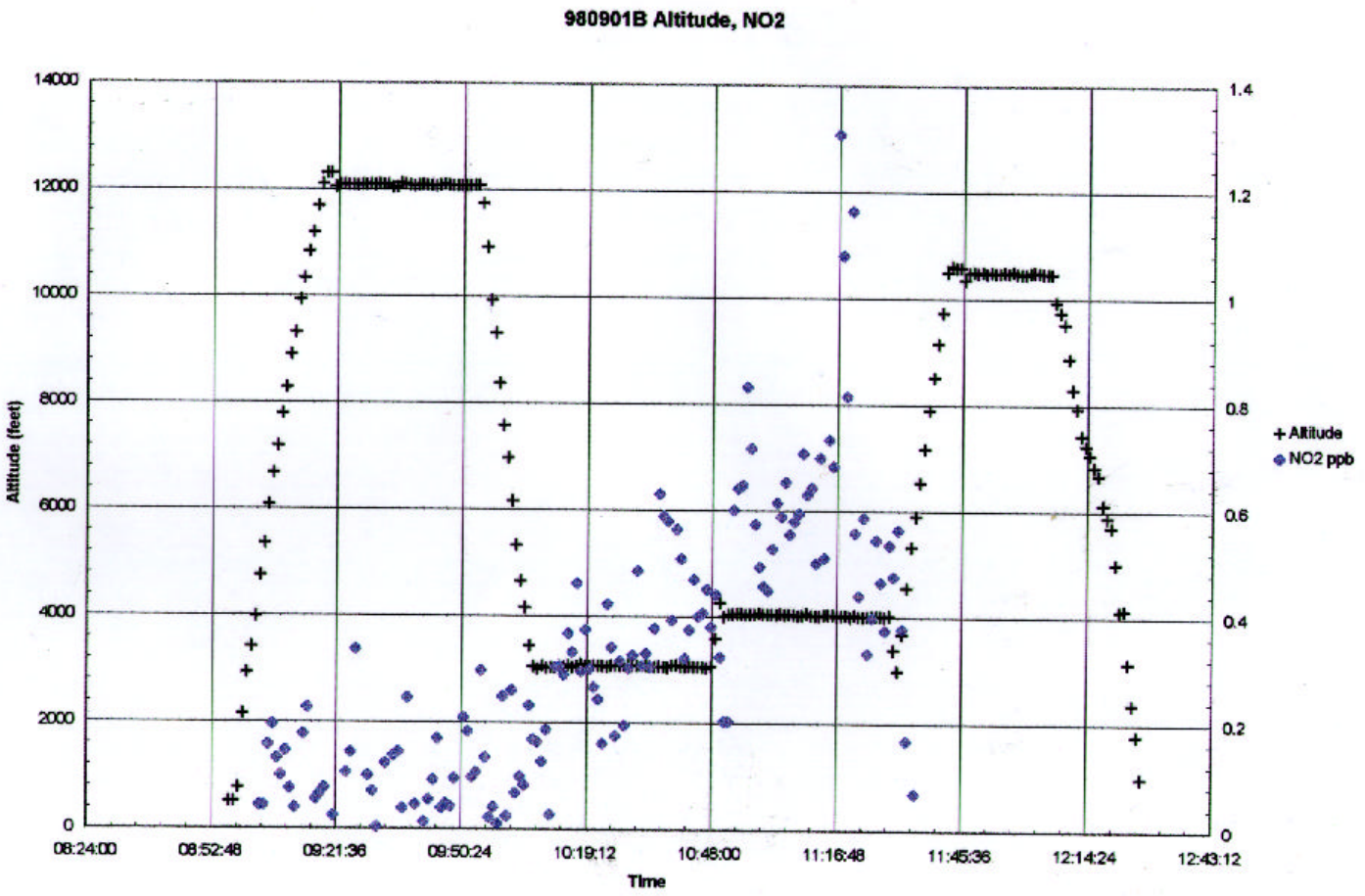
A period of very hazy air occurred during the initial period of the study. During this time both ozone and NO_2 were observed to be reduced significantly. PANs were also low during this period. Measurements in Albuquerque, NM were also consistent with this regional phenomenon, most likely due to the Mexican fires. During the latter part of the study, ozone and PAN levels were observed to be higher indicating the possible long-range transport from the South Coast Air Basin.

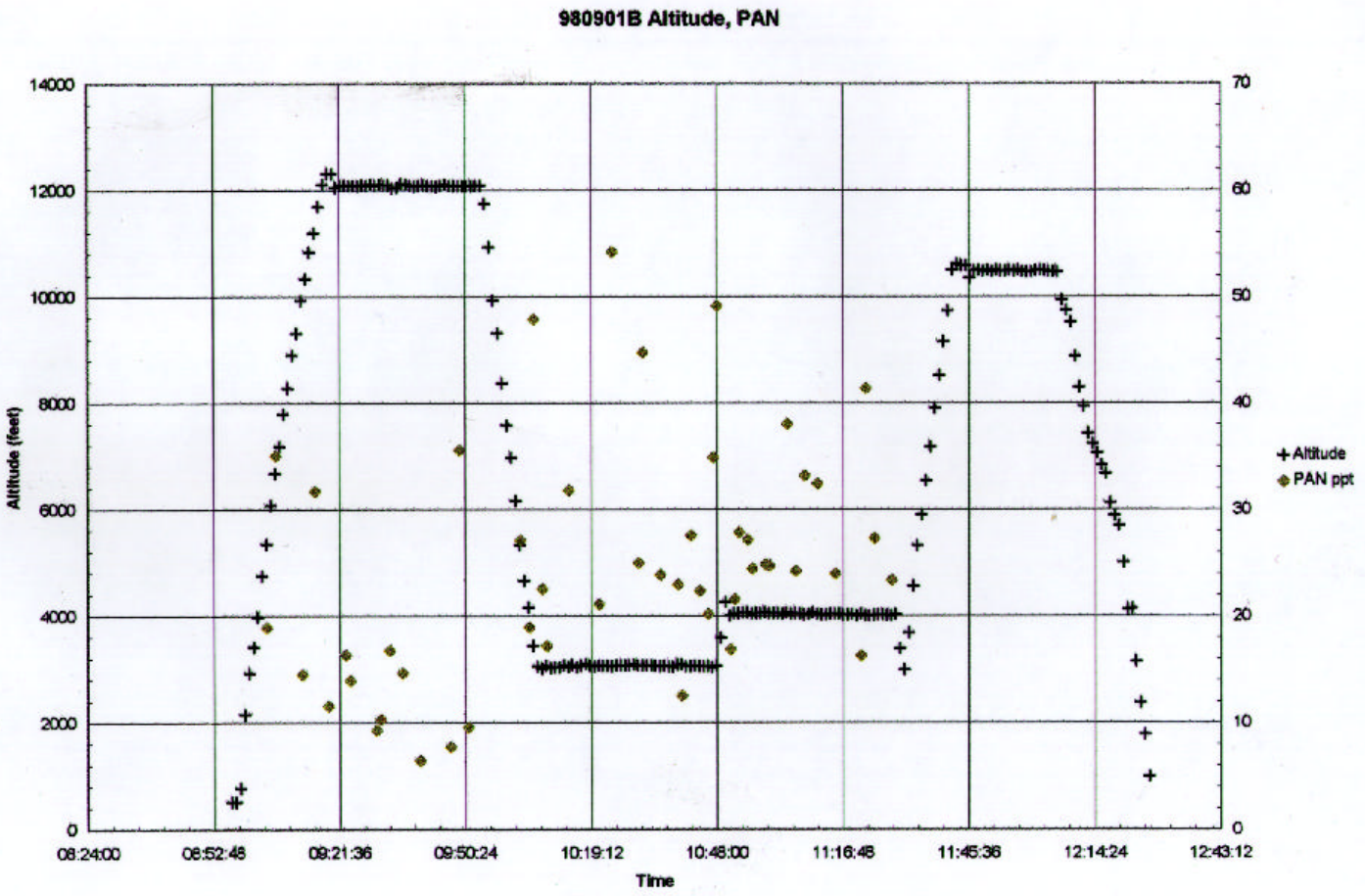

UV, NO2 Usery Pass, Mesa AZ 1998
UV uW/cm2
NO2 ppb
uW/cm2
NO2 ppb
0
5
10
15
20
25
30
0
10
20
30
40
50
60
135 137 139 141 143 145 147 149 151 153 155 157 159 161 163
Julian Date

G-1 Aircraft Studies

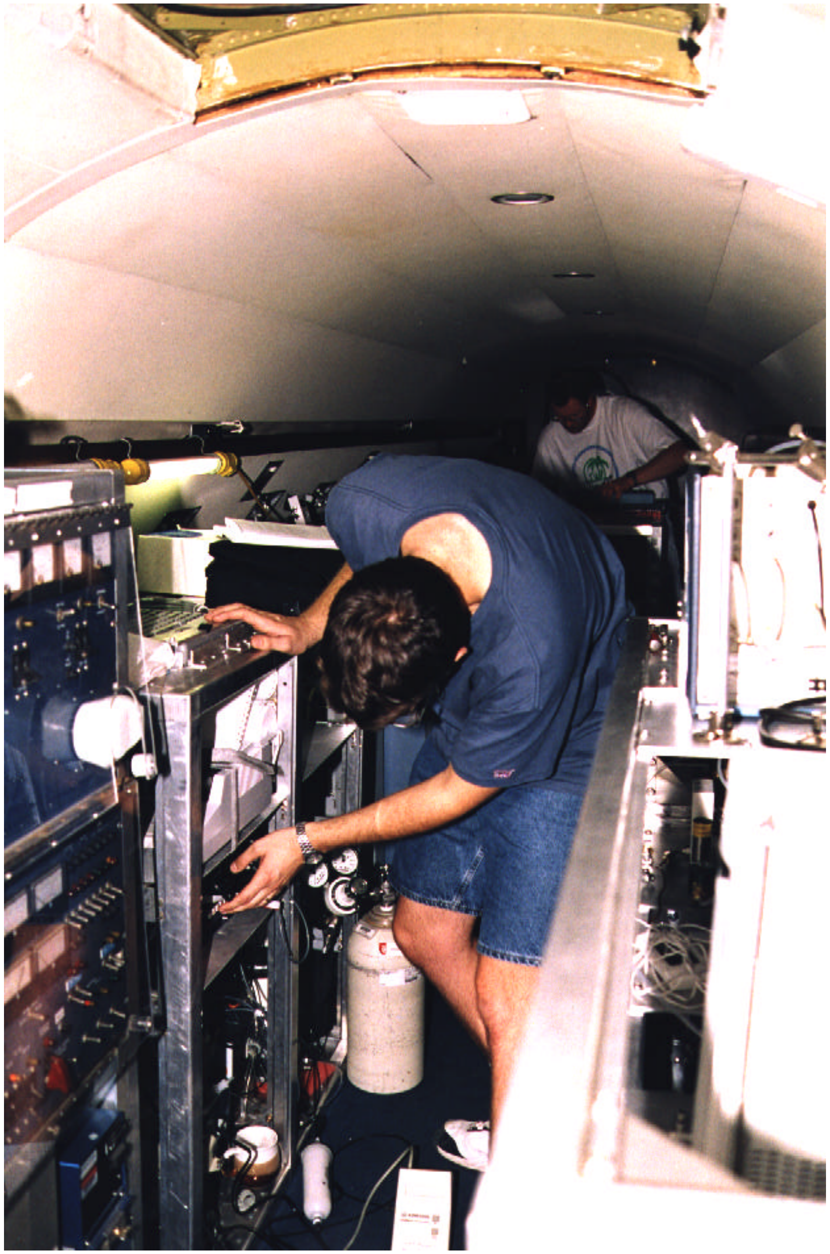
We completed four nighttime flights during September of 1998 over South Portland, Oregon. During these flights measurements of NO_2 and PAN were made using the luminol chemiluminescent monitor. These flights were done in collaboration with PNNL and Battelle, Columbus and were focused on nighttime chemistry. We are currently analyzing this data with ozone to estimate NO_3 levels.


980901A Altitude, NO2
14000
12000
10000
8000
6000
4000
2000
0
Altitude
2.8
2.4
2
1.6
1.2
0.8
0.4
0
03:36:00
04:04:48
04:33:36
05:02:24
05:31:12
06:00:00
06:28:48
06:57:36
07:26:24
Time
Altitude (feet)
NO2 (ppb)


980901B Altitude, NO2
14000
12000
10000
8000
6000
4000
2000
0
Altitude (feet)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
08:24:00
08:52:48
09:21:36
09:50:24
10:19:12
10:48:00
11:16:48
11:45:36
12:14:24
12:43:12
Time
Altitude
NO2 ppb

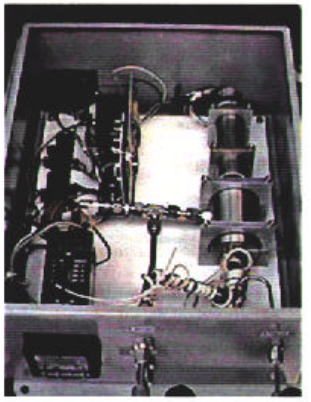

980901B Altitude, PAN
Altitude (feet)
14000
12000
10000
8000
6000
4000
2000
0
70
60
50
40
30
20
10
0
08:24:00
08:52:48
09:21:36
09:50:24
10:19:12
10:48:00
11:16:48
11:45:36
12:14:24
12:43:12
Time
Altitude
PAN ppt


Battelle



Instrumentation Development

HYDROCARBON MONITOR



Luminol Instrument – Second Generation