VII. CONTRIBUTION OF NITROARENES TO THE MUTAGENICITY OF AMBIENT POM DURING WINTER AND SUMMER AIR POLLUTION EPISODES

A. Introduction

Organic extracts of respirable ambient particulate matter have been shown to be strongly mutagenic in the Ames assay without microsomal activation (see, for example, Pitts et al. 1977, Talcott and Wei 1977, Tokiwa et al. 1977). Although the chemical compounds responsible for this direct mutagenicity (PAH themselves are not mutagenic in the absence of microsomal activation) have not yet been determined to any complete extent, nitrated PAH, many of which are strong, direct mutagens, have been reported to be present in ambient POM (Jager 1978, Ramdahl et al. 1982, Gibson 1983, Tokiwa et al. 1983, Pitts et al. 1985d, Arey et al. 1986, 1987, Ramdahl et al. 1986, Sweetman et al. 1986), diesel (Schuetzle et al. 1981, 1982, Pitts et al. 1982a, Xu et al. 1981, 1982) and gasoline (Gibson 1982, 1983) exhaust particulate matter, soot from woodburning fireplaces (Gibson 1982, 1983, Nishioka et al. 1982) and coal fly ash (Hanson et al. 1983, Harris et al. 1984).

It has also been demonstrated that these nitroarenes make a significant contribution to the direct mutagenic activity of diesel POM (Nakagawa et al. 1983, Schuetzle 1983). In addition, assays of organic extracts of ambient POM, employing Ames Salmonella strain TA98, the nitroreductase deficient strain TA98NR (Rosenkranz and Poirier 1979, Rosenkranz et al. 1981) and the transacetylase-deficient strain TA98/1,8-DNP_6 (McCoy et al. 1983) have suggested that nitroarenes may also contribute significantly to the direct mutagenic activity of ambient POM (Wang et al. 1980, Pitts et al. 1982b). Interest in these nitroarenes has been heightened by the observation of an induction of rat mammary gland tumors by 1-nitropyrene (Hirose et al. 1984) and induction of sarcomas in rats by subcutaneous injection of dinitropyrenes (Ohgaki et al. 1984, 1985).

In previous CARB-funded studies we have shown that extracts of respirable ambient POM in the CSCAB are mutagenic (Pitts et al. 1977, 1982a,b,c, 1984c, Pitts 1980, 1981, 1983, Pitts and Winer 1984) and that the particulate mutagenicity levels observed are generally higher than those reported from other major urban airsheds throughout the world (Daisey et al. 1980, Flessel et al. 1981, 1983, Alfheim and Lindskog

1984). In this section we describe our measurements of the mutagenic activity of the ambient POM collected during our summer field study at Claremont and our winter field study at Torrance, and discuss the contribution of nitroarenes to the observed activity.

B. Experimental

1. Pomona College (Claremont) Sample Collection, Extraction and Mutagenicity Testing

During the September 1985 study in Claremont the SAPRC "mega-sampler" (see Figure VII-1) was used to collect ambient POM for mutagenicity testing as well as for nitroarene analysis. The "mega-sampler" was loaded with three TIGF and one GF filter (the filters, their pretreatment and the collection times have been described above in Section VI-B) for each 6-hr collection period. The most polluted 24 hr period (0600 hr Saturday, September 14, through 0600 hr on Sunday, September 15) was chosen for mutagenicity testing to complement the nitroarene analyses.

One 16 in x 20 in filter from each time period was extracted for 18 hr with CH_2Cl_2 for mutagenicity testing (the remaining two TIGF filters were used for the nitroarene analyses). All samples were transferred to dimethyl sulfoxide (DMSO) and tested for direct activity (in the absence of S9) using the Ames Salmonella plate incorporation test (Maron and Ames 1983) with the TA98, TA98NR and TA98/1,8-DNP_6 tester strains. Our modifications to improve the accuracy and precision of the test, as described by Belser et al. (1981), were employed. Strain TA98 was used because it is the most sensitive strain to atmospheric particulate mutagens while strains TA98NR and TA98/1,8-DNP_6 were used as biological indicators of nitroarene contributions to the observed mutagenicity.

Strain TA98NR is an isolate of TA98 which is deficient in the "classical" nitroreductase required to activate many mononitroarenes such as 1-nitropyrene. It has been used in conjunction with strain TA98 as a qualitative indicator of the presence of nitroaromatics in complex mixtures. Thus, a diminished response on strain TA98NR relative to that on TA98 suggests that nitroarenes are responsible for some of the observed TA98 mutagenicity. Strain TA98/1,8-DNP_6 is another isolate of TA98 which was chosen for its resistance to the killing action of 1,8-dinitropyrene, and is deficient in a transacetylase required to fully express the

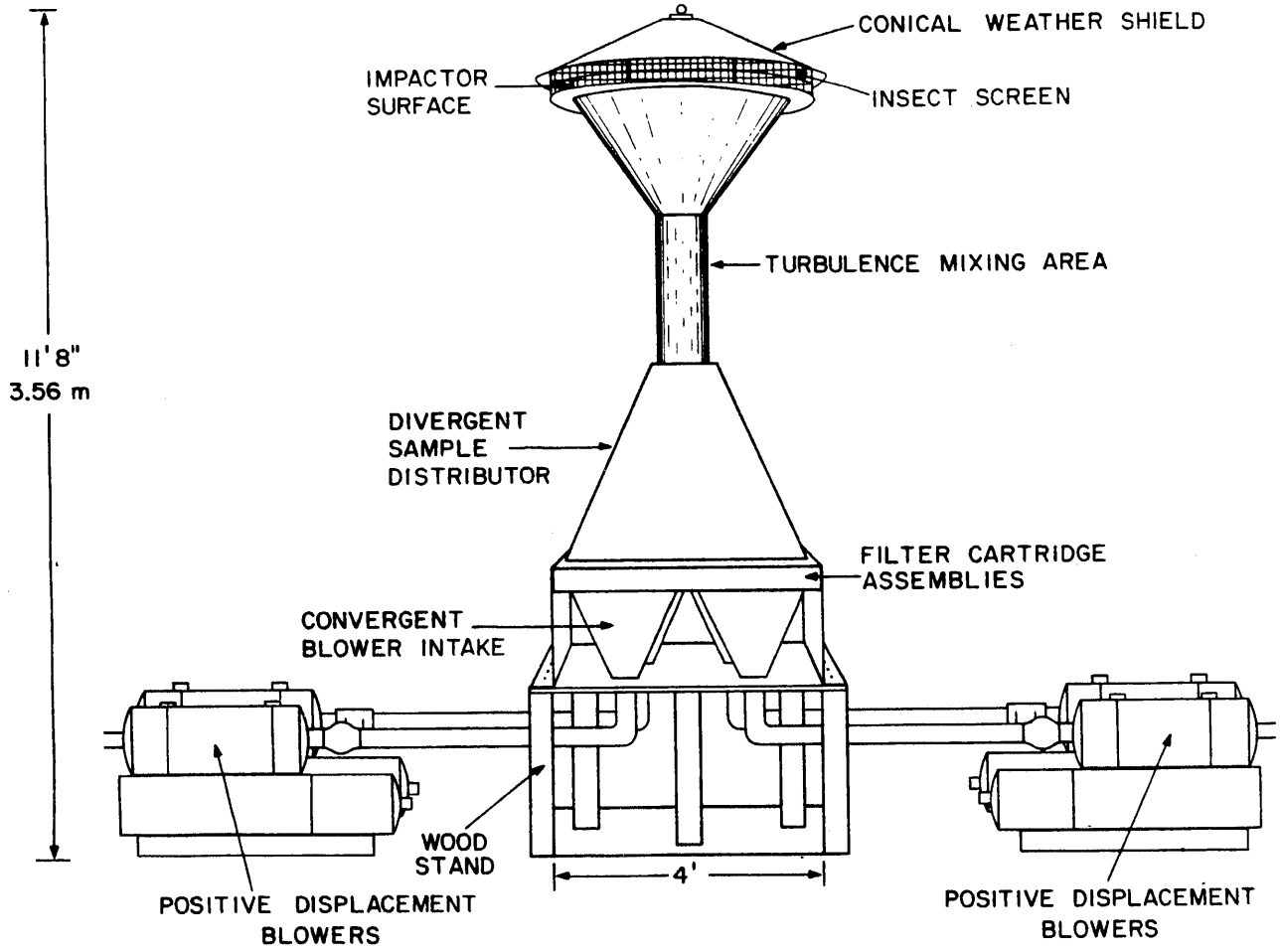

Figure VII-1. The SAPRC four-by-four high-volume mega-sampler.

activity of this potent mutagen (McCoy et al. 1983). Other nitroarenes, including many mononitroarenes, are recognized by this transacetylase as well, and thus exhibit lower mutagenicity in strain TA98/1,8-DNP$_6$ than in TA98 (see Table VII-1). Thus, although a lower response on strain TA98/1,8-DNP$_6$, relative to those of TA98NR and TA98, may indicate the presence of dinitropyrenes in a sample (Rosenkranz et al. 1981, Rosenkranz and Mermelstein 1983), when applied to ambient POM, strain TA98/1,8-DNP$_6$ must be considered as an indicator of nitroarene mutagenicity in general.

Table VII-1. Direct Mutagenicity of Standard Nitroarenes (-S9)

Chemical	M.W.	Rev μg^{-1} on Strains		
		TA98	TA98NR	TA98/ 1,8-DNP_6
2-Nitrofluorene	211	420	49	59
2-Nitrofluoranthene	247	4,200	1,000	730
3-Nitrofluoranthene	247	46,000	21,000	3,900
8-Nitrofluoranthene	247	100,000	30,000	6,000
1-Nitropyrene	247	2,300	310	1,300
2-Nitropyrene	247	16,000	1,600	2,300
1,2-Dinitrofluoranthene	292	6,200	2,600	2,500
1,3-Dinitropyrene	292	130,000	76,000	2,200
1,6-Dinitropyrene	292	420,000	410,000	180,000
1,8-Dinitropyrene	292	990,000	1,100,000	21,000
1-Nitrobenzo(a)pyrene	297	2,500	450	2,700
3-Nitrobenzo(a)pyrene	297	5,300	940	4,400
6-Nitrobenzo(a)pyrene	297	0[a]	0[a]	0[a]
1,3,6-Trinitropyrene	337	640,000	370,000	250,000
1,3,6,8-Tetranitropyrene	382	60,000	35,000	11,000

[a]6-Nitrobenzo(a)pyrene is a potent mutagen in the presence of S9 (Pitts et al. 1984d).

Cultures of the tester strains were grown for 12 hr in L-broth and diluted with sterile medium until the optical density at 550 nm reached a previously determined value corresponding to a concentration of 10^9 cells $m\ell^{-1}$. In each test, the strains were checked for the following genetic markers: (1) ampicillin sensitivity, (2) ultraviolet sensitivity, (3) crystal violet sensitivity, (4) standard spontaneous reversion and (5) mutagenic response to the standard mutagens 2-nitrofluorene, quercetin and (for strain TA98/1,8-DNP_6) 1,8-dinitropyrene.

After dilution, the cultures were kept in an ice-water bath to ensure that the culture density remained the same. Culture titers were determined directly by dilution and plating on histidine-supplemented minimal

medium. After a 63-hr incubation period, the colonies on the plates were counted with a New Brunswick Scientific Biotran II automatic colony counter directly interfaced to an Apple II microcomputer for data logging and reduction.

Eight doses were tested in triplicate and the mean of the three responses (net revertants = total revertants minus spontaneous background revertants) was used to determine the dose-response curve. Linear regression analysis was used to determine the slope of the dose-response curve in the region of linear response. This slope, or specific activity (in rev μg^{-1} of extract), was used to calculate the mutagen density (rev m^{-3}) by multiplying by the total extract weight and dividing by the volume of air sampled. Mutagen density can thus be thought of as the airborne mutagenicity "concentration." Mutagen loading, or the potency of the particulate matter (rev mg^{-1}), was calculated by multiplying the specific activity by the extract weight and dividing by the weight of the collected particulate matter.

2. El Camino Community College (Torrance) Sample Collection, Extraction and Mutagenicity Testing

For each sampling period, a single filter from a Hi-vol equipped with a 10 μm size selective inlet was Soxhlet extracted for 16 hours using CH_2Cl_2, and the resulting extract used for mutagenicity analyses. The extracts were dissolved in DMSO and tested for direct mutagenic activity at 10 doses in the range of 5 to 500 μg per plate on strains TA98, TA98NR, and TA98/1,8-DNP_6. Due to a limited amount of extract, two samples (2/24-25/86, 1800-0600 hr; 2/25/86, 0600-1800 hr) were tested only on strain TA98. The tests were performed as described above.

Table VII-1 lists the direct mutagenicities of pure nitroarene standards as determined in our laboratory, using the three TA98 strains described above. Use of these standard nitroarene mutagenicities, together with the observed ambient nitroarene concentrations (Section VI), allowed the percentage contribution of individual nitroarenes to the total mutagenicities observed at Claremont and Torrance to be calculated.

C. Results and Discussion

1. Nitroarene Mutagenicity in Ambient POM

Based upon the values for the mutagenic activity of the pure nitroarenes given in Table VII-1, the measured concentrations of these compounds in ambient POM listed in Section VI and the corresponding revertants m^{-3} of sampled air, the contributions of each of these nitroarenes to the observed activity of the ambient POM extracts have been calculated (Table VII-2). With the exception of the first nighttime sample in Torrance, the greatest contribution to the mutagenic activity in each case is that of 2-nitrofluoranthene which alone contributes up to ~5% of the observed mutagenicity.

We have observed 2-nitrofluoranthene to be the most abundant nitroarene at several locations [Riverside, Claremont, Torrance, Norway, as well as in the National Bureau of Standards, Standard Reference Materials 1648 (collected in St. Louis, MO) and 1649 (collected in Washington, D.C.)] as well as in POM collected both in summer and in winter. We have also identified 2-nitropyrene in all of the above POM samples. With the exception of a single minor industrial source (Liberti and Ciccioli 1986), 2-nitrofluoranthene and 2-nitropyrene have not been reported in emissions of primary POM and, therefore, their detection in ambient air provides evidence for the importance of atmospheric transformations of PAH to form mutagenic nitroarenes (see Section XI.C for a detailed discussion). In our Torrance POM samples, the 2-nitropyrene concentrations have been calculated to account for up to 1.4% of the direct mutagenicity of the POM extracts.

The lower contribution of 2-nitropyrene to the mutagenicity in the summer (Claremont) samples compared to the winter (Torrance) samples reflects the lower concentration of this compound in the atmosphere, which, in turn, may be related to its mechanism of formation, as discussed in Section XI.C. 1-Nitropyrene, which is present in direct particle emissions such as diesel exhaust (see, for example, Paputa-Peck et al. 1983) is a relatively minor contributor to the ambient mutagenicity (0.1-0.2%).

An interesting exception to the usual dominance of 2-nitrofluoranthene among the mononitroarene contributors to ambient POM mutagenicity was observed in the 1/27-28/86 nighttime Torrance sample. From the GC/MS-MID analysis of this sample (see Section VI), it was apparent that

Table VII-2. Contribution of Nitrofluoranthene (NF) and Nitropyrene (NP) Isomers to the Direct Mutagenicity of Ambient POM

Collection Date and Location	Collection Time (hrs)	Mutagen Density[a] rev m^{-3}	% Contribution of Nitroarenes					
			2-NF	2-NP	1-NP	8-NF	3-NF	Total
1/27-28/86 Torrance, CA	1700-0500	120	2.4 2.6[c]	0.7 0.8[c]	0.2 0.1[c]	N.Q.[b] 3.8[d]	N.Q. 2.8[d]	3.3 10
1/28/86 Torrance, CA	0500-1700	120	1.4	0.7	0.1	N.Q.	N.D.[e]	2.2
2/24-25/86 Torrance, CA	1800-0600	35[f]	3.8	1.4	0.2	N.D.	N.D.	5.4
2/25/86 Torrance, CA	0600-1800	73	1.6	0.9	0.1	N.D.	N.D.	2.6
9/14/85 Claremont, CA	0600-1200	35	1.0	0.1	0.2	N.Q.	N.D.	1.3
9/14/85 Claremont, CA	1200-1800	15	0.8	0.1	0.2	N.D.	N.D.	1.1
9/14/85 Claremont, CA	1800-2400	40	5.2	0.2	0.2	N.Q.	N.Q.	5.6
9/15/85 Claremont, CA	0000-0600	20	2.1	0.2	0.1	N.Q.	N.Q.	2.4

[a]Tested on TA98, -S9; CH_2Cl_2, extracts of POM collected on TIGF filters.
[b]N.Q. = Trace amounts detected, but not quantified.
[c]Replicate quantification using 60 m GC column (see Section VI).
[d]Additional quantification after standard compounds were purified.
[e]N.D. = None detected.
[f]Average of two six-hour samples.

8-nitrofluoranthene and 3-nitrofluoranthene were present in amounts comparable to 1- and 2-nitropyrene, and this sample was therefore reanalyzed to allow these nitrofluoranthenes to be quantified. Although these two nitroarenes were less abundant than 2-nitrofluoranthene, because of their potent mutagenicities (Table VII-1) 3- and 8-nitrofluoranthene contributed more to the ambient POM activity than did 2-nitrofluoranthene (Table VII-2). As with 2-nitrofluoranthene, 8-nitrofluoranthene is thought to be formed primarily in the atmosphere, rather than being directly emitted (see Section XI.C). Thus, at least in the South Coast Air Basin, a substantial portion of ambient particulate mutagenicity (up to 10%) can be accounted for by a relatively few highly mutagenic nitroarenes which are largely atmospheric reaction products, rather than directly-emitted species.

Table VII-3 lists several other nitroarenes which were detected in the Torrance ambient air samples, together with their direct mutagenicities towards strain TA98 taken from the existing literature. Because of their higher volatilities, 1-nitronaphthalene, 2-nitronaphthalene, and 3-nitrobiphenyl were present almost entirely in the gas phase during sampling and were detected primarily on the backup PUF plugs (Section VI). Although they are present in ambient air at concentrations greater than 2-nitrofluoranthene, they contribute little to the total inhalable mutagenicity because of their low activities. Similarly, 9-nitroanthracene, a particulate nitroarene, was detected in substantial amounts, but it, too, is a weak mutagen and does not contribute significantly. 7-Nitrofluoranthene, which is reportedly only a moderately mutagenic compound, was detected only in trace quantities, and is not thought to be an important contributor.

Although 4-nitropyrene was not quantified, it can be estimated from the relative m/z 247 ion response to be approximately an order of magnitude less abundant than 1-nitropyrene, and, thus would contribute only slightly to the observed Salmonella mutagenicity. However, 4-nitropyrene is a potent tumorigen in the newborn mouse assay (Wisocki et al. 1986) and its detection in ambient air is of major relevance in the evaluation of the human health risks of atmospheric nitroarenes.

Table VII-3. The Mutagenicity of Other Nitroarenes Detected in Ambient Air in Torrance, CA

Compound	M.W.	Mutagenicity (rev μg^{-1} TA98,-S9)	Reference
1-Nitronaphthalene	173	1.7	El-Bayoumy et al. (1981)
2-Nitronaphthalene	173	2.3	El Bayoumy et al. (1981)
3-Nitrobiphenyl	199	0	El Bayoumy et. al. (1981)
9-Nitroanthracene	223	0.30	Pitts et al. (1982a)
7-Nitrofluoranthene	247	190	Vance and Levin (1984)
4-Nitropyrene	247	10,000	Fu et al. (1985)

2. Ambient Mutagenicity of Dichloromethane Extracts on Strains TA98NR and TA98/1,8-DNP_6

The specific activities (rev μg^{-1}) for six time periods, for which nitroarene analyses were also conducted, were tested on strains TA98NR and TA98/1,8-DNP_6 as well as on TA98 and the results are given in Table VII-4. Both the nitroreductase-deficient strain TA98NR and the transacetylase-deficient strain TA98/1,8-DNP_6 exhibited lower mutagenic response than did TA98, consistent with a contribution of nitroarenes to the TA98 direct mutagenicity. The relative response of TA98NR to TA98 ranged from 0.38 to 0.62 and that of TA98/1,8-DNP_6 to TA98 from 0.08 to 0.18, values which are typical of ambient POM sampled in previous studies in the South Coast Air Basin (Pitts et al. 1984c, Pitts and Winer 1984).

From the standard mutagenicity values for 2-, 3-, and 8-nitrofluoranthene and 1- and 2-nitropyrene given in Table VII-1, the contribution of these nitroarenes to the lower response on TA98NR and TA98/1,8-DNP_6 was calculated and is shown in Table VII-5. As seen from this table, the contribution of the measured nitroarenes to the diminished response on TA98NR is proportionately greater than their contribution to the TA98 activity. In contrast, their contribution to the diminished response on TA98/1,8-DNP_6 is no greater than their contribution to the TA98 activity. These observations are generally consistent with our current knowledge of strains TA98NR and TA98/1,8-DNP_6 in that: (1) TA98NR is a better

Table VII-4. Mutagenicities of Dichloromethane Extracts of Ambient Particulate Matter Collected at Claremont and Torrance, CA

Collection Date and Location	Collection Period (hr)	Specific Activity (rev μg^{-1} extract)			Relative Response	
		TA98	TA98NR	TA98/1,8-DNP_6	TA98NR / TA98	TA98/1,8-DNP_6 / TA98
1/27-28/86 Torrance, CA	1700-0500	4.7	2.6	0.81	0.55	0.17
1/28/86 Torrance, CA	0500-1700	5.3	3.3	0.98	0.62	0.18
9/14/85 Claremont, CA	0600-1200	1.9	0.89	0.23	0.47	0.12
9/14/85 Claremont, CA	1200-1800	0.98	0.37	0.079	0.38	0.081
9/14/85 Claremont, CA	1800-2400	3.4	1.8	0.48	0.53	0.14
9/15/85 Claremont, CA	0000-0600	1.6	0.83	0.20	0.52	0.13

Table VII-5. Contributions of Measured Nitrofluoranthenes and Nitropyrenes to the Reduced Response on Strains TA98NR and TA98/1,8-DNP_6 at Claremont and Torrance, CA

Collection Date and Location	Collection Period (hr)	% Contribution to TA98 Activity[a]	% Contribution to the Reduced Response on TA98NR	% Contribution to the Reduced Response on TA98/1,8-DNP_6
1/27-28/86 Torrance, Ca	1700-0500	10	15	10
1/28/86 Torrance, CA	0500-1700	2.2	4.7	2.2
9/14/85 Claremont, CA	0600-1200	1.3	1.9	1.1
9/14/85 Claremont, CA	1200-1800	1.1	1.4	0.9
9/14/85 Claremont, CA	1800-2400	5.6	9.2	5.3
9/15/85 Claremont, CA	0000-0600	2.4	4.1	2.2

[a]From Table VII-2.

indicator of mononitroarenes than is TA98/1,8-DNP_6, and (2) the diminished response on TA98/1,8-DNP_6 is due to nitroarenes (such as the dinitropyrenes) which depend more heavily on the transacetylase for activation than do the nitroarenes quantified here. Since we did not measure any dinitropyrenes in these samples, their contribution to the mutagenicity of ambient POM or to the diminished response on TA98/1,8-DNP_6 cannot be estimated. Additionally, as yet largely unidentified polar mutagens are suspected to contribute significantly to ambient POM mutagenicity (Pitts et al. 1984c). Many of these polar mutagens in ambient POM may be nitro-substituted, for example, hydroxynitroarenes (Greenberg 1985, Nishioka et al. 1986, Gibson 1986, Gibson et al. 1986), and these compounds may contribute to the lower responses observed in strains TA98NR and TA98/1,8-DNP_6.

3. General Observations on Ambient Particulate Mutagenicity

As reported in Tables VII-2 and VII-4, the mutagenicity of the POM samples collected in Claremont over 6-hr time intervals showed a distinct variation over the four time periods studied. Figure VII-2 shows the diurnal variation of mutagenicity, in revertants mg^{-1} of particulate matter, towards Salmonella strain TA98. This diurnal variation is similar to other reported studies (Pitts et al. 1982b, 1985f), with the lowest mutagenicity being observed in the 1200-1800 hr time period. The sums of the concentrations of the three nitroarenes quantified are also given in Figure VII-2 for the different time periods, and they show a diurnal variation which is similar to the mutagenicity values. The same is also true for the NO_2 concentrations measured at the sampling site. This diurnal variation is not seen for the concentration of the particulate matter, suggesting that a different air mass with more mutagenic particles moved into the sampling site in the afternoon. Another possibility is that mutagenic compounds including 2-nitrofluoranthene are formed close to the sampling site by reaction with co-pollutants, and then sampled at the site in the following hours. Indeed, NO_3 radicals were observed during this sampling interval and thus it is possible that the formation of 2-nitrofluoranthene from the reaction of N_2O_5 with fluoranthene occurred, as discussed in Section XI.C.

The characteristic midday minima in mutagenicity may be due, in part, to greater atmospheric dispersion during the early afternoon. However,

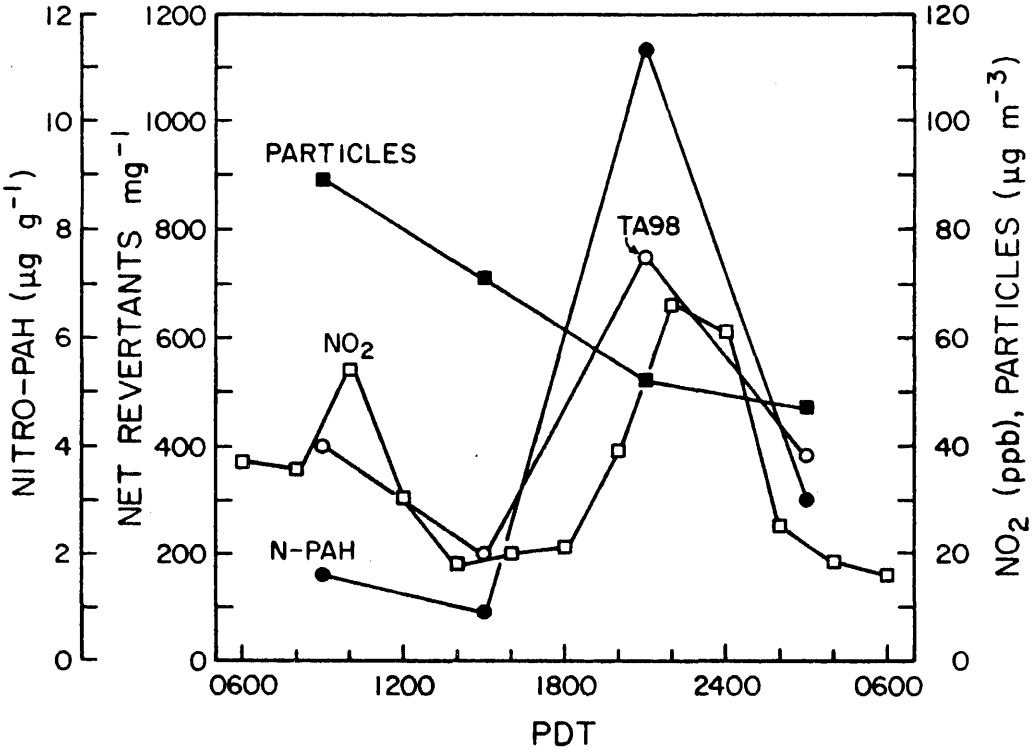

Figure VII-2. Diurnal variations of the collected particulate matter (μg m^{-3}), nitrogen dioxide concentration (ppb), nitro-PAH (N-PAH) concentration (sum of 2-NF, 1-NP and 2-NP, μg g^{-1} particulate matter) and direct mutagenicity (TA98, revertants mg^{-1} particulate matter) for September 14-15, 1985, at Claremont, CA.

the ratios of the responses of TA98NR and TA98/1,8-DNP_6 to TA98 were lower during the afternoon sampling interval than during the other three time periods (Table VII-4). This suggests that there was also a qualitative difference in the POM collected during this time period. Because this was the hottest time of day, increased volatilization of particle-adsorbed mutagens during sampling, or decreased condensation of vapor phase mutagens in the atmosphere, may have contributed to the decreased mutagenicity observed during this time period. Additionally, photolysis of mutagens or their reaction with ozone may have lead to lower activities. It should be noted that these data are for CH_2Cl_2 extracts, and are thus not subject to any of the possible extraction artifacts observed with acetonitrile (see Section IX).

Mutagen densities, mutagen loadings, and specific activities for the winter collection period in Torrance are shown in Figure VII-3, and were again determined from the CH_2Cl_2 extracts. Again, these values show considerable variation but are within the range of values we have previously observed, although they are generally higher than those observed in Claremont.

As can be seen in Figure VII-3, the atmospheric mutagen density correlates with the specific activity (extract potency) but not with mutagen loading (particulate potency). This may be because the particulate matter has variable amounts of inorganic, non-extractable material, which does not contribute to mutagenic activity. For example, on February 23 from 1800-2400 hr, the mutagen loading was very high while the mutagen density was low, indicating that a low concentration of highly potent particulate matter was present at the site. In contrast, the two collections with the highest mutagen densities (January 27-28, 1700-0500 hr and January 28, 0500-1700 hr) also had the highest mutagen loadings, the highest specific activities, and (not shown) the highest particulate concentrations. This suggests that stagnant atmospheric conditions, which produce high particulate concentrations, may also favor the formation of mutagens, resulting in higher mutagen loadings and specific activities.

Additionally, as we have observed previously, there is substantial intra-day and inter-day variation in mutagen density. Because of this wide short-term variation in mutagen density, an evaluation of the long-term trends in atmospheric mutagenicity in Southern California remains elusive. Since in the studies carried out to date, experimental parameters such as sampling time, sampling duration, extraction method and solvent were chosen with the specific research goals of each study in mind, the resulting ambient mutgenicity data are not strictly comparable. [For example, some of the past mutagenicity determinations were made on POM obtained by Soxhlet extraction using acetonitrile, a procedure which we have found can yield anomalously high values (see Section IX).] Consequently, determining the long-term trends in airborne particulate mutagenicity, in the presence of substantial short-term variations, will require a great number of observations using a standardized low-cost sampling, extraction, and testing protocol.

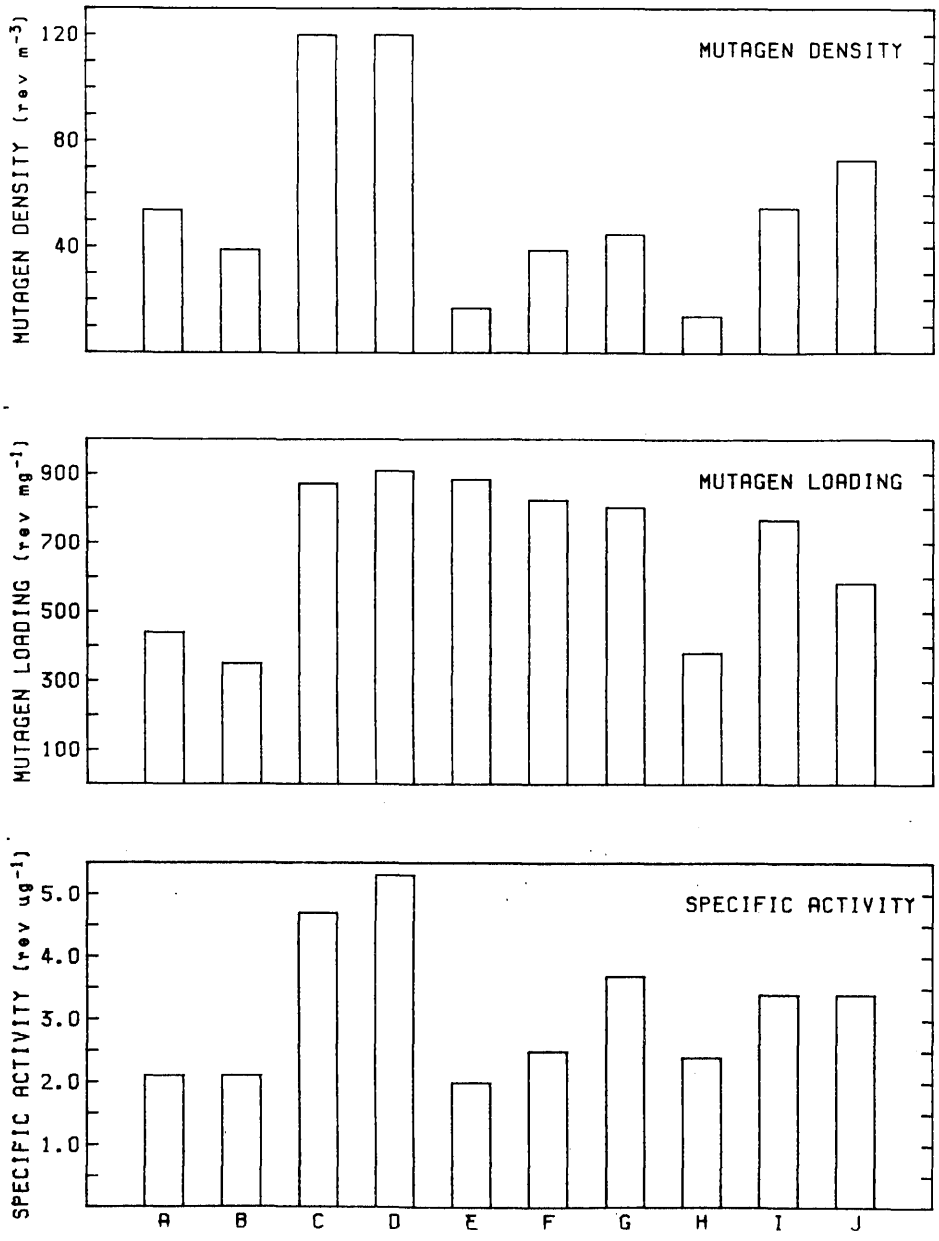

Figure VII-3. Mutagen density, mutagen loading, and specific activity, January and February 1986, Torrance, CA. A: 1/21, 0000-0700 hr; B: 1/21, 0700-1700 hr; C: 1/27-28, 1700-0500 hr; D: 1/28, 0500-1700 hr; E: 2/23, 1800-2400 hr; F: 2/24, 0000-0600 hr; G: 2/24, 0600-1800 hr; H: 2/24, 1800-2400 hr; I: 2/25, 0000-0600 hr; J:, 2/25 0600-1800 hr.

VIII. INVESTIGATION OF NITROARENE FORMATION IN THE ADSORBED PHASE DURING TRANSPORT AND SAMPLING

A. Introduction

The formation of nitroarenes from exposure of the parent PAH, adsorbed on glass fiber filters, to flows of NO_2 containing traces of HNO_3 was first reported by Pitts and co-workers (Pitts et al. 1978), and the as potential for nitroarene production during atmospheric transport as well as during Hi-vol sampling of ambient particulate organic matter (POM) was discussed (Pitts et al. 1978, Pitts 1979). Since then, a number of laboratory studies have been carried out to investigate the formation of nitroarenes from adsorbed PAH exposed to flows of NO_2 and NO_2/HNO_3 (Hughes et al. 1980, Jäger et al. 1980; Butler and Crossley 1981, Tokiwa et al. 1981, Brorström et al. 1983, Grosjean et al. 1983, Pitts 1983, Ramdahl et al. 1984, Yokley et al. 1985). The yields of the nitroarene products were observed to depend upon the specific PAH studied, the substrate on which the PAH was adsorbed, the NO_2 concentration, and the presence or absence of HNO_3 in the exposure. The relative reactivities of the PAH, and the specific nitroarene isomers formed, followed predictions for electrophilic nitration (Dewar et al. 1956, Streitwieser and Fahey 1962, Nielsen 1984).

Several studies of the conversion of PAH to nitroarenes during filter collection of diesel POM in dilution tunnels have been carried out (Gibson et al. 1981, Bradow 1982, Schuetzle 1983, Schuetzle and Perez 1983). It has been estimated that the chemical conversion of pyrene to 1-nitropyrene, a major nitroarene observed in diesel POM during sampling, could account for between 10-20% of the observed 1-nitropyrene (Schuetzle 1983).

Studies of the conversion of PAH to nitroarenes during conditions designed to represent those of ambient POM collection on filters have produced varying results. Grosjean and co-workers (Grosjean et al. 1983) reported no conversion of benzo(a)pyrene or perylene to their nitro-derivatives when these PAH were deposited on filters and ambient particles and exposed to 100 ppb of nitric acid-free NO_2 for 3 hr. Brorström and co-workers, however, reported that the addition of 1 ppm of NO_2 during Hi-vol sampling of ambient air caused degradation of pyrene, benz(a)anthracene and benzo(a)pyrene, and suggested that this was due to nitration reactions (Brorström et al. 1983).

In addition to being present in particles emitted from diesel- (Schuetzle et al. 1982, Paputa-Peck et al. 1983, Robbat et al. 1986b) and gasoline-fueled vehicles (Gibson 1982, Nishioka et al. 1982) and coal-fired power plants (Harris et al. 1984), 1-nitropyrene has also been identified in ambient POM (Ramdahl et al. 1982, Nielsen 1983, Nielsen et al. 1984, Pitts et al. 1985d, Sweetman et al. 1986, Ramdahl et al. 1986, Arey et al. 1986, 1987). The relative contributions of direct emissions versus nitration of pyrene during atmospheric transport or during sampling to the observed levels of 1-nitropyrene in collected ambient POM have not been established. Recently, 2-nitrofluoranthene and 2-nitropyrene have been identified as among the most abundant nitroarenes in ambient POM (Pitts et al. 1985d, Arey et al. 1986, 1987, Nielsen and Ramdahl 1986, Ramdahl et al. 1986, Sweetman et al. 1986). Since these two nitroarene isomers are not produced in electrophilic nitration reactions of fluoranthene and pyrene (Dewar et al. 1956, Streitwieser and Fahey 1962) [in contrast to 1-nitropyrene], they are unlikely to result from transformations occurring during the Hi-vol collection of POM. Indeed, 2-nitrofluoranthene and 2-nitropyrene have been observed in POM collected by electrostatic precipitation and bag-house collection (Sweetman et al. 1986, Ramdahl et al. 1986), as well as by Hi-vol sampling.

One goal of the work described here was to directly evaluate the significance of any formation of nitroarenes during actual Hi-vol sampling conditions. Hi-vol POM collections onto filters loaded with previously-collected POM and doped with deuterated PAH were conducted during a high-NO_x pollution episode at our winter field study site at El Camino Community College in Torrance, CA. The reactions of perdeuterated fluoranthene (FL-d_{10}) and pyrene (PY-d_{10}) were investigated since, as discussed above, 2-nitrofluoranthene and 1- and 2- nitropyrene are among the major nitroarenes present in ambient POM. Additionally, perdeuterated benzo(a)pyrene (BaP-d_{12}) and perylene (PER-d_{12}) were utilized since these PAH are highly reactive towards electrophilic nitration (Dewar et al. 1956, Nielsen 1984) and 6-nitrobenzo(a)pyrene has been reported in diesel emissions (Gibson 1982, Pitts et al. 1982a) and in ambient POM (Jäger 1978, Gibson 1982).

In addition to evaluating the potential for artifactual formation of nitroarenes during Hi-vol sampling, we sought to investigate the extent of

their formation during atmospheric transport resulting from, for example, particle-adsorbed PAH reacting with ambient light and pollutant gases. Thus, we examined the formation of deuterated nitroarenes from their parent PAH (coated onto pre-collected POM as well as onto TIGF and GF filters) during "passive" ambient exposure conditions. These "passive" exposure experiments were carried out at Torrance during one of the January sampling periods and repeated at Riverside in late August, 1986. The results from these passive (simulating atmospheric transport) and active (during Hi-vol sampling) exposures are given below.

From the measurements of the ambient profiles of nitroarenes carried out in this study (described above in Section VI) and in conjunction with laboratory studies conducted under U.S. DOE and U.S. EPA funding, it is now apparent that gas-phase atmospheric transformation of PAH to their nitro-derivatives is an important process contributing to the overall nitroarene profiles observed in ambient POM extracts. The implications of these three nitroarene formation pathways, i.e., artifactual formation during collection, and in the adsorbed- and gas-phases during atmospheric transport, are discussed in Section XI.C.

B. Experimental

1. Active Exposures of Deuterated PAH at El Camino Community College (Torrance)

Particulate matter used for the exposures was collected in Riverside with the "mega-sampler" which samples at a rate equivalent to 16 standard Hi-vol samplers (Fitz et al. 1983). Both Gelman A/E GF filters and Pallflex T60A20 TIGF filters were used, and the POM-laden filters were cut into quarters for further exposure to ambient air. Prior to the exposures the filters were doped with the deuterated PAH in pairs, each pair having a more volatile PAH (m.w. 212) and a less volatile PAH (m.w. 264). To dope the filters, 3 mℓ of a solution of either FL-d_{10} and BaP-d_{12} or of PY-d_{10} and PER-d_{12} in toluene was applied dropwise to the filter and the toluene allowed to dry. The filters were then stored in a freezer until used.

The exposures were made in Hi-vol samplers equipped with three PUF plugs located downstream from the filters and operated at somewhat reduced flow rates (~30 SCFM). The details of the sampling protocol are given in Table VIII-1.

Table VIII-1. Sampling Protocol for "Active" Exposure of Deuterated PAH January 27-28, 1986, at El Camino Community College, Torrance, CA

Date	Sampling/ Exposure Period	Deuterated PAH Added[a]	Precollected POM		Hi-vol No.[b]	Flow Rate[c] (SCFM)
			Date	Filter Type		
1/27/86	1700-2400	PY & PER	6/18/85	GF	1	27
	1700-2400	PY & PER	6/19/85	TIGF	15	26
	1700-2400	FL & BaP	6/18/85	GF	2	29
	1700-2400	FL & BaP	6/19/85	TIGF	12	26
1/28/86	0000-0700	PY & PER	6/18/85	GF	1	27
	0000-0700	PY & PER	6/19/85	TIGF	15	26
	0000-0700	FL & BaP	6/18/85	GF	2	29
	0000-0700	FL & BaP	6/19/85	TIGF	12	26
1/28/86	0700-1700	PY & PER	6/18/85	GF	1	27
	0700-1700	PY & PER	6/19/85	TIGF	15	26
	0700-1700	FL & BaP	6/18/85	GF	2	29
	0700-1700	FL & BaP	6/19/85	TIGF	12	26

[a]PY & PER = 1.0 mg PY-d_{10} and 1.0 mg PER-d_{12}. FL & BaP = 1.0 mg FL-d_{10} and 1.0 mg BaP-d_{12}.
[b]All Hi-vols were modified to hold 3 PUF plugs in the airstream below the filter.
[c]Estimated variation in flows ±10% of indicated values.

Mass Balance of Deuterated PAH. The filters and each of the three PUF plugs were separately Soxhlet extracted in CH_2Cl_2. The deuterated PAH present in each PUF plug and filter CH_2Cl_2 extract were quantified by HPLC with detection at 254 nm using a Beckman Model 334 HPLC equipped with a Beckman Model 164 uv/vis detector. Triphenylbenzene was utilized as an internal standard and the assumption was made that since one mg of the deuterated PAH was spiked onto the filter, interferences from the other components present in the POM at much lower levels would be minimal. For

the quantification of FL-d_{10} and BaP-d_{12}, an Altex Ultrasphere ODS column (4.6 mm x 25 cm) was used with CH_3CN/H_2O elution at 2 mℓ min^{-1} and the following solvent program: CH_3CN/H_2O (85%/15%) for 5 min then linearly programmed to 100% CH_3CN over 5 min, held at 100% CH_3CN for 2 min followed by re-equilibration to the starting composition. For the PY-d_{10} and PER-d_{12} quantifications the column employed was a Vydac PAH column (4.5 mm x 15 cm) with CH_3CN/H_2O elution at 1.5 mℓ min^{-1} as follows: CH_3CN/H_2O (50%/50%) for 5 min then a linear gradient to 90% CH_3CN over 5 min, and held at this composition for 6 min prior to re-equilibration.

Analysis for Nitroarenes. The filter CH_2Cl_2 extracts and 80% of the extracts from the first PUF plug under each filter were fractionated by HPLC using a Spectra-Physics Model 8100 HPLC with a Model 8400 uv/vis detector, Model 4100 computing integrator and an ISCO fraction collector. A preliminary fractionation was made on an Altex semi-preparative scale Ultrasphere ODS column (1 cm x 25 cm) employing the following mobile phase program at 3 mℓ min^{-1}: CH_3OH/H_2O (80%/20%) for 5 min, then a linear gradient to 100% CH_3OH over 5 min, and held at 100% CH_3OH for 10 min. The fraction eluting between 12 and 15 min contained the nitroarenes of interest and was further fractionated using an Altex semi-preparative Ultrasphere Si column (1 cm x 25 cm). The mobile phase program, at a flow rate of 3 mℓ min^{-1} consisted of: n-hexane/CH_2Cl_2 (90%/10%) for 5 min, then a linear gradient to n-hexane/CH_2Cl_2 (60%/40%) over 10 min, held at this composition for 10 min. The fractions eluting between 14 and 30 min were collected.

These HPLC fractions from the filter extracts containing the deuterated nitroarenes were then analyzed by GC/MS using multiple ion detection (MID). For these analyses a Finnigan 3200 GC/MS interfaced to a Teknivent data system and equipped with a cool on-column injector and a 30-m DB-5 capillary column (both from J&W Scientific, Inc.) eluting directly into the ion source was operated in the electron impact mode (70 eV). 1-Nitropyrene-d_9, 6-nitrobenzo(a)pyrene-d_{11} and 3-nitroperylene-d_{11} were quantified on the basis of external calibrations with standard solutions. To determine if deuterated nitrofluoranthene or nitropyrene was present on the PUF plugs beneath the filters, the three exposure time periods were composited prior to GC/MS-MID analyses.

2. Passive Exposures at Torrance and Riverside

Exposure Protocols. The pre-collections of POM onto GF and TIGF filters and their doping with deuterated PAH were as described above for the active exposures (Section B.1.) The "passive" exposures consisted of simply suspending the filters from a line, and thus exposing them to both ambient radiation and pollutant gases. The passive exposures at Torrance paralleled the active exposures described above. As with the active exposures, both POM-coated GF and TIGF filters doped with the deuterated PAH in pairs were exposed on January 27-28, 1986, as detailed in Table VIII-1. In addition, clean GF and TIGF filters coated with fluoranthene and pyrene were exposed for the same three exposure intervals.

The exposures at Riverside consisted of day and night exposures as follows: a 0615-1915 hr daytime exposure on August 25, 1986; a 1924-0615 hr nighttime exposure on August 25-26, 1986 and a 0615-1920 hr daytime exposure on August 27, 1986. For this study only deuterated fluoranthene (0.5 μg $filter^{-1}$) and pyrene (0.5 μg $filter^{-1}$) were coated onto separate POM-laden TIGF filters, as well as onto clean TIGF and GF filters.

Recoveries of Passively Exposed PAH and Deuterated PAH at Torrance. An aliquot of each filter extract (as above, all filters were Soxhlet extracted overnight with CH_2Cl_2) was spiked with triphenylbenzene and the exposed PAH or deuterated PAH were quantified by HPLC. The HPLC programs for the quantification of the deuterated PAH were as given above for the active exposures at Torrance. The recoveries of the fluoranthene and pyrene which were separately exposed on clean TIGF and GF filters were also quantified using the Ultrasphere ODS column, but in this case elution was isocratic with acetonitrile/water (85%/15%) at 2 $m\ell$ min^{-1}.

Analysis of Nitroarenes. The filter extracts were fractionated by HPLC prior to GC/MS-MID analyses for the nitroarenes. These fractionations were conducted to remove the large amounts of the PAH or deuterated PAH spikes as well as interfering components present on the filters coated with precollected POM.

All of the passively exposed filters from the Torrance study were fractionated first by reverse phase HPLC using an Ultrasphere ODS column (1 cm x 25 cm) and the following mobile phase program: methanol/water (80%/20%) for 5 min, then programmed linearly to 100% methanol over 10 min and held at 100% methanol for 10 min. The extracts of the filters with

precollected POM were further fractionated by normal phase chromatography on an Ultrasphere Si column (1 cm x 25 cm) employing the following mobile phase program: n-hexane/CH_2Cl_2 (90%/10%) for 5 min, then programmed over 10 min to n-hexane/CH_2Cl_2 (60%/40%), held at this composition for 10 min then re-equilibrated to the starting composition over 5 min.

The passively exposed filters from the Riverside study were first fractionated by normal phase HPLC on the Ultrasphere Si column with the following solvent program: n-hexane/CH_2Cl_2 (95%/5%) for 10 min, then a linear gradient to 100% CH_2Cl_2 over 15 min, held at this composition for 10 min, then a linear gradient to 100% CH_3CN over 10 min. The fractions containing the nitrofluoranthenes and nitropyrenes (and their deuterated analogs) from the POM-coated filters were further fractionated by reverse phase HPLC on the Ultrasphere ODS column with methanol/water elution at 80%/20%.

The GC/MS-MID analyses for the nitroarenes were as described above for the active exposures, except that for analysis of the Riverside passive exposures a 60 m DB-5 column was employed for maximum resolution of the nitrofluoranthene and nitropyrene isomers (see Section VI).

C. Results

1. Active Exposures of Deuterated PAH at Torrance

Mass balance of deuterated PAH. The recovery of the more volatile PAH exposed, i.e., FL-d_{10} and PY-d_{10}, in terms of the percent of these PAH remaining on the filters after the Hi-vol sampling and the percent of these PAH found on each of the PUF plugs under the filters are given in Tables VIII-2 and VIII-3 (the PUF plug located first in the airstream below the filter is labeled PUF plug #1, with PUF plugs #2 and #3 being in series beneath PUF plug #1). It can be seen from these tables that, under the sampling conditions employed (i.e., ~10 hrs sampling at ~30 SCFM and <30°C), two PUF plugs were adequate to collect all of the FL-d_{10} and PY-d_{10} "blown-off" the filters during sampling. This is consistent with our ambient data for fluoranthene and pyrene reported above (Tables VI-4 and VI-5).

The total recoveries of FL-d_{10} (Table VIII-2), i.e., the sum of the FL-d_{10} remaining on the filters plus the amounts collected on the PUF plugs, were 100 percent, within the error caused by additional,

Table VIII-2. Recovery of FL-d_{10} in "Active" Exposures on Filters with Pre-Collected POM During the Torrance Winter Field Study

Date	Time (hr)	Filter[a] Type	% FL-d_{10} PUF #1	PUF #2	PUF #3	Filter	Total[b] Recovery (%)
1/27/86	1700-2400	GF	78	4	0	23	105
	1700-2400	TIGF	82	2	0	21	105
1/28/86	0000-0700	GF	72	2	0	31	105
	0000-0700	TIGF	76	0	0	26	102
	0700-1700	GF	88	2	0	15	105
	0700-1700	TIGF	99	2	0	10	111

[a]FL-d_{10} was spiked onto filters loaded with pre-collected POM (see Table VIII-1).
[b]Recovery determined relative to an unexposed doped filter.

Table VIII-3. Recovery of PY-d_{10} in "Active" Exposures on Filters with Pre-Collected POM During the Torrance Winter Field Study

Date	Time (hr)	Filter[a] Type	% PY-d_{10} PUF #1	PUF #2	PUF #3	Filter	Total[b] Recovery (%)
1/27/86	1700-2400	GF	57	0	0	35	92
	1700-2400	TIGF	58	0.2	0	35	93
1/28/86	0000-0700	GF	62	0.2	0	38	100
	0000-0700	TIGF	35	0	0	56	91
	0700-1700	GF	64	2	0	28	94
	0700-1700	TIGF	57	1	0	28	86

[a]PY-d_{10} was spiked onto filters loaded with pre-collected POM (see Table VIII-1).
[b]Recovery determined relative to an unexposed doped filter.

nonresolved components present in the POM extracts. As can be seen from Table VIII-3, the recoveries of PY-d_{10} were also high, $\gtrsim$90% for all sampling periods. Thus the amount of reaction of FL-d_{10} or PY-d_{10} during sampling was small. The extracts were examined, however, for the presence of nitrofluoranthene-d_9 or nitropyrene-d_9 reaction products, and the results are given below.

As expected for the less volatile PAH BaP-d_{12} and PER-d_{12}, no blow-off from the filters was observed, i.e., less than one percent of BaP-d_{12} or PER-d_{12} was present on the first PUF plug. Table VIII-4 lists the recovery of these PAH after the Hi-vol exposure and also the recovery from an unexposed TIGF filter. Whereas recovery of fluoranthene and pyrene after spiking onto an unexposed filter was always good, benzo(a)pyrene (BaP) and perylene recoveries were often (as shown in Table VIII-4) 80% or less, even from unexposed filters. It appears that reaction of BaP-d_{12} occurred during the daytime (0700-1700 hr) exposure period, although the reaction of BaP-d_{12} during other time periods as well as reaction of PER-d_{12} cannot be excluded based upon the observed recoveries. Reaction of

Table VIII-4. Recovery of BaP-d_{12} and PER-d_{12} in "Active" Exposures on Filters with Pre-Collected POM in the Torrance Winter Field Study

Date	Time (hr)	Filter Type[a]	% PAH Recovered from Filter	
			BaP-d_{12}	PER-d_{12}
Not exposed		TIGF	84	65
1/27/86	1700-2400	GF	77	69
	1700-2400	TIGF	87	69
1/28/86	0000-0700	GF	86	69
	0000-0700	TIGF	84	71
	0700-1700	GF	55	66
	0700-1700	TIGF	48	66

[a]BaP-d_{12} and PER-d_{12} were spiked onto separate POM-laden filters (see Table VIII-1).

$BaP\text{-}d_{12}$ during the daytime sample would be consistent with the known reaction of adsorbed BaP with ozone (Pitts et al. 1986), since a maximum of 48 ppb of ozone was recorded at Torrance on January 28 (see Appendix C). The formation of nitration products from $BaP\text{-}d_{12}$ and $PER\text{-}d_{12}$ during these active exposures is discussed in the following section.

Artifactual Formation of Nitroarenes During Hi-vol Sampling. HPLC separation was used to remove the relatively large amount of the parent deuterated PAH remaining on the filters, as well as polar compounds present in the POM, by collecting a narrow fraction in which each deuterated nitroarene would elute. These fractions were then analyzed by GC/MS-MID. Any deuterated nitroarenes present would, of course, have been formed artifactually during the Hi-vol sampling, by reaction of the deuterated parent PAH (spiked onto the filter) with pollutant gases such as NO_2/HNO_3 present in the ambient air sampled.

Table VIII-5 lists the quantities of deuterated nitroarenes observed. The reaction of fluoranthene with 10 ppm of NO_2 has been reported to produce 3-nitrofluoranthene and 8-nitrofluoranthene (Tokiwa et al. 1981),

Table VIII-5. Deuterated Nitroarenes Formed Artifactually During Hi-vol Sampling[a]

Date	Time (hr)	Filter type	Nitroarenes (ng)			
			NO_2-FL-d_9	1-NO_2-PY-d_9	6-NO_2-BaP-d_{11}	3-NO_2-PER-d_{11}
1/27/86	1700-2400	GF	n.d.[b]	n.d.	100	200
	1700-2400	TIGF	n.d.	40	40	40
1/28/86	0000-0700	GF	n.d.	n.d.	200	1,000
	0000-0700	TIGF	n.d.	n.d.	<30	60
	0700-1700	GF	n.d.	n.d.	90	300
	0700-1700	TIGF	n.d.	<40	200	200

[a]The details of the initial POM collections and the spiking with deuterated PAH are given in Table VIII-1.
[b]n.d. = none detected.

the isomers expected as electrophilic nitration products of fluoranthene (Kloetzel et al. 1956). As seen from Table VIII-5, no nitrofluoranthene-d_9 was observed in the extracts from the filters which had been doped with 1 mg of FL-d_{10}. Furthermore, no nitrofluoranthene-d_9 was observed in the composited extracts of the PUF #1 plugs, although 70% or more of the FL-d_{10} was present on these PUF plugs. Thus, there was no artifactual formation of nitrofluoranthene during Hi-vol collection of POM during a high-NO_x pollution episode (see Appendix C and Sections IV and V for data concerning gaseous nitrogenous species at Torrance). Furthermore, as mentioned above, the nitrofluoranthene isomer we have consistently observed in highest quantities in collected ambient POM is 2-nitrofluoranthene (see Section VI) rather than 3-nitrofluoranthene.

The greatest amount of artifactually formed deuterated nitroarene was 1 μg of 3-nitroperylene-d_{11}, corresponding to 0.1% reaction of the spiked PER-d_{12} to form a nitro-product. There is no consistent difference between the POM-coated TIGF vs GF filters nor among the three time periods examined. This is not surprising since, in all cases, the amounts of nitroarenes formed were very low and, therefore, the quantifications of the deuterated nitroarenes were subject to large uncertainties.

Although the levels of deuterated nitroarenes present were low, as can be seen in Figures VIII-1 through VIII-3, we were able to make the isomer-specific identifications of these nitroarenes as 1-nitropyrene-d_9, 6-nitro-BaP-d_{11} and 3-nitroperylene-d_{11}. It is important to note that the analyses shown in Figures VIII-2 and VIII-3 are from co-injections of a standard solution of the non-deuterated nitro-isomer along with the exposed filter extract. The co-injection of the standard is shown to demonstrate the excellent retention time and fragment ion abundance matches upon which the identifications were based. In contrast to 1-nitropyrene (Figure VIII-1), no 6-nitro-BaP nor 3-nitroperylene was observed in the two ambient POM collections on each filter.

The composited extracts of the PUF #1 plugs under the TIGF filters doped with PY-d_{10} contained no detectable nitropyrene-d_9. The corresponding composite from the PUF plugs under the GF filters contained traces of 1-nitropyrene-d_9 (estimated at less than 40 ng) and no 2-nitropyrene-d_9.

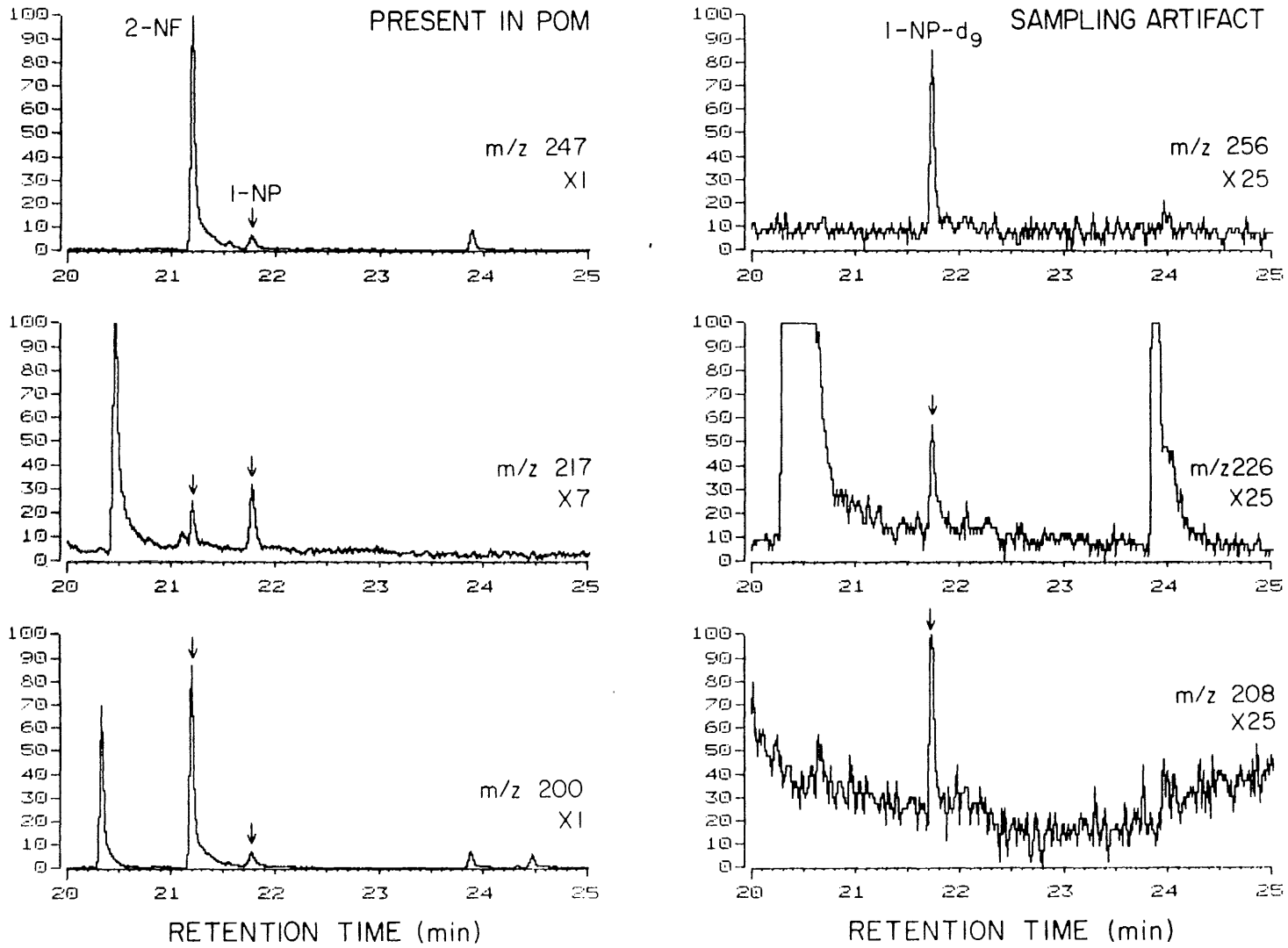

Figure VIII-1. GC/MS-MID analysis of the nitroarene fraction (from an HPLC separation) of the extract of a POM-laden TIGF filter doped with 1 mg PY-d_{10} and placed in a Hi-vol sampler operating from 1700-2400 hr on January 27, 1986 at Torrance, CA. On the left are the characteristic fragment ions of the nitrofluoranthenes (NF) and nitropyrenes (NP): $[M]^+$ = m/z 247, $[M-NO]^+$ = m/z 217, $[M-HNO_2]^+$ = m/z 200. On the right are the corresponding fragment ions for the deuterated species: $[M]^+$ = m/z 256, $[M-NO]^+$ = m/z 226, $[M-DNO_2]^+$ = m/z 208. GC separation on a 29 m DB-5 column. Injection at 50°C, then programmed at 8°C min^{-1}. The scaling factor for each ion is given.

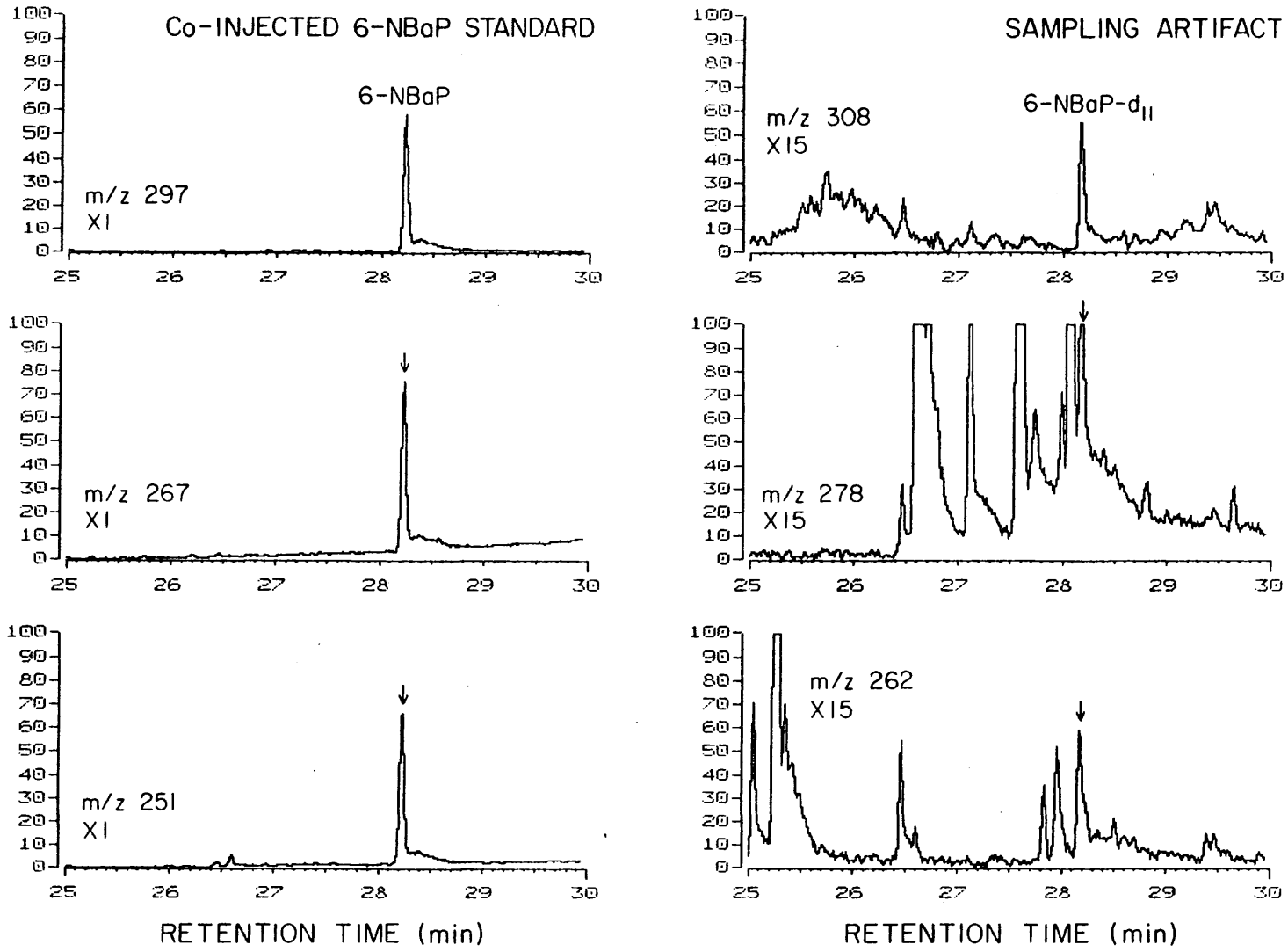

Figure VIII-2. GC/MS-MID analysis of the nitroarene fraction of the extract of a POM-laden GF filter doped with 1 mg BaP-d_{12} and placed in a Hi-vol sampler operating from 0700-1700 hr on January 28, 1986. Co-injected with this extract was a standard solution of 6-nitrobenzo(a)pyrene (6-NBaP). On the left are the characteristic fragment ions of the 6-NBaP : $[M]^+$ = m/z 297, $[M-NO]^+$ = m/z 267, $[M-NO_2]^+$ = m/z 251. On the right are the corresponding fragment ions for the artifactually formed 6-nitrobenzo(a)pyrene-d_{11} (6-NBaP-d_{11}): $[M]^+$ = m/z 308, $[M-NO]^+$ = m/z 278, $[M-NO_2]^+$ = m/z 262. GC conditions as given in Figure VIII-1; scaling factor for each ion is given.

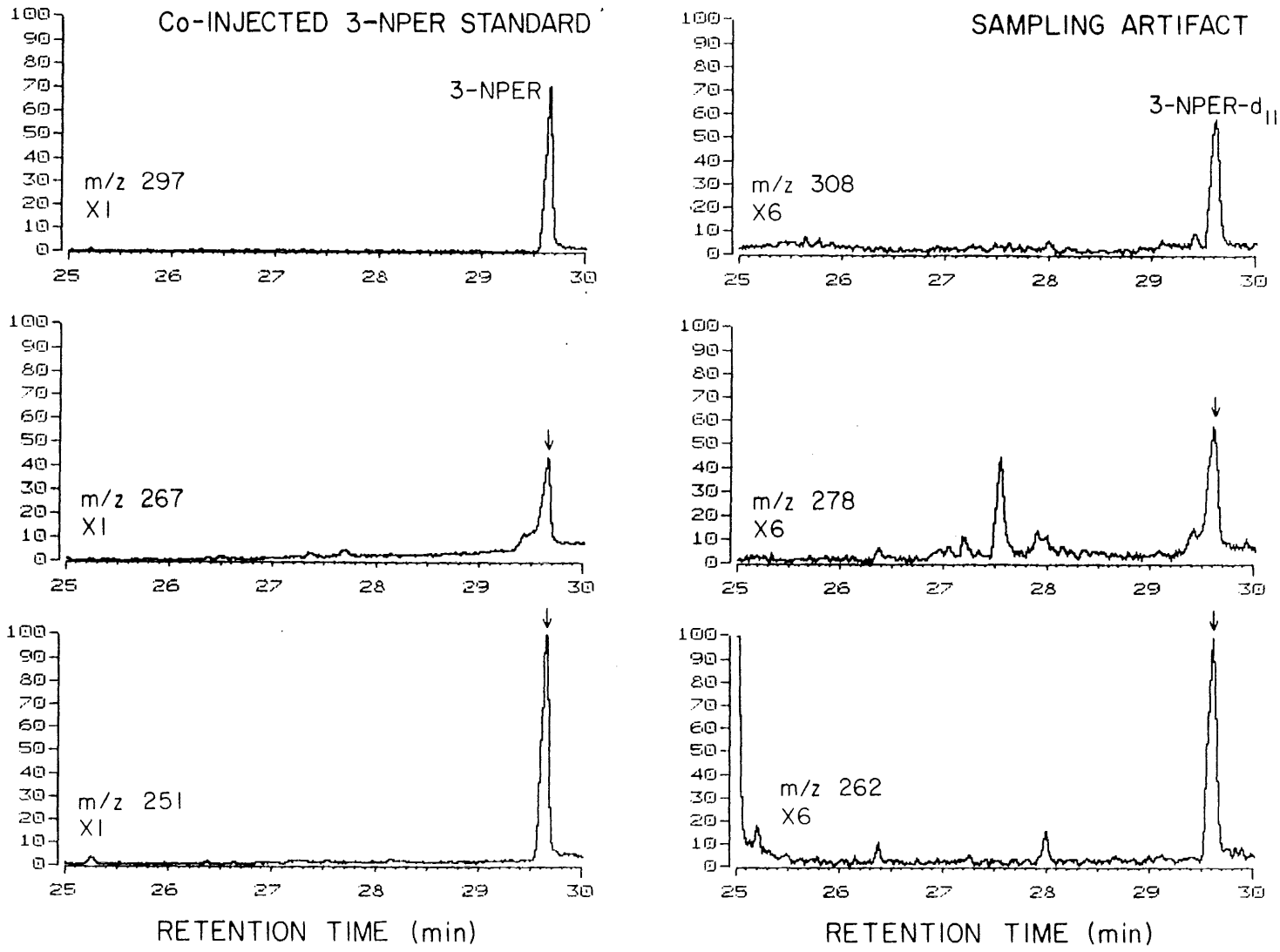

Figure VIII-3. GC/MS-MID analysis of the nitroarene fraction of the extract of a POM-laden GF filter doped with 1 mg PER-d_{12} (exposure interval as given in Figure VIII-2) and co-injected with a standard solution of 3-nitroperylene (3-NPER). On the left are the characteristic fragment ions of the 3-NPER and on the right are the corresponding fragment ions for the artifactually formed 3-nitroperylene-d_{11} (3-NPER-d_{11}). Identification of the fragment ions is as given in Figure VIII-2 for the isomeric nitrobenzo(a)pyrene. GC conditions as given in Figure VIII-1; scaling factor for each ion is given.

The significance of the 1-nitropyrene-d_9 artifact formation we observed during sampling can be evaluated, in part, by comparing the magnitude of that formed artifactually with the amount of the nitropyrenes observed in the ambient POM. Figure VIII-1 shows the GC/MS-MID traces from the analysis of the POM-laden TIGF filter doped with 1 mg of PY-d_{10} and placed in a Hi-vol sampler operated from 1700-2400 hr on January 27. The amount of 1-nitropyrene-d_9 observed in this sample was ~40 ng (Table VIII-5) and it can be estimated from the observed ion abundances that approximately four times as much 1-nitropyrene was present in the ambient POM. This sample showed the highest artifactual formation of 1-nitropyrene-d_9, i.e., $\lesssim$0.01% conversion of PY-d_{10} to its nitro-derivative (the upper limit of ~0.01% being calculated using the value of 350 μg of PY-d_{10} remaining on the filter at the end of the exposure).

The pyrene present in the POM was not measured, but it would be the sum of the pyrene present in the POM collected prior to spiking the filter with PY-d_{10} plus the pyrene collected during the filter "exposure." The latter can be estimated from our PAH analyses (see Section VI above) of POM collected concurrently with the exposures described here to be <2 μg pyrene over the 24-hr exposure period. A similar or lesser amount could be expected in the first 4-hr POM collection made prior to doping the filters. Thus, an upper limit for the pyrene present in the POM would be <10 μg. This pyrene upper limit, with a 0.01% conversion to 1-nitropyrene, would yield $\lesssim$1 ng of 1-nitropyrene produced artifactually during collection, i.e., $\lesssim$1% of the 1-nitropyrene actually observed. Some of the pyrene present in the POM is likely to be inside the particles and unavailable to react. However, this calculation assumes that the pyrene present in the POM is as available for reaction as the PY-d_{10} doped onto the POM, again making the calculated <1% 1-nitropyrene artifact an upper limit.

A further argument can be made that the amount of nitroarenes formed artifactually during Hi-vol POM collection does not significantly affect the nitrofluoranthene or nitropyrene isomer profiles observed. By examining Table VIII-5, it can be seen that the amounts of artifactually formed nitroarenes follow the ranking expected from the reactivity of the parent PAH toward electrophilic nitration, i.e., 3-nitroperylene-d_{11} > 6-nitro-BaP-d_{11} > 1-nitropyrene-d_9 (Nielsen 1984). In ambient air, the

parent PAH are all generally present at similar levels, at least within a factor of ten (see, for example, Tables VI-4 and VI-5). On particles collected by Hi-vol filtration, however, BaP is often more abundant than pyrene and fluoranthene due to blow-off of the latter PAH during sampling. Yet we have observed neither 6-nitro-BaP nor 3-nitroperylene in this ambient POM. Furthermore, those nitroarenes which have been observed are present in the order of abundance: 2-nitrofluoranthene > 1-nitropyrene ~ 2-nitropyrene, with only 1-nitropyrene being an expected electrophilic nitration product (and known to be present in primary emitted particles).

Thus, we conclude that artifact formation of nitroarenes during Hi-vol sampling does not make a significant contribution to the nitrofluoranthenes and nitropyrenes observed in ambient POM. However, other workers have reported 6-nitro-BaP (Gibson 1983) and the non-isomer specific identification of a species of molecular weight 297 (Wise et al. 1985) in ambient POM. The possibility remains that some portion of these nitroarenes was formed artifactually during particle collection.

2. Passive Exposures

Recoveries of Passively Exposed PAH and Deuterated PAH at Torrance. Table VIII-6 gives the recoveries of the deuterated PAH which were passively exposed on POM-coated filters at Torrance. As expected, the percentages of the FL-d_{10} and PY-d_{10} which remained on the filters in these passive exposures were greater than those observed for the concurrent active exposures (see Tables VIII-2 and 3). Comparing the high total recoveries in the active exposures (i.e., that on the filters plus that collected on the PUF plugs) with the approximately 50% recovery of FL-d_{10} and PY-d_{10} during the 0700-1700 hr exposure suggests that the loss of these deuterated PAH was largely due to volatilization rather than to reaction. This is substantiated by the ~90-100% recovery of FL-d_{10} from the TIGF and GF filters during nighttime periods. The absence of POM on the filters (Table VIII-7) did not significantly affect the recovery of fluoranthene or pyrene. Despite the generally low observed amounts of reaction, GC/MS-MID analyses of the nitrofluoranthene and nitropyrene isomers was undertaken because of the importance of these isomers in ambient POM.

The recoveries of the BaP-d_{12} and PER-d_{12} were quite similar to those observed for the active exposures (see Table VIII-4). No product analyses were conducted for these deuterated species.

Table VIII-6. Recovery of $FL\text{-}d_{10}$, $PY\text{-}d_{10}$, $BaP\text{-}d_{12}$ and $PER\text{-}d_{12}$ in "Passive" Exposures on Filters with Pre-Collected POM; Torrance Winter Field Study

Date	Time (hr)	Filter[a] Type	% Recovery			
			$FL\text{-}d_{10}$	$PY\text{-}d_{10}$	$BaP\text{-}d_{12}$	$PER\text{-}d_{12}$
1/27/86	1700-2400	GF	-[b]	78	-[b]	73
	1700-2400	TIGF	93	78	88	73
1/28/86	0000-0700	GF	100	88	104	76
	0000-0700	TIGF	98	79	94	73
	0700-1700	GF	53	53	68	67
	0700-1700	TIGF	40	49	51	60

[a]The deuterated PAH were spiked in pairs onto filters loaded with pre-collected POM (see Table VIII-1).
[b]Filter extract lost.

Table VIII-7. Recovery of Fluoranthene and Pyrene in "Passive" Exposures on Clean TIGF and GF Filters; Torrance Winter Field Study

Date	Time (hr)	Filter Type	% Recovery	
			Fluoranthene	Pyrene
1/27/86	1700-2400	GF	98	95
	1700-2400	TIGF	93	98
1/28/86	0000-0700	GF	99	97
	0000-0700	TIGF	97	98
	0700-1700	GF	62	51
	0700-1700	TIGF	34	50

Nitrofluoranthene and Nitropyrene Isomers Formed at Torrance and at Riverside in Passive Exposures. Tables VIII-8 and VIII-9 list the nitrofluoranthene-d_9 and nitropyrene-d_9 isomers (or their non-deuterated analogs in the case of the clean TIGF and GF filters exposed at Torrance) formed in these passive exposures in Torrance and Riverside, respectively. It can be seen from these tables that adsorbed phase reactions can produce all eight nitrofluoranthene and nitropyrene isomers.

The relative abundances listed in Tables VIII-8 and 9 were tabulated from peak heights only and, since no internal standard was added prior to the GC/MS-MID analyses, the values can only be viewed as approximate (i.e., each sample was dissolved in 20 μl of CH_2Cl_2 and approximately 1 μl was injected for the GC/MS analysis). The data shown in Table VIII-8 were obtained from analyses run on a 30 m DB-5 column on which the isomer resolution was somewhat degraded. For this reason the identification of 4-nitropyrene-d_9 is given as tentative. It can be seen, however, that the most abundant nitropyrene-d_9 isomer formed in the Torrance passive exposures was 1-nitropyrene-d_9, the isomer which is the electrophilic nitration product of pyrene-d_{10}. This was true whether the pyrene-d_{10} had been doped onto a clean TIGF or GF filter or onto POM previously collected onto a TIGF or a GF filter.

In contrast to the pyrene-d_{10} passive exposures in Torrance, which resulted in the formation of 1-nitropyrene, the electrophilic nitration product, the exposures of fluoranthene-d_{10} resulted mainly in the formation of 2-nitrofluoranthene-d_9, with generally much smaller amounts of 7- and 8-nitrofluoranthene-d_9 being formed. These are the same nitrofluoranthene isomers we have observed to be the product of the gas-phase reaction of fluoranthene with the hydroxyl radical in the presence of NO_x (Arey et al. 1986, see also Section XI.C).

In a recently published reactivity scale of PAH in electrophilic nitrations (Nielsen 1984) where group I is the most reactive group (e.g., pentacene) and group VI is the least reactive group (e.g., benzene), pyrene is ranked in group III and fluoranthene in group V. Thus, at Torrance during a high-NO_x pollution episode, passive exposures of pyrene-d_{10}, which is reactive towards electrophilic nitration, gave mainly 1-nitropyrene-d_9, but fluoranthene-d_{10}, which is less reactive toward

Table VIII-8. Results of Passive Exposures of Fluoranthene (FL) and Pyrene (PY) on GF and TIGF Filters and FL-d_{10} and PY-d_{10} on Filters Coated with POM at El Camino Community College, Torrance, CA, in January 1986. Relative Abundances[a] of Observed Nitroarenes[b]

	Nitrofluoranthenes (-d_9)					Nitropyrenes (-d_9)		
	1-	2-	3-	7-	8-	1-	2-	4-
0700-1700, 1/28/86								
GF; PY						1.5	0.32	
GF; FL		1.0		0.05	0.09			
TIGF; PY						1.25	0.09	
TIGF; FL		1.33		0.09	0.12			
POM/GF; PY-d_{10}						0.33	0.09	
POM/GF; FL-d_{10}		~0.025						
POM/TIGF; PY-d_{10}						2.4	0.21	
POM/TIGF; FL-d_{10}		0.17		~0.018	~0.030			
1700-2400, 1/27/86								
GF; PY						0.50	0.05	~0.03[c]
GF; FL		2.5[d]						
TIGF; PY						1.7		~0.04[c]
TIGF; FL		0.10		0.04	0.08			
0000-0700, 1/28/86								
GF; PY						<0.01		
GF; FL		0.07						
TIGF; PY						0.29	~0.002	0.08[c]
TIGF; FL		~0.013						
POM/TIGF; PY-d_{10}						<0.014		

[a]A full scale peak on an attenuation of 1.0 for the GC/MS-MID molecular ion peak (i.e., m/z 247 for nitrofluoranthenes and nitropyrenes or m/z 256 for their deuterated analogs) was given a value of 100.
[b]No entry means none detected. [c]Tentative Identification. [d]Possibly suspect.

Table VIII-9. Results of Passive Exposures of Fluoranthene-d_{10} (FL-d_{10}) and Pyrene-d_{10} (PY-d_{10}) at Riverside in August, 1986. Relative Abundance[a] of Observed Nitroarenes[b]

	Date	Nitrofluoranthenes-d_9					Nitropyrenes-d_9		
		1-	2-	3-	7-	8-	1-	2-	4-
Daytime									
GF; PY-d_{10}	8/27/86						0.28	0.87	
GF; FL-d_{10}	8/27/86		5.0	0.20	0.25	0.40	0.10	~0.03	
TIGF; PY-d_{10}	8/27/86						56[c]	0.3	0.2
TIGF; FL-d_{10}	8/27/86	5.0	33	22[d]	1.5	5.4	0.7		
POM/TIGF; PY-d_{10}	8/27/86						67	15	14
POM/TIGF; FL-d_{10}	8/27/86		0.34	0.17		0.22			
POM/TIGF; FL-d_{10}	8/25/86	~0.025	1.5	0.85	0.04	0.43	0.08	~0.015	
Nighttime									
GF; PY-d_{10}	8/25-26/86						0.15	0.83	
GF; FL-d_{10}	8/25-26/86		3.1		0.22	0.66			
TIGF; PY-d_{10}	8/25-26/86						12.5	~0.05	~0.15
TIGF; FL-d_{10}	8/25-26/86		8.3	5.1	1.2	4.6	1.0		
POM/TIGF; PY-d_{10}	8/25-26/86		~0.02				1.2	0.07	~0.02
POM/TIGF; FL-d_{10}	8/25-26/86		0.12						

[a]A full scale peak on an attenuation of 1.0 for the GC/MS-MID molecular ion peak (i.e., m/z 256 for deuterated nitrofluoranthenes or nitropyrenes) was given a value of 100.

[b]No entry means none detected. Note that small amounts of nitropyrene-d_9 were detected in some cases on filters coated with FL-d_{10}. This is probably due to volatilization of PY-d_{10} from another filter.

[c]Sample quantified by reanalysis after spiking with a known amount of 1-nitropyrene. The relative abundance of "56" corresponds to a total of 0.9 μg 1-nitropyrene-d_9.

[d]Sample quantified by reanalysis after spiking with a known amount of 3-nitrofluoranthene. The relative abundance of "22" corresponds to a total of 0.1 μg 3-nitrofluoranthene-d_9.

electrophilic nitration, did not yield detectable amounts of its main electrophilic nitration product, 3-nitrofluoranthene-d_9.

Examining the concentration ratios of 2-nitropyrene-d_9/1-nitropyrene-d_9 resulting from the 0700-1700 hr Torrance data given in Table VIII-8, it can be seen that this ratio was significantly higher for the GF filter (0.2) versus the TIGF filter (0.07). This was also the case for the POM-coated filters (0.3 for POM on a GF filter versus 0.09 for POM on a TIGF filter) suggesting that "run-off" of the doped PAH onto the filter probably occurred. In general, more nitration occurred on the TIGF filters than on the GF filters. This may be the result of the more basic nature of the GF filters [the pH of a water extract of a TIGF filter was ~7 (Sweetman et al. 1985) versus ~10 for a GF filter (Pitts et al. 1985c)].

Since more 2-nitrofluoranthene-d_9 and 2-nitropyrene-d_9 were seen in the daytime exposure in Torrance than in the exposures made after dark (Table VIII-8) and these two nitroarenes are products of the gas-phase reaction of fluoranthene and pyrene with the OH radical in the presence of NO_x (a process which should only occur during daylight hours) [Arey et al. 1986], we conducted daytime and nighttime passive exposures in Riverside with the nighttime filters being set in place after sunset and removed prior to sunrise. The data from these exposures shown in Table VIII-9 were obtained using a 60 m DB-5 column for the GC/MS-MID analyses and, therefore, all isomer identifications are reliable.

In order to gain perspective on the relative amounts of nitration occurring in these Riverside passive exposures, two of the samples in which high levels of nitration occurred (the samples chosen were without POM since the POM contains the non-deuterated nitroarenes) were reanalyzed after spiking with known amounts of 3-nitrofluoranthene or 1-nitropyrene for quantification of the deuterated products (see footnotes on Table VIII-8). The amount of 1-nitropyrene-d_9 formed in the passive daytime exposure of 500 μg of pyrene-d_{10} deposited on a TIGF filter was 0.9 μg, which corresponds to a 0.2% yield of nitration. Thus, the highest observed yield of pyrene-d_{10} nitration can be estimated to be $\lesssim$0.3% for the pyrene-d_{10} on POM daytime exposure (estimated by scaling the relative abundances in Table VIII-9 with 56 = 0.9 μg). This estimated $\lesssim$0.3% nitration yield includes the unusually high amounts of the 2- and 4-nitro-

isomers which were observed on the POM-coated filter. The greatest amount (0.1 μg) of 3-nitrofluoranthene-d_9 formation occurred in the passive daytime exposure of 500 μg of fluoranthene-d_{10} on a TIGF filter. Summing the contributions of all the isomers observed in this sample, the highest nitration yield for fluoranthene-d_{10} can be estimated to be <0.1% (scaling the Σ(relative abundances = 67) to 22 = 0.1 μg; not taking into account any differences in response factors of particular isomers).

It can be seen from Table VIII-9 that, surprisingly, for the Riverside passive exposures the absence of light did not affect the formation yields of those nitroarenes (2-nitrofluoranthene-d_9 and 2-nitropyrene-d_9) which are not the products of electrophilic nitration. While only minor amounts of nitration of pyrene-d_{10} were observed on the GF filters, it is interesting to note that more of the 2-nitro-isomer than of the 1-nitro-isomer was formed.

Clearly, the occurrence of adsorbed phase reactions during atmospheric transport of fluoranthene and pyrene to produce their nitro-products cannot be ruled out. As discussed in Section XI.C, the importance of these adsorbed-phase reactions in forming the nitrofluoranthene and nitropyrene isomers observed in ambient POM can best be evaluated in terms of the particular isomer patterns observed under different ambient pollutant conditions.

IX. STUDIES OF POTENTIAL MUTAGENICITY ARTIFACTS

A. Introduction

One of the goals of this program was to provide experimental data concerning the extent to which the observed direct mutagenicity of primary emissions of POM can be altered by reactions with nitrogenous and other pollutants during atmospheric transport and/or during Hi-vol collection.

In a previous CARB-supported study involving the collection of ambient particulate matter in the South Coast Air Basin, we had observed mutagenicity "filter artifacts," that is, differences in the mutagenicity of the POM extracts which were related to the type of filter media employed for collection (Pitts and Winer 1984). Specifically, POM collected on GF filters was generally lower in mutagenic activity than POM collected on TIGF filters, except during certain afternoon collection periods during which ozone and peroxyacetyl nitrate (PAN) were present at high levels. Filter artifacts may occur through reactions of POM with gaseous co-pollutants, resulting in enhancement or destruction of mutagenic activity. Because of the very high mutagenic activity of nitroarenes, nitration of collected PAH by gaseous reactants such as NO_2 and/or HNO_3 and N_2O_5 was considered to be a likely mechanism for altering mutagenic activity during collection of ambient POM. Different filter media could collect different amounts of mutagenicity because of their differing capacities for adsorption or degradation of reactive gases, or their differences, both qualitative and quantitative, in reactive surface sites. Thus, we have examined the effect on mutagenic activity of exposing precollected particulate matter to ambient gases under standard Hi-vol sampler conditions. These studies, which were conducted during a wintertime high-NO_x episode in Torrance during January and February 1986, are described in detail below.

In addition, we have carried out a comparison of mutagen densities for POM simultaneously collected on GF and TIGF filters during a summer episode at a receptor site (Claremont, September 1985) and during a winter (Torrance, January and February, 1986) air pollution episode in a source area. The POM samples collected at Claremont were sequentially Soxhlet extracted for 12 hrs with CH_2Cl_2 and acetonitrile, and the combined extracts were assayed using the Ames Salmonella bacterial reversion assay

(TA98, -S9). However, since we became aware of reports that Soxhlet extraction with acetonitrile could produce artifactual mutagenicity (Goto et al. 1981, 1982), we examined the influence of different methods of extracting POM on its mutagenic activity. The results of these studies are described below.

B. Experimental

1. Mutagen Densities of Ambient POM Collected on Two Filter Types at Claremont, CA (1985)

The filter comparison was made by simultaneously collecting POM on TIGF (Pallflex T60A20) and GF (Gelman AE) filters (precleaned by Soxhlet extraction with CH_2Cl_2 and methanol), using two standard Hi-vol samplers, equipped with 10 μm cutoff inlets, with matched flow rates of 40 SCFM each. The POM collections were begun at 1200 hr on September 13, 1985 and continued until 1200 hr on September 18, 1985, with the filters being changed every six hours.

After collection, the filters were equilibrated at 75°F and 50% relative humidity and the particulate weights determined by subtraction of the pre-exposure filter weights. Table IX-1 lists the net weight of the particles for the two filter types. As observed previously (Pitts and Winer 1984), the particulate weights on the GF filters were generally higher than those of the corresponding TIGF filters. The filters were then sequentially extracted for twelve hours with dichloromethane and acetonitrile. The combined extracts were taken up in dimethylsulfoxide (DMSO) and tested for mutagenic activity by the standard plate-incorporation Ames assay, using our modifications for more rigorous control of experimental conditions (Belser et al. 1981). Ames Salmonella strain TA98, which is most sensitive to ambient particulate mutagens, was used. The limited sample size precluded the use of other Ames tester strains.

Each sample was tested at six or more different concentrations in the range which bracketed the linear region of the dose-response curve; three replicates were run at each concentration and the averages of the three responses were used to determine the dose-response curve. The mutagenic potency (specific activity in revertants μg^{-1} of extract) was calculated from the slope of the line determined by a least-squares regression in the region of linear response. In addition, mutagen density, the airborne

Table IX-1. Net Particulate Weights for Hi-Vol POM Collections at Claremont, CA, on TIGF and GF Filters

Date	Time (hr)	Particulate Weights (mg)	
		TIGF Filter	GF Filter
9/13/85	1200-1800	37.9	48.4
	1800-2400	34.5	42.8
9/14/85	0001-0600	45.0	47.9
	0600-1200	43.6	50.4
	1200-1800	40.0	46.2
	1800-2400	28.5	32.5
9/15/85	0001-0600	27.9	30.8
	0600-1200	37.0	41.4
	1200-1800	28.5	37.2
	1800-2400	32.5	33.5
9/16/85	0001-0600	32.1	32.6
	0600-1200	51.8	50.2
	1200-1800	31.5	38.2
	1800-2400	27.6	32.0
9/17/85	0001-0600	34.7	35.2
	0600-1200	45.8	47.2
	1200-1800	37.2	48.8
	1800-2400	24.0	28.1
9/18/85	0001-0600	16.9	19.1
	0600-1200	16.7	15.6

mutagenicity concentration (revertants m^{-3}), was calculated by dividing the total activity per filter by the total volume of air sampled.

2. Effect of Extraction Method on the Mutagenicity of POM

Soxhlet Extraction Versus Ultrasonication with Acetonitrile. Two aliquots of NBS SRM 1649 (0.28 g each) were Soxhlet extracted in parallel with CH_2Cl_2 for 12 hrs. For one of these samples the extracting solvent was changed to acetonitrile and the Soxhlet extraction continued for an additional 20 hrs. The second sample, after CH_2Cl_2 extraction, was sonicated 3 times for 5 min with 50 mℓ acetonitrile each time. Both acetonitrile extracts were concentrated under vacuum, filtered through 0.45 μm Acrodiscs (Gelman Sci., Ann Arbor) and brought to dryness under a stream of nitrogen. The residues were analyzed with Ames Salmonella strain TA98 in the absence of S9.

Analogous procedures were carried out for a POM sample collected in Aurskog, Norway, during February and March of 1984 using an electrostatic precipitator. Two samples, of 0.28 g each, were employed for these analyses.

Soxhlet Extraction with Acetonitrile and Methanol. Ambient POM samples were simultaneously collected on precleaned (see above) TIGF and GF filters at Torrance, CA, on February 24-26, 1986, with the filters being changed every 12 hours. The effect of the solvent used for Soxhlet extraction on the observed mutagenicity was tested as follows. For each 12-hr collection period, two TIGF and two GF filters were individually Soxhlet extracted with CH_2Cl_2 for twelve hours. One TIGF and one GF filter were subsequently extracted with acetonitrile, while the second TIGF and GF filters were further extracted with methanol. Each of the extracts was separately concentrated and assayed for mutagenic activity using Salmonella strain TA98 in the absence of S9.

3. Investigation of Mutagenicity Artifacts During Hi-vol Collection

Testing of Sampling Uniformity of the SAPRC Mega-Sampler. Since the SAPRC Mega-sampler was used for the precollection of POM for subsequent exposure at Torrance under Hi-vol sampling conditions, it was necessary to assure the equivalence of the sixteen Hi-vol sized filters resulting from a single collection with the mega-sampler (four mega-sampler quadrants each cut into four parts). On April 16, 1985 the mega-sampler was used to collect POM at Riverside on TIGF filters between 1200-

1800 hr. The quadrants were quartered and the 16 resulting Hi-vol size pieces were separately sequentially extracted for 16 hrs with CH_2Cl_2 followed by 16 hr with acetonitrile. The combined CH_2Cl_2 and acetonitrile extracts for each filter piece were evaporated and the resulting organic material was dissolved in dimethylsulfoxide and submitted for mutagenicity testing using Ames Salmonella strain TA98. Table IX-2 gives the total activity (net revertants) measured on each of the 16 filter pieces and on a single TIGF filter used for Hi-vol sampling concurrently with the mega-sampler. The 16 filter pieces and the single Hi-vol filter showed good reproducibility in the mutagenic activities measured.

Exposures of Precollected POM. The particulate matter used for these exposures was collected in Riverside with the mega-sampler. Both GF and TIGF filters were used, and each of the POM-laden filters was cut into quarters for exposure to ambient air in standard Hi-vol samplers. A portion of this particulate matter was set aside for extraction and determination of the unexposed mutagenic activity. The precollected POM was then exposed to ambient air under standard Hi-vol sampling conditions at El Camino Community College in Torrance on January 20-21, 1986 and February 23-25, 1986.

Table IX-2. Total Activity (Net Revertants) of 16 Filter Pieces from a Single Mega-Sampler POM Collection, Compared to Single Concurrent Hi-vol Filter Sample. Carried out at Riverside, CA, 1200-1800 hr, April 16, 1986

	Filter Piece No.				
Quadrant	1	2	3	4	Avg[a]
I	4900	5900	5100	5300	5300 ± 400
II	5700	5000	4700	5100	5100 ± 400
III	5200	5500	5300	5200	5300 ± 100
IV	5100	5500	4400	4500	4900 ± 500
Hi-vol					5100[b]

[a]Uncertainty is a single standard deviation. All numbers rounded to nearest hundred.
[b]Normalized to an equivalent volume of air sampled.

Because filter media can adsorb or destroy reactive gases present in ambient air, the precollected particulate matter was not exposed with a particulate filter upstream; rather, it was exposed to unfiltered ambient air. Two Hi-vols, one fitted with a clean GF filter and one with a clean TIGF filter, collected ambient particulate matter for determination of the mutagenicity of the particles collected on top of the precollected POM. Thus, the mutagenicity artifact was determined by comparing the mutagenicities of the unexposed (original) POM to the difference of the exposed POM minus the POM collected concurrently during the exposure period.

Three daily time periods were used for these exposures: 1) daytime (sunrise to sunset), 2) sunset to midnight, and 3) midnight to sunrise. All POM samples were extracted by Soxhlet extraction with dichloromethane for 16 hours, followed by methanol for an additional 16 hours. The extracts were assayed separately using the Ames Salmonella bacterial reversion assay (TA98, -S9), as described above.

In order to minimize any effect of day-to-day variation in bacterial response on the calculations of filter artifacts, all of the CH_2Cl_2 extracts were tested in a single day's test. Similarly, all of the methanol extracts were tested in a second day's test.

C. Results and Discussion

1. Mutagen Densities of Ambient POM at Claremont

The results of the mutagenicity assays for the combined CH_2Cl_2 and acetonitrile extracts of ambient POM collected at Claremont are given in Table IX-3.

The mutagen densities (revertants m^{-3}) for POM collected on both filter types are generally lower than observed during previous photochemical smog episodes; for example, during our September 1983 field study in Riverside when mutagen densities for POM collected on TIGF filters ranged from 22 to 240 rev m^{-3} (it should be noted that the values for standard mutagens run as controls remained comparable throughout this time period). As seen from Table IX-1, the weights of particles collected on the GF filters were consistently higher than those for the TIGF filters. However, the mutagen densities were generally lower for the GF filters (Table IX-3), with the ratio of the mutagen densities for POM collected on

Table IX-3. Mutagen Densities TA98,-S9 (Revertants m^{-3}) of POM Simultaneously Collected on TIGF and GF Filters at Claremont, CA, and the Ratio of the Mutagen Densities of the Two Filter Types

Date	Time (hr)	Mutagen Densities (rev m^{-3})		GF Filter[a]
		TIGF Filter	GF Filter	TIGF Filter
9/13/85	1200-1800	37	34	0.93
	1800-2400	94	104	1.11
9/14/85	0001-0600	72	69	0.96
	0600-1200	73	70	0.97
	1200-1800	33	33	1.00
	1800-2400	64	40	0.62
9/15/85	0001-0600	35	25	0.71
	0600-1200	47	42	0.89
	1200-1800	17	13	0.79
	1800-2400	49	31	0.64
9/16/85	0001-0600	44	29	0.66
	0600-1200	45	45	0.99
	1200-1800	19	16	0.87
	1800-2400	28	21	0.76
9/17/85	0001-0600	33	24	0.74
	0600-1200	33	29	0.87
	1200-1800	31	23	0.74
	1800-2400	47	19	0.41
9/18/85	0001-0600	29	21	0.72
	0600-1200	31	14	0.44
				Avg 0.79 ± 0.18[b]

[a]TA98 mutagen density obtained for POM collected on GF filters divided by the mutagen density for POM collected on TIGF filters.
[b]Single standard deviation.

GF filters to POM simultaneously collected on TIGF filters (GF/TIGF) being unity or above for only two sampling intervals. Low values of the mutagen density ratio (GF/TIGF) may be explained, as we have earlier suggested (Pitts and Winer 1984), by three processes: (1) irreversible adsorption of the mutagenic species on the filter surface (in this case, the GF surface) leading to lower extraction efficiencies, (2) destruction of the mutagenic species catalyzed by the filter surface (again the GF surface) or, (3) transformation of nonmutagenic compounds to direct mutagens involving catalysis by the filter surface and/or surface-dependent accumulation of a reactive species present in the ambient gases flowing through the filter (in this case on the TIGF filter leading to higher mutagen densities than for the GF filter collections).

No correlation of the (GF/TIGF) mutagen density ratio with the nitric acid (Section V) or NO_2 (Section IV) data was apparent. It seems likely that the severity of the pollution episode in Claremont was not sufficient to result in the large apparent artifact on the GF filter type that we observed in our September 1983 field study, when the (GF/TIGF) mutagen density ratio was as high as 5 during certain 1500-2100 hr POM collections in Riverside, coincident with high levels of ozone and an influx of an "aged" air mass (Pitts and Winer 1984). However, as discussed in detail below, the large extraction-dependent mutagenicity differences may contribute to the filter-dependent artifact.

2. Effect of Extraction Method on the Mutagenicity of POM

Table IX-4 gives the mutagenic activities of ambient POM samples extracted with acetonitrile by two different methods, namely Soxhlet extraction and ultrasonic agitation. Both NBS SRM 1649 and Norway POM samples were Soxhlet extracted with CH_2Cl_2 for 12 hrs prior to acetonitrile extraction. Because of the differences in the weights of the extracts (Table IX-4), the mutagenicities of POM samples were compared on the basis of total activity per sample, obtained by multiplying the extract specific activity (rev μg^{-1}) by the weight of the extract.

It can be seen from Table IX-4 that the acetonitrile extracts obtained by ultrasonication showd much lower mutagenic activities than those extracts obtained by Soxhlet extraction. However, the magnitude of this phenomenâ is dramatically different for both samples, with the Norway POM sample showing much lower mutagenicity when extracted by ultrasonication.

Table IX-4. Comparison of Total Mutagenic Activities (TA98, -S9) of Ambient POM Acetonitrile Extracts, Using Soxhlet Extraction and Ultrasonication

Sample Description	Soxhlet Extraction		Ultrasonication	
	Weight of extract [mg]	10^{-3} x Total Mutagenicity in Revertants	Weight of extract [mg]	10^{-3} x Total Mutagenicity in Revertants
NBS SRM 1649	17.8	107	4.5	16
Norway POM	46.2	309	27.4	3

This discrepancy between the two methods of extraction could be due either to artifactual mutagen formation during the Soxhlet extraction with acetonitrile or (since the weights of extracts obtained by ultrasonication were consistently lower) to incomplete extraction of mutagenic compounds by ultrasonication.

In an attempt to further clarify this point, we compared the mutagenic activities of extracts of ambient POM obtained by Soxhlet extraction with acetonitrile as the second extraction solvent, with those obtained by Soxhlet extraction with methanol as the second extraction solvent. Methanol was chosen since it was expected, like acetonitrile, to efficiently extract any polar mutagenic material present. POM samples collected on GF and TIGF filters were Soxhlet extracted with CH_2Cl_2 prior to extraction with acetonitrile or methanol.

Table IX-5 summarizes the results of this study. It can be seen from this table that the acetonitrile extracts showed higher total mutagenic activities than the methanol extracts, regardless of the filter type used for POM collection and despite the generally higher weights of the methanol extracts. This suggests that artifactual mutagen formation occurred during Soxhlet extraction when acetonitrile was used as an extracting agent.

The ratio of (mutagenic activity of acetonitrile extract/mutagenic activity of methanol extract) differs significantly for GF and TIGF filters. Therefore, the type of filter used for POM collection may contribute to the large extraction-dependent mutagenicity differences observed.

Table IX-5. Comparison of the Total Mutagenic Activities (-S9) and the Weight of Extracts (mg) of Ambient POM Extracted by Soxhlet Extraction with Dichloromethane (CH_2Cl_2) Followed by Acetonitrile (ACN) or Methanol (MeOH)

Filter Type	POM Collection Day	Collection Time (hr)	10^{-3} x Total Mutagenicity in Revertants (Weight of Extracts, mg)[a]				ACN/MeOH[b]
			CH_2Cl_2	ACN	CH_2Cl_2	MeOH	
TIGF	2/24-25/86	1800-0600	36.7 (8.73)	19.8 (24.7)	38.1 (9.3)	2.52 (17.97)	7.9
TIGF	2/25/86	0600-1800	65.6 (19.28)	84.1 (11.68)	68.3 (17.5)	4.12 (42.0)	20
TIGF	2/25-26/86	1800-0600	9.41 (4.09)	13.4 (4.96)	9.26 (4.21)	2.36 (15.73)	5.7
TIGF	2/26/86	0600-1800	26.8 (10.71)	37.9 (7.57)	23.2 (10.07)	2.27 (28.74)	17
GF	2/24-25/86	1800-0600	34.7 (8.67)	30.3 (4.15)	34.8 (8.70)	5.09 (23.15)	6.0
GF	2/25/86	0600-1800	72.1 (20.61)	78.0 (10.26)	77.1 (21.41)	6.65 (80.07)	12
GF	2/25-26/86	1800-0600	6.16 (3.24)	18.5 (4.3)	5.71 (3.36)	2.18 (16.76)	8.5
GF	2/26/86	0600-1800	19.9 (10.48)	40.2 (7.89)	24.0 (10.0)	4.13 (37.50)	9.7

[a]Given in parentheses.
[b]Ratio of total activity of ACN extract to MeOH extract.

Our results are in agreement with those previously reported by Goto et al. (1981, 1982), who tested the mutagenic activities of extracts of ambient POM obtained by using 10 different organic solvents. They concluded that Soxhlet extraction of ambient POM with acetonitrile produced artifactual mutagenicity and that benzene-ethanol (4:1 v/v) or methanol were the most suitable solvents for the extraction of mutagenic compounds from ambient POM.

The results of this study led us to modify our procedure for filter extraction. Thus, Soxhlet extraction with CH_2Cl_2 followed by Soxhlet extraction with methanol was employed for the study dealing with the exposure of precollected POM to investigate the formation of artifactual mutagenicity during POM collection carried out at Torrance during January and February, 1986, as described below.

3. Investigation of Mutgenicity Artifacts During Hi-vol Collection

Particulate Mutagenicity. The mutagen densities determined in this study are shown in Table IX-6 for POM collected on TIGF and GF filters and extracted by CH_2Cl_2 followed by methanol. Most of the mutagenic activity was in the CH_2Cl_2 extracts, which accounted for 75 to 93 percent of the combined activities. For each collection period, the methanol extracts from GF filters contained a larger portion of the total activities than did those from TIGF filters, suggesting that polar species are more readily extracted from TIGF filters or that there may be a slight tendency for GF filters to increase the overall polarity of the collected mutagens. The combined values (CH_2Cl_2 plus methanol), which ranged from 16 to 84 rev m^{-3}, are within the range of values we have observed for mutagen densities in the South Coast Air Basin during previous studies. The time-weighted averages (corrected for different sampling times) were 52 rev m^{-3} for the GF filters and 49 rev m^{-3} for the TIGF filters.

The mean values of the mutagen densities for the two filter types agree well (Table IX-6), as do the individual values, which are all within the estimated error of the mutagenicity test (±10%). Thus, there is no evidence for a net filter-mediated mutagenicity increase or decrease for the ambient particulate matter collected at the Torrance site.

Exposures of Pre-collected POM. Although no net filter effect could be seen in the mutagenicity of POM collected at the Torrance site, some differences between GF and TIGF filter samples were revealed from the

Table IX-6. Mutagen Densities of POM Collected in Torrance, CA - Winter 1986

Date	Time Period (hr)	TA98 Mutagen Densities (revertants m^{-3})					
		CH_2Cl_2 Extracts		Methanol Extracts		CH_2Cl_2 + Methanol	
		GF	TIGF	GF	TIGF	GF	TIGF
1/20/86	1700-2400	37	35	5.3	5.0	42	40
1/21/86	0000-0700	58	54	6.3	3.8	64	58
1/21/86	0700-1700	40	39	6.5	3.8	47	43
1/23/86	1800-2400	14	17	4.2	4.0	18	21
2/24/86	0000-0600	39	39	6.2	4.6	45	44
2/24/86	0600-1800	50	45	8.0	6.2	58	51
2/24/86	1800-2400	12	14	3.8	2.3	16	16
2/25/86	0000-0600	45	55	9.3	5.0	54	60
2/25/86	0600-1800	76	73	8.4	6.7	84	81
Mean		41	41	6.4	4.6	48	46
S.D.		20	19	1.9	1.3	21	20

exposures of precollected POM to ambient air. Because of the differences in the weights of the extracts, the POM exposure samples were compared on the basis of total activity per filter, obtained by multiplying the extract's specific activity by the weight of the extract (given in Table IX-5). Table IX-7 gives the total mutagenic activity for each sample type in this study: (1) unexposed, precollected POM, (2) exposed, precollected POM, and (3) POM collected during the exposure period. Also tabulated is the mutagenicity artifact, the ratio of the net activity of the exposed POM to its unexposed activity. Thus, the artifact will be greater than one for a net increase in mutagenicity and less than one for a net decrease in mutagenicity.

It should be noted that the calculation of this artifact involved the subtraction of mutagenicity values which were subject to considerable error. Further error was introduced by the fact that, in these samples,

Table IX-7. Total Activities and Mutagenicity Filter Artifacts, Torrance, CA - Winter 1986

Date	Time Period (hr)	10^{-3} x Total Activity in Revertants[a] (1) Pre-collected Unexposed POM GF	(1) Pre-collected Unexposed POM TIGF	(2) Pre-collected Exposed POM GF	(2) Pre-collected Exposed POM TIGF	(3) Collected POM GF	(3) Collected POM TIGF	Mutagenicity Artifact[b] GF	Mutagenicity Artifact[b] TIGF
1/20/86	1700-2400	6.7[c]	6.9[c]	23.7	27.8	20.0	18.9	0.56	1.3
1/21/86	0000-0700	6.7[c]	6.9[c]	38.9	38.6	30.8	27.6	1.2	1.7
1/21/86	0700-1700	6.7[c]	6.9[c]	44.5	41.8	31.7	29.1	1.9	1.9
2/23/86	1800-2400	9.2[d]	9.5[d]	16.3	18.2	7.6	8.5	0.95	1.0
2/24/86	0000-0600	9.2[d]	9.5[d]	26.3	30.0	18.3	17.9	0.87	1.3
2/24/86	0600-1800	9.2[d]	9.5[d]	51.4	52.9	47.6	41.3	0.41	1.2
2/24/86	1800-2400	14[e]	5.9[e]	14.8	12.1	6.4	6.5	0.60	0.95
2/25/86	0000-0600	14[e]	5.9[e]	33.5	30.6	22.2	24.4	0.80	1.0
2/25/86	0600-1800	14[e]	5.9[e]	87	71	69	65	1.3	1.0
							Mean	1.0	1.3
							S.D.	0.5	0.4

[a]Total activity = specific activity x extract weight, TA98 (-S9), CH_2Cl_2 + methanol.
[b]Mutagenicity artifact = [(2)-(3)]/(1) for the appropriate filter type (GF or TIGF).
[c]Collected in Riverside 6/10/85.
[d]Collected in Riverside 6/7/85.
[e]Collected in Riverside 7/5/85.

the precollected POM was of lower activity than the additional POM collected. These errors should, on the average, be comparable for GF and TIGF filters.

It should be noted that the composition of the aerosol itself, both organic and inorganic, may also influence filter effects. The precollected particulate matter was sampled in Riverside in late spring and early summer and might be expected to be more hygroscopic (due to aerosol sulfate and nitrate) than the particulate matter found in the western portion of the basin in winter. For example, a large apparent

increase in extract weight in the precollected POM on January 21 (~300%), was likely due to water picked up by the precollected particulate matter when it was exposed to the foggy ambient air that day. Because wetted particles are more efficient in scrubbing gaseous co-pollutants than dry particles, hygroscopic (aged) particulate matter may react more easily on filter surfaces in high humidity environments than primary particulate matter.

Taking these sources of possible errors into account, there was little evidence for mutagenicity artifacts on TIGF filters. With perhaps one exception, all of the calculated TIGF mutagenicity artifacts were close to unity, suggesting that neither destruction nor creation of mutagenicity occurred on these filters.

Although the average artifact on GF filters was also close to unity, there was considerably more variability in the values on GF filters than on TIGF filters. Both the highest and lowest artifacts (1.9 and 0.41, respectively) occurred on GF filters, which may imply that the uncoated glass fiber surface is more reactive than the TIGF filter surface, but may increase or decrease mutagenicity depending on the distribution of atmospheric constituents and ambient air conditions during sampling. Thus we continue to believe that collections of ambient POM for mutagenicity testing should be made on TIGF, rather than GF, filters.

X. THE MUTAGENICITY OF 2-NITROFLUORANTHENE AND ITS IN VITRO HEPATIC METABOLITES

A. Introduction

We have recently identified 2-nitrofluoranthene as a major nitroarene present in ambient particulate organic matter (POM) collected at various locations in the U.S. and Europe (Pitts et al. 1985d, Sweetman et al. 1986, Ramdahl et al. 1986; see also Section VI above). This nitroarene has been shown to contribute up to 5% of the overall directly-acting mutagenicity of ambient POM (Ramdahl et al. 1985b; see also Section VII above) in the Salmonella test. The ubiquitous occurrence of 2-nitrofluoranthene in the ambient troposphere and its potent mutagenicity prompted us to investigate its in vitro mammalian metabolism.

It has been shown that in vitro metabolism by rat liver microsomes of 1-nitropyrene, another environmental mutagen, yields mainly hydroxynitro-derivatives (El-Bayoumy and Hecht 1983, Howard et al. 1985). Additionally, recent work (King et al. 1986) has shown that similar metabolites resulted from the in vitro metabolism of 1-nitropyrene by rabbit respiratory tract tissue. Thus, it appears that for nitroarenes whose route of exposure is through inhalation, the rat liver system provides a reasonable model of mammalian metabolism.

In this section we describe the results of a study of the 2-nitro-fluoranthene metabolites formed in the presence of 9000 x g supernatant (S9) obtained from the livers of Aroclor-pretreated rats. In addition, the mutagenic potency of these metabolites is reported. This study was conducted in collaboration with Drs. Robert A. Haas and Carl V. Hanson of the California Department of Health Services who co-authored the resulting journal article (see Appendix A).

B. Experimental

Chemicals. 2-Nitrofluoranthene was synthesized as described elsewhere (Zielinska et al. 1986a) and was shown by GC/MS to be >99% pure. Glucose-6-phosphate and $NADP^+$ were obtained from Sigma Chemical Co. (St. Louis, MO). Sodium phosphate, potassium phosphate, and magnesium chloride were obtained from Mallinckrodt, Inc. (St. Louis, MO). Aroclor 1254-induced rat liver S9 was purchased from Organon Teknika (Charleston,

SC). The S9 was prepared from 8-10 week old male Sprague Dawley rats according to the procedure of Ames et al. (1975) and contained 45 mg $m\ell^{-1}$ protein (manufacturer's analysis). The sterility of the preparation was confirmed in our laboratory by plating on LB medium agar.

In-vitro Incubations. Four incubations were carried out in parallel using different S9 concentrations to investigate the effect of varying the S9-to-substrate ratio on the metabolism of 2-nitrofluoranthene. Each incubation mixture was 10 mℓ in volume and contained 80 μmol of $MgCl_2$, 16.5 μmol of KCl, 50 μmol of glucose-6-phosphate, 40 μmol of $NADP^+$ and 2 μmol (0.5 mg) of 2-nitrofluoranthene dissolved in 100 μℓ of DMSO. The S9 content of the four incubation mixtures (A, B, C, and D) was as follows: A: 5 mℓ, B: 2.5 mℓ, C: 1.0 mℓ and D: 0.5 mℓ, corresponding to protein amounts of 225 mg, 112.5 mg, 45 mg and 22.5 mg, respectively. The volumes of S9 mix added to mixtures B to D were matched to that of mixture A by the addition of sterile water and sodium phosphate buffer (0.5 M, pH 7.4), so that each incubation mixture was 0.1 M with respect to phosphate. The mixtures were incubated in 125 mℓ Erlenmeyer flasks under sterile conditions in an atmosphere of air at 37°C, with shaking. After 1 hour, the reactions were quenched by the addition of 10 mℓ of chilled acetone. The mixtures were filtered to remove denaturated protein, and the acetone solutions were diluted with distilled water and extracted with ethyl acetate. Each extract was evaporated under reduced pressure and the residue redissolved in 4 mℓ of methanol and filtered through an Acrodisc (Gelman Sciences, Ann Arbor, MI) prior to analysis by HPLC.

After determining the optimum conditions to maximize the yield of the expected hydroxynitrofluoranthene metabolites, an incubation was carried out on a preparative scale with 38 μmol (9.4 mg) of 2-nitrofluoranthene and 18.8 mℓ of S9 (188 mℓ total volume), that is, with the S9 to 2-nitrofluoranthene ratio corresponding to that of incubation mixture (C). Two major metabolites were collected following HPLC separation in amounts (~300 μg each) sufficient for ^1H NMR analysis.

Control incubations were performed as described above, using heat-denaturated S9.

Instrumentation. High pressure liquid chromatography was conducted using a Beckman Model 334 HPLC system equipped with a Beckman Model 164 uv/vis detector. An Altex semi-preparative octadecylsilane column

(Ultrasphere ODS) was employed to separate the metabolites by isocratic elution with CH_3OH/H_2O (80/20) at a flow rate of 3 mℓ min^{-1}. The ^1H NMR spectra were recorded at 300 MHz with a Nicolet 300 pulsed Fourier transform spectrometer, using methanol-d_4 as the solvent. Mass spectra were recorded with a Finnigan 3200 GC/MS interfaced to a Teknivent data system and operated in the electron impact mode. The instrument was fitted with a cool on-column injector and a 29 m DB-5 capillary column (J&W Scientific) eluting directly into the ion source. Measurements of exact masses were made on a VG 70/70 high resolution mass spectrometer.

Mutagenicity Assays. Three Salmonella plate-incorporation mutagenicity tests were performed according to the standard procedure (Ames et al., 1975) with our modifications (Belser et al. 1981). 2-Nitrofluoranthene was assayed in Test 1 and its metabolites in Tests 2 and 3. The Salmonella strains used were TA98, which is sensitive to nitroarene mutagenicity, and strains TA98NR and TA98/1,8-DNP_6, which are deficient in nitroreductase (Rosenkranz and Speck 1975, McCoy et al. 1981) and transacetylase enzymes (McCoy et al. 1983, Orr et al. 1985, Saito et al. 1985), respectively. Cultures of these strains were grown for 12 hrs in LB broth, diluted to approximately 1 x 10^9 cells $mℓ^{-1}$, and maintained at ice temperature until testing.

All samples, including positive controls, were dissolved in DMSO and tested in triplicate at eight doses with the exception of Test 3 (the test of the metabolites on TA98NR and TA98/1,8-DNP_6 with S9), where a limited amount of metabolite #1 necessitated single plates at each dose. Mutagenic activity as reported here is the slope of the linear region of the dose-response curve as determined by a least-squares linear regression analysis. Positive control mutagens were quercetin, 2-nitrofluorene, 1,8-dinitropyrene and benzo(a)pyrene (with rat liver metabolic activation). The mutagenic activities of these control chemicals are given in Table X-1.

C. Results and Discussion

Figure X-1 shows the HPLC profiles of the ethyl acetate extracts obtained from the incubation of 0.5 mg of 2-nitrofluoranthene with 5 mℓ (incubation mixture A, Figure X-1A), 2.5 mℓ (B, Figure X-1B), 1 mℓ (C,

Table X-1. Mutagenicity (rev $nmol^{-1}$)[a] of 2-Nitrofluoranthene and its Hydroxylated Metabolites Towards Salmonella Typhimurium

	TA98		TA98NR		TA98/1,8-DNP_6	
	-S9	+S9[b]	-S9	+S9[b]	-S9	+S9[b]
2-Nitrofluoranthene	1030 ± 18	758 ± 33	251 ± 21	233 ± 15	180 ± 9	<20[c]
9-Hydroxy-2-nitro-fluoranthene	2220 ± 49	442 ± 27	423 ± 18	44.8 ± 6.0	49.8 ± 1.7	3.72 ± 0.89
8-Hydroxy-2-nitro-fluoranthene	614 ± 24	161 ± 3	124 ± 5	<13[c]	2.82 ± 0.73	<13[c]
Control Mutagens:						
Benzo(a)pyrene	-	129(87)[d]	-	180(56)[d]	-	126(53)[d]
2-Nitrofluorene	107(116)[d]	-	13.7(17.7)[d]	-	16.8(12.0)[d]	-
Quercetin	4.39(3.66)[d]	-	4.09(3.11)[d]	-	3.53(3.08)[d]	-
1,8-Dinitropyrene	3.72×10^5 (4.18×10^5)[d]	-	4.09×10^5 (4.44×10^5)[d]	-	7220(5260)[d]	-

[a]Slope of a least squares regression of dose-response curve together with the standard error of the slope.
[b]2% v/v mix was used.
[c]Regression not significant at 95% confidence level. Upper limit is based on the highest dose tested and the estimated minimum detectable response (25 revertants above spontaneous response).
[d]Numbers in parentheses are controls for Test 2 or 3, hydroxynitrofluoranthene assays.

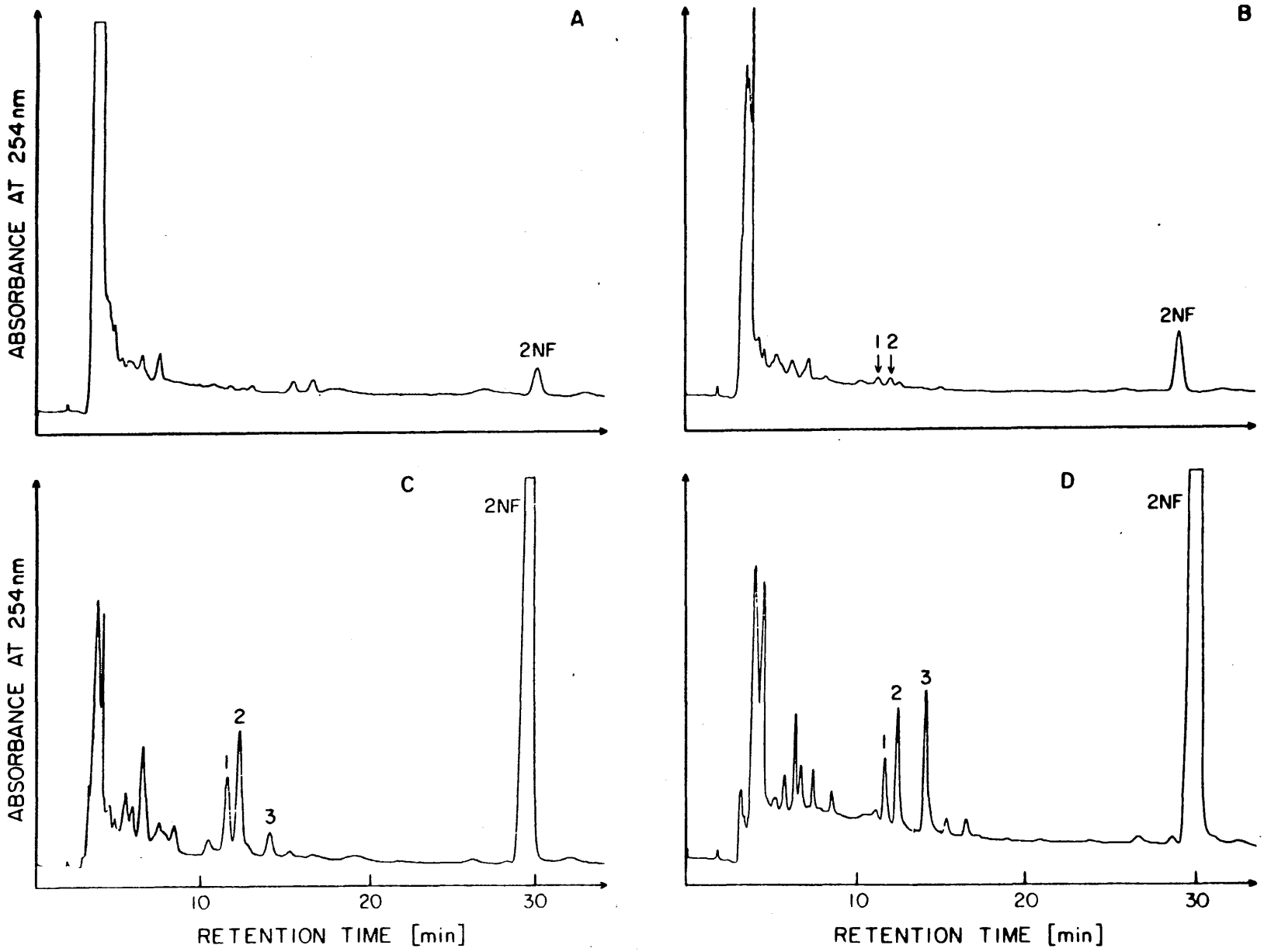

Figure X-1. HPLC traces (semi-preparative Ultrasphere ODS column: CH_3OH/H_2O, 80%/20%, 3 mℓ min^{-1}) of extracts of four incubation mixtures of 2-nitrofluoranthene with varying amounts of S9. S9/2-nitrofluoranthene ratios (mℓ mg^{-1}) were as follows: A, 10; B, 5; C, 2; D, 1.

Figure X-1C) and 0.5 mℓ (D, Figure X-1D) of S9 mix. The 2-nitrofluoranthene was almost totally consumed (~98-99%) in incubations A and B, whereas ~20 and 40% of the 2-nitrofluoranthene remained after incubations C and D, respectively. The metabolites eluting as chromatographic peaks #1, 2 and 3 were analyzed by mass spectrometry and found to be hydroxynitrofluoranthene isomers. All three isomers have very similar mass spectra (Figure X-2) with a molecular ion at m/z 263 and major fragment ions at m/z 217 $[M-NO_2]^+$, m/z 189 $[M-NO_2-CO]^+$ (exact mass m/z 189.0700, Δ=2.2 ppm), m/z 188 $[M-CHNO_3]^+$ and m/z 187 $[M-CH_2NO_3]^+$ (exact mass m/z 187.0547, Δ=0.4 ppm).

The S9/2-nitrofluoranthene concentration ratio of incubation mixture C was used for the preparative scale incubation, and an HPLC profile of metabolites similar to that of mixture C was observed.

The metabolites eluting in chromatographic peaks #1 and #2 (Figure X-1C) were collected and analyzed by ^1H NMR. Figure X-3 shows the 300 MHz proton NMR spectra of the metabolites (Fig. X-3.1 and X-3.2) and of 2-nitrofluoranthene (Fig. X-3.3). The NMR resonance assignments of the metabolites were determined by homonuclear decoupling experiments as well as by comparison with the spectrum of 2-nitrofluoranthene (Paputa-Peck et al. 1983, Zielinska et al. 1986a). From a comparison of each metabolite spectra with that of 2-nitrofluoranthene, it is obvious that the multiplet due to H-8 and H-9, observed at 7.65 ppm in the 2-nitrofluoranthene spectrum (Fig. X-3.3) is missing from these metabolite spectra (Fig. X-3.1 and X-3.2) suggesting that the OH substitution occurred in the C ring. In addition, the upfield signals at 6.81 ppm and 6.80 ppm in the spectrum of metabolite #1 and #2, respectively, are expected to be due to the protons ortho to the OH group. The downfield singlets in the ~8.4-9 ppm region (Fig. X-3.1 and X-3.2), show meta coupling to each other (J=2.1 Hz) and are clearly due to the protons ortho to the NO_2 group.

The presence of upfield singlets at 7.34 ppm (Fig. X-3.1) and 7.40 ppm (Fig. X-3.2) showing meta coupling (J=2.1 Hz for both metabolites) implied that the OH group occupied either the C-8 or C-9 position in these two hydroxynitrofluoranthene metabolites, as confirmed by the following homonuclear decoupling experiments. Irradiation of the doublet present at 6.81 ppm (1H, J=8.1 Hz) in the spectrum of metabolite #1, caused the doublet at 7.79 ppm (J=8.1 Hz, partially superimposed on a triplet at 7.76

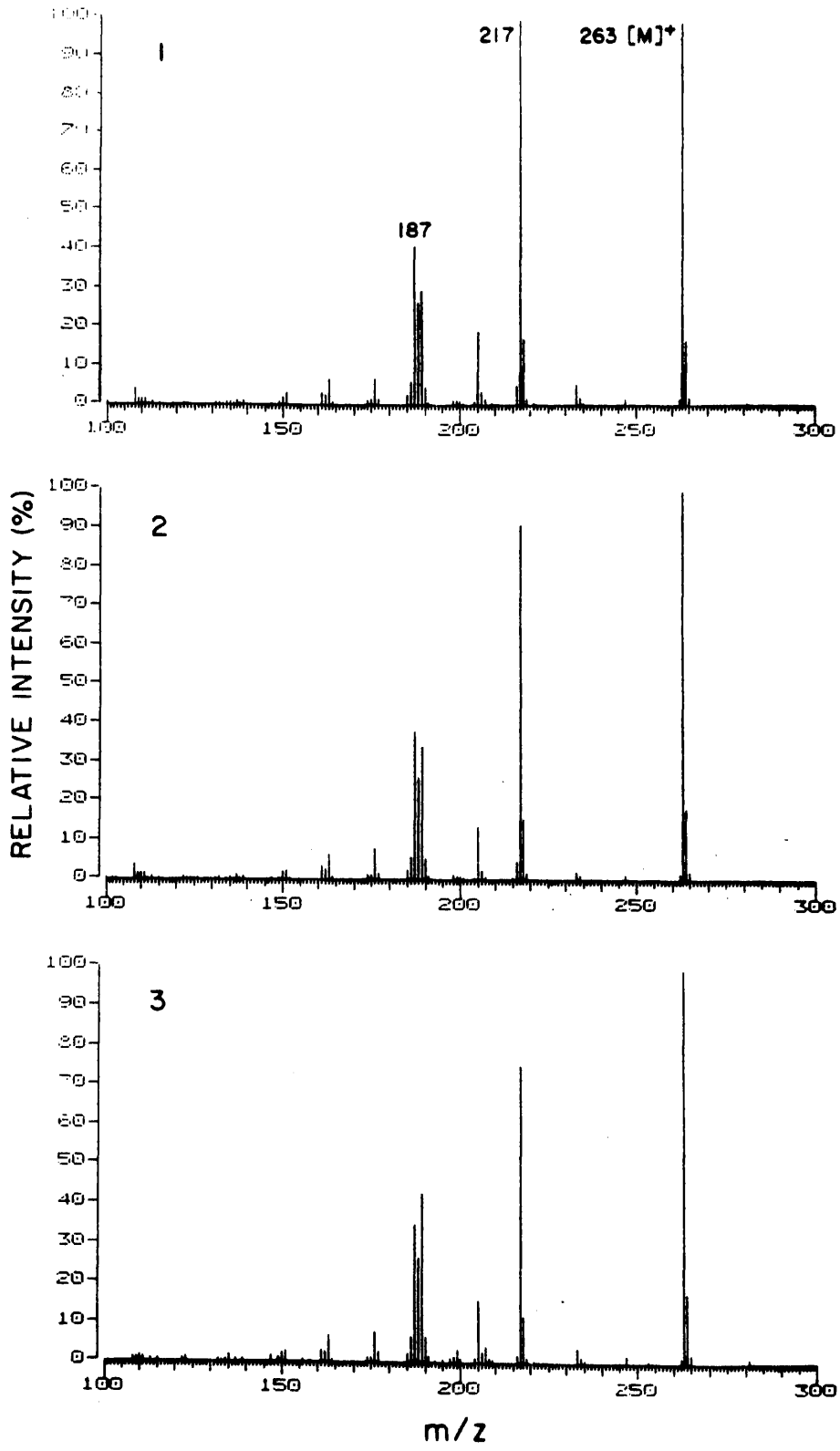

Figure X-2. Mass spectra of the three metabolites of 2-nitrofluoranthene labelled 1, 2, and 3 according to their HPLC retention times (RT) as shown in Figure X-1. The spectra were recorded by GC/MS using a 29 m DB-5 capillary column with injection at 50°C followed by temperature programming at 8°C min^{-1}. The GC RT of the isomers were as follows: 1, 25.7 min; 2, 25.6 min; 3, 25.3 min.

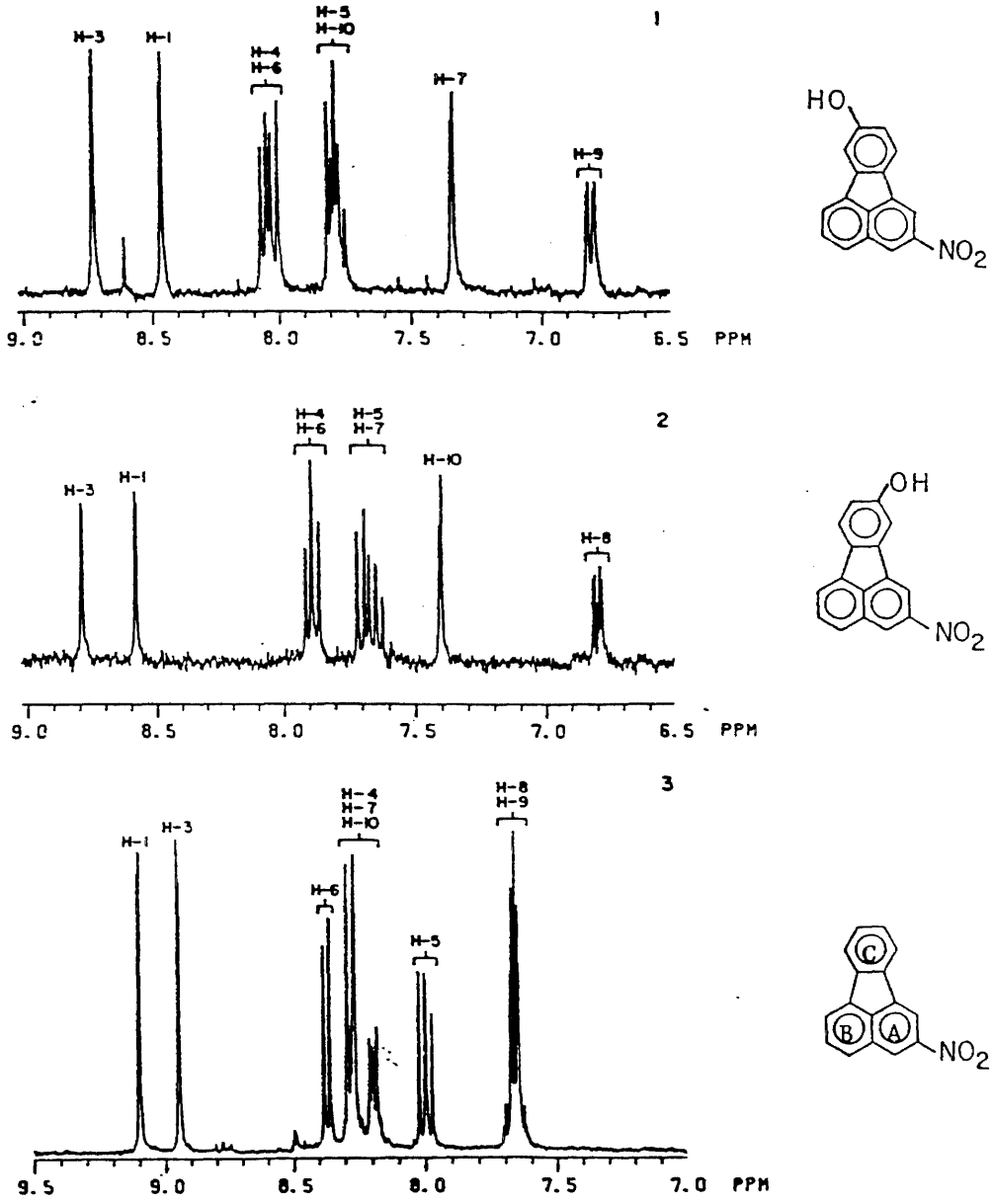

Figure X-3. 300 MHz ^{1}H NMR spectra of the metabolites 1 and 2 (in CD_3OD), identified as 8-hydroxy-2-nitrofluoranthene (1) and 9-hydroxy-2-nitrofluoranthene (2) and the spectrum of 2-nitrofluoranthene (3) in CD_3OD.

ppm) to collapse to a singlet. In addition, this irradiation caused the meta coupling of the singlet at 7.34 ppm (J=2.1 Hz) to disappear. For metabolite #2, irradiation of the multiplet at 7.88 ppm (2H, doublet over doublet) resulted in the collapse of the triplet at 7.65 ppm.

The identity of the metabolites was established on the basis of a nuclear Overhauser effect (NOE) measurement carried out for metabolite #2: the irradiation of the singlet at 7.40 ppm (H-7 or H-10) caused NOE enhancement (~6%) of the singlet at 8.58 ppm. We therefore concluded that the signals at 8.79 ppm and 8.58 ppm were due to H-3 and H-1, respectively, and that the proton giving rise to the singlet at 7.40 ppm was H-10. These assignments for H-1 and H-3 are reversed from those which were previously assumed for 2-nitrofluoranthene (Paputa-Peck et al. 1983, Zielinska et al. 1986a), suggesting that the influence of the OH group on the chemical shift of H-1 is greater than on that of H-3. Irradiation of the singlet present at 7.34 ppm in the spectrum of metabolite #1 did not produce any measurable NOE effect. Therefore, metabolite #1 was identified as 8-hydroxy-2-nitrofluoranthene and metabolite #2 as 9-hydroxy-2-nitrofluoranthene. The third observed hydroxynitrofluoranthene metabolite (peak #3) was obtained in insufficient quantity for full structural identification.

No significant transformation of 2-nitrofluoranthene was seen using heat-denaturated S9. When the incubation was performed in an atmosphere of air but without shaking, thus reducing the level of oxygen (an inhibitor of nitroreductase activity) in the incubation medium, 2-aminofluoranthene was the only detectable product.

It has been reported by Howard and Mateescu (1985) that the metabolism of 3-nitrofluoranthene by rat liver microsomes resulted in the formation of essentially one phenolic derivative, 8-hydroxy-3-nitrofluoranthene, along with one major dihydrodiol derivative. Other investigators have suggested that as many as six hydroxynitrofluoranthene isomers may be formed from 3-nitrofluoranthene (Ball et al. 1985). Our preliminary results show that ring oxidation is also an important metabolic pathway for 2-nitrofluoranthene and that the metabolism of this nitroarene by rat liver microsomes leads to at least three hydroxynitrofluoranthene isomers, two of which have been identified as 8- and 9-hydroxy-2-nitrofluoranthene. Although no major dihydrodiol derivatives were detected in our preparative

scale incubation, they may have been formed as minor products or may have decomposed during our work-up procedure.

It has been shown (El-Bayoumy and Hecht 1983, Manabe et al. 1985) that one of the nitrophenolic metabolites of 1-nitropyrene, 3-hydroxy-1-nitropyrene, is a more potent mutagen that 1-nitropyrene itself, while two other phenolic products (6- and 8-hydroxy-1-nitropyrene) are less potent. It was interesting, therefore, to investigate the mutagenicity of the observed 2-nitrofluoranthene metabolites. Table X-1 gives the mutagenic activities (rev $nmol^{-1}$) of 2-nitrofluoranthene and two of its metabolites, 8- and 9-hydroxy-2-nitrofluoranthene, in Salmonella strains TA98, TA98NR and TA98/1,8-DNP_6, with and without microsomal activation.

2-Nitrofluoranthene exhibited its maximum direct-acting mutagenicity (e.g. without S9) towards strain TA98 (1030 rev $nmol^{-1}$). This mutagenicity was 4-fold lower in strain TA98NR, deficient in the "classical" nitroreductase enzyme (Rosenkranz and Speck 1975, McCoy et al. 1981) and 6-fold lower in strain TA98/1,8-DNP_6, deficient in a transacetylase enzyme (McCoy et al. 1983, Orr et al. 1985, Saito et al. 1985). These data suggest that the bacterial activation of 2-nitrofluoranthene required nitroreduction to the N-hydroxyarylamine followed by O-acetylation.

The direct-acting mutagenicity of 9-hydroxy-2-nitrofluoranthene in strain TA98 was higher (2220 rev $nmol^{-1}$), while that of 8-hydroxy-2-nitrofluoranthene was lower (614 rev $nmol^{-1}$) than that of the parent 2-nitrofluoranthene. As with 2-nitrofluoranthene, the direct-acting mutagenicities of 9- and 8-hydroxy-2-nitrofluoranthene were lower in strains TA98NR (5-fold for both compounds) and TA98/1,8-DNP_6 (44 and 200-fold, respectively) than in strain TA98. These results indicate that the mutagenicities of the metabolites were dependent upon nitroreduction and further O-acetylation of the resulting N-hydroxyarylamine intermediates.

The presence of S9 slightly lowered the mutagenicity of 2-nitrofluoranthene in strain TA98, had no effect in TA98NR, and practically abolished mutagenic activity in strain TA98/1,8-DNP_6. These data imply that ring oxidation of 2-nitrofluoranthene was not the predominant activating process in the Salmonella test system in the presence of S9. The mutagenicity of 9- and 8-hydroxy-2-nitrofluoranthene was substantially suppressed by the addition of S9 in all three strains tested (with the exception of 8-hydroxy-2-nitrofluoranthene tested in strain TA98/1,8-DNP_6, for which

the results are inconclusive). This result suggests that further oxidation of 8- and 9-hydroxy-2-nitrofluoranthene by S9 leads to less mutagenic or nonmutagenic products, or that non-specific binding of the nitrophenols to S9 proteins occurs.

The greater mutagenic potency of 9-hydroxy-2-nitrofluoranthene suggests that both nitro-reduction and ring oxidation may be important in the activation of 2-NF and that the hydroxylated metabolites of 2-nitrofluoranthene (at least the 9-hydroxy isomer) cannot be viewed as detoxification products. Ring hydroxylation of nitroarenes has been demonstrated in vivo (Howard et al. 1985, Ball and King 1985), and it has been found (Ball and King 1985) that the major urinary metabolites of 1-nitropyrene are both ring-oxidized and nitro-reduced. It has also been postulated (Stanton et al. 1985) that the DNA adducts found in vivo following interperitoneal injection of 1-nitropyrene are a mixture that may include ring-oxidized metabolites.

In conclusion, in this work, we have identified 8- and 9-hydroxy-2-nitrofluoranthene as in vitro hepatic metabolites of 2-nitrofluoranthene, a major nitroarene in ambient airborne particulate matter. The role of ring oxidation or nitro-reduction, or both, in the in vivo metabolic pathways of 2-nitrofluoranthene remains to be explored.

XI. CONCLUSIONS AND RECOMMENDATIONS

A. Introduction

During this two year program, the experimental resources and research expertise of the atmospheric chemistry group of the Statewide Air Pollution Research Center were employed to carry out three field studies. Two of these were conducted at mid-basin receptor areas under summer/fall air pollution episode conditions, with the third being at a site in the western end of the South Coast Air Basin under characteristic high-NO_x winter episode conditions. As discussed in Sections II and III, the original experimental focus of this program was to monitor a spectrum of gaseous nitrogenous species (NO_2, HONO, HNO_3, the NO_3 radical, NH_3, and possibly N_2O_5) by long pathlength differential optical absorption and FT-IR absorption spectroscopy, while simultaneously collecting ambient air and particulate samples for the analysis of gas and particle phase PAH and nitroarenes and particulate mutagenicity.

However, subsequent to initiation of this program, the CARB expressed a strong interest in obtaining in situ absolute and interference-free measurements of key gas-phase species using the SAPRC long pathlength optical spectrometers during two intercomparison studies to serve as benchmark data against which other experimental methods could be evaluated prior to the 1987 Southern California Air Quality Study. Thus, some shift in emphasis of the program with respect to the role of the long pathlength FT-IR and differential optical absorption spectrometers took place in the case of the Pomona College (Claremont) and Citrus College (Glendora) studies.

In the remainder of this section, the major conclusions derived from the extensive measurements of gaseous atmospheric species and of particle-associated PAH, nitroarenes and mutagenicity carried out during this program are summarized. The original research objectives concerning the role of nitrogenous pollutants in producing mutagenic nitroarenes were fully met and, as summarized in Section XI.C below, a wealth of information was obtained during this program concerning the atmospheric transformations of polycyclic aromatic hydrocarbons in both the gaseous and particulate phases.

B. In Situ Spectroscopic Measurements of Gas-Phase Atmospheric Species

As discussed in Sections II, III, IV and V, the SAPRC long pathlength optical spectrometers were employed at three locations in the California South Coast Air Basin to determine the ambient concentrations of a variety of trace gas pollutants. Specifically, the DOAS system was used to monitor the concentrations of NO_2, HONO, HCHO and the NO_3 radical, while the FT-IR spectroscopic technique was used to measure HNO_3, NH_3 and HCHO. Due to the strong interest of the CARB in the participation of these two absolute (and "continuous") spectroscopic techniques at the methods intercomparison studies held at Pomona College, Claremont, during September 1985 and at Citrus College, Glendora, during August 1986, the original goals of this aspect of our experimental program changed somewhat.

As discussed briefly in Sections IV and V, and as will be documented in much more detail in forthcoming peer-reviewed journal articles (for example, those of Hering et al. 1987 and Biermann et al. 1987), the SAPRC long pathlength spectroscopic instruments were successfully used as benchmark standards for the assessment of the other experimental methods employed at these intercomparison studies. This was successful despite the generally low levels of atmospheric pollution observed at the Claremont study which resulted in the gas-phase nitric acid concentrations being below the detection limit of the FT-IR system for a significant portion of the study period.

In particular, during the Nitrogenous Species Measurement Methods Intercomparison Study at Claremont, SAPRC's measurements of HNO_3 and NH_3 (by FT-IR spectroscopy) and HONO (by DOAS) were used as primary standards, and the DOAS data for NO_2 were also used for comparison with a second spectroscopic technique, the tunable diode laser system (TDLS), as well as with continuous analyzer data. At the Carbonaceous Species Intercomparison study held at Glendora during August 1986, further comparison of the FT-IR and TDLS data for HNO_3 was carried out, while our measurements of HCHO by FT-IR spectroscopy were used as standards for comparison with the TDLS and other HCHO measurement methods such as the diphenylhydrazone derivatization technique. Several selected examples of the data we obtained, and of comparisons between our spectroscopic data and those

obtained by either other investigators or by our own continuous analyzers, are given below.

For the Claremont study the 52 data points obtained for HNO_3 by the FT-IR system on September 14 and September 17, which represented the FT-IR's most definitive measurements during this study, are compared with the coincident five-minute averages from the two TDLS instruments (operated by Unisearch Associates and Atmospheric Environment Service, Canada, respectively) in Figure XI-1. The ratio of the mean for the HNO_3 (TDLS/FT-IR) measurements was equal to 0.84. For the six highest reported HNO_3 values, the TDLS measurements were significantly lower than those of the FT-IR, with the ratio being 0.72.

The data for the sampling period 1200-1600 PDT on September 14 permit a direct comparison between the FT-IR measurements and the data obtained by the non-continuous sampling methods employed in the Claremont study. The ratios of the mean of each method to the FT-IR average of 15.2 ppb for this period were as follows: TDLS, 0.84; ADM (annular denuder method), 0.95; DDM (denuder difference method), 1.03; FP (filter pack), 1.32. The closest agreement for this period was with the DDM value of 15.7 ppb, which was within 4% of the FT-IR value. The mean of the FP, DDM, ADM and TDLS results was 15.7 ppb.

Sufficient data were obtained by FT-IR absorption spectroscopy to yield hourly average values for two or three of the four hours during the sampling intervals 0800-1200 hr and 1600-2000 hr on September 14 and for 1200-1600 hr on September 17. Period averages, calculated as described in Section V, are compared with those of the TDLS, FP, DDM and ADM for the above 4 hr sampling periods in Figure XI-2. The uncertainty in the FT-IR data was ±4 ppb, although an additional error of ±1 ppb may be assigned for periods with missing data. While the FT-IR data were closest to the measurements of the DDM method, all methods agreed within their reported ranges of uncertainty.

For NH_3 measurements, the closest agreement with the FT-IR spectroscopic data was for the filter pack method designated as CF1 (Hering et al. 1987), which employed a citric acid impregnated filter to collect NH_3 after Teflon (which remove particulates) and Nylon (which collect HNO_3) filters. The linear regression of CF1 vs. the FT-IR spectroscopic data for 33 sampling periods yields the relationship CF1 = -0.17 + 0.89 (FT-IR),

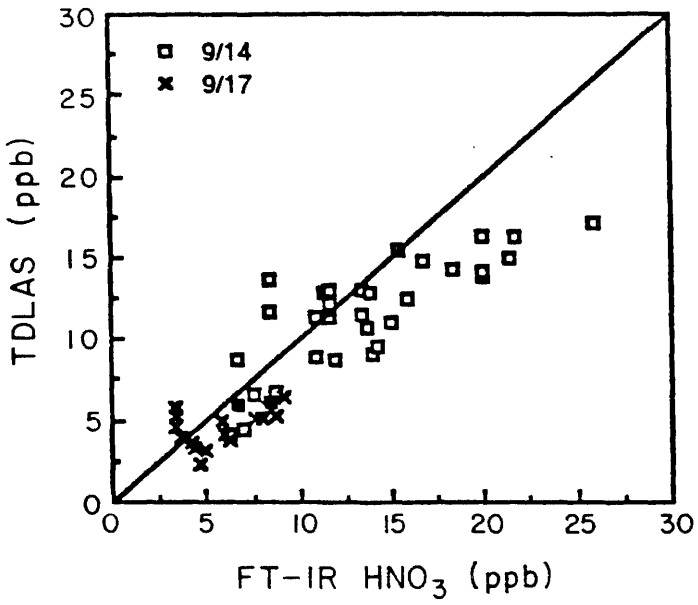

Figure XI-1. Comparison of 5-minute average concentrations from the TDLS and FT-IR methods. The 1:1 line is shown (adapted from Hering et al. 1987).

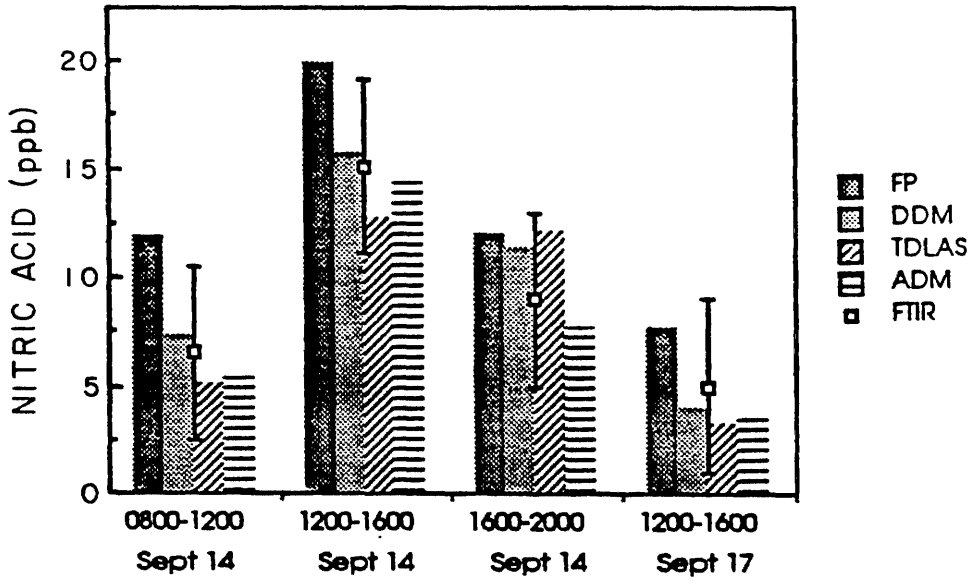

Figure XI-2. Period averages measured by FT-IR compared to those of the other methods (adapted from Hering et al. 1987).

with a correlation coefficient of r = 0.987. Another comparison made was with the technique designated QA1 (Hering et al. 1987), which employed a train of annular denuders, one of which was coated with citric acid to collect NH_3. The QA1 vs FT-IR linear regression for 34 sampling periods showed r = 0.939, but had a slope of only 0.56. Poor collection efficiency of the denuder segment at higher NH_3 levels was apparent from the comparison of individual data points. Similarly, the techniques which employed tungstic acid coated tubes gave erratic comparisons.

Of the methods used at the Claremont nitrogenous species intercomparison study, the HONO data obtained with the DOAS system were consistently lower, by as much as factors of 2 to 3, than those obtained by the other techniques. As discussed in Section IV, the reasons for these discrepancies are not presently known, but it is clear that the DOAS data cannot be in error by more than approximately 30%.

During the carbonaceous species intercomparison study carried out at Glendora during August 1986, we measured a wide range of gaseous species. Since significantly elevated pollution levels were encountered during this study period, with maximum ozone concentrations exceeding 200 ppb on all but one day, the concentrations of the species we sought to measure were, for the majority of the time, above the detection limits of the DOAS and FT-IR systems. The ambient concentrations of HNO_3, NH_3 and HCHO measured by the long pathlength FT-IR spectrometer for the entire study period are shown in Figure XI-3.

Figure XI-4 shows the time-concentration profile for NO_2 from 0000 hr on August 13 to 0800 hr on August 21 at Glendora. The solid line corresponds to the DOAS data, while the dashed line shows measurements made by our chemiluminescence oxides of nitrogen analyzer. The two curves track each other very well during the nighttime and early morning hours. In the afternoon the NO_x analyzer consistently read 10 to 30 ppb higher; since the DOAS values at those times were as low as 15-25 ppb this caused a discrepancy of a factor of two or more. However, the higher values measured by the chemiluminescence method are attributed to the known interferences of HNO_3 and PAN in this detection method, and indeed the levels of HNO_3 and PAN in the afternoon periods were approximately equivalent to this difference between the DOAS NO_2 and chemiluminescence NO_x-NO readings.

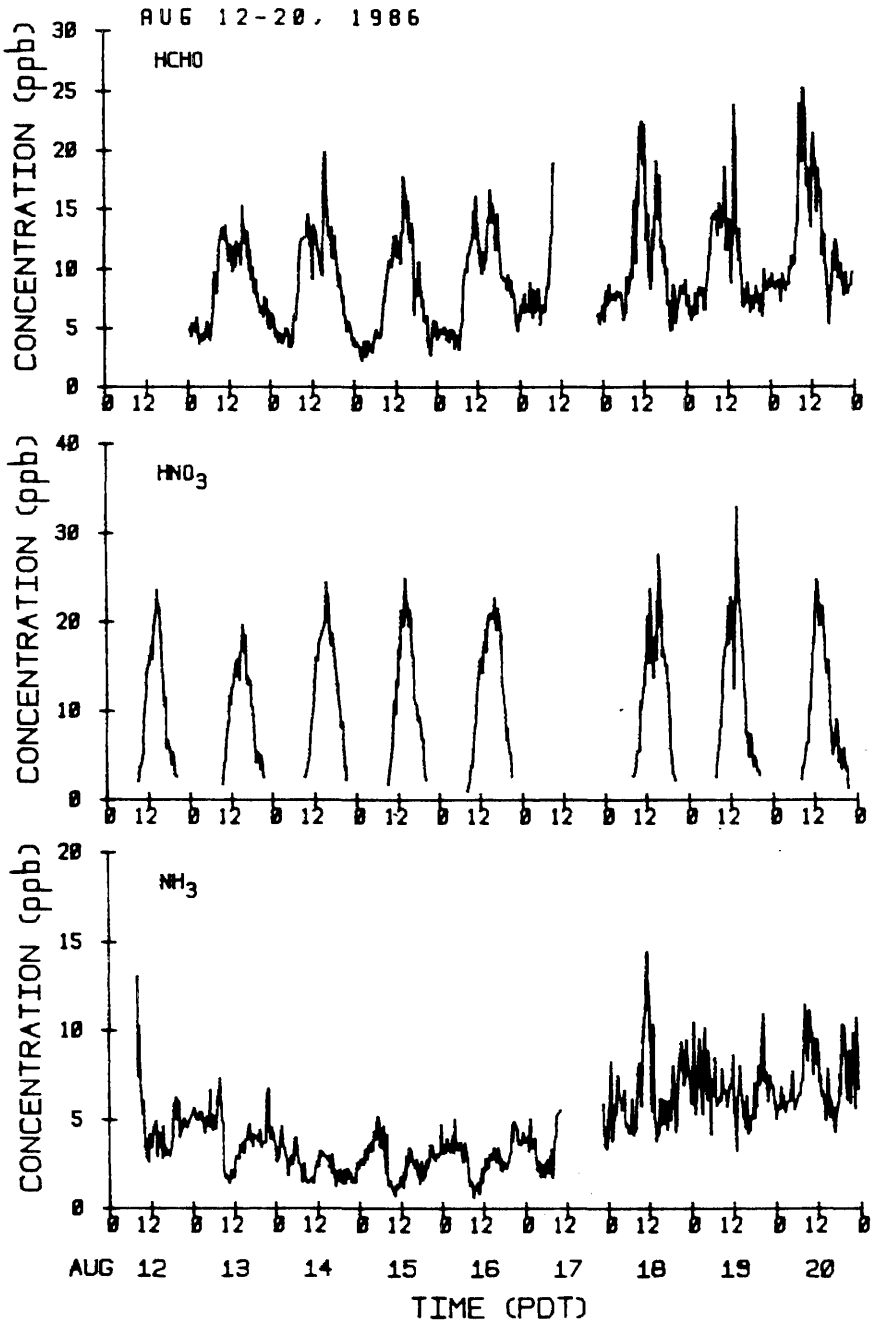

Figure XI-3. Time-concentration profiles for formaldehyde, nitric acid and ammonia measured by long pathlength FT-IR spectroscopy during the Citrus College study.

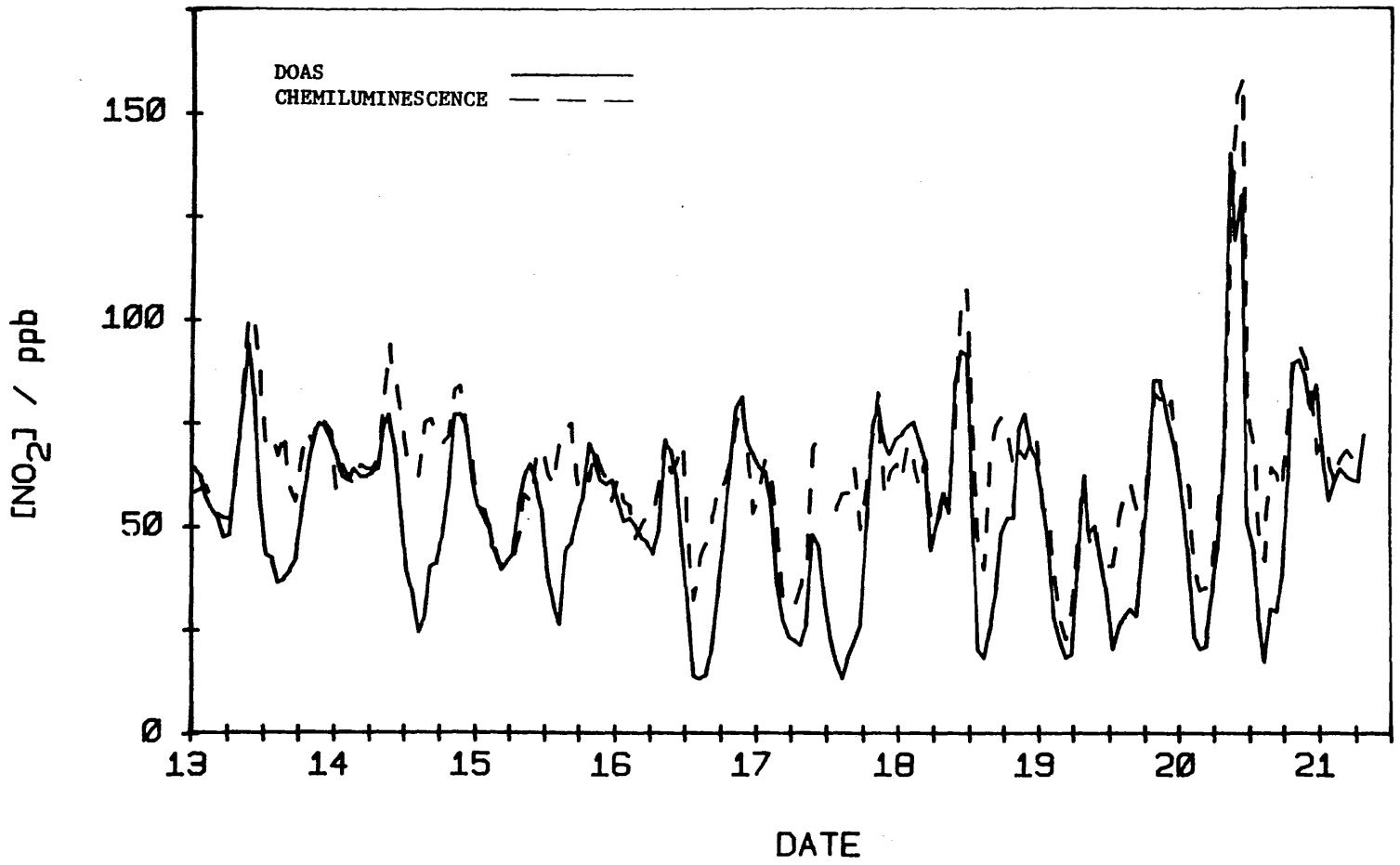

Figure XI-4. Time concentration profiles for nitrogen dioxide measured by DOAS and chemilunminescence (NO_x-NO) at Citrus College (Glendora) in August 1986.

Figure XI-5 shows the time concentration profile for HCHO as determined by DOAS (solid line) and for comparison, the FT-IR data (Section V) are also shown (dashed line). The agreement between the two methods is very good, with the discrepancies being within the error limits. Additionally, preliminary data from the TDLS system and from a diphenylhydrazone-derivatization method show similar good agreement (Lawson, private communication 1987), indicating that reliable methods other than spectroscopy are available for monitoring ambient levels of HCHO.

Throughout all three of the field studies conducted during this program, a major objective of the spectroscopic measurements was to provide the ambient air data necessary to assess the importance of the various atmospheric formation routes to the directly mutagenic nitroarenes we and others have observed in ambient POM. As discussed in Section XI.C and elsewhere (Arey et al. 1986, 1987, Atkinson et al. 1987, Atkinson and Aschmann 1987), the nitroarenes observed in ambient POM can be formed in the atmosphere from the gas-phase reactions of PAH with the OH radical (in the presence of NO_x) during daylight hours and with N_2O_5 during nighttime hours, as well as from adsorbed-phase reactions.

Research conducted in this program and in complementary laboratory programs at SAPRC during this project period showed that the gas- and adsorbed-phase reactions of PAH with NO_2 and/or HNO_3 are not important routes to the formation of nitroarenes. N_2O_5, however, was determined to play an important role in the formation of certain nitroarenes (Section XI.C) and thus it was critical to determine whether or not N_2O_5 was present during early evening and nighttime hours. Unfortunately, during the periods that the FT-IR spectrometer was operating at its optimum capability, ambient N_2O_5 concentrations remained below the FT-IR detection limit of approximately 4 ppb. However, NO_2, NO_3 radicals and N_2O_5 are maintained in equilibrium through the reactions

$$NO_2 + NO_3 \underset{\leftarrow}{\overset{M}{\rightarrow}} N_2O_5$$

and therefore measurements of NO_3 radical concentrations by the DOAS system provided the needed information concerning the presence or absence of N_2O_5. As discussed below (Section XI.C), these DOAS NO_3 radical

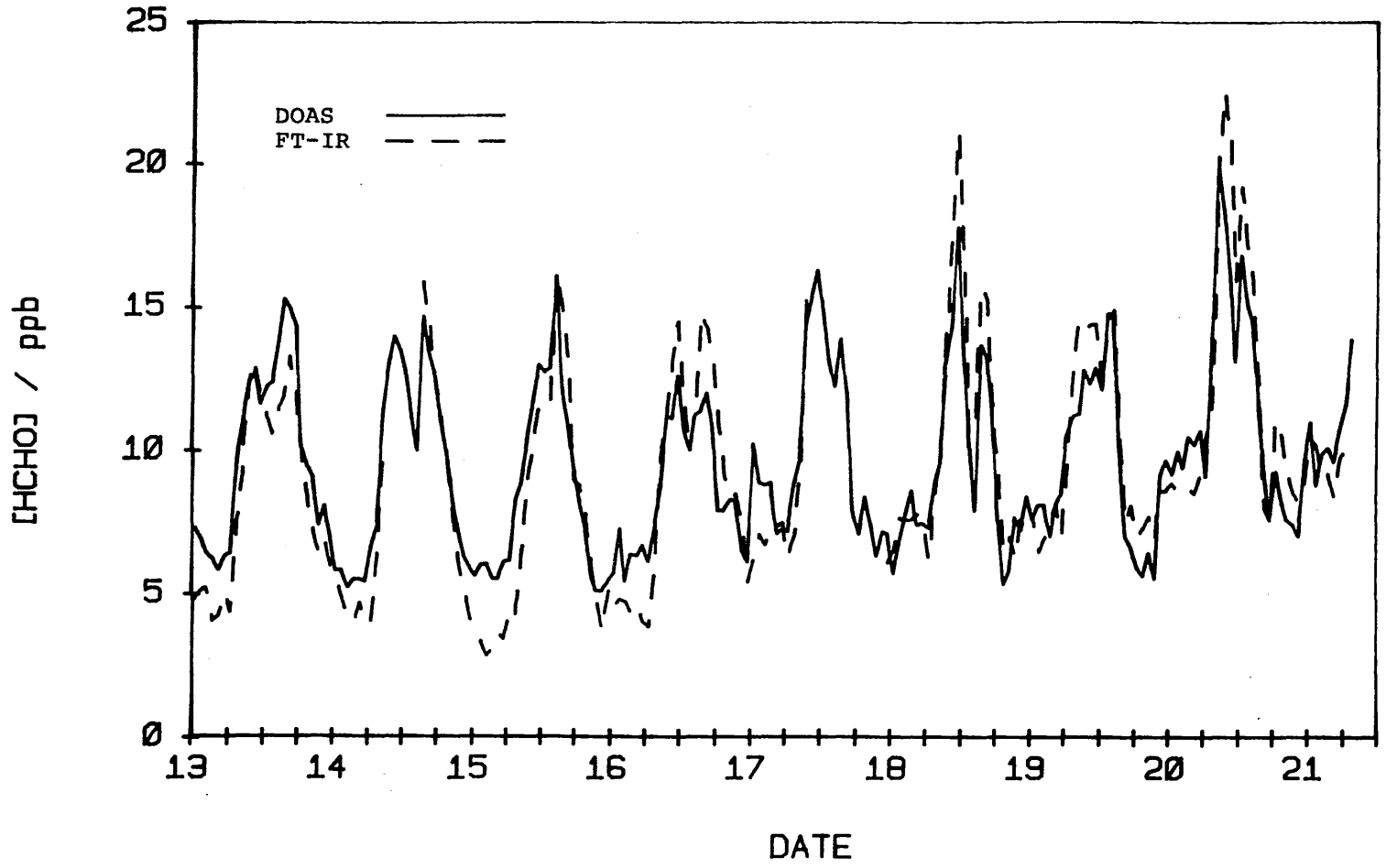

Figure XI-5. Time concentration profiles for formaldehyde measured by long pathlength DOAS and FT-IR spectrometers at Citrus College (Glendora) in August 1986.

measurements allowed us to delineate the reaction pathways leading to nitroarenes which were operating during the ambient measurement periods. Additionally, the DOAS measurements of HONO, a photolytic precursor to the OH radical

$$HONO + h\nu \rightarrow OH + NO$$

during predawn hours were of importance in assessing, in a qualitativ# manner, the involvment of daytime OH radicals in the formation of nitroarenes. Thus, the high HONO concentrations observed by DOAS at Torrance (up to 11 ppb) were consistent with the very high ratios observed for nitroarenes to their parent PAH, as shown, for example, by the observed 3-nitrobiphenyl/biphenyl concentration ratio of 0.1 (Section VI and Arey et al. 1987).

C. Nitroarene Formation During Atmospheric Transport and Sampling: Implications for Health Effects and Ambient Mutagenicity

A variety of PAH are formed in combustion systems at high temperature (Bockhorn et al. 1982, Prado et al. 1985, Toqan et al. 1985), and are hence emitted into the atmosphere from combustion sources (Nikolaou et al. 1984). These PAH exhibit a range of volatilities (Table XI-1) and are partitioned between the gas and particle phases. As discussed in previous sections (see, for example, Section VII), the PAH themselves are not responsible for the direct-acting mutagenicities of ambient POM extracts. Therefore, any assessments of the health impacts of PAH emissions, as well as the sources of the direct activity of ambient POM, must take into account the atmospheric transformation products of the initially emitted PAH.

Those PAH present in the gas-phase are known to react in the atmosphere with the hydroxyl (OH) radical and, to a lesser extent, with N_2O_5. The room temperature rate constants for the OH radical, O_3 and N_2O_5 reactions which we have determined in laboratory studies carried out under U.S. Department of Energy (DOE) and U.S. Environmental Protection Agency (EPA) funding are given in Table XI-2. Use of these kinetic data in conjunction with estimated or measured ambient atmospheric concentrations of OH radicals, N_2O_5 and O_3 then allows the atmospheric lifetimes of the PAH

Table XI-1. Vapor Pressures at 298 K for a Series of PAH[a]

PAH	Vapor Pressure at 298 K (torr)
Naphthalene	8.0×10^{-2}
Phenanthrene	1.2×10^{-4}
Anthracene	6.0×10^{-6}
Fluoranthene	9.2×10^{-6}
Pyrene	4.5×10^{-6}
Benzo(a)anthracene	2.1×10^{-7}
Benzo(a)pyrene	5.6×10^{-9}[b]
Chrysene	6.4×10^{-9}[b]

[a]From Sonnefeld et al. (1983), except as indicated.
[b]From Yamasaki et al. (1984).

Table XI-2. Room Temperature Rate Constants for the Gas-Phase Reaction of OH Radicals, O_3 and N_2O_5 with PAH

PAH	Rate Constant (cm^3 $molecule^{-1}$ s^{-1})		
	OH	O_3	N_2O_5
Naphthalene	2.2×10^{-11}[a]	$<2 \times 10^{-19}$[b]	1.4×10^{-17}[c]
1-Methylnaphthalene	5.3×10^{-11}[d]	$<1.3 \times 10^{-19}$[d]	3.3×10^{-17}[d]
2-Methylnaphthalene	5.2×10^{-11}[e]	$<4 \times 10^{-19}$[e]	4.2×10^{-17}[d]
2,3-Dimethylnaphthalene	7.7×10^{-11}[e]	$<4 \times 10^{-19}$[e]	5.7×10^{-17}[d]
Phenanthrene	3.2×10^{-11}[f]		
Anthracene	1.3×10^{-10}[f]		
Biphenyl	7×10^{-12}[a]	$<2 \times 10^{-19}$[b]	$<2 \times 10^{-19}$[c]

[a]From Atkinson (1986).
[b]From Atkinson et al. (1984).
[c]From Atkinson et al. (1987).
[d]From Atkinson and Aschmann (1987).
[e]From Atkinson and Aschmann (1986).
[f]From Biermann et al. (1985).

due to these gas-phase reactions to be calculated. Using ambient concentrations of 7 x 10^{11} molecule cm^{-3} (30 ppb) of O_3 over a 24-hr period, 1 x 10^6 molecule cm^{-3} of OH radicals over a 12-hr daytime period, and 2 x 10^{10} molecule cm^{-3} of N_2O_5 over a 12-hr nighttime period, the resulting atmospheric lifetimes due to each of these gas-phase removal processes are given in Table XI-3. Clearly, the daytime reaction with the OH radical appears to be the most important atmospheric loss process for the gas-phase PAH, with calculated lifetimes of the order of hours for the fused-ring PAH.

Also under U.S. DOE and U.S. EPA funding, we have investigated the products formed from these reactions and have shown that the nitroarenes we observe in ambient air are formed from both the OH radical reaction (in the presence of NO_x) and the N_2O_5 reaction. Furthermore, based upon the nitroarene formations yields in these reactions, it is clear that both of these reaction pathways must be considered with respect to nitroarene production during atmospheric transport. These studies of the gas-phase reactions of PAH with OH radicals and with N_2O_5 were carried out in the

Table XI-3. Calculated Atmospheric Lifetimes for Gas-Phase PAH Due to Reaction with OH Radicals, O_3 and N_2O_5

PAH	Lifetime Due to Reaction with		
	OH[a]	O_3[b]	N_2O_5[c]
Naphthalene	13 hr	>80 day	80 day
1-Methylnaphthalene	5 hr	>120 day	35 day
2-Methylnaphthalene	5 hr	>40 day	25 day
2,3-Dimethylnaphthalene	4 hr	>40 day	20 day
Phenanthrene	9 hr		
Anthracene	2 hr		
Biphenyl	3 day	>80 day	>15 yr

[a]For 12-hr daytime average of 1 x 10^6 molecule cm^{-3} (Crutzen 1982).
[b]For 24-hr average of 7 x 10^{11} molecule cm^{-3} (Singh et al. 1978).
[c]For 12-hr nighttime average of 2 x 10^{10} molecule cm^{-3} (Atkinson et al. 1986).

SAPRC 5800 liter evacuable and 6400 liter all-Teflon environmental chambers (Pitts et al. 1985a, Arey et al. 1986, Atkinson et al. 1987, Sweetman et al. 1986, Zielinska et al. 1986a,b, 1987).

In the remainder of this Section, we discuss our present knowledge concerning the gas-phase reactions of PAH and the gas-phase formation routes to nitroarenes. We then discuss the results of our passive exposures of PAH, which were designed to simulate adsorbed-phase reactions of PAH during atmospheric transport, as well as our study of artifactual formation of nitroarenes during high-volume sampling. The significance of these nitroarene formation pathways are then evaluated in terms of the nitroarenes we have observed in ambient air.

Gas-Phase Reactions of PAH to Form Nitroarenes. To date, the PAH studied with respect to the products formed from their gas-phase OH radical-initiated and N_2O_5 reactions have been biphenyl, naphthalene, fluoranthene, pyrene and acephenanthrylene. The nitroarene products formed from these reactions are given in Table XI-4, and the yields of these nitroarenes, either experimentally measured or approximately estimated, are also given in this table. It should be noted that exposures of gaseous fluoranthene and pyrene to NO_2 and NO_2/HNO_3 mixtures in the dark produced no detectable nitroarene products (Sweetman et al. 1986; unpublished data, this laboratory), and this finding is in agreement with the lack of reaction of naphthalene and the alkyl-naphthalenes with gas-phase NO_2 and NO_2/HNO_3 (Atkinson and Aschmann 1986).

As seen from Table XI-4, the 1- and 2-nitronaphthalenes and 2-nitrofluoranthene are formed from the gas-phase reactions of the parent PAH with OH radicals (in the presence of NO_x) and with N_2O_5, 2-nitropyrene and 3-nitrobiphenyl are formed from the gas-phase OH radical-initiated reactions, and 4-nitropyrene is formed from the gas-phase N_2O_5 reaction.

Adsorbed-phase Reactions of PAH to Form Nitroarenes. As discussed in Section VIII above, we carried out studies to evaluate the adsorbed-phase reactions of selected PAH to form nitroarenes during both high-volume sampling and during transport through the atmosphere. Fluoranthene and pyrene were most extensively studied because of the importance of their nitro-derivatives in ambient air (although benzo(a)pyrene and perylene were also included in the high-volume sampling study).

Table XI-4. Nitroarene Products Formed from the Gas Phase Reactions of PAH, Known to be Present in Ambient Air, with OH Radicals (in the Presence of NO_x) and N_2O_5, Together with their Yields

PAH	Reaction with OH	Reaction with N_2O_5
Naphthalene	1-Nitronaphthalene (0.3%)[a] 2-Nitronaphthalene (0.3%)[a]	1-Nitronaphthalene (17%)[a,b] 2-Nitronaphthalene (7%)[a,b]
Pyrene	2-Nitropyrene[c]	4-Nitropyrene[d]
Fluoranthene	2-Nitrofluoranthene (~0.5%)[c] 7-Nitrofluoranthene (minor)[c] 8-Nitrofluoranthene (minor)[c]	2-Nitrofluoranthene[e,f]
Acephenanthrylene	Two nitroarene isomers[g]	None observed[g]
Biphenyl	3-Nitrobiphenyl (5%)[a]	No reaction observed[a]

[a]Atkinson et al. (1987).
[b]Pitts et al. (1985a).
[c]Arey et al. (1986).
[d]Zielinska et al. (1986b).
[e]Sweetman et al. (1986).
[f]Zielinska et al. (1986a).
[g]Zielinska et al. (1987).

The studies conducted to assess the contribution of nitroarene formation during Hi-vol sampling of ambient air show that any artifact formation of the m/z 247 nitroarenes during sampling will affect only 1-nitropyrene. Furthermore, the contribution of this artifact formation of 1-nitropyrene to the observed ambient levels of 1-nitropyrene is expected to be insignificant. However, the experiments carried out to assess the importance of the formation of nitroarenes from adsorbed phase reactions of fluoranthene and pyrene show that all possible isomers can be formed, although only in low yields during 12-hr ambient exposures.

Table XI-5 summarizes the possible formation routes which we have identified for the m/z 247 nitroarenes under atmospheric conditions. While these studies concerning the transformation of adsorbed-phase PAH suggest that nitroarene formation via these reaction pathways will be minor under atmospheric conditions, further assessment can only be made on the basis of the nitroarenes observed in ambient POM and concurrent levels of key atmospheric species such as OH and NO_3 radicals, the latter acting as a surrogate species for N_2O_5 since N_2O_5, NO_3 and NO_2 are in equilibrium through the reactions

$$NO_2 + NO_3 \underset{\leftarrow}{\overset{M}{\rightarrow}} N_2O_5$$

Table XI-5. The Possible Formation Routes to the m/z 247 Nitroarenes Under Atmospheric Conditions

	Nitrofluoranthenes					Nitropyrenes			Nitroacephenanthrylenes
	1-	2-	3-	7-	8-	1-	2-	4-	
Gas Phase									
OH Radical reaction in the presence of NO_x		+[a]		+	+		+		+[b]
N_2O_5 Reaction		+						+[c]	None observed
Adsorbed Phase									
Dark simulated Hi-vol sampling	None observed					+			
Exposed to atmosphere	+	+	+	+	+	+	+	+	Not tested

[a]Major nitrofluoranthene isomer formed.
[b]Two isomers observed, distinct from the two isomers formed in solution phase reactions with N_2O_4 and N_2O_5.
[c]Formed in low yield relative to 2-nitrofluoranthene from fluoranthene.

Evaluation of Formation Routes to Nitroarenes in Ambient Air. The nitroarenes observed in what is certainly the best characterized combustion emission, namely diesel POM, have been those expected from electrophilic nitration of PAH (Schuetzle 1983), presumably being formed after the combustion process but before extensive dilution after emission occurs (Kittelson et al. 1985).

The specific isomers and the relative abundance of the nitroarenes present in diesel POM can be rationalized on the basis of the abundance of the parent PAH and their reactivities toward electrophilic nitration. For example, 1-nitropyrene is the primary nitroarene observed in diesel POM, together with much lower amounts of the 3- and 8- nitrofluoranthenes (Paputa-Peck et al. 1983, Liberti and Ciccioli 1986, Robbat et al. 1986b). Fluoranthene and pyrene are among the most abundant PAH in diesel POM and are emitted in similar quantities (Schuetzle et al. 1981); however, pyrene is more reactive toward electrophilic nitration than is fluoranthene (Nielsen 1984). As shown in Section VI, Tables VI-4 and VI-5, we observed that fluoranthene and pyrene were also present in ambient air at very similar concentrations. Of relevance to the following discussion, the isomeric PAH acephenanthrylene was also present in ambient air, though in much smaller amounts.

In addition to being the most abundant nitroarene in diesel POM, 1-nitropyrene has been reported to be present in particulate emissions from gasoline-fueled vehicles (Gibson 1982, Nishioka et al. 1982) and coal-fired power plants (Harris et al. 1984). However, neither 2-nitrofluoranthene nor 2-nitropyrene has been reported to be present in any of these emission sources, although both are present in ambient POM (Nielsen et al. 1984, Pitts et al. 1985d, Liberti and Ciccioli 1986, Nielsen and Ramdahl 1986, Ramdahl et al. 1986, Sweetman et al. 1986, Tables VI-3 through VI-6). Indeed, we have shown that 2-nitrofluoranthene is often the most abundant nitroarene in ambient POM. In addition to the present work, we have shown this to be true for POM collected at several locations in the U.S. and Europe by various collection methods, including Hi-vol filtration, electrostatic precipitation and bag-house collection (Pitts et al. 1985d, Arey et al. 1986, Ramdahl et al. 1986, Sweetman et al. 1986).

It should be noted, however, that a single report of the presence of 2-nitrofluoranthene and 2-nitropyrene in an industrial emission (from a

plant in Italy manufacturing carbon electrodes) has recently appeared (Liberti and Ciccioli 1986). This particular emission source seems unlikely to be a major contributor to ambient 2-nitrofluoranthene and 2-nitropyrene concentrations, except perhaps on a very local scale, and no such plants exist in the California South Coast Air Basin, where the present ambient measurements were conducted. As discussed in Section VI, the most abundant m/z 247 nitroarenes observed in ambient air are 2-nitrofluoranthene and 1- and 2-nitropyrene (Figure XI-6 and Table XI-6).

As noted above, while 1-nitropyrene is a direct emission from combustion sources, 2-nitrofluoranthene and 2-nitropyrene have not been reported in emissions in the California South Coast Air Basin. Thus, these two nitroarenes must be formed during atmospheric transport from source to receptor. 2-Nitrofluoranthene can be formed in the gas-phase from both the daytime OH radical (in the presence of NO_x) and the nighttime N_2O_5 reactions, while 2-nitropyrene is formed in the gas phase only from the daytime OH radical-initiated reaction. The large amounts of these two m/z 247 nitroarenes, relative to the other m/z 247 isomers, argues that the adsorbed-phase reactions of fluoranthene and pyrene cannot be responsible for the formation of 2-nitrofluoranthene and 2-nitropyrene, since the adsorbed-phase reactions form the complete spectrum of nitrofluoranthene and nitropyrene isomers, with 1-nitropyrene being the major m/z 247 isomer formed from these adsorbed-phase reactions (Section VIII).

Further evidence for the importance of gas-phase reactions for the formation of 2-nitrofluoranthene and 2-nitropyrene arises from comparison of our data at Claremont and at Torrance. As shown in Figure XI-6 and Table XI-6, for the nighttime ambient air samples collected at Claremont on 9/13 and 9/14/85 from 1800-2400 hr, where NO_3 radicals were present during the early evening hours and thus N_2O_5 was expected to be present (Section IV), the 2-nitrofluoranthene/2-nitropyrene concentration ratios were significantly higher than those for the samples collected at Torrance when NO_3 radicals, and hence N_2O_5, were not present. Furthermore, the samples collected at Torrance during January and February 1986, when the sole gas-phase reaction pathway leading to formation of nitroarenes was the daytime OH radical reaction, have similar 2-, 7- and 8-nitrofluoranthene and 2-nitropyrene concentration profiles as do our environmental chamber OH radical-initiated experiments (Figure XI-7).

Table XI-6. Comparison of 2-Nitrofluoranthene (2-NF), 1-Nitropyrene (1-NP) and 2-Nitropyrene (2-NP) Concentrations in Winter- and Summertime Ambient POM Samples

Collection Date	Collection Time (hrs)	Concentration, pg m^{-3} ($\mu g\ g^{-1}$)				$\frac{2\text{-NF}}{2\text{-NP}}$	$\frac{2\text{-NF}}{\text{BeP}} \times 100$	$\frac{2\text{-NP}}{\text{BeP}} \times 100$
		2-NF	1-NP	2-NP	BeP			
1/19-20/86	1700-0500	40 (0.7)	3 (0.05)	1 (0.025)	270 (4.7)	28	15	0.5
1/20/86	0500-1700	60 (0.8)	10 (0.140)	1 (0.02)	340 (4.8)	41	17	0.4
1/27-28/86	1700-0500	690 (5.1)	90 (0.7)	50 (0.35)	2,800 (21)	15	24	1.7
		750[a]	50[a]	60[a]				
1/28/86	0500-1700	410 (3.4)	60 (0.5)	50 (0.4)	3,500 (29)	8	12	1.4
2/24-25/86	1800-0600	320 (4.1)	30 (0.37)	30 (0.37)	2,100 (26)	11	16	1.4
2/25/86	0600-1800	280 (1.7)	40 (0.24)	40 (0.24)	2,100 (13)	7	13	1.8
9/13/85	1200-1800	40 (0.5)	2 (0.03)	0.9 (0.01)	-	50	-	-
9/13/85	1800-2400	1,700 (22)	11 (0.14)	8 (0.11)	-	200	-	-
9/14/85	0600-1200	80 (0.9)	30 (0.4)	3 (0.025)	280 (3.7)	36	24	0.7
9/14/85	1200-1800	30 (0.4)	10 (0.2)	1 (0.01)	130 (2.6)	40	15	0.4
9/14/85	1800-2400	500 (10)	30 (0.6)	5 (0.1)	360 (7.2)	100	140	1.4
9/14/85	0000-0600	100 (2.1)	10 (0.3)	2 (0.3)	130 (3.9)	54	54	0.8

[a]Replicate quantification. See Section VI.C for a detailed discussion.

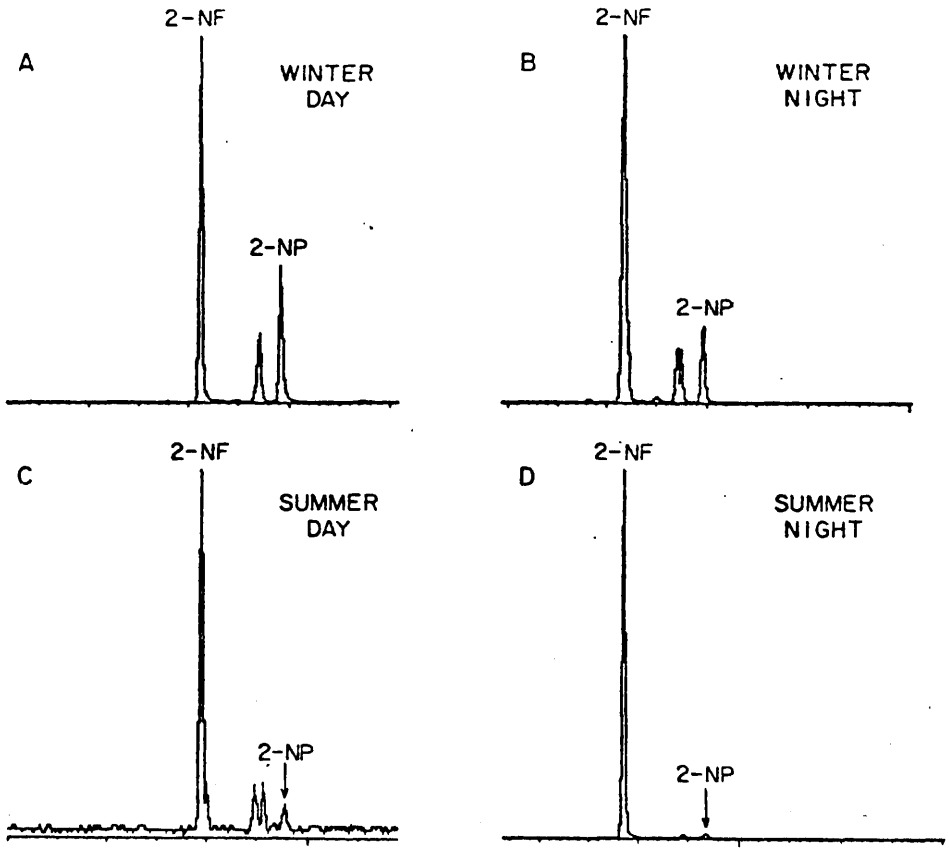

Figure XI-6. GC/MS-MID traces of the molecular ions of the NF and NP isomers present in ambient POM. The sample extraction and clean-up procedures have been described above (Section VI). The ambient particulate samples were collected as follows:
(A) At Torrance, CA on January 28, 1986 from 0500-1700 hr.
(B) At Torrance, CA on January 27-28, 1986 from 1700-1500 hr.
(C) At Claremont, CA on September 13, 1985 from 1200-1800 hr.
(D) At Claremont, CA on September 13, 1985 from 1800-2400 hr.

Figures XI-8 and XI-9 show further examples of GC/MS-MID m/z 247 nitroarene molecular ion traces obtained from analyses of ambient air sample extracts at Claremont and Torrance. Also shown in Figure XI-8 are analogous GC/MS-MID traces for the entire set of nitrofluoranthene (NF) and nitropyrene (NP) isomers from a standard mixture and for the two nitroacephenanthrylene isomers formed from the gas-phase reaction of acephenanthrylene with OH radicals in the presence of NO_x [entirely

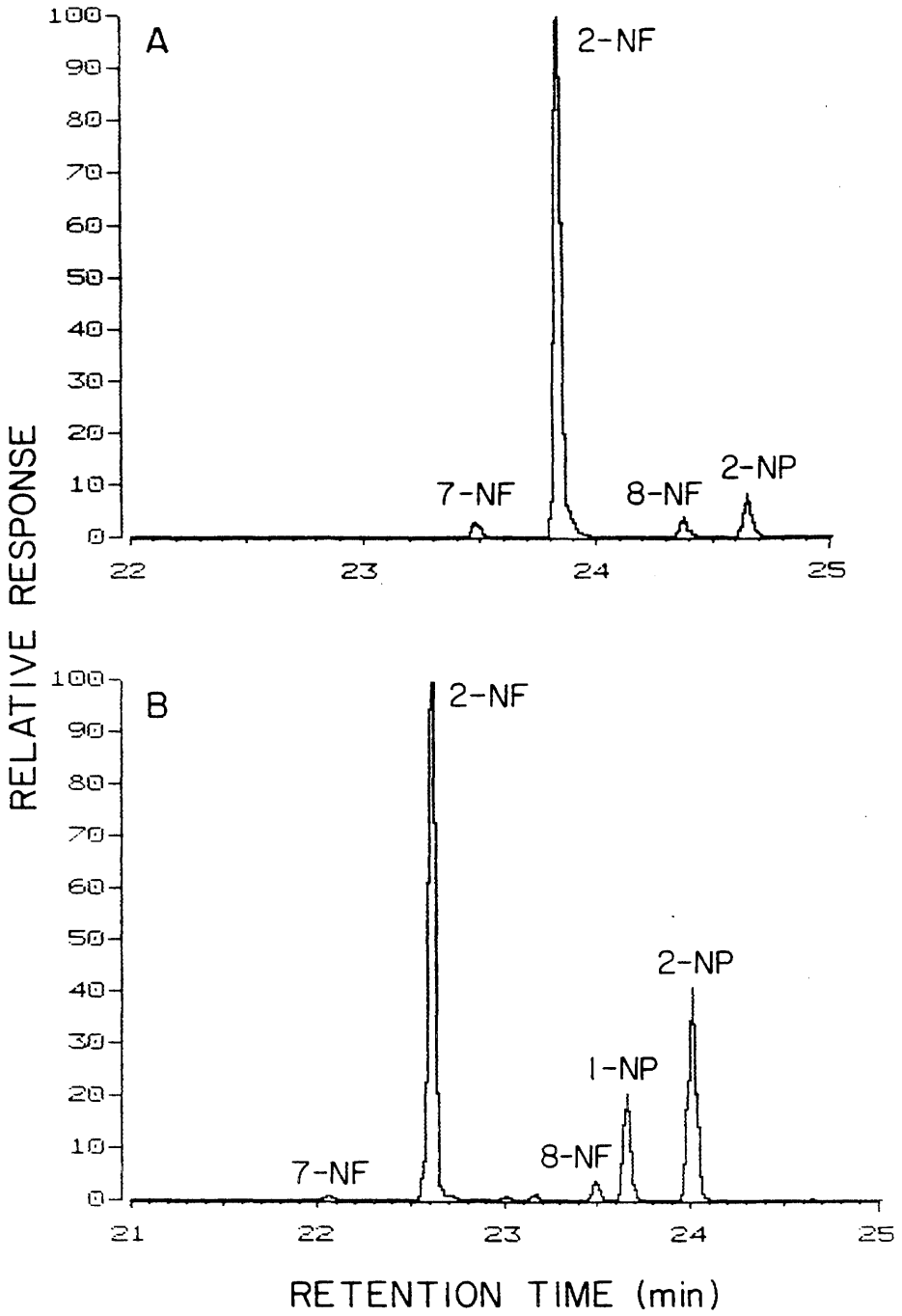

Figure XI-7. GC/MS-MID traces of the molecular ions of the NF and NP isomers present: (A) As products from the gas-phase reactions of fluoranthene and pyrene with the OH radical in the presence of NO_x; (B) In the extract of an ambient POM sample collected at Torrance, CA on January 28, 1986 from 0500-1700 hr. Two different (~30 m) GC columns were used for these analyses and thus the retention times are slightly different. The ambient sample is that shown in Figure XI-6(A) with the 2-nitrofluoranthene peak plotted off-scale to allow the minor isomers to be readily identified.

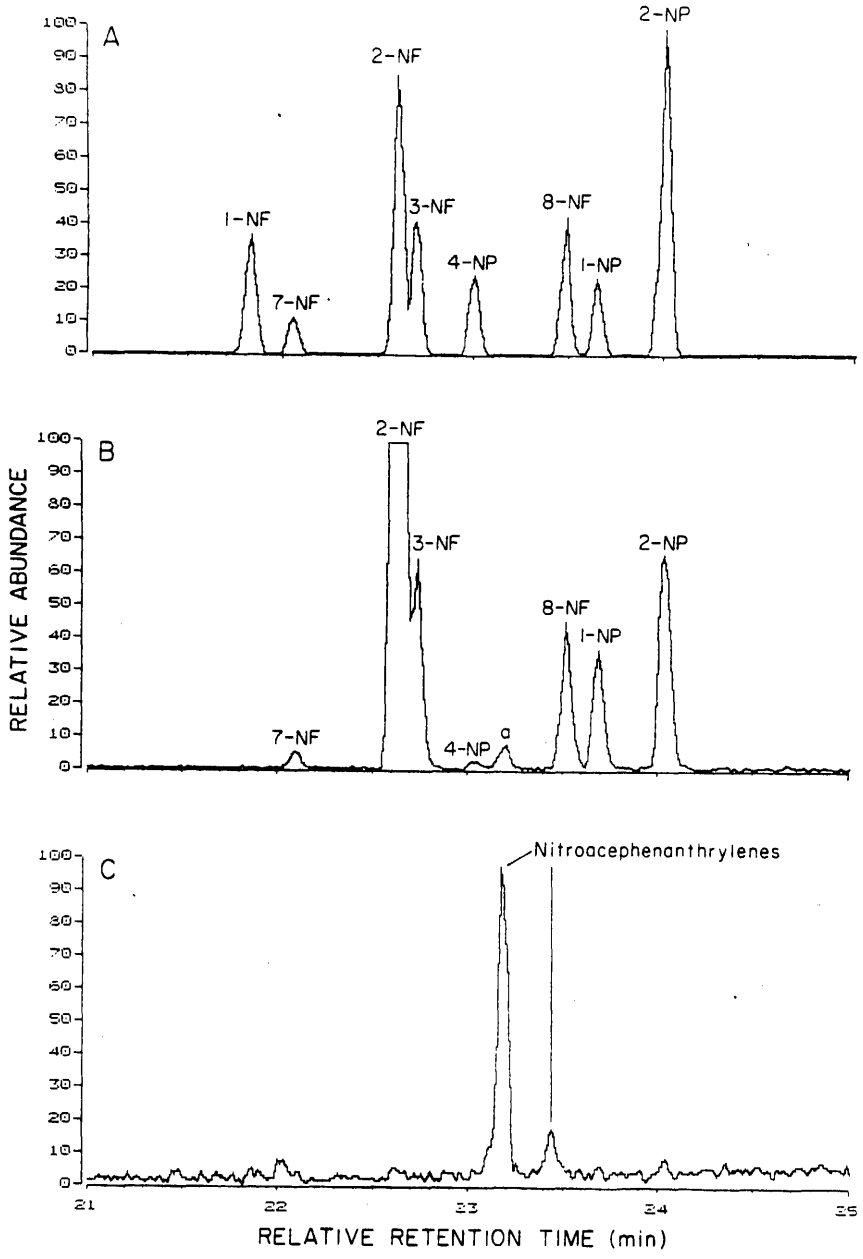

Figure XI-8. GC/MS-MID traces of the m/z 247 molecular ions of: (A) A standard mixture containing all eight NF and NP isomers. (B) The NF and NP isomers present in the ambient POM sampler collected at Torrance, CA on January 27-28, 1986 from 1700-0500 hr [(the peak labeled "a" can be seen to elute at the retention time of the most abundant nitroacephenanthrylene isomer shown in (C)]. (C) The nitroarene products of the gas-phase reaction of acephenanthrylene with the OH radical in the presence of NO_x. GC column and conditions: 60 m DB-5N column, injection at 50°C, then programmed at 20°C min^{-1} to 200°C, then at 4°C min^{-1}. 2-Nitrofluoranthene-d_9 was used as an internal standard to give the precise relative retention times. See Appendix E for additional ion traces.

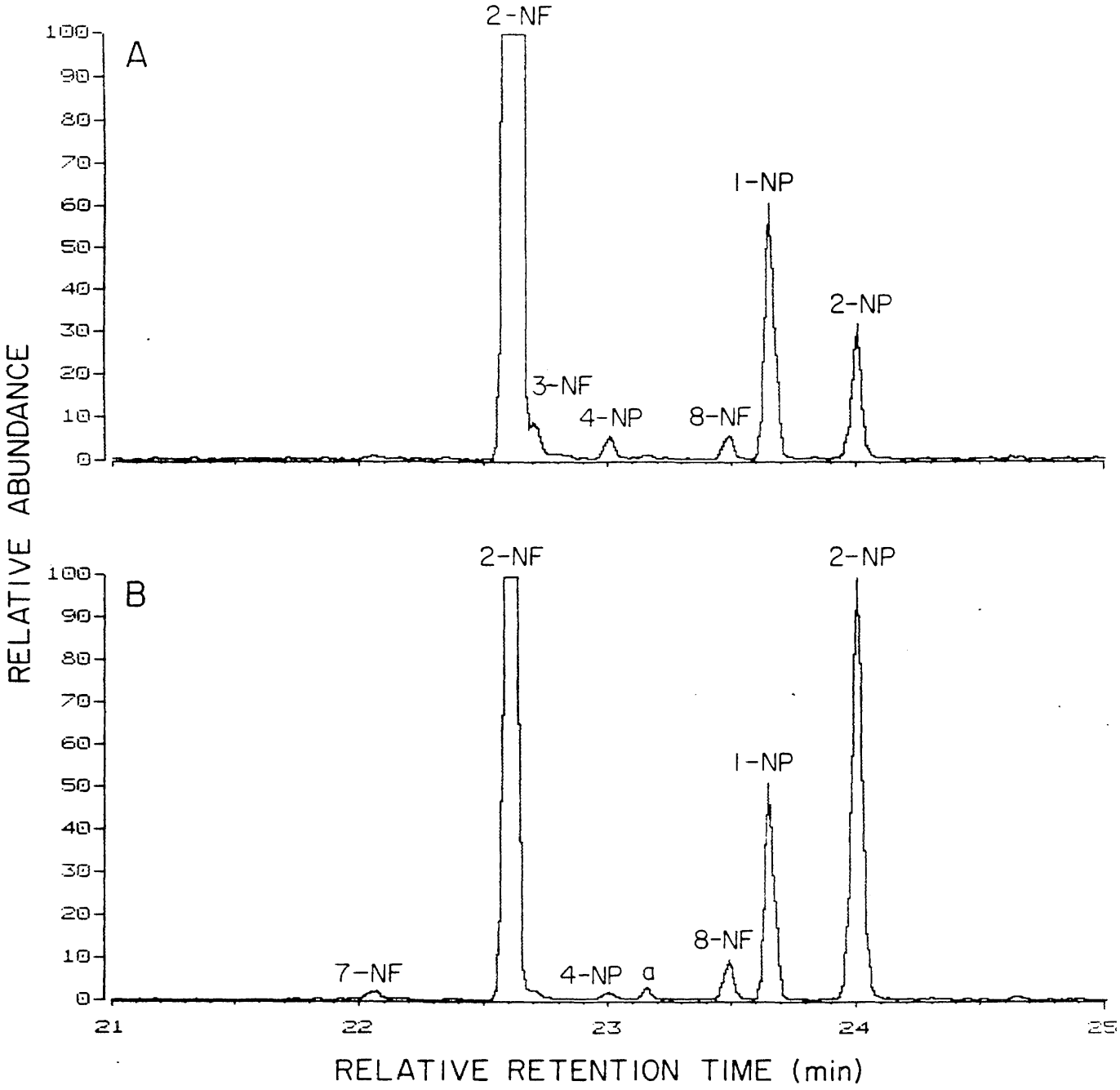

Figure XI-9. GC/MS-MID traces of the m/z 247 molecular ion of the NF, NP and nitroacephenanthrylene (labeled "a") isomers present in ambient POM samples collected at: (A) Claremont, CA on September 14, 1985 from 1800-2400 hr. (B) Torrance, CA on January 28, 1986 from 0500-1700 hr. GC column and conditions as given in Figure XI-8.

different nitroacephenanthrylene isomers are formed from the solution phase reactions of acephenanthrylene with N_2O_4 or N_2O_5, and no nitro-isomers were detected from the gas-phase reaction of acephenanthrylene with N_2O_5 (Zielinska et al. 1987)]. Consistent with Figure XI-6, these figures (as well as the additional data given in Appendix E) show that the m/z 247 nitroarene isomers observed in ambient air typically have the following approximate order of abundance: 2-nitrofluoranthene > 1-nitropyrene ~ 2-nitropyrene > 8-nitrofluoranthene > 3-nitrofluoranthene ~ 4-nitropyrene ~ 7-nitrofluoranthene ~ nitroacephenanthrylene [formed from the gas-phase OH radical reaction with acephenanthrylene].

Although it is difficult to provide quantitative answers, as discussed above it appears that the adsorbed phase reactions of fluoranthene and pyrene can provide only a minor amount of the 2-nitrofluoranthene and 2-nitropyrene observed in ambient air. However, these adsorbed phase reactions are potentially significant for the formation of the lesser amounts of 4-nitropyrene and 3- and 8-nitrofluoranthene observed in ambient POM.

Based upon our ambient air and chamber data, we believe that the following are the major formation routes to the m/z 247 nitroarene isomers observed in ambient air:

- 1-nitropyrene is a direct emission from combustion sources, with a small amount being formed in the atmosphere from adsorbed-phase reactions of pyrene.
- 2-nitropyrene is formed in the atmosphere, predominantly via the gas-phase OH radical-initiated reaction with pyrene during daylight hours.
- 4-nitropyrene is formed in the atmosphere, both from the gas-phase reaction of pyrene with N_2O_5 (when present) during nighttime hours and from the adsorbed-phase reaction of pyrene during atmospheric transport from source to receptor.
- 2-nitrofluoranthene is formed in the atmosphere, both from the gas-phase reactions of fluoranthene with OH radicals, in the presence of NO_x, during daytime hours and with N_2O_5 (when present) during nighttime hours.
- 3-nitrofluoranthene is a minor direct emission from combustion sources, and can also be formed from adsorbed-phase reactions during atmospheric transport conditions.

• The 7- and 8-nitrofluoranthenes can be formed from both the gas-phase reactions of the OH radical with fluoranthene during daylight hours and from adsorbed-phase reactions of fluoranthene during atmospheric transport conditions, although it is appears likely that 7-nitrofluoranthene is formed mainly via the OH radical-initiated reaction.

Thus, for example, the nitroarene profile given in Figure XI-8B from a nighttime Torrance sample (when N_2O_5 was not present) is consistent with laboratory experiments which predict that the 2-nitrofluoranthene, 7-nitrofluoranthene, some of the 8-nitrofluoranthene, the nitroacephenanthrylene and the 2-nitropyrene were formed from gas-phase OH radical-initiated reaction, and that the 4-nitropyrene and some of the 3- and 8-nitrofluoranthenes were formed from adsorbed-phase reactions (some of the 3-nitrofluoranthene could also be a direct emission). The data shown in Figure XI-9A for an ambient sample collected during nighttime hours in Claremont when NO_3 radicals (and hence N_2O_5) were present are consistent with the majority of the observed 2-nitrofluoranthene and 4-nitropyrene arising from gas-phase N_2O_5 reactions, with the 3- and 8-nitrofluoranthenes arising from direct emissions (3-nitrofluoranthene), gas-phase OH radical reaction (8-nitrofluoranthene) and/or adsorbed phase reactions. Since no nitroacephenanthrylene nor 7-nitrofluoranthene were observed, any contribution to these m/z 247 nitroarenes from OH radical reactions was probably small. In contrast, the data shown in Figure XI-9B for a daytime sample from Torrance indicate that the 2-, 7- and 8-nitrofluoranthenes, the nitroacephenanthrylene and 2-nitropyrene were formed predominantly from gas-phase reactions of fluoranthene, acephenanthrylene and pyrene with the OH radical in the presence of NO_x. Since N_2O_5 was not present at this study site, the 4-nitropyrene observed probably arose from adsorbed-phase reactions.

Clearly, under atmospheric conditions there is more than one formation route for most of these m/z 247 nitroarenes and, especially for the more minor species such as 3-, 7- and 8-nitrofluoranthene and 4-nitropyrene, the dominant formation routes can vary significantly with location, time and atmospheric conditions.

Less data are available concerning the atmospheric concentrations of the more volatile nitroarenes, but it is extremely likely that the 3-nitrobiphenyl observed during our study at Torrance (Section VI) arose

from the gas-phase reaction of OH radicals with biphenyl, since this particular nitrobiphenyl isomer is not expected to be a direct emission and 3-nitrobiphenyl is not the electrophilic nitration product of biphenyl (see above). Moreover, environmental chamber experiments show that 3-nitrobiphenyl is the sole nitrobiphenyl isomer formed from the OH radical initiated reaction of biphenyl, in the presence of NO_x (Atkinson et al. 1987).

Nitroarene Contribution to Mutagenicity. As discussed in detail in Sections VII and above, we have shown that directly-acting mutagenic nitroarenes are formed from the atmospheric reactions of emitted PAH with gaseous reactive species such as N_2O_5 and the OH radical in the presence of NO_x. In particular, we have identified and, for selected POM samples, quantified a number of mutagenic nitroarenes which have not been reported in emissions from combustion sources. These nitroarenes include 2- and 8-nitrofluoranthene and 2- and 4-nitropyrene. The contribution of these nitroarenes to the overall mutagenicity of several ambient POM samples from southern California has been calculated (see Section VII, Table VII-2) to range from ~1 to 10%. In one sample, 2-nitrofluoranthene alone contributed as much as 5% to the observed mutagenicity. Thus, it is clear that the mutagenicity of ambient POM can be enhanced during transport through the atmosphere due to the formation of mutagenic nitroarenes.

Mutagenicity Artifacts. As discussed in detail in Section IX, we have exposed precollected ambient POM, for which mutagen assays have been carried out, to ambient air under active conditions, e.g., corresponding to normal POM collection on Hi-vol samplers. In addition, since we have previously observed differences in the mutagenicity of POM collected on different filters materials, GF and TIGF filters were used for POM collection. Because filter media can adsorb or destroy reactive gases present in ambient air, the precollected POM was not exposed with a particulate filter upstream; instead it was exposed to unfiltered ambient air. Thus, any mutagenicity artifacts were observed by comparing the mutagenicities of the unexposed (original) POM to the difference of the exposed POM minus the POM collected (by using separate Hi-vols) during the exposure period.

Although this calculation of mutagenicity artifact is subject to considerable error, we have no evidence for the occurrence of such artifacts on TIGF filters (see Table IX-7). Our results for GF filters

imply that the uncoated glass fiber surface is more reactive, and hence we intend to continue to use TIGF filters for Hi-vol collection of ambient POM for mutagenicity determinations.

Of much more significance, however, to the determination of the mutagenicity of ambient POM was our observation that the method of POM extraction had a considerable effect on its measured mutagenicity (see Section IX). Specifically, we have established that the Soxhlet extraction of POM with acetonitrile produces artifactual mutagenicity (see Table IX-5). Therefore, our procedure for POM extraction has been modified to sequential Soxhlet extraction with CH_2Cl_2 followed by methanol, and we recommend that acetonitrile not be used for extraction of POM for mutagenicity testing.

Implications for Health Effects and Ambient Mutagenicity. In conclusion, our laboratory and ambient atmospheric measurements show that most of the nitroarenes present in ambient air arise from atmospheric transformations in either the gas- or adsorbed phases during transport from source-to-receptor. As discussed above, the m/z 247 nitroarenes contributed up to ~10% of the direct acting mutagenicity of extracts of ambient POM collected during our field studies, with the majority of this nitroarene-mutagenicity arising from atmospheric transformations. In one sample, 2-nitrofluoranthene alone contributed as much as 5% to the observed mutagenicity. Additionally, we observed for the first time the presence in low concentration of several highly mutagenic nitroarenes (7- and 8-nitrofluoranthene and 4-nitropyrene) in ambient POM. Although the observed levels of 4-nitropyrene did not contribute significantly to the ambient mutagenicities, this isomer has recently been found to be a potent tumorigen in the newborn mouse assay (Wisocki et al. 1986). These findings must be taken into account in any risk assessments of PAH and nitroarene emissions from combustion sources.

Additionally, although the PAH which are carcinogenic (Jacob et al. 1986) are the higher molecular weight (m.w. >200), mainly particle-associated species, this may not be the case for the nitroarenes. For example, 2-nitronaphthalene and 4-nitrobiphenyl have both been shown to be carcinogenic in animal feeding studies (Tokiwa and Ohnishi 1986). In our ambient measurements in Torrance, CA, of volatile nitroarenes we found

these species, in particular 1- and 2-nitronaphthalene and 3-nitrobiphenyl, to be more abundant than the particle-associated nitroarene species. Clearly, the health implications of these lower molecular weight nitroarenes should be studied.

D. Recommendations for Future Research

In summary, we believe that the main goals of this program have been fulfilled during our two-year study. Thus, our data allow the relative importance of the formation of mutagenic nitroarenes during transport and during Hi-vol collection of ambient POM and the role of nitrogenous pollutants in these processes to be assessed. However, results from this program also suggest further research to resolve remaining key issues or to address certain gaps in our present knowledge. In this context we make the following recommendations for future research.

- For the nitroarene species present in ambient air, the main goals of this program, as detailed in Section II, have been achieved. We now know that these species are indeed formed from their parent PAH as the particle emissions travel from source to receptor and that nitrogenous species such as N_2O_5 can play a major role in their formation. We have elucidated both the formation pathways for these nitroarenes and their contribution to the observed direct mutagenic activity of ambient POM. However, in terms of the risk assessment of PAH emissions, important questions remain.

Thus, although a fraction of ambient POM mutagenicity can be attributed to a relatively few nitroarenes, the majority of the activity remains to be explained. From previous tests of HPLC fractions of ambient POM, we have seen that a substantial portion of the TA98 direct mutagenicity is due to compounds which are more polar than simple nitroarenes. Additionally, based in part on our chamber studies of the reactions of gas-phase PAH with the OH radical in the presence of NO_x, we anticipate that more polar, possibly highly mutagenic compounds (for example, hydroxynitroarenes) may be formed from the parent PAH during transport through the atmosphere. Indeed, our chamber studies show that the formation of nitroarenes from the gas-phase OH radical-initiated reactions in the presence of NO_x account for $\lesssim$ 5% of the overall OH radical reaction, with hydroxy-derivatives accounting for a further $\lesssim$ 20%. Thus

in excess of 75% (and often in excess of 95%) of the products of these reactions remain to be accounted for. Clearly, one important goal for future research on characterizing atmospheric mutagenicity should be to investigate these more polar mutagenic species, including their modes of formation during atmospheric transport, and to assess their contribution to the total mutagenic activity of ambient POM.

- In conducting the FT-IR measurements described above, we chose operating parameters with the objective of attaining the best sensitivity for HNO_3, NH_3 and HCHO in order to ensure a successful comparison with the other analytical methods during the CARB-sponsored methods intercomparison studies. This was not entirely compatible with our original objective of attempting to detect N_2O_5 for the first time in a polluted airshed. We have previously noted that for N_2O_5 the use of a pathlength about half of that used in the present study, i.e., ~500 meters, might be advantageous since it would reduce H_2O interferences. Due to the demanding schedules of both the Claremont and Glendora intercomparison studies and the need to preserve the continuity of the data sets being taken, no experimentation on the optimum detection of N_2O_5 could be conducted, at Claremont or Glendora. The limited number of such experiments conducted in the 1986 Torrance study yielded no data on N_2O_5, as expected from the presence of high concentrations of NO. Obviously, several episodes of various degrees of severity must be examined under optimum parameterization of the FT-IR system in order to experimentally test the recent predictions (Atkinson et al. 1986) of nighttime N_2O_5 levels and this remains an important research goal.

- As we have observed in previous studies concerned with determining the mutagen burden to which populations in the South Coast Air Basin are exposed, there were substantial intra-day and inter-day variations in mutagen density (revertants m^{-3}) during both the summer study at Claremont and the winter study at Torrance. Because of these wide short-term variations in mutagen density, an evaluation of the long-term trends in atmospheric mutagenicity in Southern California remains elusive. In order to determine these long-term trends in airborne particulate mutagenicity, which can then be used to evaluate, for example, the effectiveness of certain pollutant control measures, it will be necessary to use a standardized, low-cost sampling, extraction, and testing protocol. Such a

protocol should be developed, involving, for example, weekly integrated samples taken with a low volume sampler at specific locations in the air basin over the period of several years with testing for mutagenicity via a simplified Ames assay.

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APPENDIX A

Research Papers, and Publications Resulting from Technical Presentations, Arising Wholly or in Part from this Research Program

"Determination of Nitrofluoranthenes and Nitropyrenes in Ambient Air and Their Contribution to Direct Mutagenicity"
T. Ramdahl, J. A. Sweetman, B. Zielinska, W. P. Harger, A. M. Winer and R. Atkinson
Presented at the 10th International Symposium on PAH, Battelle, Columbus, Ohio, October 21-23, 1985

"Ubiquitous Occurrence of 2-Nitrofluoranthene and 2-Nitropyrene in Air"
T. Ramdahl, B. Zielinska, J. Arey, R. Atkinson, A. M. Winer and J. N. Pitts, Jr.
Nature, 321, 425-427 (1986)

"The Formation of Nitropolycyclic Hydrocarbons and Their Contribution to the Mutagenicity of Ambient Air"
R. Atkinson, J. Arey, B. Zielinska, A. M. Winer, and J. N. Pitts, Jr.
Presented at the 5th Symposium on the Application of Short-Term Bioassays in the Analysis of Complex Environmental Mixtures, Durham, N.C., October 20-23, 1986

"Polycyclic Aromatic Hydrocarbons and Nitroarene Concentrations in Ambient Air During a Wintertime High-NO_x Episode in the Los Angeles Basin"
J. Arey, B. Zielinska, R. Atkinson and A. M. Winer
Atmospheric Environment, in press (1987)

"The Mutagenicity of 2-Nitrofluoranthene and Its In Vitro Hepatic Metabolites"
B. Zielinska, W. P. Harger, J. Arey, A. M. Winer, R. A. Haas and C. V. Hanson
Mutation Research Letters, in press (1987)

"Simultaneous Absolute Measurements of Gaseous Nitrogen Species in Urban Ambient Air by Long Pathlength Infrared and Ultraviolet-Visible Spectroscopy"
H. W. Biermann, E. C. Tuazon, A. M. Winer, T. J. Wallington and J. N. Pitts, Jr.
Submitted to Atmospheric Environment (1987)

"Field Comparison of Measurement Methods for Nitric Acid"
S. V. Hering et al.
Submitted to Atmospheric Environment (1987)

APPENDIX B

DOAS Data for HONO, HCHO and NO_2 from the
Pomona College, Claremont (September 1985) [Tables B-1 and B-2]
and Citrus College, Glendora (August 1986) [Table B-3] Studies

Table B-1. Nitrogen Dioxide Concentrations (ppb) Determined by Long Pathlength DOAS System at Pomona College (Claremont) in September 1985

Date	Hr[a]	Concentration	Date	Hr[a]	Concentration
9/11	8	25	9/12	20	121
9/11	9	22	9/12	21	136
9/11	10	22	9/12	22	107
9/11	11	16	9/12	23	93
9/11	12	17	9/13	0	90
9/11	13	12	9/13	1	42
9/11	14	16	9/13	2	31
9/11	15	16	9/13	3	23
9/11	16	17	9/13	4	20
9/11	17	22	9/13	5	23
9/11	18	28	9/13	6	48
9/11	19	40	9/13	7	71
9/11	20	53	9/13	8	73
9/11	21	53	9/13	9	59
9/11	22	53	9/13	10	51
9/11	23	43	9/13	11	45
9/12	0	47	9/13	12	17
9/12	1	48	9/13	13	29
9/12	2	40	9/13	14	26
9/12	3	36	9/13	15	28
9/12	4	39	9/13	16	33
9/12	5	42	9/13	17	47
9/12	6	47	9/13	18	56
9/12	7	51	9/13	19	71
9/12	8	47	9/13	20	95
9/12	9	50	9/13	21	129
9/12	10	48	9/13	22	121
9/12	11	47	9/13	23	112
9/12	12	28	9/14	0	88
9/12	13	14	9/14	1	54
9/12	14	9	9/14	2	54
9/12	15	33	9/14	3	48
9/12	16	34	9/14	4	43
9/12	17	37	9/14	5	42
9/12	18	50	9/14	6	45
9/12	19	71	9/14	7	37

(continued)

Table B-1 (continued) - 2

Date	Hr[a]	Concentration	Date	Hr[a]	Concentration
9/14	8	68	9/15	20	54
9/14	9	98	9/15	21	68
9/14	10	68	9/15	22	73
9/14	11	37	9/15	23	65
9/14	12	40	9/16	0	57
9/14	13	23	9/16	1	36
9/14	14	17	9/16	2	20
9/14	15	19	9/16	3	39
9/14	16	28	9/16	4	40
9/14	17	25	9/16	5	40
9/14	18	34	9/16	6	37
9/14	19	50	9/16	7	28
9/14	20	56	9/16	8	45
9/14	21	76	9/16	9	62
9/14	22	91	9/16	10	48
9/14	23	91	9/16	11	31
9/15	0	88	9/16	12	20
9/15	1	43	9/16	13	19
9/15	2	48	9/16	14	16
9/15	3	42	9/16	15	17
9/15	4	43	9/16	16	19
9/15	5	31	9/16	17	29
9/15	6	17	9/16	18	33
9/15	7	39	9/16	19	36
9/15	8	37	9/16	20	37
9/15	9	64	9/16	21	54
9/15	10	42	9/16	22	65
9/15	11	25	9/16	23	62
9/15	12	12	9/17	0	51
9/15	13	11	9/17	1	48
9/15	14	9	9/17	2	31
9/15	15	11	9/17	3	16
9/15	16	14	9/17	4	19
9/15	17	14	9/17	5	14
9/15	18	31	9/17	6	20
9/15	19	47	9/17	7	25

(continued)

Table B-1 (continued) - 3

Date	Hr[a]	Concentration	Date	Hr[a]	Concentration
9/17	8	20	9/18	9	34
9/17	9	26	9/18	10	36
9/17	10	34	9/18	11	29
9/17	11	29	9/18	12	22
9/17	12	23	9/18	13	42
9/17	13	25	9/18	14	23
9/17	14	20	9/18	15	29
9/17	15	22	9/18	16	42
9/17	16	31	9/18	17	37
9/17	17	34	9/18	18	31
9/17	18	45	9/18	19	47
9/17	19	47	9/18	20	47
9/17	20	64	9/18	21	43
9/17	21	62	9/18	22	37
9/17	22	57	9/18	23	31
9/17	23	53	9/19	0	23
9/18	0	42	9/19	1	20
9/18	1	39	9/19	2	19
9/18	2	42	9/19	3	16
9/18	3	43	9/19	4	22
9/18	4	39	9/19	5	34
9/18	5	40	9/19	6	34
9/18	6	40	9/19	7	34
9/18	7	39	9/19	8	37
9/18	8	37			

[a]Start of hour in 24 hr time.

Table B-2. Nitrous Acid Concentrations (ppb) Determined by Long Pathlength DOAS System at Pomona College (Claremont) in September 1985 .

Date	Hr[a]	Concentration	Date	Hr[a]	Concentration
9/11	16	0.00	9/13	2	0.73
9/11	17	0.00	9/13	3	0.62
9/11	18	0.00	9/13	4	0.64
9/11	19	0.00	9/13	5	0.62
9/11	20	0.26	9/13	6	0.26
9/11	21	0.19	9/13	7	0.00
9/11	22	0.62	9/13	8	0.00
9/11	23	0.77	9/13	9	0.00
9/12	0	0.74	9/13	10	0.00
9/12	1	0.74	9/13	11	0.00
9/12	2	0.73	9/13	12	0.00
9/12	3	0.87	9/13	13	0.00
9/12	4	0.73	9/13	14	0.00
9/12	5	0.96	9/13	15	0.00
9/12	6	1.07	9/13	16	0.00
9/12	7	0.88	9/13	17	0.00
9/12	8	0.05	9/13	18	0.00
9/12	9	0.00	9/13	19	0.00
9/12	10	0.00	9/13	20	0.00
9/12	11	0.00	9/13	21	0.40
9/12	12	0.00	9/13	22	1.15
9/12	13	0.00	9/13	23	1.44
9/12	14	0.00	9/14	0	1.32
9/12	15	0.00	9/14	1	0.96
9/12	16	0.00	9/14	2	0.85
9/12	17	0.00	9/14	3	0.93
9/12	18	0.00	9/14	4	0.98
9/12	19	0.00	9/14	5	1.05
9/12	20	0.03	9/14	6	0.85
9/12	21	0.81	9/14	7	0.71
9/12	22	1.44	9/14	8	0.26
9/12	23	1.81	9/14	9	0.00
9/13	0	1.64	9/14	10	0.00
9/13	1	1.05	9/14	11	0.00

(continued)

Table B-2 (continued) - 2

Date	Hr[a]	Concentration	Date	Hr[a]	Concentration
9/14	12	0.00	9/15	22	0.99
9/14	13	0.00	9/15	23	1.63
9/14	14	0.00	9/16	0	2.57
9/14	15	0.00	9/16	1	2.01
9/14	16	0.00	9/16	2	1.38
9/14	17	0.00	9/16	3	1.41
9/14	18	0.00	9/16	4	1.30
9/14	19	0.00	9/16	5	1.36
9/14	20	0.39	9/16	6	1.30
9/14	21	0.64	9/16	7	0.87
9/14	22	1.26	9/16	8	0.42
9/14	23	1.49	9/16	9	0.00
9/15	0	1.44	9/16	10	0.00
9/15	1	0.67	9/16	11	0.00
9/15	2	0.88	9/16	12	0.00
9/15	3	0.93	9/16	13	0.00
9/15	4	0.90	9/16	14	0.00
9/15	5	0.81	9/16	15	0.00
9/15	6	0.68	9/16	16	0.00
9/15	7	0.64	9/16	17	0.00
9/15	8	0.11	9/16	18	0.00
9/15	9	0.00	9/16	19	0.00
9/15	10	0.00	9/16	20	0.00
9/15	11	0.00	9/16	21	0.00
9/15	12	0.00	9/16	22	0.37
9/15	13	0.00	9/16	23	1.05
9/15	14	0.00	9/17	0	0.90
9/15	15	0.00	9/17	1	0.67
9/15	16	0.00	9/17	2	0.48
9/15	17	0.00	9/17	3	0.00
9/15	18	0.00	9/17	4	0.00
9/15	19	0.29	9/17	5	0.00
9/15	20	0.48	9/17	6	0.00
9/15	21	0.22	9/17	7	0.00

(continued)

Table B-2 (continued) - 3

Date	Hr[a]	Concentration	Date	Hr[a]	Concentration
9/17	8	0.00	9/18	18	0.00
9/17	9	0.00	9/18	19	0.05
9/17	10	0.00	9/18	20	0.71
9/17	11	0.00	9/18	21	0.95
9/17	12	0.00	9/18	22	0.64
9/17	13	0.00	9/18	23	0.36
9/17	14	0.00	9/19	0	0.00
9/17	15	0.00	9/19	1	0.00
9/17	16	0.00	9/19	2	0.00
9/17	17	0.00	9/19	3	0.00
9/17	18	0.00	9/19	4	0.09
9/17	19	0.00	9/19	5	0.53
9/17	20	0.00	9/19	6	0.60
9/17	21	0.00	9/19	7	0.59
9/17	22	0.00	9/19	8	0.22
9/17	23	0.00	9/19	9	0.17
9/18	0	0.00	9/19	10	0.00
9/18	1	0.00			
9/18	2	0.14			
9/18	3	0.60			
9/18	4	0.76			
9/18	5	0.20			
9/18	6	0.12			
9/18	7	0.00			
9/18	8	0.00			
9/18	9	0.00			
9/18	10	0.00			
9/18	11	0.00			
9/18	12	0.00			
9/18	13	0.00			
9/18	14	0.00			
9/18	15	0.00			
9/18	16	0.00			
9/18	17	0.00			

[a]Start of hour in 24 hr time.

Table B-3. Ambient Concentrations Determined by DOAS During Citrus College Study

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
13-AUG-86	00:14-00:33	2.1	7.9	65.0
	00:33-00:47	1.8	6.7	63.7
	01:08-01:22	1.9	7.8	62.3
	01:22-01:36	2.0	7.0	64.2
	01:56-02:10	2.3	6.8	59.6
	02:10-02:24	2.2	6.4	60.9
	02:45-02:59	2.4	6.4	55.8
	02:59-03:13	2.4	7.8	56.8
	03:34-03:48	2.8	5.3	52.4
	03:48-04:02	1.9	6.5	55.7
	04:22-04:37	1.9	5.5	54.7
	04:37-04:51	3.2	5.6	47.6
	05:11-05:25	3.1	7.3	49.1
	05:25-05:39	3.7	5.3	46.0
	06:00-06:14	4.1	6.6	44.1
	06:14-06:28	3.0	7.4	49.9
	06:49-07:03	3.5	5.9	46.3
	07:03-07:17	3.1	7.8	52.3
	07:37-07:51	2.0	10.0	65.7
	07:51-08:06	1.5	10.8	74.2
	08:11-08:31	1.1	11.0	73.0
	08:31-08:46	1.3	9.7	76.3
	08:46-09:01	1.2	12.5	87.3
	09:01-09:16	0.9	10.7	91.7
	09:16-09:31	0.8	12.6	91.7
	09:31-09:46	ND	12.2	97.5
	09:46-10:01	ND	14.0	93.8
	10:01-10:16	ND	13.0	89.3
	10:16-10:31	ND	14.2	83.2
	10:31-10:46	ND	11.9	78.0
	10:46-11:01	ND	11.6	72.5
	11:01-11:16	ND	11.4	66.2
	11:16-11:31	ND	12.2	57.7
	11:31-11:46	ND	11.3	53.5
	11:46-12:01	ND	11.5	49.3
	12:01-12:16	ND	11.0	43.8
	12:16-12:31	ND	13.1	43.7
	12:31-12:46	ND	13.3	41.2
	12:46-13:01	ND	11.3	44.0
	13:01-13:16	ND	11.8	48.7
	13:16-13:31	ND	10.0	43.8
	13:31-13:46	ND	14.9	40.2
	13:46-14:01	ND	13.1	35.5

(continued)

Table B-3 (continued) - 2

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
13-AUG-86	15:46-16:01	ND	15.8	37.1
	16:01-16:16	ND	14.0	38.1
	16:16-16:31	ND	14.4	38.4
	16:31-16:46	ND	15.7	35.8
	16:46-17:01	ND	15.4	43.2
	17:01-17:16	ND	16.0	36.9
	17:16-17:31	ND	14.8	41.1
	17:31-17:46	ND	13.7	43.1
	17:46-17:53	ND	13.2	47.4
	18:00-18:17	ND	10.7	52.8
	18:17-18:32	ND	11.0	53.9
	18:32-18:47	ND	9.5	52.7
	19:10-19:21	ND	9.4	61.4
	19:42-19:53	ND	9.6	62.2
	20:15-20:26	ND	9.1	67.9
	20:50-21:01	0.8	9.1	73.0
	21:22-21:33	ND	6.8	76.1
	22:37-22:49	1.8	8.5	73.7
	23:21-23:35	2.2	6.8	71.4
	23:35-23:49	1.9	6.6	68.2
14-AUG-86	00:10-00:24	1.6	7.4	67.3
	00:24-00:38	1.9	5.4	65.8
	00:58-01:12	2.0	6.1	67.8
	01:12-01:26	2.1	5.9	64.2
	01:47-02:01	2.4	5.8	60.5
	02:01-02:15	2.3	5.9	61.7
	02:36-02:50	2.5	5.2	59.6
	02:50-03:04	2.0	ND	63.1
	03:25-03:39	2.0	6.4	63.6
	03:39-03:53	2.0	4.9	65.2
	04:13-04:27	3.1	6.1	60.5
	04:27-04:41	2.3	5.5	62.5
	05:02-05:16	2.5	ND	60.9
	05:16-05:30	2.5	7.0	62.8
	05:51-06:05	2.7	ND	60.9
	06:05-06:19	2.9	4.8	60.9
	06:40-06:54	2.5	7.9	65.1
	06:54-07:08	2.5	5.4	60.0
	07:28-07:42	2.1	8.0	61.5
	07:42-07:56	1.5	7.6	68.8
	08:18-08:33	1.3	11.0	70.7
	08:33-08:48	0.9	13.4	77.4
	08:48-09:03	ND	11.2	81.8
	09:03-09:18	ND	12.1	79.2

(continued)

Table B-3 (continued) - 3

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
14-AUG-86	09:18-09:33	ND	14.2	68.6
	09:48-10:03	ND	12.5	79.9
	10:03-10:18	ND	13.6	73.2
	10:33-10:48	ND	14.0	65.7
	10:48-11:03	ND	14.4	63.7
	11:03-11:18	ND	13.3	47.8
	11:18-11:33	ND	13.6	55.9
	11:33-11:48	ND	13.4	50.2
	12:18-12:33	ND	13.3	27.8
	12:33-12:48	ND	11.6	44.7
	12:48-13:03	ND	12.7	50.2
	13:03-13:18	ND	14.4	37.5
	13:18-13:33	ND	8.8	33.2
	13:33-13:48	ND	10.1	29.0
	13:48-14:03	ND	11.6	28.8
	14:03-14:14	ND	7.8	23.0
	15:06-15:21	ND	13.8	26.2
	15:21-15:36	ND	16.4	26.2
	15:36-15:51	ND	14.7	30.7
	16:08-16:23	ND	13.4	40.4
	16:23-16:38	ND	15.0	39.7
	16:38-16:53	ND	12.5	39.6
	17:09-17:24	ND	13.8	39.6
	17:24-17:43	ND	12.9	40.0
	17:43-18:00	ND	11.1	44.6
	18:00-18:15	ND	10.1	45.8
	18:15-18:35	ND	11.7	46.8
	19:18-19:38	ND	10.4	56.7
	19:59-20:10	ND	9.6	62.2
	20:31-20:42	ND	8.3	80.5
	21:02-21:14	1.2	8.1	79.7
	21:28-21:43	1.3	7.2	77.2
	22:22-22:36	1.2	6.3	74.4
	22:36-22:50	1.3	6.0	72.6
	23:10-23:24	1.4	6.0	62.2
	23:24-23:38	1.6	5.7	57.4
15-AUG-86	00:00-00:14	1.6	5.6	54.6
	00:14-00:28	1.5	5.3	55.7
	00:48-01:02	1.5	5.7	53.9
	01:02-01:16	1.7	5.4	53.0
	01:36-01:50	1.8	6.3	51.2
	01:50-02:04	1.2	5.9	51.9
	02:25-02:39	1.9	5.9	48.9
	02:39-02:53	1.9	6.2	47.8

(continued)

Table B-3 (continued) - 4

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
15-AUG-86	03:14-03:28	1.9	5.3	42.7
	03:28-03:42	2.0	5.4	42.0
	04:02-04:16	2.0	5.7	42.1
	04:16-04:30	2.1	5.9	39.8
	04:51-05:05	2.4	5.3	38.9
	05:05-05:19	2.6	5.6	39.6
	05:39-05:53	1.9	6.2	41.6
	05:53-06:07	1.9	6.5	43.5
	06:28-06:42	2.3	4.7	39.8
	06:42-06:56	1.9	8.1	46.7
	07:17-07:31	1.7	7.2	51.2
	07:31-07:45	1.8	7.8	51.8
	07:55-08:09	1.2	8.6	57.2
	08:10-08:25	1.2	8.6	61.1
	08:25-08:40	1.3	8.0	60.0
	08:40-08:55	1.4	9.6	63.6
	08:55-09:10	1.1	10.4	65.3
	09:25-09:40	ND	9.8	66.5
	09:40-09:55	ND	10.2	62.9
	09:55-10:10	ND	11.6	63.7
	10:10-10:25	0.9	10.8	58.3
	10:25-10:40	ND	12.0	60.8
	10:40-10:58	ND	12.2	61.9
	10:58-11:13	ND	13.5	57.5
	11:13-11:29	ND	13.2	57.4
	11:29-11:43	ND	12.0	51.9
	11:43-11:58	ND	13.4	47.4
	11:58-12:13	ND	12.8	39.7
	12:13-12:28	ND	12.2	39.3
	12:28-12:43	ND	12.9	39.9
	12:43-12:58	ND	12.9	36.1
	12:58-13:18	ND	12.9	31.3
	13:18-13:34	ND	13.5	28.3
	13:34-13:49	ND	11.3	31.6
	13:49-14:04	ND	14.1	34.3
	14:04-14:19	ND	18.9	30.2
	14:19-14:34	ND	15.8	24.8
	14:34-14:49	ND	14.4	21.6
	14:49-15:04	ND	15.9	24.7
	15:04-15:19	ND	16.8	29.9
	15:19-15:34	ND	15.0	35.9
	15:34-15:54	ND	13.7	45.8
	15:55-16:13	ND	12.0	43.6
	16:13-16:28	ND	11.4	45.4
	16:28-16:43	ND	10.4	47.2

(continued)

Table B-3 (continued) - 5

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
15-AUG-86	18:58-19:14	ND	7.7	59.9
	19:30-19:46	ND	7.5	72.8
	20:59-21:14	1.2	4.5	63.3
	21:30-21:53	1.4	5.3	60.0
	22:15-22:33	1.5	4.7	59.8
	23:03-23:22	2.0	6.2	61.1
	23:22-23:36	1.5	6.6	60.3
	23:52-24:00	2.1	4.8	60.6
16-AUG-86	00:00-00:02	2.1	4.8	60.6
	00:16-00:22	2.0	7.1	56.7
	00:34-00:49	2.3	5.4	56.7
	00:49-01:04	2.7	5.4	55.2
	01:04-01:19	2.9	6.9	54.1
	01:19-01:34	3.6	8.4	48.5
	01:34-01:49	3.3	7.8	50.4
	01:49-02:04	3.4	6.6	49.0
	02:04-02:19	2.7	5.9	53.7
	02:19-02:34	3.0	4.7	52.6
	02:34-02:49	2.8	4.5	51.6
	02:49-03:04	3.1	6.3	50.4
	03:04-03:19	2.8	7.7	52.6
	03:19-03:34	3.2	6.2	47.5
	03:34-03:49	2.9	6.0	49.5
	03:49-04:04	2.6	5.6	51.9
	04:04-04:19	3.0	7.1	46.5
	04:19-04:34	3.6	4.7	46.0
	04:34-04:48	3.5	7.2	47.2
	04:48-05:03	3.5	6.6	45.4
	05:03-05:18	3.5	7.1	46.9
	05:18-05:33	3.5	5.6	45.0
	05:33-05:48	3.5	7.2	46.0
	05:48-06:03	3.5	6.9	46.8
	06:03-06:18	2.9	ND	46.9
	06:18-06:37	3.3	7.2	44.9
	06:37-06:54	3.6	6.2	38.5
	06:54-07:11	3.2	5.7	39.4
	07:11-07:28	2.9	6.9	45.1
	07:28-07:47	2.2	8.3	51.9
	07:47-08:02	1.3	7.7	59.6
	08:02-08:17	1.6	7.1	70.5
	08:17-08:32	0.9	8.1	73.6
	08:32-08:47	1.2	9.5	71.1
	08:47-09:02	0.9	10.4	65.4
	09:02-09:17	ND	9.2	68.1

(continued)

Table B-3 (continued) - 6

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
16-AUG-86	09:17-09:32	0.8	10.7	70.7
	09:32-09:47	ND	12.6	71.0
	09:47-10:02	0.9	12.6	62.9
	10:02-10:17	ND	8.7	61.9
	10:17-10:32	ND	9.9	61.5
	10:32-10:47	ND	13.1	59.8
	10:47-11:01	ND	12.5	59.0
	11:01-11:16	ND	12.6	54.3
	11:16-11:31	ND	13.5	52.6
	11:31-11:46	ND	13.1	41.6
	11:46-12:01	ND	11.3	38.4
	12:01-12:18	ND	9.6	33.7
	12:18-12:33	ND	11.7	30.8
	12:33-12:48	ND	12.9	24.2
	12:48-13:03	ND	8.1	19.3
	13:03-13:18	ND	10.1	14.3
	13:18-13:33	ND	11.9	16.0
	13:33-13:48	ND	9.6	13.1
	13:48-14:03	ND	8.4	12.8
	14:03-14:18	ND	14.0	14.1
	14:18-14:34	ND	10.4	11.8
	14:34-14:49	ND	10.2	13.2
	14:49-15:04	ND	10.4	13.7
	15:04-15:19	ND	11.6	11.8
	15:19-15:34	ND	11.7	15.4
	15:34-15:49	ND	11.3	15.4
	15:49-16:04	ND	11.4	14.4
	16:04-16:19	ND	10.2	16.3
	16:19-16:34	ND	11.7	19.4
	16:34-16:52	ND	13.7	21.4
	16:52-17:07	ND	12.6	23.6
	17:09-17:27	ND	11.3	28.2
	17:27-17:42	ND	11.3	35.5
	17:42-17:57	ND	9.6	37.1
	17:57-18:12	ND	10.8	36.7
	18:12-18:27	ND	10.1	38.9
	18:27-18:43	ND	9.2	38.1
	18:59-19:15	ND	6.8	52.0
	19:35-19:46	ND	8.3	64.2
	20:08-20:19	1.4	8.1	75.4
	20:40-20:51	1.5	8.4	77.9
	21:12-21:23	1.7	7.8	83.3
	21:43-21:54	1.7	8.6	81.1
	22:14-22:26	2.0	6.8	65.0
	22:48-23:02	2.0	6.3	73.0

(continued)

Table B-3 (continued) - 7

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
16-AUG-86	23:02-23:16	2.0	5.0	68.1
	23:37-23:51	2.1	6.6	66.7
	23:51-24:00	2.4	6.2	66.2
17-AUG-86	00:00-00:05	2.4	6.2	66.2
	00:25-00:39	2.7	8.1	58.2
	00:40-00:54	3.2	10.4	64.6
	01:14-01:28	3.7	8.9	62.8
	01:28-01:42	3.6	8.7	64.3
	02:03-02:17	3.8	8.3	60.8
	02:17-02:31	4.0	8.0	60.4
	02:52-03:05	3.7	9.3	53.9
	03:05-03:20	2.6	8.4	47.8
	03:40-03:54	3.0	9.0	34.5
	03:54-04:08	1.9	9.2	23.7
	04:29-04:43	2.5	6.5	26.7
	04:43-04:57	2.4	6.6	30.4
	05:18-05:32	1.5	6.6	21.9
	05:32-05:46	1.7	8.4	23.7
	06:06-06:20	1.6	6.9	18.7
	06:20-06:34	1.7	6.0	19.0
	06:55-07:09	1.5	8.0	24.2
	07:09-07:23	1.2	9.2	28.1
	07:45-08:00	ND	8.6	18.2
	08:10-08:25	ND	8.3	21.5
	08:25-08:40	ND	10.1	25.1
	08:40-08:55	ND	10.2	33.6
	08:55-09:09	ND	13.1	36.8
	09:09-09:24	ND	14.1	45.9
	09:24-09:39	ND	16.1	50.4
	09:39-09:54	ND	13.8	52.3
	09:54-10:09	ND	14.7	56.6
	10:09-10:24	ND	12.5	48.0
	10:24-10:39	ND	16.2	42.2
	10:39-10:54	ND	17.3	39.7
	12:45-13:00	ND	14.3	20.1
	13:00-13:15	ND	13.4	16.0
	13:15-13:30	ND	13.4	18.3
	13:30-13:45	ND	12.6	15.2
	13:45-14:00	ND	12.9	17.6
	14:00-14:15	ND	12.5	16.0
	14:15-14:30	ND	12.2	13.2
	14:30-14:45	ND	12.0	11.3
	14:45-15:00	ND	11.9	10.6
	15:00-15:15	ND	11.4	11.7

(continued)

Table B-3 (continued) - 8

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
17-AUG-86	15:15-15:30	ND	15.3	15.3
	15:30-15:45	ND	14.4	22.3
	15:45-16:00	ND	14.6	21.5
	16:00-16:17	ND	14.6	22.3
	16:17-16:32	ND	13.7	22.5
	16:32-16:47	ND	11.0	22.4
	16:47-17:02	ND	7.7	20.2
	17:02-17:17	ND	8.0	21.0
	17:17-17:32	ND	8.1	24.4
	17:32-17:47	ND	7.2	26.8
	17:47-18:02	ND	8.6	33.7
	18:02-18:17	ND	6.0	40.5
	18:17-18:32	ND	7.5	51.4
	18:32-18:47	ND	5.3	51.1
	18:47-19:02	ND	9.8	58.9
	19:02-19:17	ND	7.7	63.5
	19:43-19:54	ND	8.7	78.9
	20:15-20:26	1.2	8.3	81.8
	20:47-20:58	ND	7.2	77.4
	21:19-21:30	1.2	5.4	69.8
	21:51-22:02	1.0	6.8	70.6
	22:23-22:34	1.0	7.2	69.5
	22:55-23:06	ND	7.2	65.7
	23:30-23:41	1.1	7.7	69.7
	23:41-23:55	1.3	6.2	76.2
18-AUG-86	00:18-00:30	1.4	5.7	75.1
	00:30-00:44	1.9	5.7	69.6
	01:05-01:19	1.8	6.0	76.0
	01:19-01:33	1.7	6.8	76.0
	01:53-02:07	2.1	6.9	73.5
	02:07-02:21	2.1	7.2	75.7
	02:42-02:56	1.5	8.0	75.2
	02:56-03:10	1.7	7.8	72.7
	03:31-03:45	2.3	8.9	69.5
	03:45-03:59	1.9	8.6	67.4
	04:20-04:34	2.5	8.9	65.9
	04:34-04:48	2.8	5.1	67.4
	05:08-05:22	2.0	8.7	53.4
	05:22-05:37	2.3	9.5	51.1
	05:58-06:11	1.5	5.9	38.3
	06:11-06:25	1.5	6.9	46.0
	06:46-07:00	1.2	7.5	53.5
	07:00-07:14	1.7	7.1	55.3
	07:36-07:50	1.3	8.6	55.1

(continued)

Table B-3 (continued) - 9

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
18-AUG-86	07:51-08:06	1.3	8.9	58.3
	08:06-08:21	1.2	8.1	52.4
	08:21-08:36	1.2	9.5	43.8
	08:36-08:51	ND	10.2	49.1
	08:51-09:06	1.4	12.0	72.1
	09:06-09:21	1.9	15.5	106.4
	09:21-09:36	1.0	12.5	72.8
	10:05-10:20	ND	12.0	83.1
	10:20-10:35	ND	15.0	87.7
	10:35-10:50	ND	15.2	102.1
	10:50-11:05	0.9	16.4	101.0
	11:05-11:20	0.9	17.1	100.4
	11:20-11:35	ND	19.8	96.0
	11:35-11:50	ND	17.9	82.0
	11:50-12:05	ND	16.5	75.6
	12:05-12:20	ND	14.9	71.0
	12:20-12:35	ND	14.4	60.7
	12:35-12:50	ND	11.4	36.8
	12:50-13:05	ND	13.4	35.9
	13:05-13:20	ND	11.1	26.1
	13:20-13:35	ND	10.7	16.6
	13:35-13:50	ND	9.8	16.2
	13:50-14:06	ND	7.1	14.8
	14:06-14:21	ND	6.9	16.0
	14:21-14:36	ND	7.5	14.7
	14:36-14:51	ND	8.9	20.6
	14:51-15:06	ND	9.2	23.2
	15:06-15:21	ND	11.0	24.5
	15:21-15:38	ND	14.3	21.2
	15:38-15:53	ND	16.8	27.9
	15:53-16:08	ND	15.0	30.6
	16:08-16:23	ND	13.4	24.5
	16:23-16:38	ND	12.3	32.4
	16:38-16:53	ND	13.2	47.7
	16:53-17:08	ND	12.3	42.8
	17:08-17:23	ND	10.4	42.8
	17:23-17:38	ND	11.9	49.2
	17:38-17:53	ND	11.4	50.6
	17:53-18:08	ND	11.3	54.1
	18:08-18:23	ND	10.4	50.8
	18:23-18:38	ND	6.9	52.9
	18:38-18:53	ND	5.7	52.0
	18:53-19:09	ND	5.0	53.9
	19:31-19:42	ND	5.4	50.4
	20:05-20:11	ND	5.3	57.3

(continued)

Table B-3 (continued) - 10

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
18-AUG-86	20:32-20:43	ND	5.7	80.2
	21:04-21:15	1.0	6.9	63.3
	21:36-21:47	0.9	8.0	82.5
	22:10-22:24	1.8	7.8	74.1
	22:24-22:38	1.6	7.1	70.0
	22:59-23:13	1.5	7.2	68.3
	23:13-23:27	1.5	8.3	68.4
	23:48-24:00	1.5	8.4	64.4
19-AUG-86	00:00-00:02	1.5	8.4	64.4
	00:02-00:16	1.5	7.2	61.9
	00:37-00:51	1.7	7.7	56.4
	00:51-01:05	1.8	7.7	49.2
	01:25-01:39	2.0	8.4	46.6
	01:39-01:54	1.5	7.8	44.4
	02:14-02:28	1.2	8.6	27.1
	02:28-02:42	1.2	7.7	25.1
	03:03-03:17	1.2	7.8	26.7
	03:17-03:31	0.9	8.3	18.5
	03:52-04:06	ND	6.3	23.7
	04:06-04:20	ND	8.9	19.4
	04:41-04:55	ND	8.0	18.3
	04:55-05:09	ND	7.1	15.2
	05:30-05:44	ND	8.4	14.8
	05:44-05:58	1.0	9.6	27.6
	06:18-06:32	1.5	11.9	40.3
	06:32-06:47	1.5	9.2	41.6
	07:07-07:21	1.8	12.3	56.1
	07:21-07:35	1.6	11.4	65.6
	07:57-08:11	1.0	11.0	58.5
	08:11-08:26	ND	11.3	49.9
	08:26-08:41	ND	11.1	43.8
	08:41-08:56	ND	11.4	42.8
	08:56-09:11	ND	12.5	41.5
	09:11-09:27	ND	12.6	46.9
	09:27-09:42	ND	13.1	57.4
	09:42-09:57	ND	13.1	52.7
	09:57-10:13	ND	11.6	38.0
	10:13-10:28	ND	12.8	34.3
	10:28-10:43	ND	12.0	50.0
	10:43-10:58	ND	12.3	41.6
	10:58-11:13	ND	14.7	46.2
	11:13-11:28	ND	13.7	37.3
	11:28-11:43	ND	11.4	25.4
	11:43-11:58	ND	12.0	23.9

(continued)

Table B-3 (continued) - 11

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
19-AUG-86	11:58-12:13	ND	13.4	25.0
	12:13-12:28	ND	13.1	33.8
	12:29-12:44	ND	12.5	23.6
	12:44-12:59	ND	11.9	17.0
	12:59-13:14	ND	9.8	13.7
	13:14-13:29	ND	14.4	25.5
	13:29-13:44	ND	15.0	24.4
	13:44-13:59	ND	19.5	40.5
	13:59-14:14	ND	18.9	31.5
	14:14-14:29	ND	15.6	25.5
	14:29-14:44	ND	11.9	27.9
	14:44-14:59	ND	12.3	26.3
	14:59-15:14	ND	11.6	30.4
	15:14-15:29	ND	11.7	31.4
	15:29-15:44	ND	9.3	30.5
	15:44-15:59	ND	8.1	27.4
	15:59-16:14	ND	7.5	25.5
	16:14-16:29	ND	6.9	25.9
	16:29-16:44	ND	5.6	26.7
	16:44-16:59	ND	8.0	34.5
	17:04-17:19	ND	6.3	38.5
	17:19-17:34	ND	7.4	43.4
	17:34-17:49	ND	7.4	43.4
	17:49-18:04	ND	4.8	48.5
	18:04-18:20	ND	6.9	56.1
	18:20-18:35	ND	5.6	61.5
	18:35-18:50	ND	5.9	62.8
	18:50-19:05	ND	5.0	65.2
	19:05-19:20	ND	6.0	74.6
	19:42-19:53	ND	5.4	89.5
	20:14-20:25	0.9	5.4	82.6
	20:46-20:57	1.0	6.8	86.6
	21:18-21:29	0.9	5.9	80.8
	21:50-22:01	ND	5.3	76.1
	22:22-22:33	1.9	8.1	76.7
	22:54-23:05	2.1	9.9	68.8
	23:26-23:40	2.5	9.9	68.0
	23:40-23:54	2.0	9.2	60.5
20-AUG-86	00:15-00:29	1.8	9.5	58.5
	00:29-00:43	2.1	8.9	53.8
	01:04-01:18	2.1	9.8	47.2
	01:18-01:32	2.7	10.8	54.6
	01:53-02:07	1.7	9.5	36.7
	02:07-02:21	2.2	9.6	33.5

(continued)

Table B-3 (continued) - 12

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
20-AUG-86	02:41-02:55	1.3	9.3	19.3
	02:55-03:09	1.7	9.6	18.2
	03:30-03:44	1.8	10.4	20.5
	03:44-03:58	1.7	11.4	21.6
	04:14-04:33	2.1	10.1	20.9
	04:32-04:47	1.6	9.9	20.8
	05:03-05:21	1.8	10.5	25.9
	05:56-06:10	2.2	10.8	40.3
	06:10-06:24	2.1	9.2	44.0
	06:45-06:59	2.0	8.9	45.4
	06:59-07:13	3.1	12.8	52.7
	07:34-07:49	2.3	13.2	64.5
	07:49-08:04	1.9	13.1	71.9
	08:04-08:20	2.3	14.9	99.4
	08:20-08:35	2.5	16.7	116.2
	08:36-08:51	2.8	20.9	142.0
	08:51-09:06	2.0	18.3	138.1
	09:06-09:21	2.1	18.3	136.5
	09:21-09:36	1.8	17.1	12.9
	09:36-09:51	1.7	19.7	165.1
	09:51-10:06	1.4	18.8	173.7
	10:06-10:21	1.2	17.4	166.3
	10:21-10:36	1.3	16.2	141.5
	10:36-10:51	0.8	13.8	97.1
	10:51-11:06	ND	15.9	77.7
	11:06-11:21	ND	13.4	74.9
	11:36-11:51	ND	13.2	46.2
	11:51-12:06	ND	12.7	41.7
	12:06-12:21	ND	16.2	53.1
	12:21-12:36	ND	15.9	44.9
	12:36-12:51	ND	20.7	43.6
	12:51-13:06	ND	15.2	32.9
	13:06-13:21	ND	16.8	30.4
	13:21-13:36	ND	15.4	26.2
	13:36-13:51	ND	14.0	21.7
	13:51-14:06	ND	13.7	18.6
	14:06-14:21	ND	15.6	17.6
	14:21-14:36	ND	14.9	16.8
	14:36-14:51	ND	14.0	15.9
	14:51-15:06	ND	12.5	16.2
	15:06-15:21	ND	11.6	22.1
	15:21-15:36	ND	10.5	34.5
	15:36-15:51	ND	12.2	37.0
	15:51-16:06	ND	12.2	32.7
	16:06-16:21	ND	9.8	28.8

(continued)

Table B-3 (continued) - 13

Date	Scan Period	Concentration (ppb) HONO	HCHO	NO_2
20-AUG-86	16:21-16:36	ND	9.5	30.9
	16:36-16:51	ND	8.7	29.3
	16:51-17:06	ND	6.8	25.8
	17:06-17:21	ND	6.8	32.5
	17:21-17:36	ND	7.5	40.4
	17:36-17:51	ND	8.7	40.9
	17:51-18:06	ND	8.7	43.6
	18:06-18:21	ND	9.2	57.0
	18:21-18:36	ND	8.4	59.8
	18:36-18:51	ND	9.6	67.5
	18:51-18:56	ND	11.0	75.4
	19:16-19:27	ND	7.7	83.6
	19:48-19:59	0.9	8.7	91.1
	20:20-20:31	1.0	7.4	89.0
	20:52-21:03	1.5	7.7	90.3
	21:23-21:35	1.2	7.4	85.7
	21:55-22:06	2.1	7.4	85.4
	22:28-22:42	1.1	7.4	73.6
	22:42-22:56	1.0	6.2	78.1
	23:16-23:30	1.8	10.2	84.6
	23:30-23:44	2.0	9.8	84.8
21-AUG-86	00:05-00:19	2.2	8.9	78.7
	00:19-00:33	2.4	11.0	78.8
	00:54-01:08	2.4	11.0	63.4
	01:08-01:22	2.4	10.5	56.2
	01:43-01:57	2.4	8.1	54.9
	01:57-02:11	2.6	8.7	57.4
	02:32-02:46	3.1	10.5	64.3
	02:46-03:00	2.7	9.9	56.6
	03:20-03:34	2.9	9.6	55.4
	03:34-03:48	3.4	10.8	75.6
	04:09-04:23	2.6	8.7	68.3
	04:23-04:37	3.3	7.5	62.2
	04:58-05:12	3.6	11.3	62.0
	05:12-05:26	3.6	11.1	59.8
	05:47-06:01	4.1	10.7	61.6
	06:01-06:15	4.2	10.5	61.1
	06:36-06:50	5.0	11.6	60.6
	06:50-07:04	4.0	12.8	61.6
	07:24-07:38	3.1	14.7	71.1
	07:38-07:53	2.6	13.4	81.8

ND - below detection limit: 0.8 ppb for HONO,
4.5 ppb for HCHO
3.5 ppb for NO_2

APPENDIX C

Supplementary Ambient Air Data from the El Camino Community College Study At Torrance, January/February 1986

Table C-1. Supplementary Ambient Air Data from El Camino Community College Study

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1/16/86					
1600	7	26	27	28	69
1700	4	33	33	18	65
1800	6	47	47	17	65
1900	25	56	72	11	64
2000	17	69	76	4	66
2100	109	82	177	12	66
2200	110	72	170	6	64
2300	83	67	136	5	67
2400	223	59	270	6	62
1/17/86					
100	150	61	197	5	63
200	217	64	266	6	61
300	193	47	227	7	62
400	194	63	243	5	63
500	224	54	263	5	60
600	278	56	320	11	62
700	346	82	411	13	61
800	>500	104	>500	15	64
900	297	147	432	5	71
1000	183	220	386	14	77
1100	87	219	292	18	76
1200	46	243	275	28	80
1300	38	122	148	19	77
1400	11	65	68	37	75
1500	0	35	34	24	72
1600	4	39	40	22	69
1700	18	54	64	0	69
1800	46	59	93	0	65
1900	58	53	101	0	64
2000	61	50	99	0	64
2100	79	46	113	0	62
2200	125	48	160	0	62
2300	153	48	189	16	62
2400	189	45	222	0	64

(continued)

Table C-1 (continued) - 2

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1/18/86					
100	290	50	334	0	63
200	379	65	432	8	60
300	417	71	476	8	61
400	412	58	462	10	59
500	445	63	498	10	58
600	494	73	>500	12	55
700	422	91	499	3	61
800	317	104	411	1	65
900	231	162	382	0	76
1000	61	136	184	13	78
1100	30	121	141	26	82
1200	19	114	126	35	87
1300	32	186	206	33	90
1400	21	172	184	42	89
1500	11	110	114	51	82
1600	6	124	127	54	83
1700	6	123	123	32	80
1800	31	104	124	1	69
1900	14	72	127	9	67
2000	132	123	192	1	66
2100	184	174	247	0	70
2200	268	72	328	10	66
2300	>500	86	>500	12	68
2400	461	82	>500	9	69
1/19/86					
100	>500	88	>500	3	65
200	>500	94	498	6	67
300	426	87	>500	9	67
400	?	82	498	3	65
500	440	110	>500	3	~63-64
600	483	96	498	10	~62-63
700	315	87	392	3	61
800	252	117	355	9	65
900	68	142	197	5	70
1000	38	137	158	20	81
1100	28	186	204	37	85
1200	21	142	152	37	85
1300	12	138	143	46	82
1400	11	118	122	50	84
1500	9	64	67	22	77
1600	4	56	57	28	72
1700	17	57	67	16	69

(continued)

Table C-1 (continued) - 3

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1800	0	56	57	2	67
1900	72	71	132	0	66
2000	0	62	59	12	65
2100	0	43	39	25	66
2200	0	34	30	37	65
2300	0	42	39	30	65
2400	0	35	33	35	65
1/20/86					
100	0	29	27	39	64
200	0	26	23	45	66
300	0	27	24	41	65
400	0	26	22	35	67
500	0	32	28	37	65
600	0	44	42	22	66
700	7	56	58	18	66
800	16	67	77	14	66
900	9	64	67	14	69
1000	6	53	54	26	76
1100	13	69	74	23	78
1200	16	81	87	27	78
1300	6	65	66	35	79
1400	8	59	62	30	72
1500	0	36	34	37	69
1600	0	29	26	33	70
1700	0	33	29	33	66
1800	0	65	63	14	65
1900	52	92	130	3	65
2000	208	100	297	11	63
2100	46	106	139	2	63
2200	164	105	257	4	64
2300	144	100	232	8	64
2400	246	96	328	8	61
1/21/86					
100	275	92	353	2	62
200	256	89	332	3	60
300	253	82	322	2	61
400	221	83	291	3	62
500	113	74	174	0	62
600	138	70	199	1	62
700	154	72	217	0	63
800	196	79	263	8	62
900	177	82	258	8	65

(continued)

Table C-1 (continued) - 4

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1000	71	97	156	9	73
1100	29	96	114	2	74
1200	14	92	95	35	76
1300	18	149	160	34	80
1400	3	57	56	51	73
1500	0	41	41	50	70
1600	0	47	46	50	68
1700	0	38	34	45	66
1800	0	57	55	27	64
1900	0	64	62	36	66
2000	0	79	76	26	64
2100	2	97	97	15	63
2200	57	112	154	3	61
2300	31	107	127	9	62
2400	17	90	198	13	64
1/22/86					
100	54	107	147	3	66
200	89	97	173	9	61
300	56	107	148	3	63
400	12	86	87	1	66
500	54	88	129	1	66
600	0	66	63	14	66
700	18	81	93	9	68
800	113	107	207	13	65
900	48	98	154	12	67
1000	22	101	114	24	69
1100	22	121	133	30	72
1200	20	135	145	32	77
1300	0	56	55	55	73
1400	0	47	45	53	73
1500	0	41	40	55	68
1600	0	38	36	43	67
1/22/86					
1800	0	75	85	50	65
1900	0	69	65	18	65
2000	0	70	67	17	64
2100	0	35	30	35	64
2200	0	40	36	29	64
2300	3	72	73	13	64
2400	72	74	128	1	60

(continued)

Table C-1 (continued) - 5

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(°F)
1/23/86					
100	97	78	165	0	61
200	96	74	158	1	61
300	85	72	145	1	64
400	136	125	148	1	64
500	98	70	157	0	66
600	62	131	131	1	65
700	0	49	46	20	65
800	0	54	53	24	67
900	22	131	89	18	71
1000	23	91	204	18	74
1100	27	104	119	17	72
1200	16	132	138	23	72
1300	16	87	96	34	73
1400	1	62	62	41	74
1500	0	58	56	46	72
1600	0	44	43	45	69
1700	0	40	38	36	67
1800	0	58	58	26	64
1900	57	91	133	1	63
2000	58	88	135	1	64
2100	192	85	261	11	62
2200	216	92	293	10	62
2300	214	94	296	2	63
2400	264	90	339	9	60
1/24/86					
100	233	91	309	1	59
200	227	99	315	2	58
300	226	91	305	10	59
400	220	104	312	9	58
500	225	101	314	1	58
600	239	96	317	9	57
700	392	98	478	4	57
800	407	131	>500	11	62
900	301	150	438	5	63
1000	108	169	266	14	70
1100	22	145	157	34	72
1200	9	115	119	56	78
1300	17	175	176	59	80
1400	7	148	150	34	75
1500	0	39	37	78	71
1600	0	58	57	82	67

(continued)

Table C-1 (continued) - 6

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1700	1	31	31	18	66
1800	0	67	67	16	64
1900	0	66	66	20	65
2000	43	171	117	1	66
2100	177	90	254	2	63
2200	193	269	269	2	62
2300	222	87	298	8	61
2400	321	108	416	12	62
1/25/86					
100	338	103	423	11	60
200	236	90	313	3	61
300		81	288	9	60
400	128	72	198	1	59
500	70	72	132	1	60
600	45	76	104	1	62
700	85	72	144	3	60
800	115	80	204	2	63
900	70	88	146	12	72
1000	36	82	106	18	72
1100	17	67	80	24	81
1200	16	66	75	32	83
1300	11	73	77	41	84
1400	6	75	77	46	88
1500	14	100	105	38	86
1600	11	89	92	33	75
1700	0	94	94	23	73
1800	1	104	104	13	70
1900	25	107	122	0	69
2000	158	108	255	9	67
2100	222	106	317	11	67
2200	226	110	365	11	63
2300	279	98	364	12	64
2400	128	76	192	1	67
1/26/86					
100		81	404	11	63
200	325	76	382	9	63
300		74	314	3	60
400		67	294	2	61
500	196	67	237	2	62
600	177	62	228	1	60
700	83	56	122	1	66

(continued)

Table C-1 (continued) - 7

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
800	23	50	64	3	69
900	26	50	66	12	72
1000	34	69	93	13	78
1100	33	82	104	14	77
1200	23	80	95	20	80
1300	11	54	55	30	85
1400	7	56	58	40	89
1500	20	83	95	20	83
1600	16	76	85	19	81
1700	1	63	63	23	75
1800	34	93	115	2	72
1900	118	96	201	2	68
2000	137	95	218	3	65
2100	253	95	335	11	65
2200	287	86	357	9	65
2300	206	75	374	9	68
2400	149	65	205	0	66
1/27/86					
100	116	64	167	9	65
200	96	61	142	1	66
300	58	62	111	9	64
400	58	57	112	0	62
500	43	56	87	0	63
600	97	56	143	0	62
700	121	58	172	9	63
800	446	92	>500	4	70
900	270	118	366	9	78
1000	86	100	181	10	83
1100	57	147	193	18	88
1200	26	112	129	27	90
1300	25	165	129	38	90
1400	25	117	132	25	82
1500	7	70	70	43	82
1600	4	100	100	49	78
1700	8	57	157	34	72
1800	24	174	190	12	69
1900	76	160	220	12	68
2000	169	157	320	12	69
2100	129	138	254	11	65
2200	147	125	256	1	63
2300	242	148	374	12	63
2400	226	156	364	13	61

(continued)

Table C-1 (continued) - 8

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1/28/86					
100	261	150	390	3	60
200	234	146	364	11	61
300	219	142	347	11	60
400	210	142	340	12	59
500	238	140	363	10	62
600	318	126	423	11	55
700	>500	137	>500	12	58
800	>500	161	>500	11	65
900	424	221	>500	14	74
1000	116	230	333	13	77
1100	68	169	213	15	82
1200	24	114	125	30	83
1/28/86					
1300	0	51	51	36	83
1400	0	49	50	35	81
1500	0	53	53	48	79
1600	0	70	70	43	77
1700	0	76	75	45	72
1800	0	117	116	18	70
1900	8	121	123	15	69
2000	0	90	87	21	67
2100	60	127	172	2	66
2200	40	118	143	2	65
2300	64	118	168	0	66
2400	116	116	221	4	61
1/29/86					
100	195	128	323	4	60
200	198	117	304	3	61
300	228	124	338	4	60
400	252	117	357	4	61
500	244	102	332	4	58
600	254	103	343	2	61
700	>500	105	>500	13	59
800		129	>500	15	63
900	412	173	>500	11	72
1000	176	182	345	3	73
1100	62	117	168	3	80
1200	12	45	48	18	79
1300	0	43	42	19	76

(continued)

Table C-1 (continued) - 9

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1400	7	63	64	12	74
1500	12	63	66	3	71
1600	35	72	97	0	68
1700	30	65	88	0	64
1800	88	67	141	0	62
1900	10	103	105	12	59
2000	5	48	50	11	60
2100	15	59	65	0	62
2200	0	44	41	11	60
2300	0	34	30	18	60
2400	0	30	25	18	61
1/30/86					
100	0	22	18	18	57
200	0	23	19	19	58
300	0	27	22	14	58
400	0	30	25	6	59
500	0	34	31	12	60
600	22	44	55	0	61
700	0	35	32	13	64
800	4	35	35	13	65
900	0	29	25	19	67
1000	4	34	34	19	68
1100	14	32	37	13	72
1200	3	26	26	18	72
1300	12	30	35	13	69
1400	4	29	30	15	71
1500	0	23	22	21	73
1600	0	20	18	24	76
1700	6	38	38	7	69
1800	23	52	63	3	68
1900	126	55	186	3	66
2000	198	60	243	12	65
2100	167	55	208	0	68
2200	142	52	182	0	65
2300	93	50	132	0	65
2400	132	48	173	0	64
1/31/86					
100	133	49	169	0	63
200	110	52	148	0	64
300	95	46	129	0	67
400	120	50	157	0	65

(continued)

Table C-1 (continued) - 10

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
500	140	49	177	1	65
600	15	52	154	0	65
700	153	50	190	0	64
800	67	52	107	0	67
900	67	54	108	0	68
1000	41	52	131	1	69
1100	8	28	31	15	70
1200	16	41	48	12	70
1300	8	35	37	14	66
1400	2	30	29	15	67
1500	0	36	35	19	69
1600	32	61	82	0	67
1700	68	64	119	0	68
1800	57	64	105	0	67
1900	61	64	32	0	66
2000	31	59	79	0	67
2100	23	58	71	0	66
2200	22	57	68	0	67
2300	16	57	64	0	66
2400	14	57	62	0	62
2/1/86					
100	57	58	104	0	62
200	96	55	149	3	62
300	108	57	150	0	63
400	88	62	138	2	64
500	128	48	169	5	63
600	127	56	174	1	63
700	293	55	334	11	61
800	284	67	337	4	65
900	138	75	197	2	67
1000	63	75	129	5	74
1100	22	59	69	16	76
1200	17	62	69	20	70
1300	7	46	47	31	75
1400	2	44	44	36	75
1500	2	43	43	31	72
1600	0	34	32	25	69
1700	0	36	34	16	67
1800	0	44	41	15	66
1900	16	58	64	3	65
2000	38	40	90	2	65
2100	13	61	68	12	66
2200	33	66	87	5	65
2300	0	48	43	18	66
2400	76	62	125	2	66

(continued)

Table C-1 (continued) - 11

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(°F)
2/2/86					
100	164	66	216	2	65
200	190	59	237	2	63
300	214	53	254	11	63
400	158	55	227	3	60
500	201	60	249	5	63
600	206	55	251	3	63
700	224	58	267	3	62
800	298	74	359	4	67
900	90	82	149	2	71
1000	24	61	73	18	78
1100	15	43	48	24	78
1200	2	38	41	25	77
1300	0	25	22	30	75
1400	0	25	22	30	71
1500	0	21	17	29	70
1600	0	29	27	23	69
1700	0	35	33	19	68
1800	0	45	35	13	67
1900	0	38	34	16	67
2000	0	39	38	16	66
2100	29	52	71	2	63
2200	8	48	50	13	65
2300	9	51	54	3	67
2400	9	52	54	3	66
2/3/86					
100	17	52	55	0	65
200	23	47	58	0	64
300	8	47	48	0	63
400	35	48	71	2	62
500	37	47	72	0	63
600	150	43	186	11	60
700	276	54	311	11	60
800	307	77	372	12	68
900	86	128	157	0	73
1000	53	83	124	4	77
1100	22	63	78	16	75
1200	2	27	27	30	73
1300	1	32	32	28	73
1400	0	21	19	26	70
1500	15	27	32	19	68
1600	0	23	21	29	67

(continued)

Table C-1 (continued) - 12

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1700	11	31	31	19	64
1800	1	26	26	19	63
1900	10	36	36	19	62
2000	20	41	50	14	61
2100	79	60	123	1	62
2200	47	57	92	1	62
2300	98	57	145	4	61
2400	0	41	33	19	61
2/4/86					
100	0	27	24	16	61
200	0	24	20	25	61
300	0	22	18	21	61
400	0	25	20	25	60
500	0	24	20	22	61
600	1	32	32	20	60
700	20	55	66	4	61
800	30	45	61	7	63
900	19	40	50	20	65
1100	18	32	43	25	73
1200	9	28	38	31	74
1300	12	32	35	29	76
1400	6	32	32	27	77
1500	14	39	44	22	76
1600	4	42	42	24	74
1700	19	58	67	15	73
1800	54	67	107	0	69
1900	67	67	120	0	70
2000	22	58	69	13	65
2100	30	56	72	2	63
2200	38	57	82	0	65
2300	86	59	130	0	60
2400	68	57	112	0	62
2/5/86					
100	180	62	252	1	63
200	171	57	215	0	59
300	178	57	218	1	56
400	215	63	264	1	59
500	212	68	266	0	58
600	375	74	427	10	57
700	496	76	>500	6	56
800	>500	96	>500	14	63

(continued)

Table C-1 (continued) - 13

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(°F)
900	176	90	251	1	69
1000	47	78	112	16	72
1100	50	102	138	17	79
1200	47	156	190	25	79
1300	19	64	73	26	74
1400	12	56	58	35	73
1500	10	38	66	41	70
1600	3	31	31	33	69
1700	0	35	32	25	67
1800	1	30	30	13	64
1900	56	68	111	1	64
2000	44	67	96	0	64
2100	18	56	65	0	64
2200	6	56	56	1	65
2300	125	69	182	3	61
2400	95	85	167	1	58
2/6/86					
100	61	72	120	0	58
200	106	71	166	1	58
300	142	81	210	2	58
400	135	77	200	1	59
500	166	72	224	3	54
600	169	67	223	1	59
700	228	72	286	2	59
800	225	88	297	4	64
900	112	94	194	2	63
1000	47	35	98	7	70
1100				18	72
1200				24	72
1300				21	70
1400	4	30	36	25	69
1500	10		30	24	68
1600	9	30	30	24	66
1700	7	33	34	24	64
1800	12	50	55	4	62
1900	15	53	62	12	61
2000	2	49	49	12	61
2100	24	53	68	10	58
2200	27	51	61	3	57
2300	8	52	54	2	57
2400	27	55	71	2	59

(continued)

Table C-1 (continued) - 14

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
2/7/86					
100	30	52	75	0	58
200	96	54	140	0	58
300	103	48	133	1	53
400	166	57	210	2	55
500	202	54	247	2	50
600	237	61	287	3	54
700	493	62	>500	6	56
800	>500	72	>500	14	59
900	230	78	296	3	66
1000	102	83	173	4	68
1100	123	92	194	12	75
1200	16	51	56	17	77
1300	4	35	35	26	73
1400	0	32	32	26	72
1500	0	36	36	23	68
1600	0	32	30	31	65
1700	0	32	29	23	59
1800	0	44	40	16	60
1900	28	62	75	4	57
2000	15	56	59	12	55
2100	0	58	58	1	56
2200	10	57	62	1	55
2300	0	57	43	19	54
2400	0	51	49	7	54
2/8/86					
100	0	49	44	1	53
200	0	30	24	26	53
300	0	31	25	21	52
400	0	36	31	20	53
500	0	37	34	16	54
600	3	50	50	3	54
700	36	54	77	1	53
800	60	56	99	5	59
900	28	51	68	7	59
1000	26	52	67	20	65
1100	12	37	40	27	74
1200	4	24	24	30	72
1300	0	31	31	31	80
1400	0	30	27	31	73
1500	9	47	47	26	66
1600	0	40	37	32	64

(continued)

Table C-1 (continued) - 15

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1700	0	30	29	31	65
1800	0	42	37	26	64
1900	7	72	72	4	64
2000	51	73	112	3	62
2100	115	125	122	12	64
2200	155	71	212	15	60
2300	292	72	348	14	56
2400	232	73	288	5	54
2/9/86					
100	182	67	243	5	55
200	287	75	339	12	56
300	282	67	385	5	57
400	292	65	337	13	52
500	262	63	309	5	55
600	177	62	224	5	52
700	258	57	300	6	54
800	169	73	229	5	60
900	97	84	168	14	66
1000	22	50	56	22	64
1100	5	3	3	18	75
1200	5	3	3	28	72
1300	5	3	3	32	69
1400	5	3	3	30	68
1500	5	3	3	29	70
1600	5	3	3	31	67
1700	5	3	3	27	64
1800	5	3	3	22	62
1900	5	3	3	22	61
2000	5	3	3	16	59
2100	5	3	3	12	58
2200	5	3	3	15	57
2300	5	3	3	5	56
2400	5	3	3	5	57
2/10/86					
100	5	3	3	12	56
200	5	3	3	5	55
300	5	3	3	5	54
400	5	3	3	3	56
500	5	3	3	3	53
600	5	3	3	3	55
700	5	3	3	16	49

(continued)

Table C-1 (continued) - 16

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
800	5	3	3	3	58
900	5	3	3	15	65
1000	5	3	3	15	68
1100	5	3	3	20	75
1200	5	3	3	27	72
1300	5	3	3	32	71
1400	5	3	3	37	70
1500	5	3	3	36	69
1600	5	3	3	28	65
1700	5	3	3	32	64
1800	5	3	3	25	61
1900	5	3	3	4	61
2000	5	3	3	12	61
2100	5	3	3	3	61
2200	5	3	3	3	58
2300	0	0	0	4	56
2400	0	0	0	5	55
2/11/86					
100	0	0	0	5	58
200	0	0	0	11	59
300	0	0	0	5	56
400	0	0	0	3	55
500	0	0	0	3	59
600	0	0	0	4	56
700	0	0	0	12	56
800	0	0	0	11	57
900	0	0	0	4	61
1000	0	0	0	12	65
100	0	0	0	7	72
1200	0	0	0	19	74
2/11/86					
1200					
1300				18	74
1400				23	71
1500				15	67
1600				24	65
1700				25	65
1800				3	63
1900				0	64
2000				9	63
2100				13	62

(continued)

Table C-1 (continued) - 17

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
2200				10	61
2300				12	62
2400				9	61
2/12/86					
100				0	60
200				0	61
300				1	62
400				0	60
500				0	63
600				1	62
700				1	62
800				1	61
900				0	63
1000				0	65
1100				0	70
1200				19	70
1300				19	68
1400				22	71
1500				24	70
1600				19	67
1700				26	65
1800				26	65
1900				20	65
2000				19	65
2100				20	64
2200				20	63
2300				16	63
2400				24	62
2/13/86					
100				19	61
200				19	58
300				16	58
400				20	57
500				20	58
600				0	58
700				0	58
800				0	59
900				1	60
1000				13	61
100				14	63
1200				12	63

(continued)

Table C-1 (continued) - 18

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1300				9	64
1400				10	65
1500				0	64
1600				0	65
1700				0	63
1800				0	63
1900				0	64
2000				0	65
2100				0	63
2200				0	63
2300				0	64
2400				0	64
2/14/86					
100				0	64
200				0	64
300				0	64
400				2	64
500				0	64
600				0	65
700				0	66
800				0	68
900				0	69
1000				0	70
1100				1	71
1200				12	68
1300				18	65
1400				16	66
1500				20	68
1600				14	66
1700				13	65
1800				15	64
1900				1	63
2000				13	63
2100				14	63
2200				6	60
2300				14	60
2400				1	61
2/15/86					
100				1	60
200				14	60
300				4	60

(continued)

Table C-1 (continued) - 19

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
400				13	60
500				1	61
600				0	61
700				0	63
800				0	63
900				0	68
1000				25	70
1100				22	74
1200				26	74
1300				21	75
1400				25	75
1500				22	73
1600				25	70
1700				16	69
1800				15	65
1900				20	66
2000				21	65
2100				14	66
2200				19	65
2300				14	67
2400				25	65
2/16/86					
100				25	66
200				25	66
300				22	66
400				22	66
500				26	68
600				22	68
700				21	66
800				20	70
900				20	72
1000				25	72
1100				22	77
1200				25	76
1300				26	75
1400				26	73
1500				26	72
1600				26	68
1700				26	66
1800				21	64
1900				16	64
2000				3	67
2100				12	67

(continued)

Table C-1 (continued) - 20

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(°F)
2200				15	66
2300				16	66
2400				22	66
2/17/86					
100				24	66
200				25	65
300				22	65
400				22	66
500				16	65
600				0	65
700				1	67
800				15	67
900				21	72
1000				24	73
1100				25	72
1200				22	77
1300				25	76
1400				26	80
1500				22	75
1600				25	70
1700				21	67
1800				22	65
1900				25	65
2000				22	67
2100				20	65
2200				16	63
2300				22	67
2400				16	65
2/18/86					
100				14	67
200				2	68
300				2	68
400				0	67
500				0	64
600				0	66
700				2	66
800				0	77
900				0	79
1000				10	80

(continued)

Table C-1 (continued) - 21

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
2/22/86					
1300		26	43	37	79
1400		33	60	42	78
1500		19	41	39	76
1600		21	42	32	74
1700		22	44	32	72
1800	32	24	45	26	68
1900	35	34	56	5	66
2000	44	35	67	4	66
2100	64	35	85	4	64
2200	90	34	109	4	63
2300	103	42	132	5	63
2400	142	39	169	6	63
2/23/86					
100	189	45	221	14	64
200	247	50	283	15	64
300	208	48	244	6	64
400	192	43	222	15	61
500	198	50	257	7	61
600	183	43	198	4	61
700	164	50	215	7	64
800	135	49	172	5	73
900	55	48	92	20	79
1000	49	45	80	26	85
1100	40	40	66	44	91
1200	32	26	46	65	93
1300	31	30	49	62	92
1400	32	22	41	51	89
1500	32	29	50	52	84
1600	32	24	45	49	81
1700	40	40	65	23	79
1800	32	35	55	5	73
1900	34	33	55	3	71
2000				5	70
2100				3	71
2200				4	71
2300				6	66
2400				3	67

(continued)

Table C-1 (continued) - 22

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
2/24/86					
100				14	67
200				4	65
300				3	64
400				4	67
500				14	66
600				4	68
700				12	68
800				5	80
900				5	83
1000				25	89
1100				49	91
1200				55	95
1300	23	108	121	56	95
1400	18	73	83	65	92
1500	10	68	77	52	89
1600	0	55	42	55	85
1700	0	54	45	60	81
1800	0	69	55	26	74
1900	0	74	54	7	73
2000	0	63	52	12	72
2100	0	63	52	12	72
2200	103	68	156	0	72
2300	68	67	122	0	71
2400	117	75	180	0	69
2/25/86					
100	175	82	244	2	69
200	166	96	246	0	68
300	220	95		0	66
700					
800	395	156	>500	10	79
900	162	173	310	15	82
1000	92	253	356	20	91
1100	16	222	220	37	95
1200	0	149	141	52	90
1300	14	130	140	75	88
1400	4	104	105	84	86
1500	15	84	87	84	84
1600	17	72	79	90	80
1700	17	58	66	62	76
1800	14	83	88	19	71

(continued)

Table C-1 (continued) - 23

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(^oF)
1900	14	74	80	0	69
2000	23	78	92	0	69
2100	46	78	112	0	69
2200	27	69	90	9	67
2300	19	45	56	19	68
2400	17	38	42	19	66
2/26/86					
100	18	27	39	18	65
200	25	27	40	24	66
300	20	32	43	24	66
400	20	44	55	18	66
500	22	52	62	17	65
600	24	65	130	0	66
700	67	67	125	0	67
800	145	79	227	9	68
900	158	116	262	9	80
1000	72	176	237	15	85
1100	49	210	246	35	87
1200	27	76	95	40	77
1300	25	56	72	48	80
1400	20	45	55	59	75
1500	17	35	46	58	68
1600	21	34	46	41	66
1700	13	32	38	35	65
1800	0	42	41	34	65
1900	0	27	27	40	65
2000	18	27	39	46	64
2100	29	34	53	45	65
2200	23	24	40	40	67
2300	27	28	47	39	67
2400	25	37	52	26	68
2/27/86					
100	33	50	74	15	65
200	32	44	65	15	65
300	38	72	98	2	67
400	45	80	108	0	68
500	50	92	130	0	67
600	52	94	135	0	65
700	45	96	131	2	66
800	65	112	174	10	67
900	32	111	132	18	73
1000					

(continued)

Table C-1 (continued) - 24

	Concentration (ppb)				
	NO	NO_2	NO_x	O_3	T(°F)
2/23/86					
1600	4				
1700	6				
1800	9				
1900					
2000	34				
2100	89				
2200	139				
2300	151				
2400	140				
2/24/86					
100	179				
200	264				
300	272				
400	280				
500	276				
600	229				
700	>370				
800	>370				
900	172				
1000	78				
1100					

APPENDIX D

FT-IR Spectroscopic Data for HNO_3, NH_3, and HCHO Concentrations During the Citrus College Study (Glendora), August 12-21, 1986

(HCHO was not included in the measurement during the first day. No entries for HNO_3 mean below detection limit. Asterisks mark the times where gaps in the data occur.)

Table D-1. Simultaneous HNO_3, NH_3, and HCHO Concentrations (ppb) in Glendora, CA, August 12-21, 1986 by Long Pathlength FT-IR Spectroscopy

PST	HNO_3	NH_3	HCHO
8/12/86			
0758		13.1	
0811		8.1	
0825		7.4	
0837		10.3	
0851	2.1	8.1	
0905	2.1	6.9	
0917	2.6	6.7	
0930	3.9	6.1	
0944	3.9	5.3	
0957	4.5	6.1	
1010	4.4	4.9	
1024	5.3	3.3	
1037	8.9	3.9	
1052	9.7	2.9	
1119	11.8	2.6	
1136	14.4	3.9	
1149	14.5	4.2	
1202	15.2	3.5	
1221	15.3	3.4	
1234	16.3	3.7	
1250	16.3	4.6	
1305	17.7	4.7	
1320	15.8	4.7	
1339	19.5	5.0	
1353	20.0	2.9	
1406	20.6	3.5	
1419	21.6	4.3	
1433	23.7	4.2	
1447	22.2	3.9	
1503	21.5	3.5	
1517	21.6	2.8	
1532	18.9	4.7	
1546	18.7	3.8	
1608	13.9	3.4	
1622	12.4	3.0	
1635	10.5	3.4	
1651	11.6	3.1	
1705	5.8	3.2	
1718	5.7	3.2	
1732	6.7	2.9	
1745	5.9	3.1	
1802	5.9	3.4	
1816	4.6	4.1	
1828	4.0	5.9	
1848	5.4	5.6	
1904	4.8	6.3	
1920	3.5	6.2	
1934	2.8	5.0	
1947	2.6	6.1	
2000	2.6	6.0	
2014		4.0	
2106		4.5	
2118		4.6	
2132		5.1	
2144		5.1	
2201		4.7	
2215		4.6	
8/13/86			
0027		5.7	4.8
0043		5.1	5.1
0059		5.3	4.3
0114		5.0	5.4
0130		5.2	5.1
0146		5.0	5.1
0201		5.5	5.4
0217		5.5	4.6
0233		5.5	5.9
0249		5.1	5.3
0304		4.6	4.0
0320		4.3	3.6
0336		4.2	4.3
0351		5.2	4.0
0407		4.7	3.9
0423		4.7	4.5
0439		4.6	4.0
0454		6.7	4.6
0510		5.1	4.5
0526		4.9	5.5
0541		4.4	5.5
0557		5.3	4.2
0612		4.6	4.4
0628		5.0	3.9
0644		4.5	4.3
0659		5.4	5.2
0715		6.6	6.2
0731		5.9	7.0
0746		7.4	9.7
0802		6.1	9.0

Table D-1 (continued) - 2

PST	HNO_3	NH_3	HCHO	PST	HNO_3	NH_3	HCHO
0818		5.8	9.0	2018	3.4	3.7	7.9
0833		4.9	7.9	2034	5.1	3.7	7.1
0849		4.8	10.3	2113	2.4	3.7	6.2
0904	1.7	2.2	10.7	2133		5.9	6.7
0920	1.7	1.8	12.5	2146		6.4	6.3
0936	3.8	1.8	12.6	2206		6.8	5.9
0951	4.3	1.9	13.4	2226		4.3	7.6
1007	4.5	1.7	13.5	2245		3.9	6.9
1035	7.6	1.4	12.5	2305		4.6	7.4
1048	8.0	1.8	13.7	2324		4.2	5.0
1101	8.7	1.7	12.6	2344		3.8	6.5
1114	8.7	2.2	12.2				
1128	11.8	1.8	12.7	8/14/86			
1145	10.7	1.9	11.3				
1158	12.5	1.8	10.6	0004		3.7	4.8
1211	12.6	1.9	11.4	0023		2.6	5.5
1229	12.9	3.0	12.0	0043		2.7	6.2
1248	14.0	3.0	10.9	0102		2.9	5.9
1309	15.5	3.0	9.7	0122		3.6	5.0
1331	13.9	2.8	10.6	0142		3.7	4.3
1344	15.9	3.6	11.9	0201		4.7	4.7
1357	14.8	3.2	10.1	0221		3.5	3.7
1410	15.5	3.6	12.3	0241		3.4	4.2
1423	13.4	3.5	11.6	0300		3.0	4.5
1440	16.6	3.8	11.2	0320		2.6	4.2
1453	16.9	3.1	11.1	0339		1.9	3.6
1506	17.9	3.1	11.3	0359		2.4	4.0
1522	19.7	3.9	12.1	0419		2.7	4.5
1535	18.1	4.0	10.3	0438		3.0	5.0
1548	17.3	3.9	12.4	0458		2.5	4.9
1601	16.5	4.1	15.3	0518		2.9	4.5
1614	18.5	4.5	13.9	0537		4.0	3.4
1630	13.0	4.8	13.0	0557		4.1	3.3
1643	13.9	3.9	12.7	0616		3.4	3.4
1655	12.9	3.9	12.1	0636		2.8	3.8
1706	13.4	3.7	13.1	0656		2.5	6.0
1718	13.5	3.9	13.1	0716		2.4	6.2
1734	13.0	3.5	10.9	0735		2.1	5.7
1747	10.4	4.2	12.6	0755		1.5	7.4
1800	10.6	4.0	9.8	0815		2.6	8.2
1813	9.7	4.1	11.6	0834		1.8	10.9
1827	8.3	4.1	9.0	0854	2.6	1.5	12.2
1850	6.0	4.1	10.1	*0914	2.6	1.4	12.5
1913	4.3	3.8	8.3	*1033	5.1	1.7	12.8
1926	5.4	4.5	7.9	*1059	8.2	1.5	14.6
1939	5.2	4.1	8.1	*1153	10.4	2.4	11.8
1952	4.5	3.6	9.1	1208	12.8	2.7	12.1
2005	4.4	3.4	7.5	1221	14.5	2.6	9.1

Table D-1 (continued) - 3

PST	HNO_3	NH_3	HCHO
1240	16.1	2.4	13.7
1253	16.1	3.3	13.3
1309	15.7	2.9	13.0
*1322	17.5	3.2	12.5
*1507	20.1	2.7	9.4
1520	22.3	3.0	15.3
1531	24.6	2.3	17.4
1543	22.2	2.9	18.7
1555	23.1	2.3	19.9
1606	22.2	2.0	16.8
1620	19.6	3.1	15.3
1643	17.5	1.9	13.2
1655	18.2	2.2	12.7
1711	18.8	1.7	13.3
1723	18.1	1.2	12.6
1735	17.1	1.6	12.4
1746	16.3	2.1	13.5
1801	15.9	2.0	10.9
1818	13.8	1.6	10.8
1830	12.8	2.2	10.9
1842	13.0	2.2	12.8
1853	11.5	1.5	11.6
1925	10.2	2.0	10.3
1938	8.1	1.4	9.5
1951	8.4	2.2	8.4
2004	8.7	1.4	9.5
2017	5.6	1.8	8.5
2030	5.3	2.0	8.3
2044	3.4	2.3	7.6
2057	3.8	1.7	7.2
2110	2.1	2.0	7.7
2123		2.1	6.0
2136		2.1	6.0
2210		1.5	4.7
2229		1.7	5.5
2249		1.5	5.3
2309		1.5	4.9
2328		2.6	4.2
2348		2.3	3.6
8/15/86			
0008		2.5	4.1
0027		2.8	3.4
0047		2.5	3.8
0107		2.8	3.6
0126		2.5	3.4
0146		3.4	3.1
0206		3.1	2.7
0225		2.8	2.2
0245		3.6	3.0
0305		3.2	3.9
0324		3.8	2.6
0344		3.2	2.8
0404		3.3	3.9
0424		4.4	3.5
0443		3.9	3.6
0503		4.2	3.1
0523		5.2	2.9
0543		4.9	3.8
0602		3.5	4.0
0622		3.4	4.9
0641		4.0	4.4
0701		4.7	4.2
0721		2.9	4.2
0741		2.0	4.3
0800		4.2	4.6
0820		1.3	6.1
0840		1.3	7.4
0859	1.7	1.6	7.3
0919	3.1	1.1	8.8
1016	6.2	0.7	10.5
1029	8.4	1.3	10.7
1043	9.9	1.2	10.3
1100	11.3	1.4	10.1
1112	9.7	1.2	10.8
1126	13.5	1.3	11.3
1138	12.8	1.3	12.4
1151	13.1	1.8	12.8
1203	14.5	1.4	12.2
1219	17.1	1.4	12.8
1231	16.0	1.9	11.7
1244	17.1	1.2	11.0
1256	21.4	2.1	11.1
1309	21.2	1.7	11.1
1325	20.9	2.1	12.2
1341	19.6	3.0	10.4
1353	20.2	2.4	13.1
1410	25.0	2.7	13.1
1425	22.6	3.5	17.8
1440	22.2	2.9	17.6
1453	21.6	3.3	16.4
1505	21.4	3.1	16.2
1518	19.6	2.7	15.1
1530	21.4	2.5	14.3
1542	20.5	2.5	15.8

Table D-1 (continued) - 4

PST	HNO_3	NH_3	HCHO
1604	17.1	2.3	12.9
1616	16.2	2.3	13.8
1629	16.2	2.8	12.2
1641	11.5	2.1	13.5
1653	10.9	1.9	13.8
1707	10.8	2.0	12.5
1720	10.5	1.4	9.1
1732	9.4	2.1	6.1
1744	9.0	2.3	7.9
1757	9.4	2.7	9.1
1830	8.2	1.6	7.7
1842	6.7	2.2	9.0
1854	6.8	1.8	10.6
1907	6.8	1.9	8.8
1919	4.3	2.1	8.1
1938	2.9	2.8	8.1
1950	2.6	2.3	6.8
2003	2.2	2.7	7.2
2015		2.7	7.4
2027		3.6	5.5
2106		3.6	5.4
2125		2.9	6.0
2145		2.9	3.4
2205		2.7	3.4
2224		3.1	2.7
2244		3.0	4.4
2323		3.2	5.7
2343		4.8	4.4
8/16/86			
0003		3.1	5.5
0022		3.1	4.0
0042		3.6	4.3
0101		3.2	4.9
0121		4.0	4.9
0141		3.5	4.9
0200		3.6	4.5
0220		3.2	5.1
0240		3.2	4.8
0259		4.2	4.0
0319		3.1	4.7
0339		5.1	3.7
0359		3.8	4.9
0418		3.6	4.2
0438		3.3	4.9
0458		3.6	4.7
0517		3.8	3.2
0537		3.4	4.3
0557		2.7	4.4
0616		2.6	4.0
0636		3.8	3.1
0656		3.3	4.4
0715		2.8	5.0
0735		1.8	5.7
0755	0.9	1.3	7.9
0815	3.0	1.6	9.8
0834	2.1	1.5	10.0
0854	4.1	0.6	9.7
0914	3.8	1.1	11.2
0933	3.8	1.1	11.2
1015	8.1	1.5	12.2
1028	8.7	0.9	12.6
1048	10.3	0.9	14.4
1100	11.6	1.8	14.9
1118	13.8	1.8	14.9
1131	13.7	2.3	16.1
1143	15.5	1.5	12.6
1155	15.8	2.0	13.8
1207	15.6	2.2	12.4
1219	16.0	2.2	12.3
1231	14.4	2.9	11.3
1243	15.5	2.2	11.8
1255	17.7	2.4	10.3
1308	17.5	2.3	10.1
1320	17.1	2.8	9.6
1332	19.2	2.3	9.6
1344	16.6	3.1	11.4
1356	19.7	2.8	9.9
1409	19.4	2.8	10.9
1421	20.8	3.2	10.5
1433	20.3	2.8	10.9
1445	20.3	3.1	11.7
1457	21.1	3.5	14.2
1509	20.8	3.1	14.1
1522	20.5	3.3	13.8
1534	20.5	2.6	16.7
1546	20.5	2.6	14.3
1558	22.8	2.6	15.5
1610	19.8	3.5	13.8
1623	20.5	3.1	15.2
1635	19.1	3.1	13.9
1647	20.9	2.2	14.4
1659	21.6	2.9	12.7
1711	19.9	2.3	11.6
1724	20.9	2.1	13.5

Table D-1 (continued) - 5

PST	HNO_3	NH_3	HCHO
1736	19.6	2.7	14.7
1748	16.9	2.4	13.4
1800	18.7	2.6	12.6
1812	13.1	2.3	12.1
1902	10.3	2.3	9.2
1917	7.9	2.8	9.3
1924	6.7	2.7	9.1
1942	8.2	3.1	8.9
1954	6.8	3.2	8.9
2006	5.3	4.7	9.1
2024	5.4	4.8	8.2
2036	5.1	3.8	8.1
2049	2.6	5.0	9.5
2144		4.5	7.6
2152		3.9	9.0
2212		3.6	8.0
2232		3.8	7.7
2251		3.6	6.8
2311		3.7	5.3
2331		4.3	4.7
2350		3.8	5.9
8/17/86			
0010		3.7	5.6
0030		4.0	6.9
0049		4.1	6.2
0109		3.2	7.4
0129		5.1	7.9
0148		3.4	6.2
0208		3.4	6.6
0228		3.7	6.9
0248		4.0	6.3
0307		2.9	8.9
0327		2.1	7.5
0347		2.7	5.8
0406		2.6	8.2
0426		1.8	7.8
0446		2.5	6.3
0506		2.1	7.9
0525		1.8	8.3
0545		2.6	7.1
0605		2.1	5.2
0624		2.8	6.9
0644		2.0	6.2
0704		2.2	7.0
0723		3.4	6.3
0743		1.7	7.4
0803		2.2	8.5
0823		3.8	8.3
0843		4.2	10.4
0902		5.3	11.7
0922		5.4	13.1
0942		5.5	18.5
*1002		5.6	18.9
*2235		5.9	6.0
2253		4.2	6.2
2306		3.5	5.3
2317		4.6	6.0
2337		3.3	6.3
2356		4.0	6.4
8/18/86			
0016		5.0	6.9
0036		5.9	5.5
0056		8.3	7.2
0115		3.8	8.1
0135		3.9	6.9
0155		5.2	8.7
0214		5.9	7.2
0234		5.3	7.9
0254		7.5	7.4
0313		6.5	7.7
0333		6.2	7.9
0353		6.0	7.3
0412		5.6	7.5
0432		5.8	8.1
0452		6.7	7.7
0511		4.6	7.9
0531		4.8	8.0
0550		4.3	6.5
0610		4.4	5.6
0630		4.2	6.0
0649		4.7	6.4
0709		6.2	9.3
0729		4.1	7.9
0748	2.8	4.6	8.4
0808	2.7	4.3	8.9
0828	3.1	4.6	9.9
0847	3.7	7.5	9.2
0907	5.6	8.2	15.0
0926	5.5	7.1	15.8
0946	5.6	5.7	10.5
1004	9.9	8.4	15.3

Table D-1 (continued) - 6

PST	HNO_3	NH_3	HCHO
1017	11.2	9.4	17.0
1029	10.3	9.7	15.3
1057	12.3	11.5	21.5
1111	12.8	14.3	22.0
1123	13.1	14.5	20.5
1140	15.0	12.8	22.4
1156	15.5	11.5	18.8
1207	20.7	9.8	22.2
1220	19.2	9.0	19.3
1233	20.7	6.2	15.2
1245	15.4	5.5	12.4
1256	23.9	10.4	13.6
1308	20.7	10.1	14.6
1320	17.7	7.0	10.3
1333	15.4	5.0	9.3
1345	15.9	4.7	9.1
1357	13.7	3.8	8.2
1409	16.7	4.3	10.6
1421	16.7	4.1	8.9
1433	18.5	4.6	13.2
1445	18.5	4.2	11.6
1451	15.7	4.6	11.7
1509	22.4	6.2	14.4
1521	19.5	4.7	14.5
1534	27.7	6.2	15.1
1546	26.2	6.1	19.1
1558	26.2	5.8	16.3
1610	21.2	5.3	15.1
1622	21.3	4.8	14.1
1635	16.1	5.6	14.6
1647	17.2	6.1	17.9
1700	16.4	5.4	12.4
1712	16.3	5.7	11.8
1724	15.0	4.4	12.3
1737	15.2	6.1	10.4
1750	13.0	5.4	11.9
1802	12.8	5.5	10.8
1814	13.1	5.0	9.6
1826	9.9	6.9	9.7
1839	5.7	6.6	10.0
1852	5.4	8.1	6.9
1932	2.8	5.3	7.1
1944	2.8	4.3	4.7
1956	2.5	4.8	5.8
2009	2.2	4.7	4.8
2021		6.8	6.7
2035		7.9	8.6
2047		8.7	8.1
2059		8.2	7.1
2111		9.4	5.4
2124		9.0	5.8
2206		6.9	7.2
2226		7.6	7.8
2246		9.5	8.5
2305		8.5	8.0
2325		7.7	8.5
2345		7.1	7.8
8/19/86			
0004		5.9	9.1
0024		5.9	6.9
0044		10.5	7.6
0103		6.9	7.7
0123		5.3	6.2
0143		6.9	5.6
0202		7.5	6.7
0222		9.6	6.0
0242		8.0	7.5
0301		6.7	7.9
0321		5.3	6.1
0341		8.5	7.9
0400		10.2	8.4
0420		7.1	8.1
0439		6.1	7.7
0459		8.9	8.3
0519		7.8	6.4
0538		4.2	6.5
0558		7.3	7.9
0618		6.4	9.0
0637		6.4	10.0
0657		8.5	11.1
0717		5.8	11.2
0737	2.6	5.9	14.3
0757	2.6	6.0	14.6
0816	4.9	6.3	14.2
0836	6.0	6.1	14.9
0855	6.7	7.9	14.2
0915	8.4	6.8	12.7
0935	11.5	6.5	15.5
1006	16.2	6.6	13.8
1018	16.1	5.7	13.4
1030	17.3	6.0	14.3
1043	17.3	6.4	15.2
1057	18.1	7.0	15.3
1109	21.9	6.9	18.6

Table D-1 (continued) - 7

PST	HNO_3	NH_3	HCHO
1121	17.5	6.9	15.9
1133	19.5	6.9	11.5
1148	20.6	8.7	13.4
1200	22.9	6.4	11.5
1213	18.2	5.4	13.7
1225	21.6	5.5	14.2
1237	22.3	4.9	13.8
1249	12.5	3.9	9.2
1305	13.4	3.2	8.7
1317	16.6	5.8	10.8
1329	22.4	6.6	12.2
1346	29.2	7.1	19.0
1355	33.1	8.1	23.8
1405	27.2	7.8	21.3
1415	27.3	6.5	16.5
1426	23.4	6.4	13.3
1436	22.3	6.1	13.0
1448	21.2	5.8	12.7
1501	20.0	5.1	11.9
1512	18.5	5.7	10.6
1522	17.2	5.1	13.3
1532	16.6	4.5	10.9
1542	12.5	6.4	9.4
1554	11.6	4.7	9.0
1604	10.7	4.2	6.8
1614	8.3	4.7	7.6
1624	7.5	4.3	8.2
1634	7.1	4.9	6.7
1645	7.6	4.4	8.1
1655	6.2	5.2	7.0
1705	4.8	5.1	7.6
1720	6.5	5.3	8.1
1733	6.8	5.1	8.3
1747	7.4	5.1	8.8
1759	7.2	7.1	7.4
1811	4.7	5.1	7.6
1823	3.7	6.0	6.2
1835	5.0	6.8	6.7
1847	5.0	5.8	7.2
1902	4.6	8.1	7.6
1914	4.0	7.0	6.6
1927	3.3	6.9	7.2
1939	3.4	7.1	7.1
2007	3.3	9.1	8.5
2017	2.7	8.1	8.1
2029		11.0	7.7
2042		9.5	7.0
2054		7.2	7.7
2106		7.1	6.3
2118		7.7	7.2
2130		7.0	7.1
2142		6.5	7.8
2155		6.0	5.9
2207		6.7	6.8
2219		7.2	9.3
2231		7.5	9.9
2243		7.0	8.7
2314		6.9	8.1
2334		5.8	8.6
2353		6.0	9.1
8/20/86			
0013		5.0	8.4
0032		5.8	9.6
0052		5.7	8.5
0112		5.6	8.4
0131		6.9	8.2
0151		5.8	8.8
0210		6.4	8.8
0230		5.7	9.0
0250		5.4	8.2
0309		5.8	7.1
0329		6.0	9.6
0348		6.1	9.2
0408		6.0	8.9
0428		6.9	8.0
0447		7.8	8.4
0507		5.9	8.8
0527		5.6	8.6
0546		5.8	10.1
0606		6.1	10.0
0625		6.3	11.0
0645		6.5	10.3
0705		6.4	10.4
0724		7.1	10.7
0744		7.2	13.0
0803	2.3	9.5	13.9
0823	3.7	11.5	18.0
0843	3.8	9.3	23.9
0902	5.0	8.3	22.2
0923	5.6	9.8	18.9
0942	6.4	11.2	25.2
1001	6.5	10.0	25.1
1013	9.2	9.4	23.5
1025	10.4	9.9	23.3

Table D-1 (continued) - 8

PST	HNO_3	NH_3	HCHO
1038	10.0	7.5	16.9
1050	12.1	8.8	18.5
1104	14.1	8.9	16.9
1117	14.5	8.8	17.6
1129	17.5	9.6	14.7
1141	18.3	8.9	16.4
1153	17.5	8.1	13.4
1208	18.7	9.5	17.4
1220	23.4	8.7	18.9
1232	22.0	7.1	20.5
1244	24.9	7.5	21.4
1300	24.5	6.3	17.7
1311	21.7	6.5	19.3
1321	20.1	6.3	17.9
1331	19.6	6.6	15.4
1341	22.0	6.2	14.7
1352	21.0	5.9	17.5
1402	20.0	5.5	18.4
1414	20.0	5.0	16.8
1424	21.8	4.9	16.7
1434	19.0	6.3	16.7
1444	18.0	6.4	16.1
1454	15.8	7.9	11.1
1507	15.4	7.0	13.1
1517	14.8	6.3	12.3
1530	14.3	6.3	11.9
1540	14.3	5.1	11.9
1550	15.0	6.1	12.8
1600	15.7	5.9	10.4
1610	12.8	5.1	9.9
1621	8.5	5.4	8.8
1631	7.9	5.0	8.0
1643	7.3	4.6	7.1
1656	5.0	4.3	5.2
1706	5.7	5.0	6.4
1716	6.3	5.7	7.6
1727	6.5	5.2	6.8
1737	6.0	5.4	8.4
1747	6.3	5.7	8.0
1757	6.7	6.0	9.0
1807	9.1	5.9	10.2
1817	9.0	7.6	11.3
1828	7.5	6.4	11.3
1839	7.1	8.7	11.4
1849	4.2	8.1	12.1
1900	5.8	9.3	9.8
1910	5.7	10.4	12.4
1920	4.1	9.8	11.7
1930	3.4	10.3	11.1
1940	4.6	9.8	9.1
2023	5.8	6.6	9.1
2035	4.3	6.1	10.4
2050	3.3	8.9	8.4
2110	3.7	6.3	8.7
2129	1.2	5.9	7.6
2149		8.3	9.7
2209		9.9	8.4
2228		8.2	7.8
2248		5.6	8.3
2307		10.8	8.5
2327		9.1	8.6
2347		6.7	9.7
8/21/86			
0006		5.1	10.5
0026		6.2	9.8
0046		6.5	10.6
0106		6.0	11.8
0125		5.5	9.2
0145		7.5	10.1
0204		8.3	9.4
0224		7.5	9.3
0244		7.2	8.6
0303		6.7	9.3
0323		6.1	7.9
0343		8.1	10.8
0402		7.9	8.5
0422		6.8	8.4
0442		7.0	8.4
0501		6.8	8.5
0521		7.1	10.5
0541		5.8	9.6
0601		6.6	10.1
0620		6.1	10.5
0640		6.5	9.0
0700		6.3	11.6
0717		6.1	13.0
0730		7.0	14.3

APPENDIX E

GC/MS-MID Traces for Ambient POM Collected at
Pomona College (Claremont), and
El Camino Community College (Torrance) Studies

GC/MS-MID traces of nitrofluoranthene (NF), nitropyrene (NP) and nitroacephenanthrylene analyses (NAce) are presented. The GC column and conditions employed were: a 60 m DB-5 narrow-bore fused silica capillary column; injection temperature 50°C, followed by programming at 20°C min^{-1} to 200°C, then at 4°C min^{-1}. The mass spectrometer was run in the electron impact multiple ion detection mode (70 eV).

All of the ambient POM extracts for which the analyses are shown were spiked with the deuterated internal standards, 1-nitropyrene-d_9 and 2-nitrofluoranthene-d_9. The extracts were fractionated twice by HPLC (see Section VI for details) prior to the GC/MS-MID analyses.

The ion traces (% abundance vs. retention time in min) for each sample injection are given in two formats. The first (A) shows four ion traces as follows: m/z 247, the $[M]^+$ ion for the NF, NP and NAce isomers; m/z 217, the $[M-NO]^+$ fragment ion (this ion may be characteristically low for some isomers, e.g., 2-NF, 2-NP and the NAce); m/z 200, the $[M-HNO_2]^+$ fragment ion; and m/z 256, the $[M]^+$ ion for the deuterated 2-NF-d_9 and 1-NP-d_9 internal standards. The attenuation is given on each ion trace.

The second format (B) shows only the $[M]^+$ ions. The 2-NF-d_9 peak which elutes at ~22.5 min has been used as a precise retention time marker. In this second format, the ambient samples are shown with the 2-NF peak off-scale and the minor nitroarene isomers have been identified by comparison with the standard mixtures [shown in (1) and (2)]. The analyses included are as follows:

(1) A standard mixture of all eight NF and NP isomers and 2-NF-d_9.

(2) Nitroacephenanthrylenes (NAce) resulting from the gas-phase reaction of acephenanthrylene (Zielinska et al. 1987) with the OH radical in the presence of NO_x, co-injected with 2-NF-d_9.

Extracts of ambient POM Collected at:

(3) Claremont, CA, 1200-1800 hr, 9/13/85.

(4) Claremont, CA, 1800-2400 hr, 9/13/85.

(5) Claremont, CA, 1800-2400 hr, 9/14/85.

(6) Claremont, CA, 0000-0600 hr, 9/15/85.

(7) Torrance, CA, 1700-0500 hr, 1/27-28/86.

(8) Torrance, CA, 0500-1700 hr, 1/28/86.

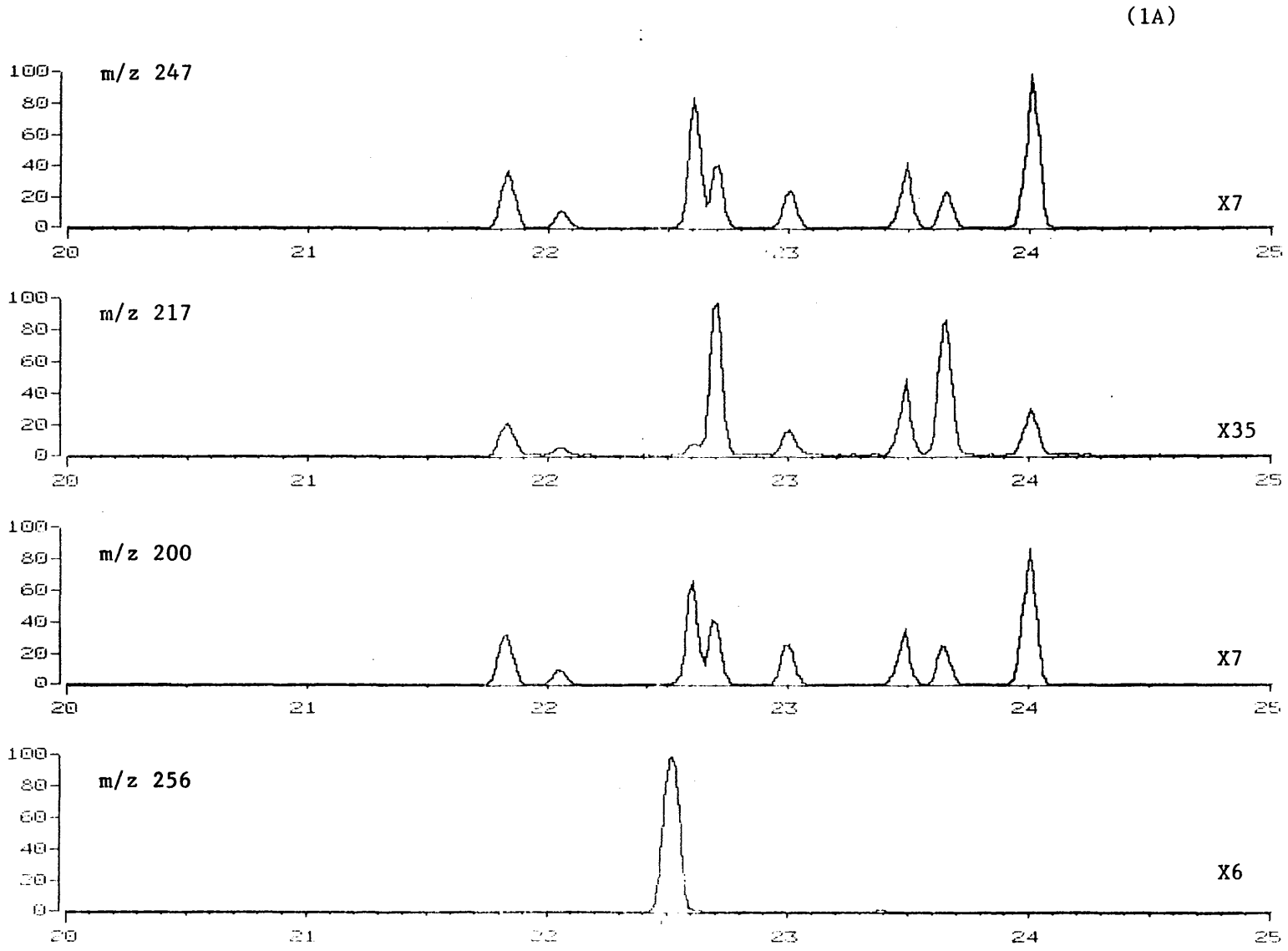

Figure E-1A. GC/MS-MID traces of ions characteristic for NF and NP isomers and the $[M]^+$ ion of 2-NF-d_9. Shown is a standard mixture of all eight NF and NP isomers and 2-NF-d_9.

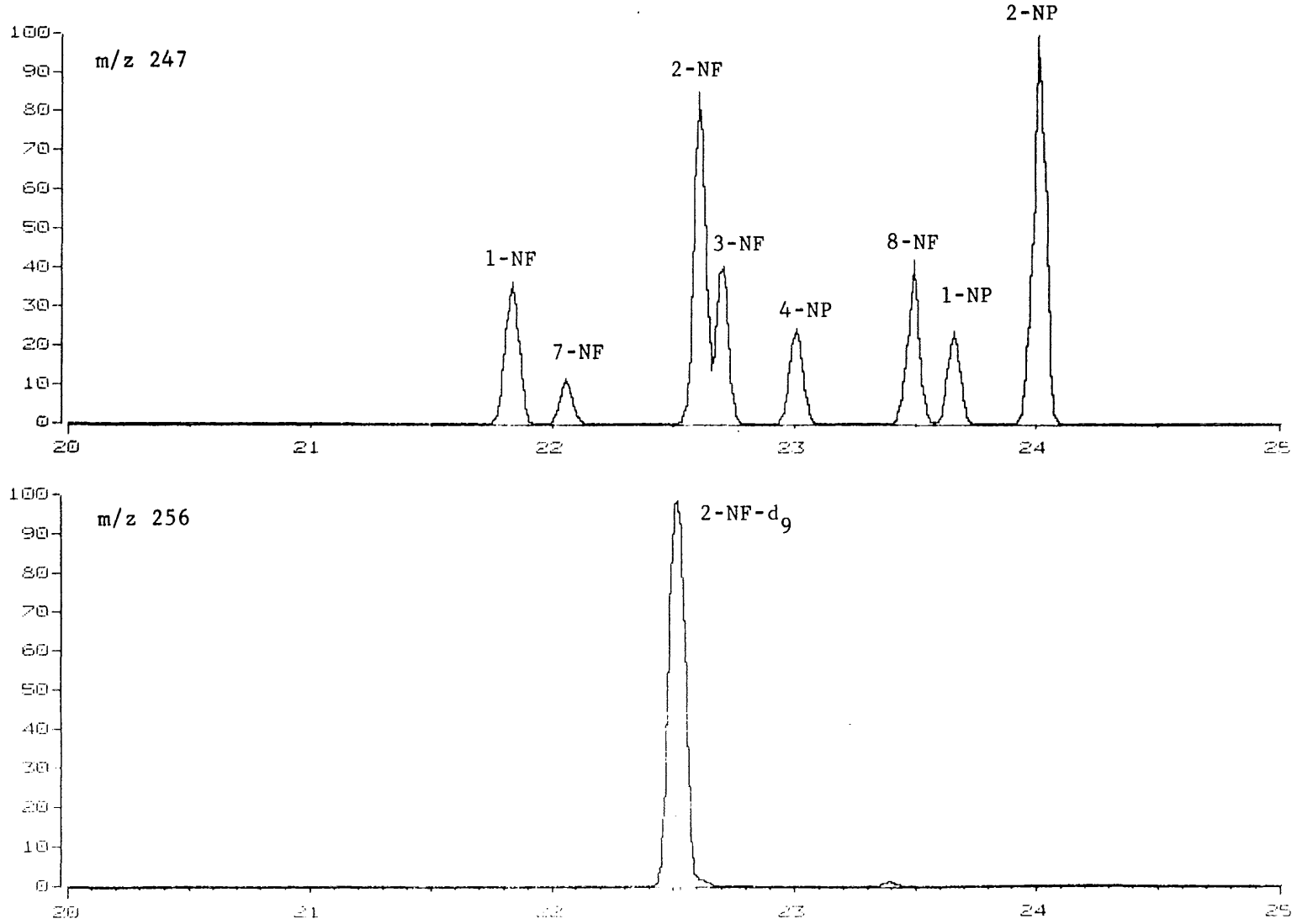

Figure E-1B. GC/MS-MID traces of the molecular ion for NF and NP isomers (m/z 247) and for the deuterated analogues (m/z 256). Shown is a standard mixture of all eight NF and NP isomers and 2-NF-d_9.

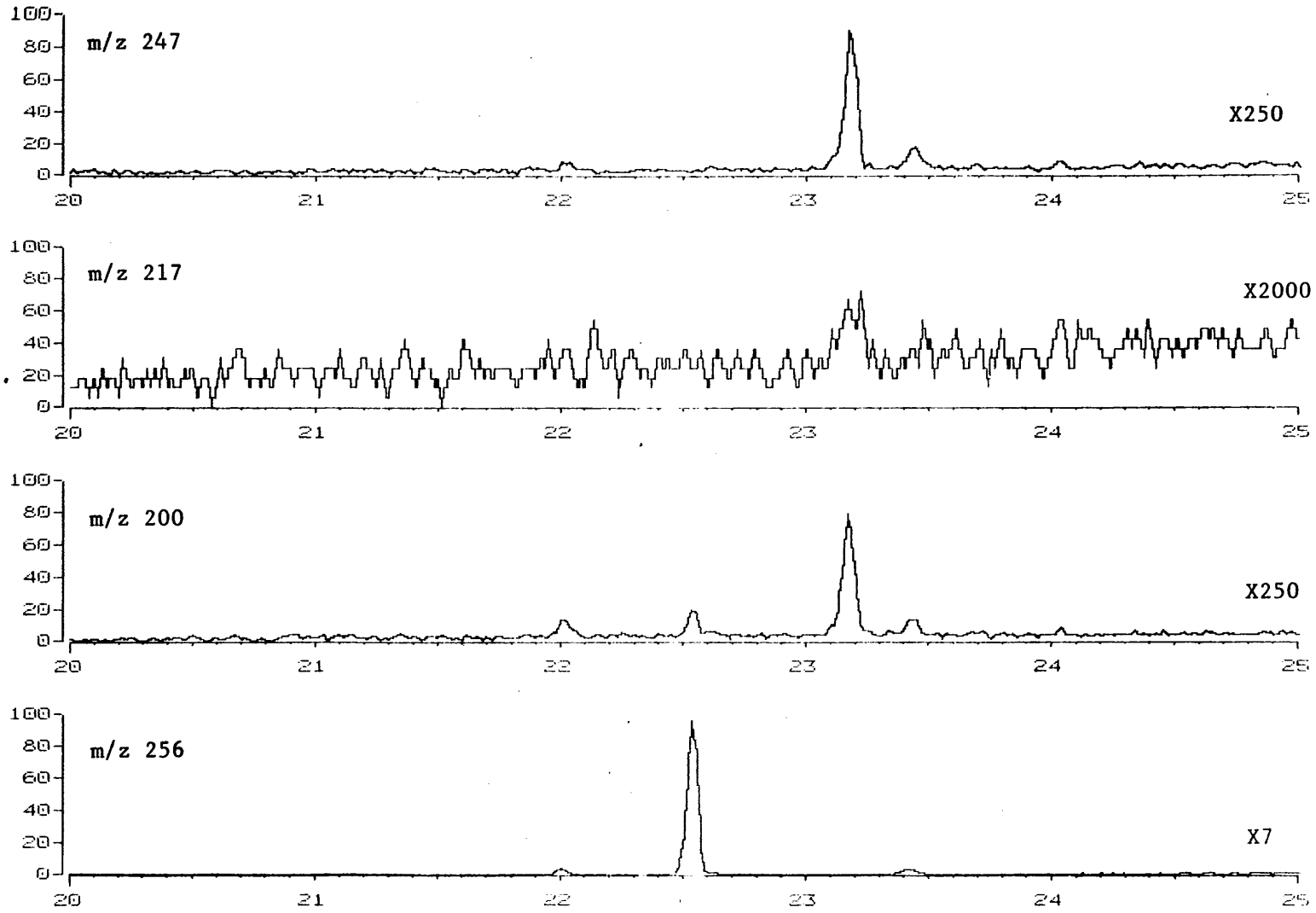

Figure E-2A. GC/MS-MID traces of ions characteristic for nitroacephenanthrylene (NAce) isomers and the $[M]^+$ ion of 2-NF-d_9. Shown are the NAce resulting from the gas-phase reaction of acephenanthrylene with the OH radical in the presence of NO_x, co-injected with 2-NF-d_9.

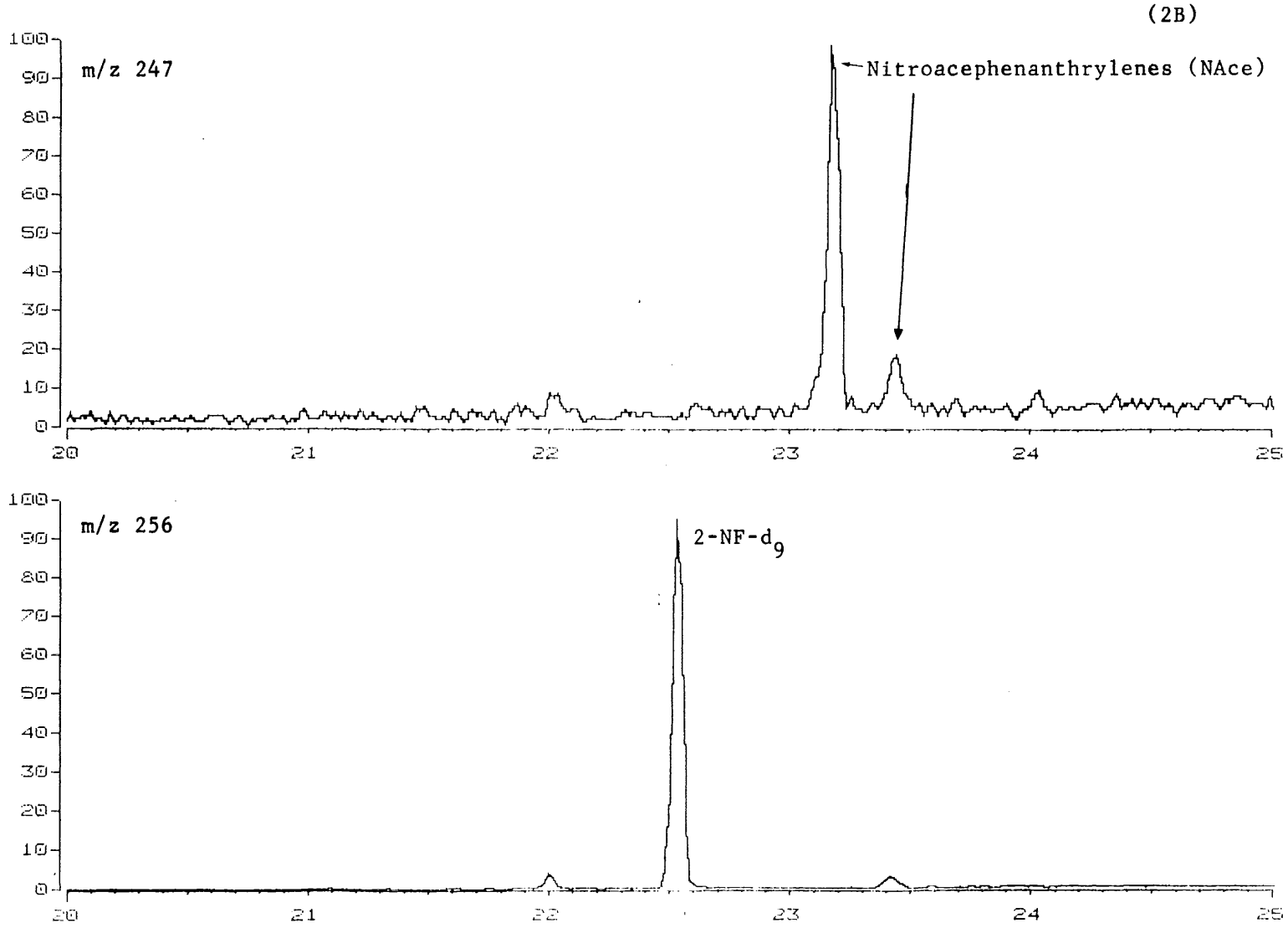

Figure E-2B. GC/MS-MID traces of the molecular ion for NAce isomers (m/z 247) and for 2-NF-d_9 (m/z 256). Shown are the NAce resulting from the gas-phase reaction of acephenanthrylene with the OH radical in the presence of NO_x, co-injected with 2-NF-d_9.

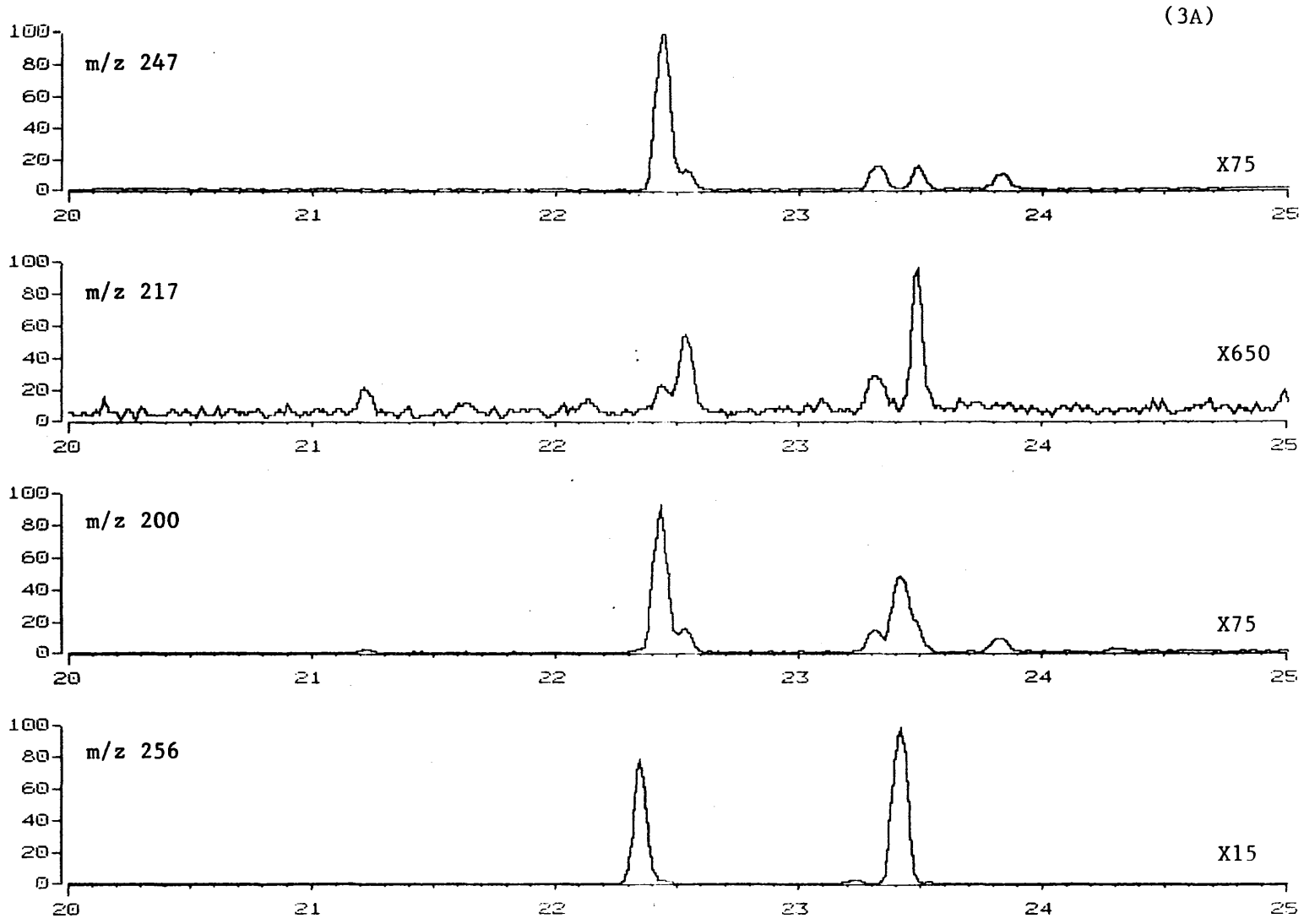

Figure E-3A. GC/MS-MID traces of ions characteristic for NF, NP and NAce isomers and the $[m]^+$ ion of their deuterated analogues. Shown is an extract of ambient POM collected at Claremont, CA, 1200-1800 hr, 9/13/85. 2-NF and 1-NP were added as internal standards.

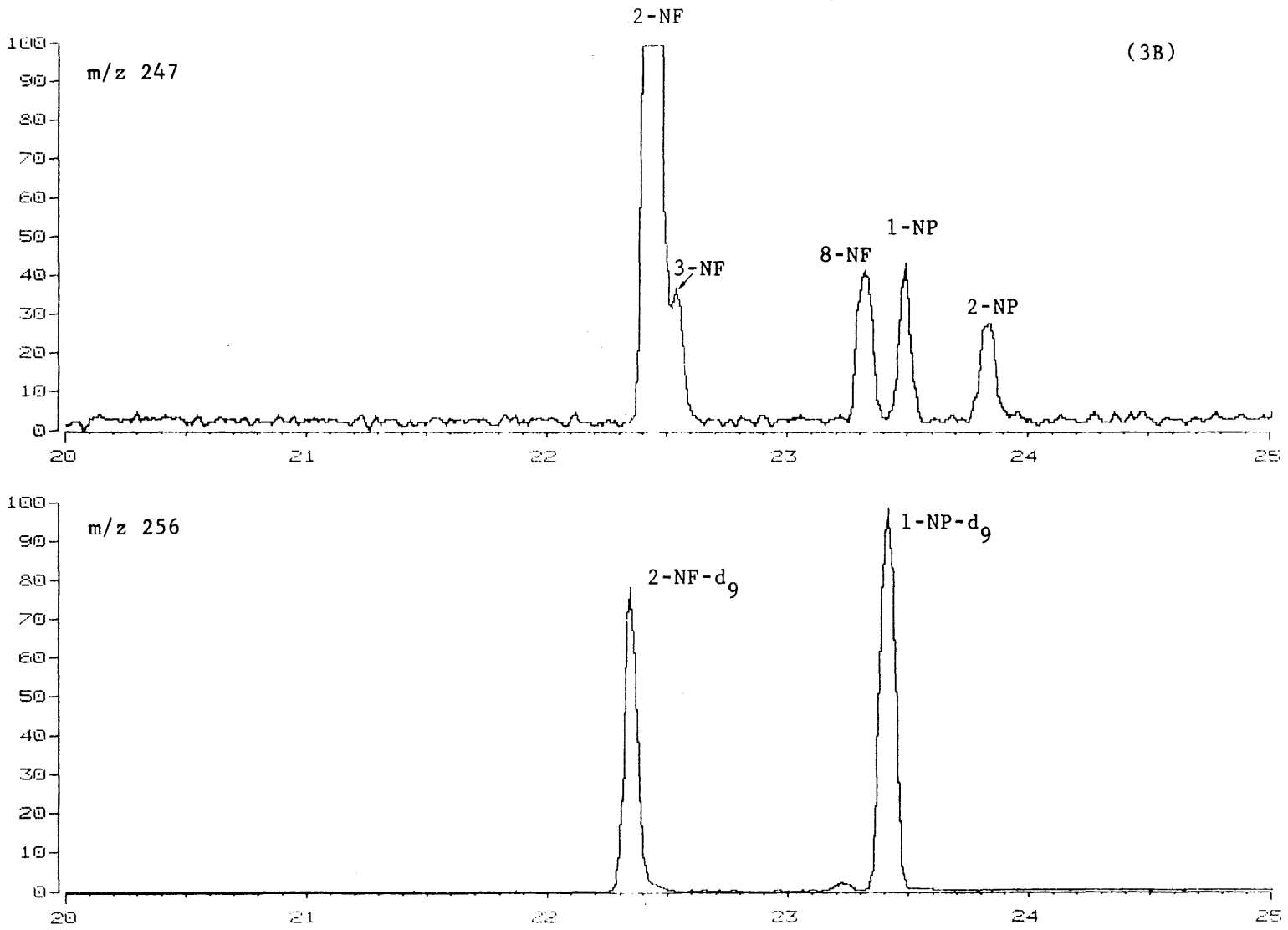

Figure E-3B. GC/MS-MID traces of the molecular ion for NF, NP and NAce isomers (m/z 247) and their deuterated analogues. Shown is an extract of ambient POM collected at Claremont, CA, 1200-1800 hr, 9/13/85. 2-NF and 1-NP were added as internal standards.

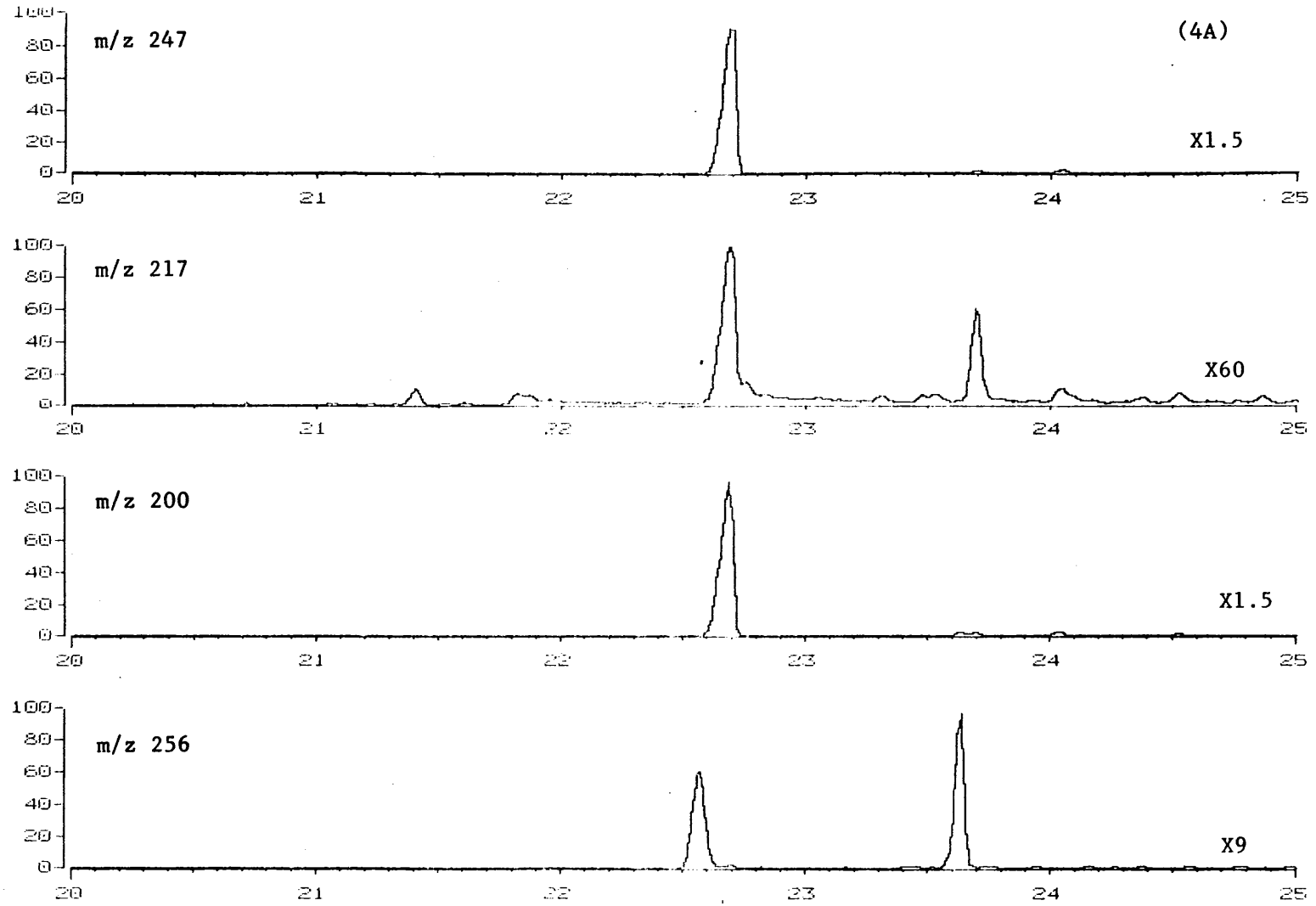

Figure E-4A. GC/MS-MID traces of ions characteristic for NF, NP and NAce isomers and the $[m]^+$ ion of their deuterated analogues. Shown is an extract of ambient POM collected at Claremont, CA, 1800-2400 hr, 9/13/85. 2-NF and 1-NP were added as internal standards.

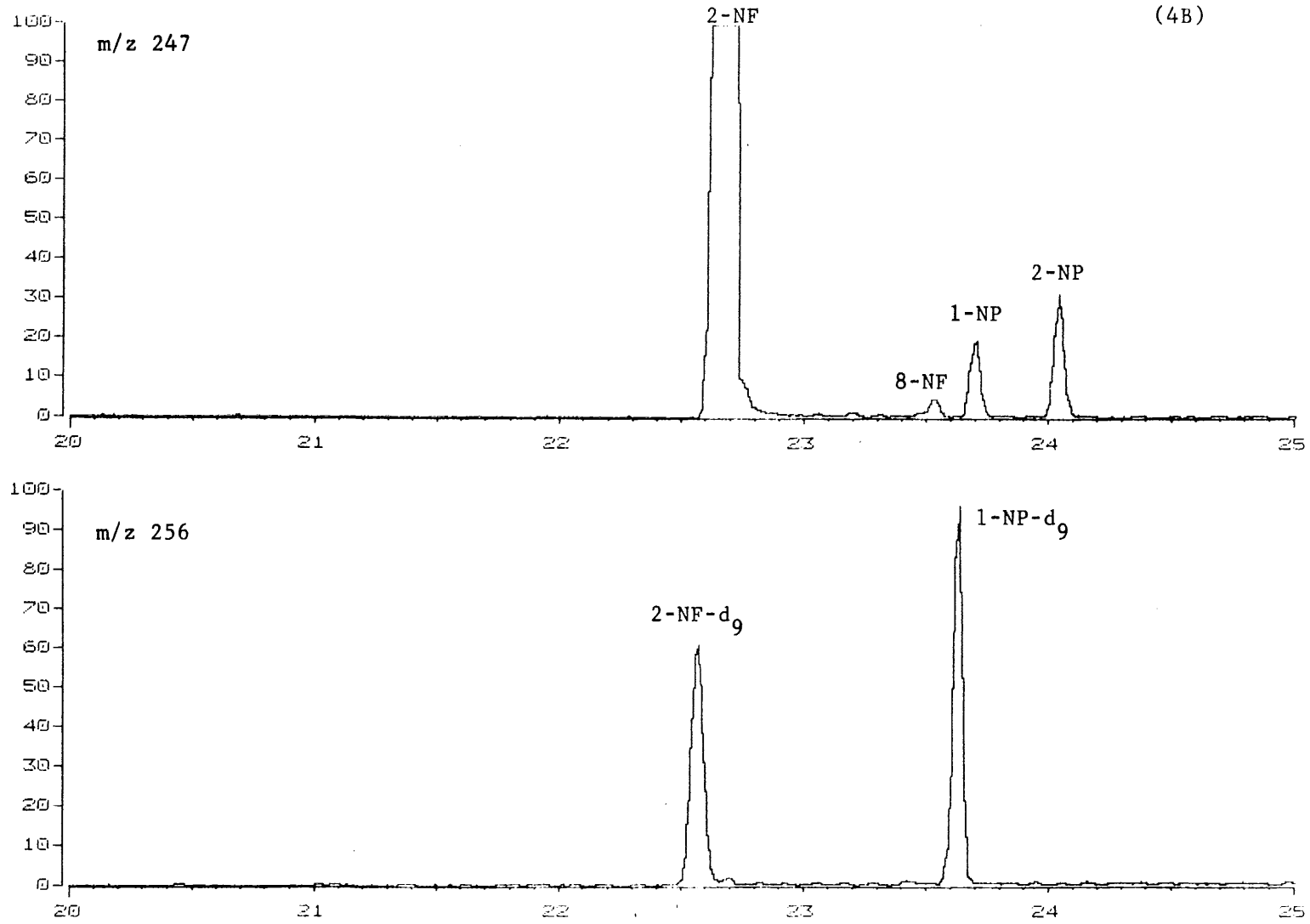

Figure E-4B. GC/MS-MID traces of the molecular ion for NF, NP and NAce isomers (m/z 247) and their deuterated analogues. Shown is an extract of ambient POM collected at Claremont, CA, 1800-2400 hr, 9/13/85. 2-NF and 1-NP were added as internal standards.

(5A)

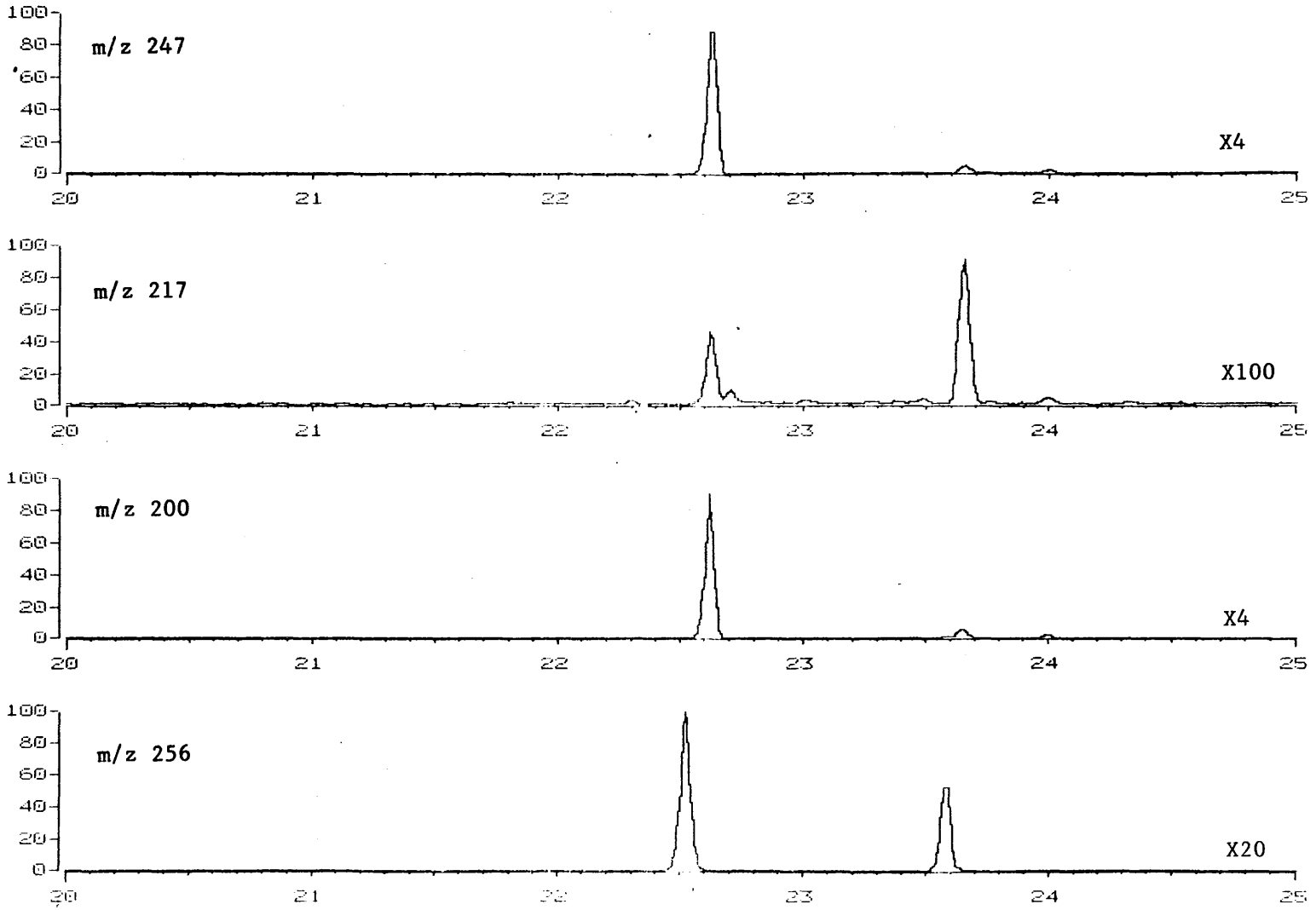

Figure E-5A. GC/MS-MID traces of ions characteristic for NF, NP and NAce isomers and the $[m]^+$ ion of their deuterated analogues. Shown is an extract of ambient POM collected at Claremont, CA, 1800-2400 hr, 9/14/85. 2-NF and 1-NP were added as internal standards.

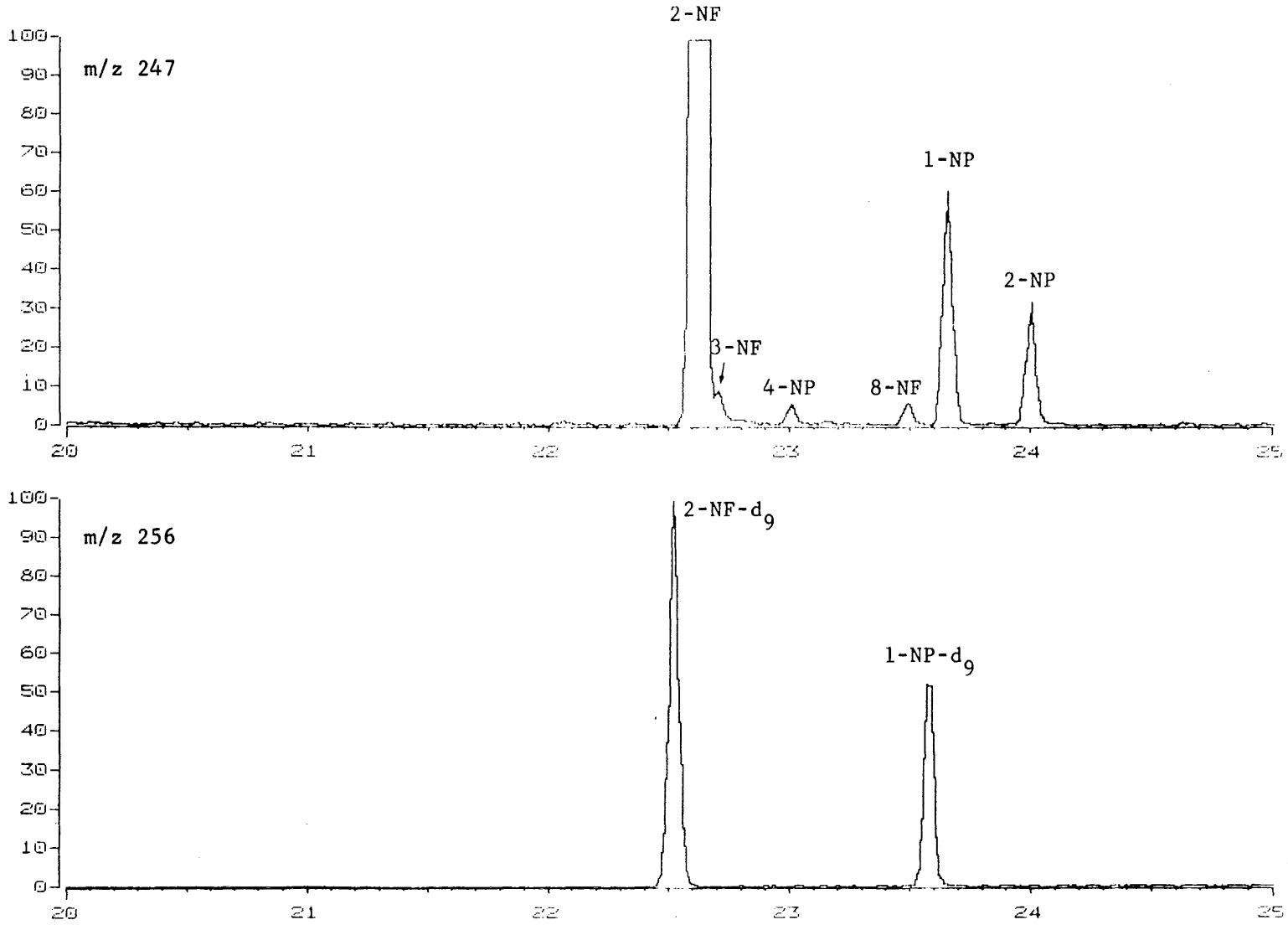

Figure E-5B. GC/MS-MID traces of the molecular ion for NF, NP and NAce isomers (m/z 247) and their deuterated analogues. Shown is an extract of ambient POM collected at Claremont, CA, 1800-2400 hr, 9/14/85. 2-NF and 1-NP were added as internal standards.

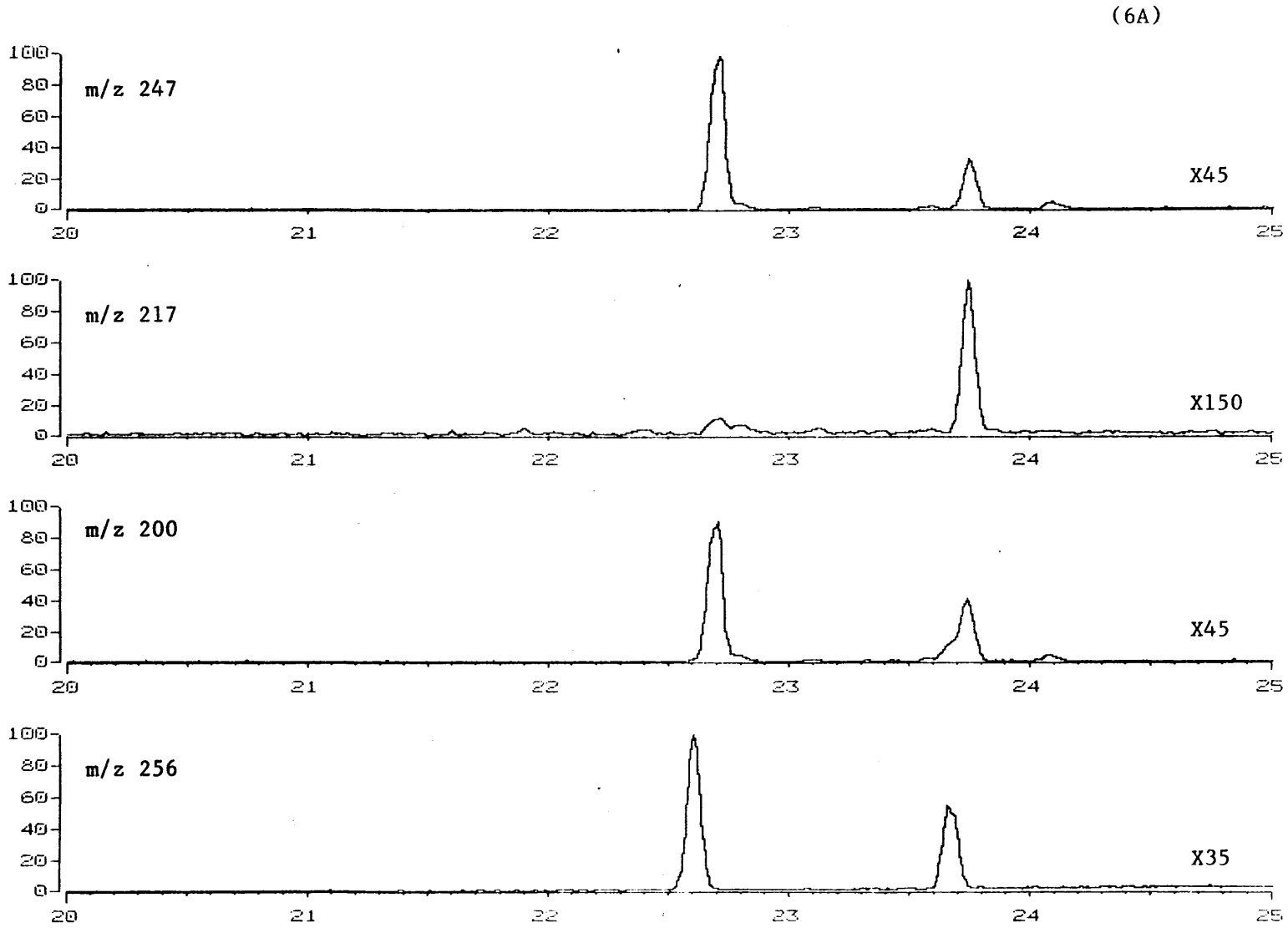

Figure E-6A. GC/MS-MID traces of ions characteristic for NF, NP and NAce isomers and the $[m]^+$ ion of their deuterated analogues. Shown is an extract of ambient POM collected at Claremont, CA, 0000-0600 hr, 9/15/85. 2-NF and 1-NP were added as internal standards.

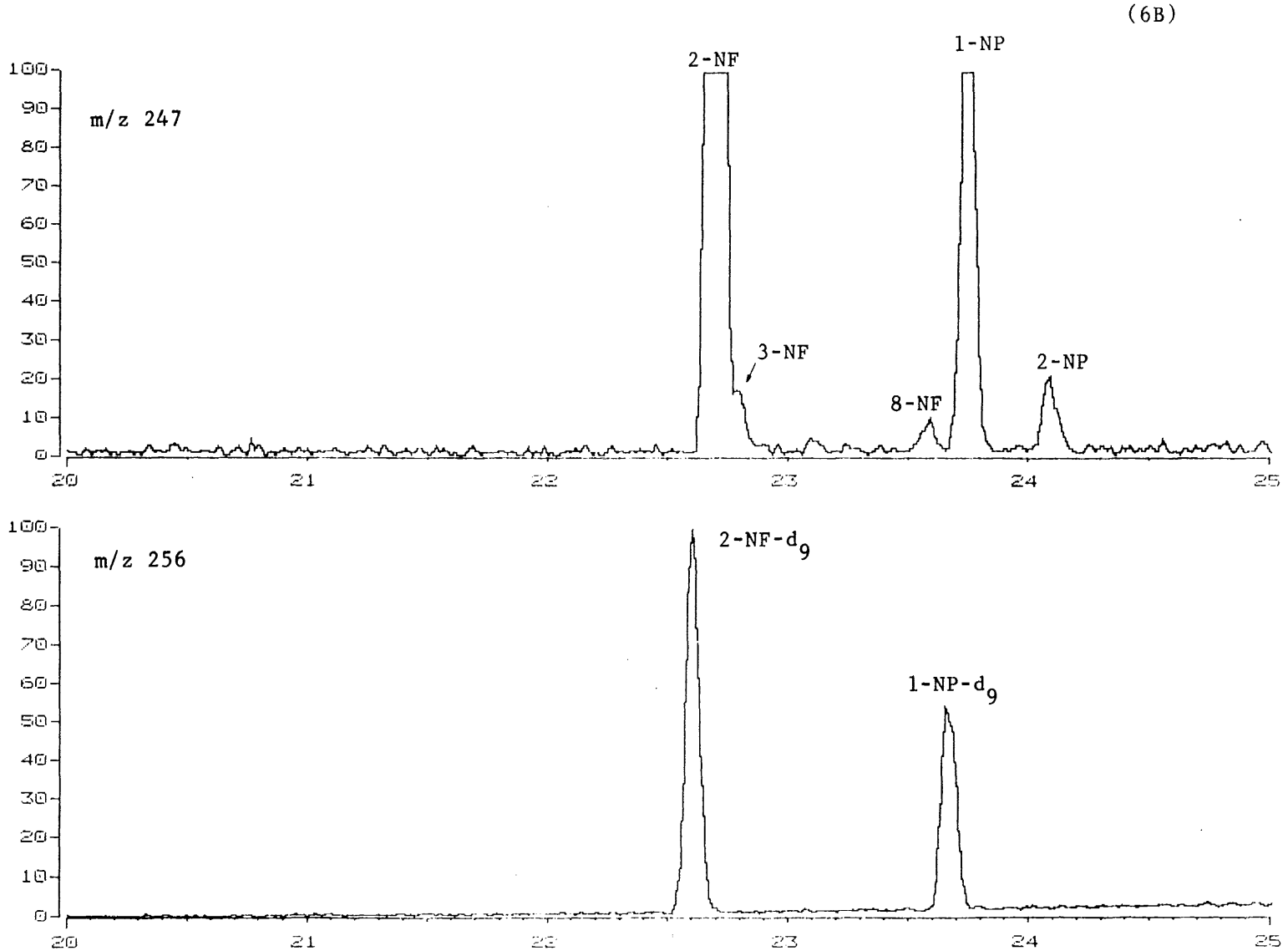

Figure E-6B. GC/MS-MID traces of the molecular ion for NF, NP and NAce isomers (m/z 247) and their deuterated analogues. Shown is an extract of ambient POM collected at Claremont, CA, 0000-0600 hr, 9/15/85. 2-NF and 1-NP were added as internal standards.

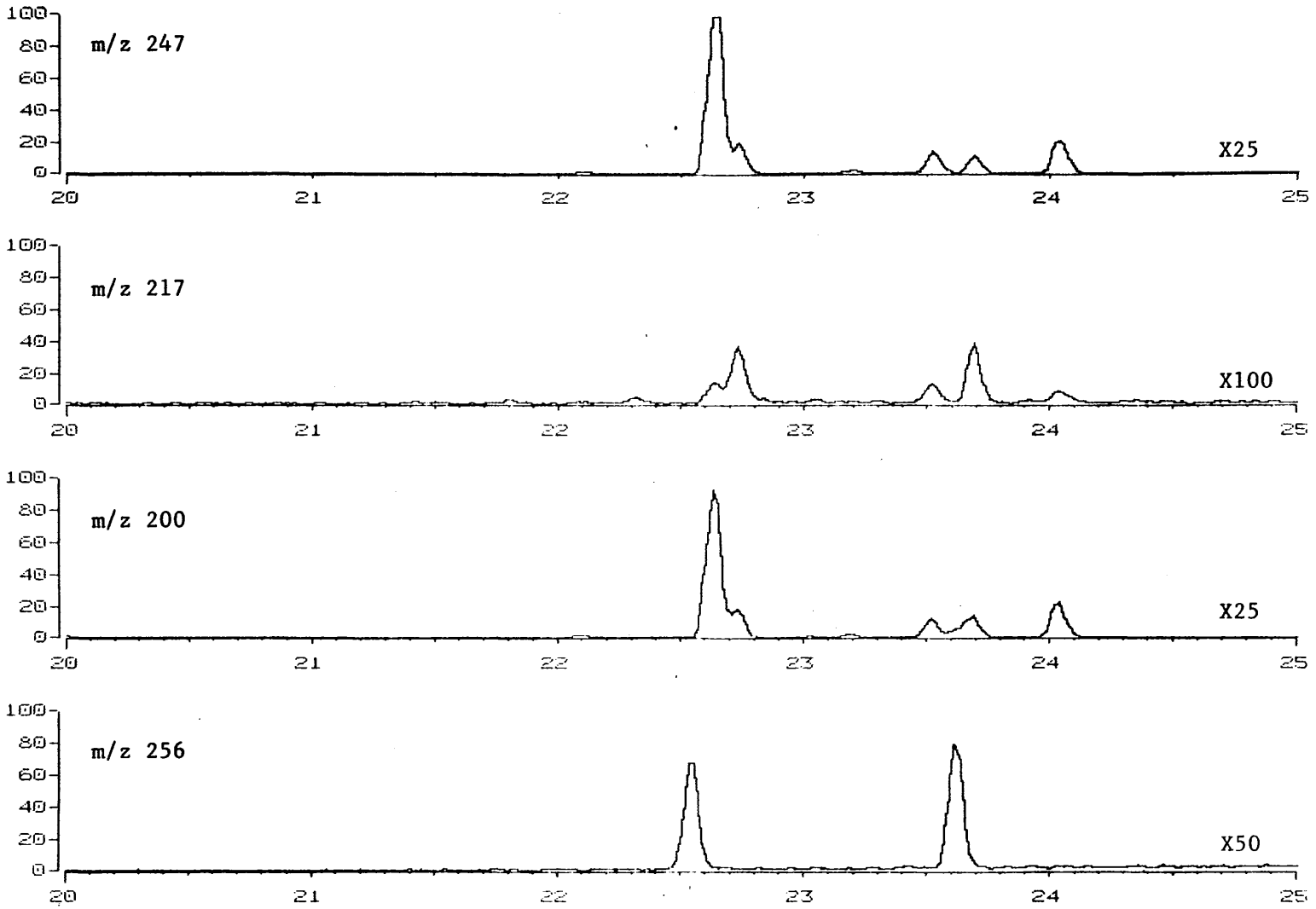

Figure E-7A. GC/MS-MID traces of ions characteristic for NF, NP and NAce isomers and the $[m]^+$ ion of their deuterated analogues. Shown is an extract of ambient POM collected at Torrance, CA, 1700-0500 hr, 1/27-28/86. 2-NF and 1-NP were added as internal standards.

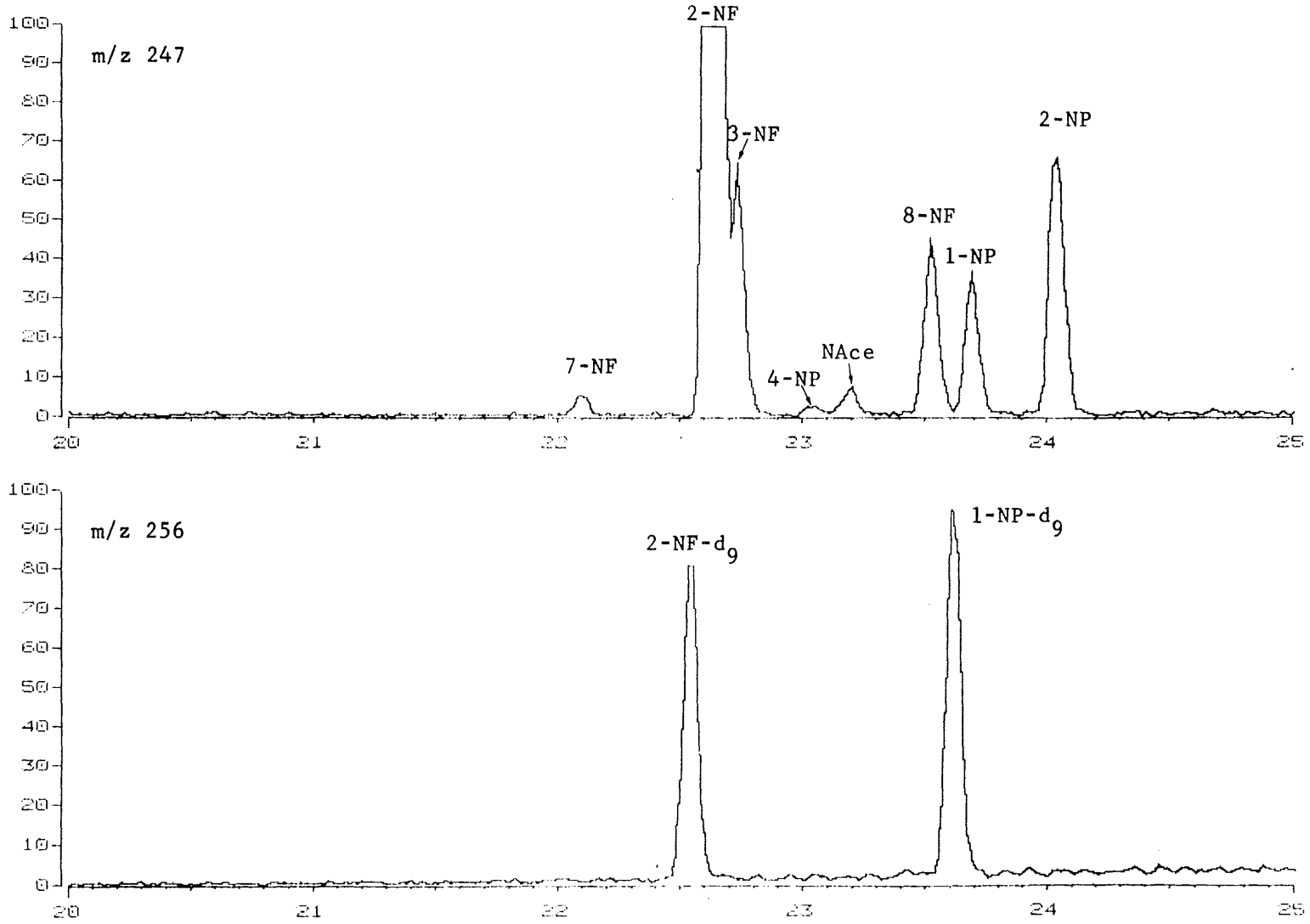

Figure E-7B. GC/MS-MID traces of the molecular ion for NF, NP and NAce isomers (m/z 247) and their deuterated analogues. Shown is an extract of ambient POM collected at Torrance, CA, 1700-0500 hr, 1/27-28/86. 2-NF and 1-NP were added as internal standards.

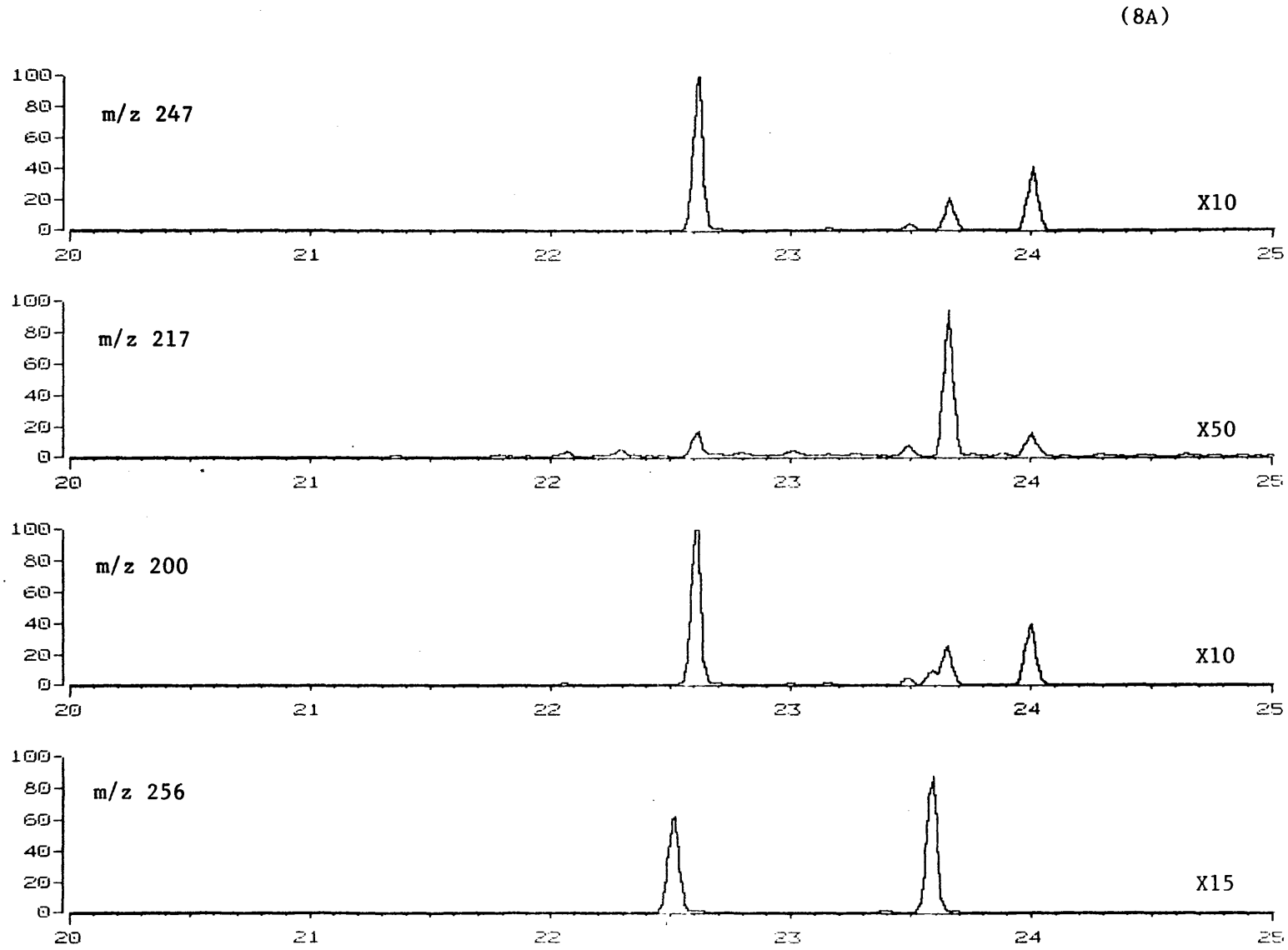

Figure E-8A. GC/MS-MID traces of ions characteristic for NF, NP and NAce isomers and the $[m]^+$ ion of their deuterated analogues. Shown is an extract of ambient POM collected at Torrance, CA, 0500-1700 hr, 1/28/86. 2-NF and 1-NP were added as internal standards.

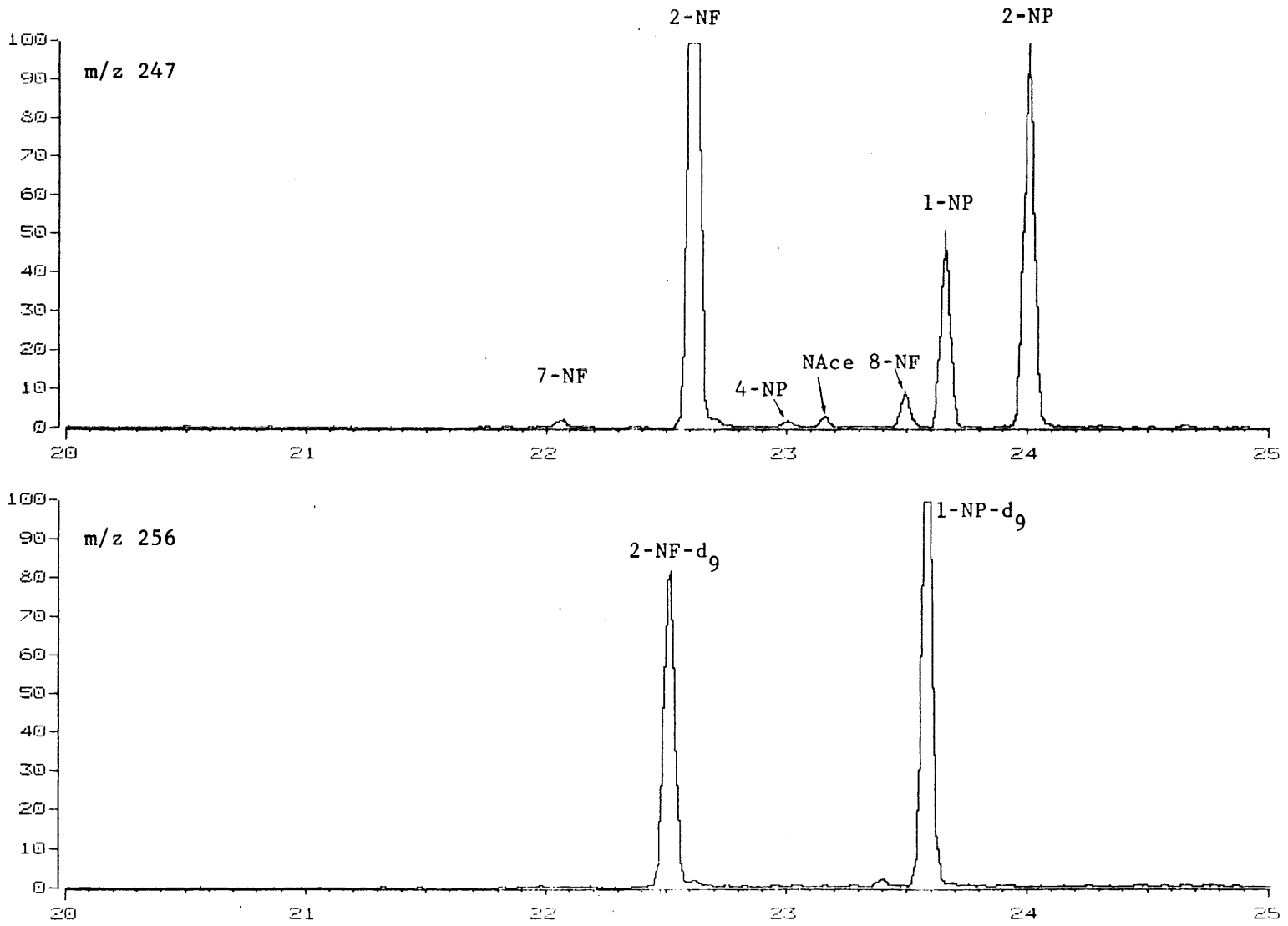

Figure E-8B. GC/MS-MID traces of the molecular ion for NF, NP and NAce isomers (m/z 247) and their deuterated analogues. Shown is an extract of ambient POM collected at Torrance, CA, 0500-1700 hr, 1/28/86. 2-NF and 1-NP were added as internal standards.